

Hydroformylation of High-Molecular-Weight *cis*-1,4-Polybutadiene Catalyzed by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

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Received 11 July 2003; accepted 7 January 2004

DOI 10.1002/app.20479

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The kinetics of the hydroformylation of high-molecular-weight *cis*-1,4-polybutadiene in the presence of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and monochlorobenzene as a solvent were studied. The degree of conversion was examined by spectroscopic characterization with Fourier transform infrared and ¹H-NMR analysis. According to the 2⁴-factorial experimental design, the temperature, catalyst concentration, and pressure appear to be significant factors for the hydroformylation of *cis*-1,4-polybutadiene. The kinetic studies indicated that the hydroformylation was first-order with respect to the

catalyst and carbon-carbon double-bond concentrations and H₂/CO pressure (1:1 ratio). The effects of the H₂/CO ratio in the synthesis gas and added triphenyl phosphine were also studied. The apparent activation energy for the hydroformylation of *cis*-1,4-polybutadiene over the temperature range of 60–80°C was estimated to be 41 kJ/mol. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 854–869, 2004

Key words: catalysts; kinetics (polym.); polybutadiene; rubber

INTRODUCTION

The chemical modifications of polymers includes reactions such as crosslinking, grafting, degradation, oxidation, isomerization, and cyclization. Their principal utility is to produce desirable physical and chemical properties within polymers that are often difficult or impossible to achieve with standard polymerization techniques. Polymers generally used as substrates for chemical modifications are unsaturated polymers or polymers containing olefinic unsaturation within the polymer structure. One of the most interesting methods for chemically modifying polymers is adding functional groups onto backbone polymers. McManus and Rempel¹ reviewed chemical modifications such as hydrogenation, hydrosilylation, hydrocyanation, hydrocarboxylation, hydroformylation, and hydroxymethylation for diene-based polymers and copolymers.

The catalytic hydroformylation of unsaturated polymers is a process by which aldehyde groups are introduced into the backbone polymer by a treatment with H₂ and CO in the presence of a catalyst. The common catalyst generally used for this process is a

Co or Rh complex.^{2–10} The most effective catalysts for the hydroformylation of C=C are rhodium complexes. Hydridocarbonyltris(triphenyl phosphine)-rhodium [$\text{HRh}(\text{CO})(\text{PPh}_3)_3$] is a catalyst that has been widely used for the hydroformylation of olefins and polymers under moderate conditions.^{3–11} There are many applications for hydroformylated polymers, such as protective coatings,^{12–15} smooth and wrinkle-free films,¹⁶ and sizing for glass fibers.¹⁷ Because of the reactivity of the aldehyde group, the hydroformylated products can be reacted via further reactions to produce nitrile, alcohol, acetate, and amine functionalities. The most often used subsequent reaction is hydrogenation, which produces a polymer with hydroxy methyl groups. The hydroxymethylated product can be used as a substrate for producing polyurethane.¹⁷

Most studies of the hydroformylation of diene polymers, that is, polybutadiene (PBD) and poly(styrene butadiene) (SBR), were carried out in the presence of rhodium catalysts. However, the earliest study showed that the hydroformylation of 1,4-PBD and high-styrene SBR could be achieved at high pressures and temperatures with a cobalt catalyst,² but there was considerable gel formation during this process. The first report of the use of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ in the hydroformylation of a polypentenamer was by Sanui et al.,³ and the reaction was carried out under moderate conditions with no gel formation. Later, Tremont and Remsen⁴ studied the hydroformylation of low-molecular-weight 1,2-PBD and 1,4-PBD in the presence of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with excess triphenyl phos-

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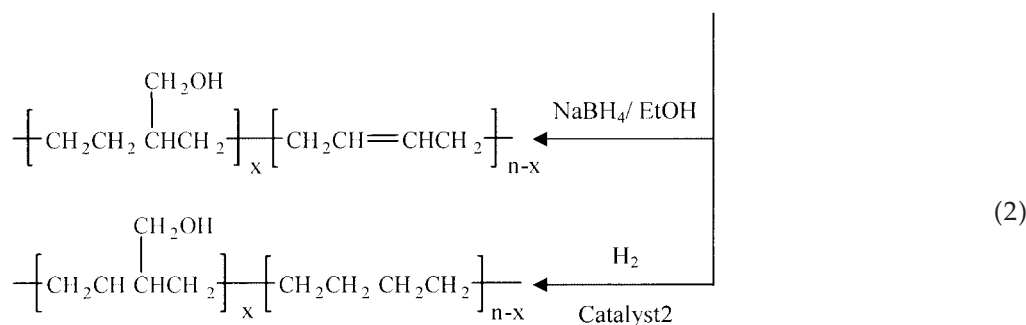
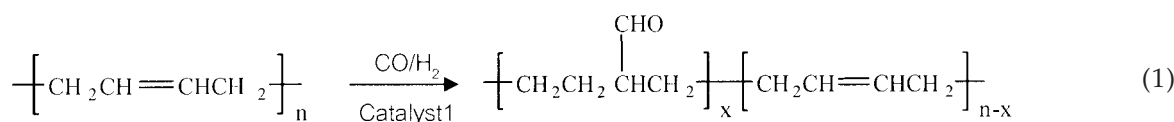
Contract grant sponsor: Thailand Research Fund (through the Royal Golden Jubilee Project).

Contract grant sponsor: Natural Science and Engineering Research Council of Canada.

phine. Scott and Rempel⁵ investigated the kinetics of the hydroformylation of SBR with the same catalyst. Furthermore, they postulated a possible reaction mechanism and presented an understanding of the catalyst species in solution.

Azuma et al.⁶ reported the preparation of a functional polydiene by a two-step process for the hydroxymethylation of a polybutadiene and *cis*-1,4-PBD. The initial reaction was hydroformylation with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, and the subsequent reaction was hydrogenation with a reducing agent such as sodium borohydride [eq. (1)]. The higher conversion led to a problem with the solubility because of the crosslinking of the hydroxyl group with the formyl group. The use of a selective reducing agent for the reduction of the formyl groups without hydrogenation at double bonds was critical. In the same

manner, McGrath et al.⁷ reported the synthesis of a novel ethylene-propylene-diene monomer and PBD polyols. The hydroformylation reaction was accomplished at high pressures and temperatures, and later the aldehyde groups were reduced to hydroxymethyl groups on the polymer. They also reported the production of polyurethane by a further reaction with diisocyanates. The synthesis and characterization of hydroformylated 1,2-PBD were also reported by Mohammadi,⁸ and the subsequent hydrogenation was achieved with $\text{RuCl}(\text{C}_6\text{H}_5\text{COO})(\text{CO})(\text{PPh}_3)_2$ as the catalyst [eq. (2)]. Sibtain and Rempel⁹ investigated this hydroformylation and hydroxymethylation of SBR with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$, respectively. Moreover, they reported the development of IR calibration curves to estimate the degree of hydroformylation:



All previous investigations reported the use of low-molecular-weight polymers with a weight-average molecular weight (M_w) of less than 200,000 for hydroformylation with moderate conversions. Recently, Chen et al.¹⁰ studied the hydroformylation of higher molecular weight styrene-butadiene copolymers ($M_w \sim 200,000$) under more severe reaction conditions in the presence of various rhodium catalysts, and conversions greater than 50% were achieved. The main purpose of this study was to prepare and characterize the hydroformylation products of high-molecular-weight *cis*-1,4-PBD. Because of its structure, *cis*-1,4-PBD can serve as a primary material for the study of this process for the further investigation of other polydienes such as synthetic *cis*-1,4-polyisoprene and natural rubber. The determination of the significant parameters was achieved with a 2⁴ experimental design. This work was also aimed at studying the detailed kinetics of the hydroformylation of *cis*-1,4-PBD to obtain further understanding of the reaction at high conversions and conditions, and this led to the postulation of a reaction mechanism.

EXPERIMENTAL

Materials

The polymer used in this study was high-molecular-weight PBD with a *cis* concentration of 98 wt % and an M_w value of about 2,000,000–3,000,000 (Aldrich, Milwaukee, WI). The hydroformylation catalyst, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, was prepared according to a literature procedure.¹⁸ The IR spectrum of the catalyst showed two bands at 2060 and 1990 cm^{-1} , which were indicative of $\nu(\text{RhH})$ and $\nu[\text{Rh}(\text{CO})]$, respectively. Analytical-grade monochlorobenzene, obtained from Fisher Scientific, Ltd. (Fairlawn, NJ), was used as received. A high-purity synthesis gas (1:1 H_2/CO) was obtained from Praxair, Inc. (Kitchener, Ontario, Canada).

Hydroformylation reaction

The hydroformylation reaction was carried out in a Parr 300-mL autoclave (Moline, IL) fitted with a catalyst addition device, a thermocouple controlled-temperature monitoring system, a gas-release and poly-

TABLE I
Results for the Hydroformylation of PBD in 2⁴-Factorial Design: Temperature (A), Pressure (B), Polymer Concentration (C), and Catalyst Concentration (D)

Experiment	Factor				Conversion (%)		Factor level	
	A	B	C	D			Low (-)	High (+)
(1)	-	-	-	-	11.7	A (°C)	40	80
a	+	-	-	-	28.1	B (bar)	13.8	68.9
b	-	+	-	-	17.3	C (mM)	222	370
ab	+	+	-	-	28.8	D (μM)	109	326
c	-	-	+	-	9.8			
ac	-	-	+	-	17.9			
bc	-	+	+	-	4.9			
abc	+	+	+	-	68.0			
d	-	-	-	+	27.1			
ad	+	-	-	+	58.8			
bd	-	+	-	+	12.4			
abd	+	+	-	+	90.0			
cd	-	-	+	+	22.8			
acd	+	-	+	+	46.3			
bcd	-	+	+	+	14.4			
abcd	+	+	+	+	90.9			

The polymer concentration is defined as the weight of PBD divided by the molecular weight of the repeating unit.

mer-sampling outlet, and a high-speed stirrer. A certain amount of the purified polymer was dissolved in 100 mL of monochlorobenzene. The catalyst was weighed in a glass bucket, and the bucket was placed in the catalyst addition device. The polymer solution was degassed by pressurization with the synthesis gas to about 24 bar and was then vented out at a temperature below 14°C and at a stirring speed of 200 rpm. This degassing of the solution was repeated three times. Subsequently, the reaction system was pressurized to slightly below the desired pressure with the synthesis gas. The reactor was heated to the desired temperature, and the stirring speed was increased to 600 rpm. When the system was stable and had reached liquid-vapor thermal equilibrium, the catalyst addition device was connected to the synthetic gas cylinder and then pressurized to slightly higher than the system pressure. This caused the catalyst to be dropped into the solution, and the reaction was initiated. To determine the incorporation of functional groups within the polymer and to investigate the conversion and the rate of the hydroformylation reaction, we sampled the polymer solution at intervals during the reaction.

Characterization

All Fourier transform infrared (FTIR) spectra were obtained with a Bio-Rad FTS 3000X spectrometer (Cambridge, MA). The IR samples were prepared through the casting of the polymer solution onto sodium chloride disks, which were then kept in the fume hood to evaporate the solvent. ¹H-NMR spectra of the polymer samples were obtained with a Bruker 300-MHz spectrometer (Milton, Ontario, Canada). A com-

parison of the sum of the aldehyde proton and unsaturated proton integration and paraffin proton integration was used to calculate the degree of hydroformylation. The sample solutions were collected in Schlenk tubes and evaporated to dryness *in vacuo*. The rubber was then dissolved in degassed CDCl₃ to make samples for NMR analysis. However, it was necessary to retain some small amount of the solvent in the NMR samples because polyaldehyde would have been unstable if the solvent had been completely removed.

Experimental design

To determine the significant factors for the hydroformylation of PBD, we used a 2^k-factorial design to design the experiment. This method is widely used for screening system factors.¹⁹ The chosen factors for the hydroformylation reaction were the temperature, pressure, polymer concentration, and catalyst concentration ($k = 4$). In this experimental design method, there are two levels: low (-1) and high (+1). Each reaction condition is summarized in Table I. The response was considered the quantitative value of the degree of hydroformylation over a specified period of time. The hydroformylation reaction was performed with the observation of the final conversion after 24 h of reaction. The determination was obtained from the consideration of the treatment combination in standard order according to the factorial design procedure.

Kinetic study and univariate experiments

The important parameters from the 2⁴-factorial experimental design were obtained to determine the nature

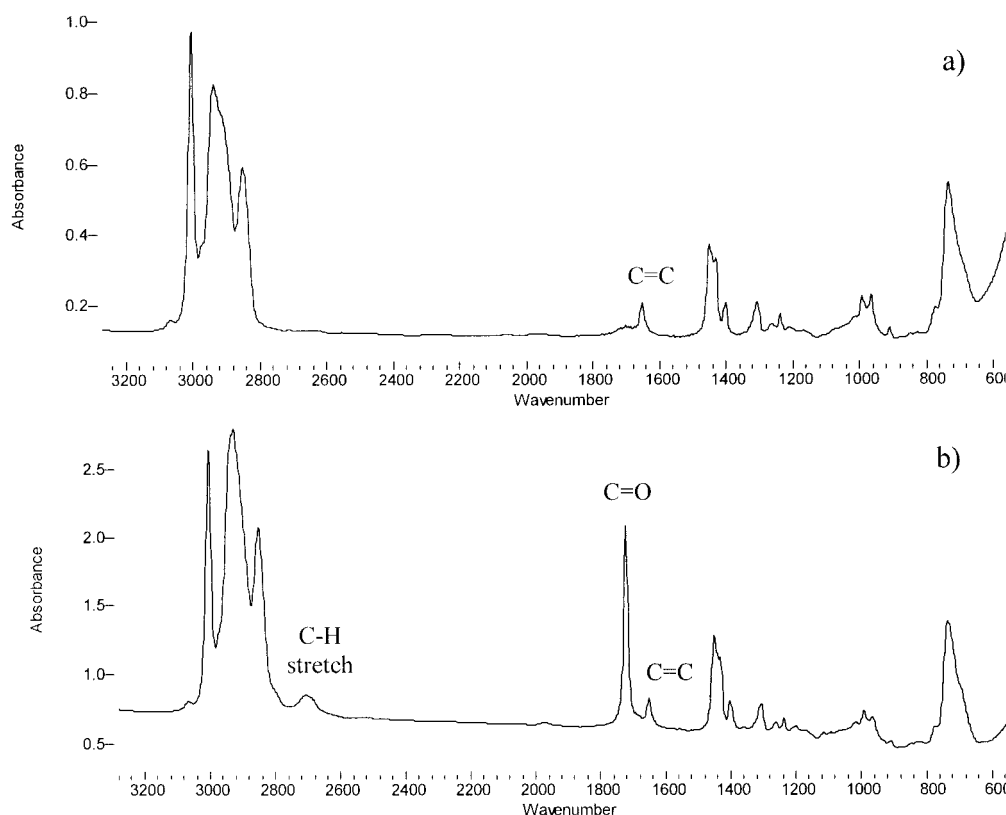


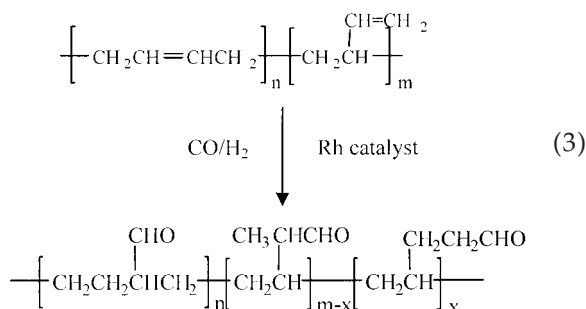
Figure 1 FTIR spectra of (a) *cis*-1,4-PBD and (b) hydroformylated *cis*-1,4-PBD ($[C=C] = 370 \text{ mM}$; $[Rh] = 326 \mu\text{M}$; H_2/CO pressure = 13.8 bar; $H_2/CO = 1:1$; temperature = 40°C ; time = 24 h).

of the univariate kinetic study. For the kinetic study, the degree of hydroformylation was detected through the sampling of the polymer solutions every hour during the reaction. The polymer solutions were characterized with $^1\text{H-NMR}$ spectroscopy, and the conversion was determined. The reaction was carried out, the conversion being followed with time for a 10 h.

RESULTS AND DISCUSSION

Product identification

The PBD used in this experiment was 98 wt % *cis* (1,4-PBD) and 2 wt % vinyl (1,2-PBD). According to the microstructure of PBD, there are three possible hydroformylated products, as shown in eq. (3). The possible products may be not only these products but also products from side reactions, such as chain degradation or hydrogenation of unsaturated polymer or aldehyde.⁵



IR spectra of *cis*-1,4-PBD and a partially hydroformylated product are shown in Figure 1. It is apparent from the spectra that in addition to a decrease in the intensity of the bands at 912 , 968 , 995 , and 1655 cm^{-1} , which can be attributed to $C=C$ bonds, two new bands appeared at 1725 and 2700 cm^{-1} . The band at 1725 cm^{-1} is due to carbonyl ($C=O$) stretching vibrations, and that at 2700 cm^{-1} can be attributed to the $C-H$ stretching vibrations of the aldehyde group. No observation at 3500 cm^{-1} due to OH stretching was made. This confirmed that there was no appreciable hydrogenation of aldehyde under the reaction conditions used.

Figure 2 shows $^1\text{H-NMR}$ spectra of *cis*-1,4-PBD and a partially hydroformylated product. The signals from 1.0 to 2.0 ppm are associated with the paraffin protons. The allylic protons occur at about 2.2 ppm, whereas the olefinic protons due to 1,4-PBD or an internal double bond occur at 5.4 ppm, and those due to 1,2-PBD or a vinyl double bond occur from 4.7 to 5.6 ppm. The characterization of the aldehyde products is difficult because of the lack of signal splitting. However, this can be distinguished through the use of some model compounds. According to the data, peaks attributable to aldehyde groups are at 9.5 and 9.7 ppm. The peak at 9.5 ppm corresponds to the aldehyde group resulting from internal or anti-Markovnikov addition. The smaller peak at 9.7 ppm can be assigned

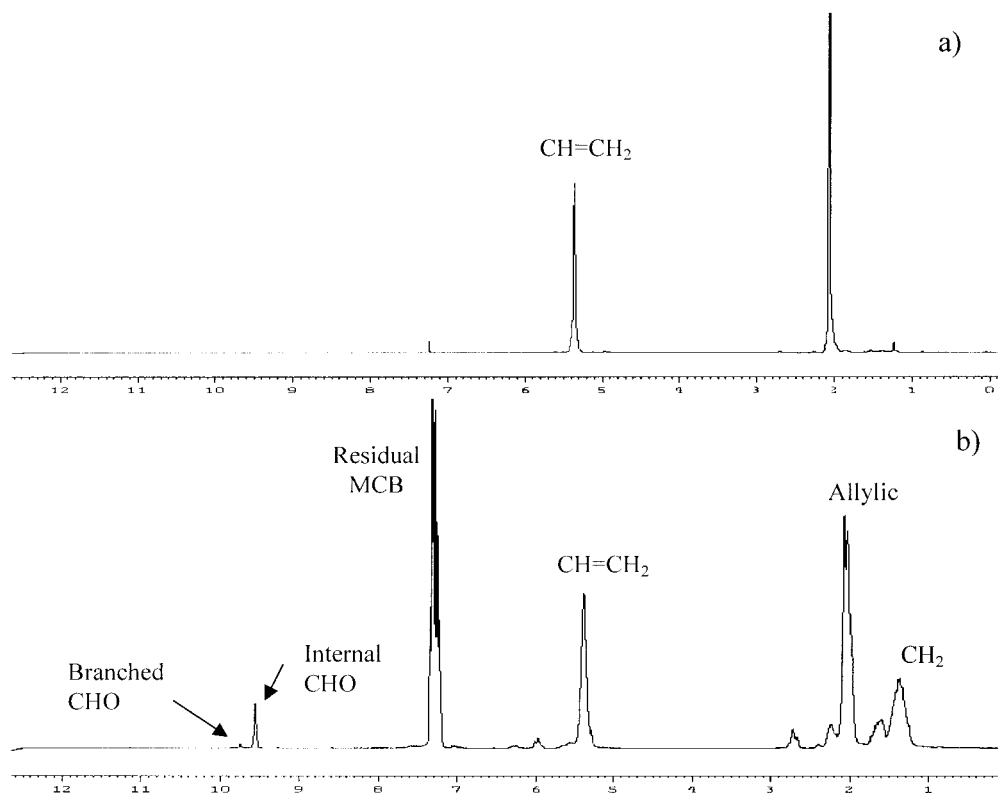


Figure 2 $^1\text{H-NMR}$ spectra of (a) *cis*-1,4-PBD and (b) *cis*-1,4-hydroformylated PBD ($[\text{C}=\text{C}] = 370 \text{ mM}$; $[\text{Rh}] = 326 \mu\text{M}$; H_2/CO pressure = 13.8 bar; $\text{H}_2/\text{CO} = 1:1$; temperature = 40°C ; time = 15 h).

to the aldehyde group, which can be the outcome of the hydroformylation of 1,2-PBD as a Markovnikov product.^{4,5,8}

2^4 -factorial experimental design

Factorial experimental design is an effective method for determining how various reaction parameters affect the system. It is very useful in a primary experimental study when there are many factors to determine. The interesting parameters in this work are the temperature, pressure, polymer concentration, and catalyst concentration. For the two-level factorial design, the final conversion of hydroformylation was defined as the response to a change in the levels of these factors. The treatment combination in standard order can be written as follows: (1), a, b, c, d, ab, ac, bc, ad, bd, cd, abc, abd, acd, bcd, and abcd (Table I). The experiments were designed to run a single replicate to obtain the response data as the final conversions over 24 h, and the conversion results are also shown in Table I.

The procedure used to analyze the data from unreplicated factorial design was provided through an examination of a normal probability plot. The contrast constants for the 2^4 design were calculated, and the normal probability plot is given in Figure 3. According

to the normal probability plot, all of the effects that lie along the line are negligible, whereas larger effects deviate from the line. Thus, the important effects that emerge from this analysis are the main effects of the temperature, pressure, and catalyst concentration and the temperature/pressure and temperature/catalyst-concentration interactions.

The main effects of the temperature, pressure, polymer concentration, and catalyst concentration are plotted in Figure 4. The temperature, pressure, and catalyst concentration positively affect the average conversion of hydroformylation of PBD, but the polymer concentration does not. For the maximum conversion, the temperature, pressure, and catalyst concentration should be at high levels. However, it is necessary to examine any interactions that are important. Main effects do not have as much meaning when they are also involved in significant interactions. Pressure/polymer-concentration, pressure/catalyst-concentration, temperature/polymer-concentration, and polymer-concentration/catalyst-concentration interactions do not affect one another because the slope value between the two factors are similar. Figure 3 shows that the temperature/pressure and temperature/catalyst-concentration interactions are significant. For the temperature/pressure interaction, the temperature effect is very small when the pressure is low and very

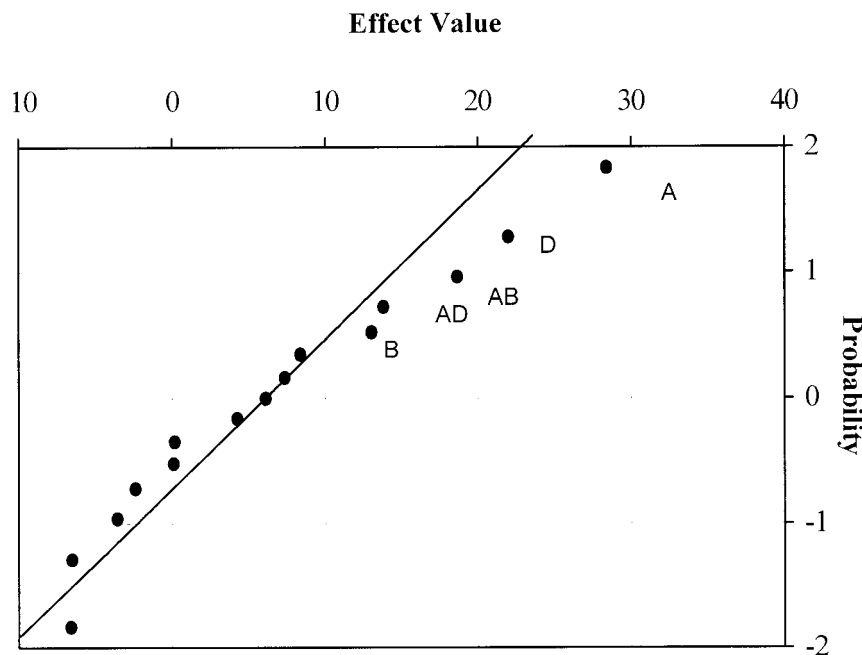


Figure 3 Normal probability plot for the 2^4 -factorial design in the hydroformylation of PBD (A = temperature; B = pressure; D = catalyst concentration).

large when the pressure is high; therefore, a high conversion is obtained at a high pressure and a high temperature. The temperature/catalyst-concentration interaction indicates that the catalyst concentration has little effect at low temperatures but a large positive effect at high temperatures. Therefore, the best conversion for the hydroformylation of PBD appears to be obtained when the temperature, pressure, and catalyst concentration are.

Kinetics of hydroformylation

Kinetic results for the hydroformylation of PBD were obtained with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ after 10 h of reaction. To obtain the kinetics, we observed the conversion of hydroformylation with time, as shown by the representative plot in Figure 5. In addition, the conversion of double-bond hydrogenation, a side reaction, was also obtained from $^1\text{H-NMR}$ spectra. The conversion of hydroformylation followed a first-order rate equation. The rate constant (k) was derived from the slope of the relationship between $\ln(1 - x)$ and the reaction time, as shown in Figure 6, where x is the conversion. Under the hydroformylation conditions for Figures 5 and 6, the final conversion at 10 h was nearly 80%, and the pseudo first-order reaction rate constant was $3.7 \times 10^{-5} \text{ s}^{-1}$. This can be compared with the results reported by Tremont and Remsen,⁴ who found that the hydroformylation of *cis*-1,4-PBD ($M_w \sim 156,800$) with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with excess PPh_3 at 20 bar and 87°C yielded a conversion of only 55% in 23 h. The

results of the hydroformylation of PBD and SBR with the same rhodium catalyst, reported by various investigators, are also presented in Table II.

From factorial design, the significant parameters for the hydroformylation of PBD were the temperature, catalyst concentration, and total pressure of the synthesis gas. Thus, it was worth carrying out an investigation of the effects of these parameters on the reaction rate constant. Furthermore, the effects of triphenyl phosphine and the percentage of CO in the synthesis gas were also studied to obtain detailed kinetic information. The results of univariate experiments are presented in Table III and are discussed in detail later.

Effect of the stirring speed

To approach the kinetic regime, we studied the effect of the stirring speed on the rate of hydroformylation from 400 to 700 rpm, as shown in Figure 7. The reaction was performed at 70°C and 41.3 bar with a 1:1 synthesis gas mixture. The catalyst concentration was maintained at $326 \mu\text{M}$, and no PPh_3 was added. The reaction rate constant increased slightly with increasing stirring speed. With a further increase in agitation above 600 rpm, the reaction rate tended to be independent of the stirring speed, and so the reaction was not affected by mass-transfer limitations when the experiments were performed at an agitation above 600 rpm.

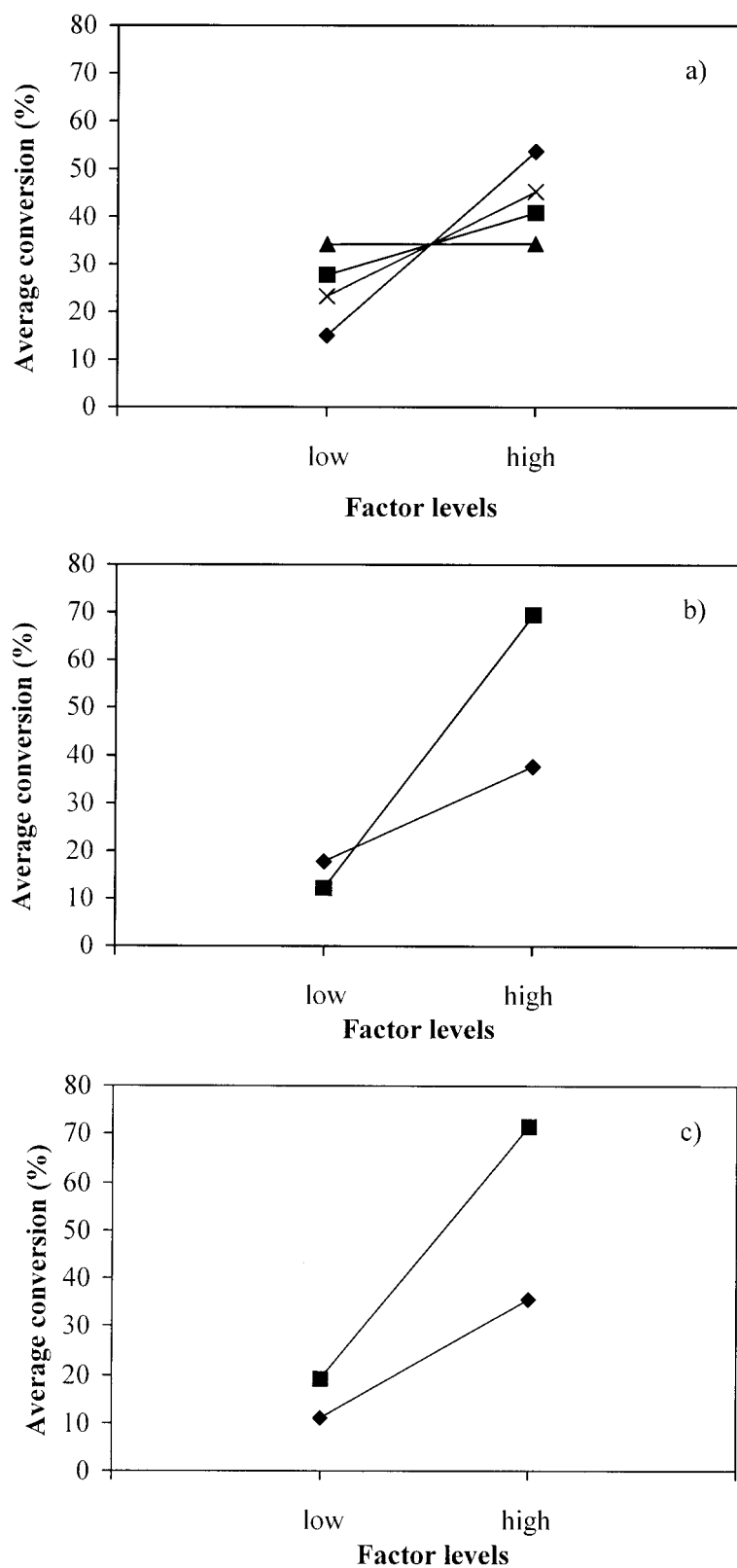


Figure 4 Plots of (a) the main effects, (b) temperature/pressure interactions, and (c) temperature/catalyst-concentration interactions for the hydroformylation of PBD: (●) temperature, (■) pressure, (▲) polymer concentration, and (×) catalyst concentration.

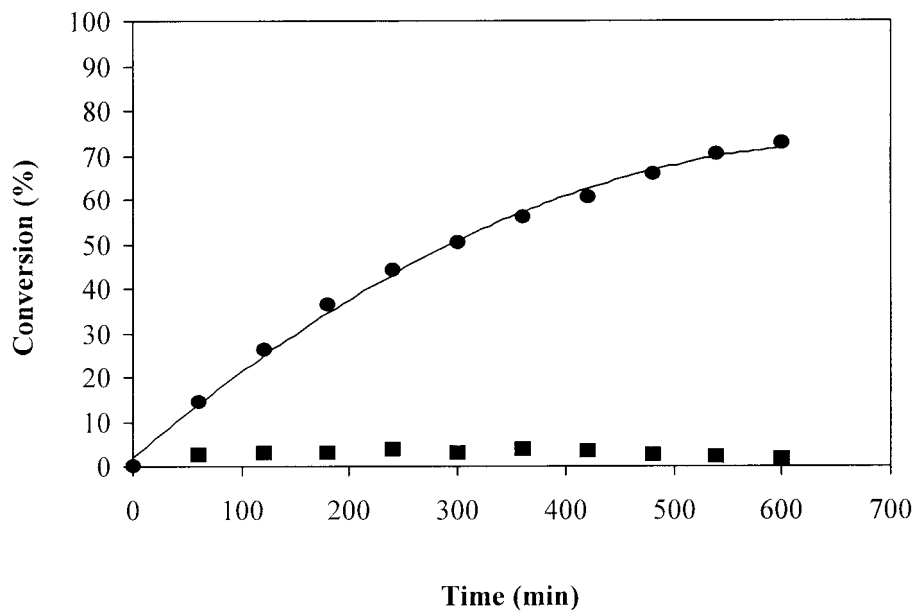


Figure 5 Conversion profile for (●) the hydroformylation and (■) hydrogenation of PBD ($[C=C] = 370 \text{ mM}$; $[Rh] = 326 \text{ } \mu\text{M}$; H_2/CO pressure = 68.9 bar; $H_2/CO = 1:1$; temperature = 70°C).

Effect of the temperature

The effect of the temperature on the rate constant and final conversion is shown in Figure 8. The reaction conditions were kept constant ($[C=C] = 370 \text{ mM}$; $[Rh] = 326 \text{ } \mu\text{M}$; $[PPh_3] = 0$; $H_2/CO = 1:1$; total pressure = 55.1 bar). The rate constant increased with increasing temperature over the range of $60\text{--}80^\circ\text{C}$ and

decreased when the temperature was above 80°C . A possible reason for this behavior is that the rhodium catalyst may no longer have been active because of decomposition at temperatures above 80°C in the absence of excess PPh_3 . The apparent activation energy was obtained from the slope of an Arrhenius plot, as shown in Figure 9. Over this range of temperatures, it was estimated to be 41.0 kJ/mol . For the hydroformy-

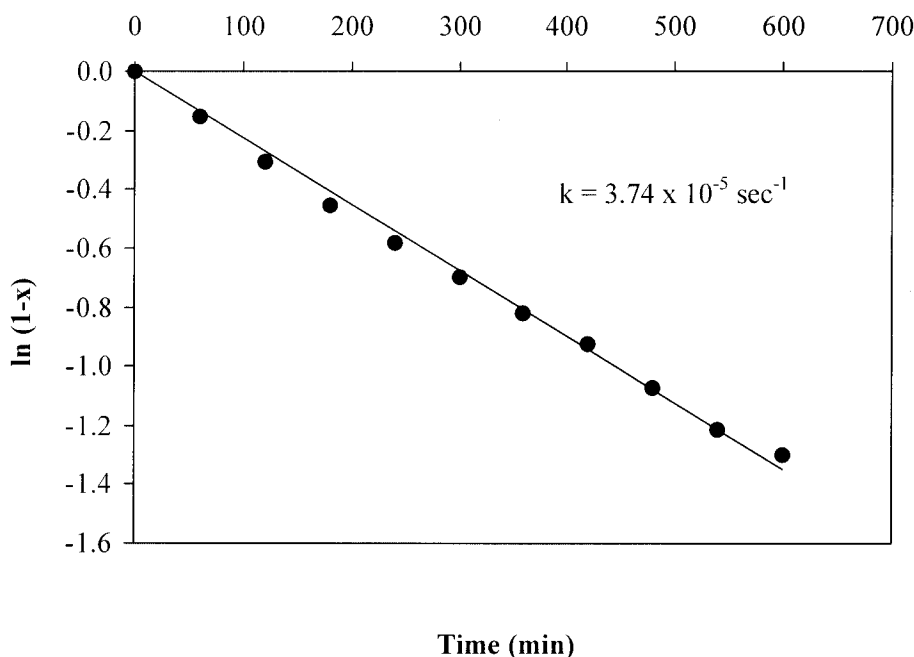


Figure 6 First-order $\ln(1-x)$ plot for the hydroformylation of PBD ($[C=C] = 370 \text{ mM}$; $[Rh] = 326 \text{ } \mu\text{M}$; H_2/CO pressure = 68.9 bar; $H_2/CO = 1:1$; temperature = 70°C).

TABLE II
Hydroformylation of Polydiene by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

Investigators	Polymer	M_w	[Rh] (μM) ^b	Condition			Conversion (%)
				Temperature ($^\circ\text{C}$)	H_2 CO pressure (bar) ^d	Time (h)	
This work	<i>cis</i> -1,4-PBD (98%)	2,000,000	326	70	55.1	10	80
Azuma et al. ⁶	<i>cis</i> -1,4-PBD (97%)	420,000	1850	40	7	4	27
			3800	40	12	4	20
			925	40	12	4	29
Mohammadi ⁸	1,2-PBD (92%)	30,000 ^a	580	60	2	—	5–40
Tremont and Remsens ⁴	<i>cis</i> -1,4-PBD	156,800	354 ^c	87	20	23	55
			45,790	87	20	23	69
Sibtain and Rempel ⁹	SBR	—	408	50	1	—	1–17
Scott and Rempel ⁵	SBR (82% butadiene)	160,000	2080	51	0.9	~1.5	30
Chen et al. ¹⁰	SBR (23.5% styrene)	222,800	437	40	13.8	19	27
			437	40	13.8	16	22
			437	40	55.1	72	80
			437	40	55.1	36	53

^a M_w .

^b $[\text{Rh}] = [\text{HRh}(\text{CO})(\text{PPh}_3)_3]$.

^c $\text{PPh}_3/[\text{Rh}] = 165$ (by mole).

^d $\text{H}_2/\text{CO} = 1:1$.

lation of SBR with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, an activation energy value of 64.3 kJ/mol was reported by Scott and Rempel.⁵ Although the observed apparent activation energy of 41.0 kJ/mol was fairly low, it still was indicative of a reaction that was subject to chemical reaction control.

Effect of the percentage of CO in the synthesis gas

The effect of the CO percentage in the synthesis gas on the reaction rate and final conversion, as shown in Figure 10, was included in this study to extend our understanding of the mechanism of hydroformylation. The reaction conditions were 70 $^\circ\text{C}$ and a total pressure of 41.3 bar. The polymer concentration and catalyst concentration were 370 mM and 326 μM , respectively, and no triphenyl phosphine was added. Figure 10 indicates that the reaction rate was inversely proportional to the CO percentage in the synthesis gas mixture in the CO range of 25–67%, and the highest reaction rate was achieved with 25% CO in the synthesis gas. This can be explained by an examination of the possible species of rhodium proposed by Scott and Rempel.⁵ In solution, the rhodium catalyst is dissociated into other species, as shown in Scheme 1, and $\text{HRh}(\text{CO})(\text{PPh}_3)_2$ is the first species from dissociation between the rhodium catalyst and PPh_3 .²⁰ They noted that under an atmosphere of hydrogen, the formation of $\text{Rh}(\text{CO})_2(\text{PPh}_3)_2$ is preferred because of its activity toward hydroformylation. However, under an atmosphere of carbon monoxide, inactive species are formed, such as $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]_2$ and $[\text{Rh}(\text{CO})_3(\text{PPh}_3)_2]_2$. Furthermore, the dicarbonyl species, $\text{Rh}(\text{COR})(\text{CO})_2(\text{PPh}_3)_2$, that is formed in the catalytic

cycle is also an inactive species. This effect was also studied by Scott and Rempel. Nevertheless, they reported that the optimum CO percentage in the synthesis gas mixture for their system was about 30%, which gave the highest conversion for the hydroformylation of SBR under moderate conditions. From the study of the CO percentage in the synthesis gas in this study, we found that the reaction rate constant also increased as the CO percentage decreased. This led to an examination of the effects of the catalyst concentration and total pressure at both 25 and 50% CO in the synthesis gas mixture.

Effect of the catalyst concentration

The effect of the catalyst concentration on the rate constant is shown in Figure 11. The temperature was 70 $^\circ\text{C}$, the total pressure was 41.3 bar with a 1:1 synthesis gas mixture, the polymer concentration was 370 mM, and the PPh_3 concentration was 0 μM . At catalyst concentrations of 109–435 μM , the reaction rate was first-order with respect to the catalyst concentration up to approximately 350 μM , at which point the reaction rate tended toward a zero-order behavior. A similar observation was made by Scott and Rempel⁵ for the hydroformylation of SBR with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. Also included in this plot is an effect study of the catalyst concentration with a 3:1 H_2/CO mixture. The reaction rate constant increased linearly with increasing catalyst concentration. The reaction rate of the 3:1 H_2/CO mixture was much higher than that of the 1:1 H_2/CO mixture at a catalyst concentration above 350 μM because of the first-order rate dependence of the catalyst concentration for the whole range investigated.

TABLE III
Kinetic Results of the Univariate Experiments

Experiment	[Rh] (μM) ^a	Molar ratio of added PPh ₃ /[Rh] ^a	H ₂ /CO Pressure (bar)	CO in gas mixture (%)	Temperature (°C)	Stirring speed (rpm)	$k \times 10^5$ (s ⁻¹)	Conversion (%) at 10 h
1	327	0	41.3	50	70	400	3.74	42.9 ^b
2	327	0	41.3	50	70	500	4.09	43.6 ^b
3	327	0	41.3	50	70	600	4.26	45.9 ^b
4	327	0	41.3	50	70	700	4.35	47.5 ^b
5	326	0	55.1	50	60	600	2.22	57.4
6	327	0	55.1	50	65	600	3.12	69.3
7	327	0	55.1	50	70	600	4.05	76.0
8	327	0	55.1	50	75	600	5.01	81.1
9	327	0	55.1	50	80	600	5.60	81.4
10	326	0	55.1	50	90	600	6.31	87.2
11	326	0	55.1	50	100	600	5.75	80.4
12	326	0	41.3	25	70	600	5.55	81.8
13	326	0	41.3	42	70	600	4.33	76.4
14	322	0	41.3	50	70	600	3.54	71.4
15	327	0	41.3	67	70	600	2.35	66.3
16	109	0	41.3	50	70	600	1.39	35.7
17	109	0	41.3	25	70	600	1.68	28.0 ^b
18	163	0	41.3	50	70	600	2.00	45.6
19	218	0	41.3	50	70	600	2.85	60.0
20	218	0	41.3	25	70	600	3.05	31.0 ^b
21	272	0	41.3	50	70	600	3.45	68.1
22	326	0	41.3	50	70	600	4.14	80.4
23	326	0	41.3	25	70	600	5.09	51.3 ^b
24	435	0	41.3	50	70	600	4.57	78.3
25	435	0	41.3	25	70	600	6.36	56.0 ^b
26	329	0	13.8	50	70	600	2.03	47.4
27	327	0	13.8	25	70	600	2.55	40.7 ^b
28	326	0	20.7	50	70	600	2.52	52.3
29	327	0	27.6	50	70	600	3.14	64.0
30	327	0	27.6	25	70	600	3.93	49.6 ^b
31	326	0	41.3	50	70	600	4.14	80.4
32	327	0	41.3	25	70	600	5.09	51.3 ^b
33	327	0	55.1	50	70	600	4.05	76.0
34	327	0	55.1	25	70	600	4.57	47.8 ^b
35	326	0	68.9	50	70	600	3.74	72.8
36	326	0	68.9	25	70	600	3.91	35.6 ^b
37	322	0	41.3	50	70	600	3.54	71.4
38	327	10	41.3	50	70	600	3.36	69.7
39	326	25	41.3	50	70	600	2.97	66.4
40	326	75	41.3	50	70	600	1.67	53.1
41	326	100	41.3	50	70	600	1.42	40.7

Polymer concentration for all conditions: [C=C] = 370 mM.

^a [Rh] = [HRh(CO)(PPh₃)₃].

^b The conversion at 5 h.

Effect of the total pressure

The variation of the reaction rate constant with the total pressure of the 1:1 H₂/CO synthesis gas is shown in Figure 12. The temperature was 70°C, the polymer concentration was 370 mM, and the catalyst concentration was 326 μM ; there was no added triphenyl phosphine. The total pressure of the synthesis gas was varied from 13.8 to 68.9 bar. The reaction rate was first-order with respect to the total pressure until around 41.3 bar. Above this pressure, the reaction rate constant decreased. It is evident

that this catalyst was most suitable under moderate pressure. In addition, Scott and Rempel⁵ reported that the reaction rate was first-order with respect to the total pressure and became zero-order at a higher pressure for the hydroformylation of SBR with a rhodium catalyst. In parallel, an effect study of the total pressure with a 3:1 H₂/CO mixture also showed that the reaction rate was first-order with respect to the total pressure. The reaction rate constant reached a maximum at a total pressure of about 41.3 bar and then decreased.

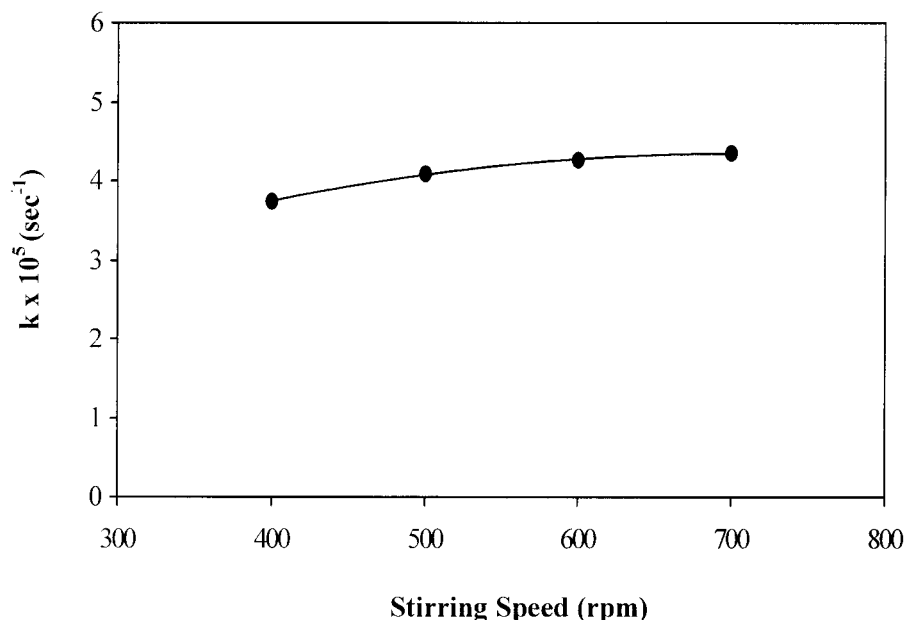


Figure 7 Effect of the stirring speed on k ($[\text{C}=\text{C}] = 370 \text{ mM}$; $[\text{Rh}] = 326 \text{ }\mu\text{M}$; H_2/CO pressure = 41.3 bar; $\text{H}_2/\text{CO} = 1:1$; temperature = 70°C).

Effect of added PPh_3

Figure 13 shows the variation of the rate constant and final conversion with the molar ratio of triphenyl phosphine to rhodium catalyst. The reaction was kept at 70°C and 41.3 bar, and a 1:1 H_2/CO mixture was used. The polymer concentration and catalyst concentration were 370 mM and 326 μM , respectively. The

molar ratio of triphenyl phosphine to the rhodium catalyst was varied over the range of 0–100. The reaction rate appeared to be inverse first-order with respect to the molar ratio of triphenyl phosphine to the rhodium catalyst up to about a molar ratio of 75:1. Triphenyl phosphine had an inhibiting effect on the rhodium catalyst because of the retardation of triphenyl phosphine dissociation in the catalytic

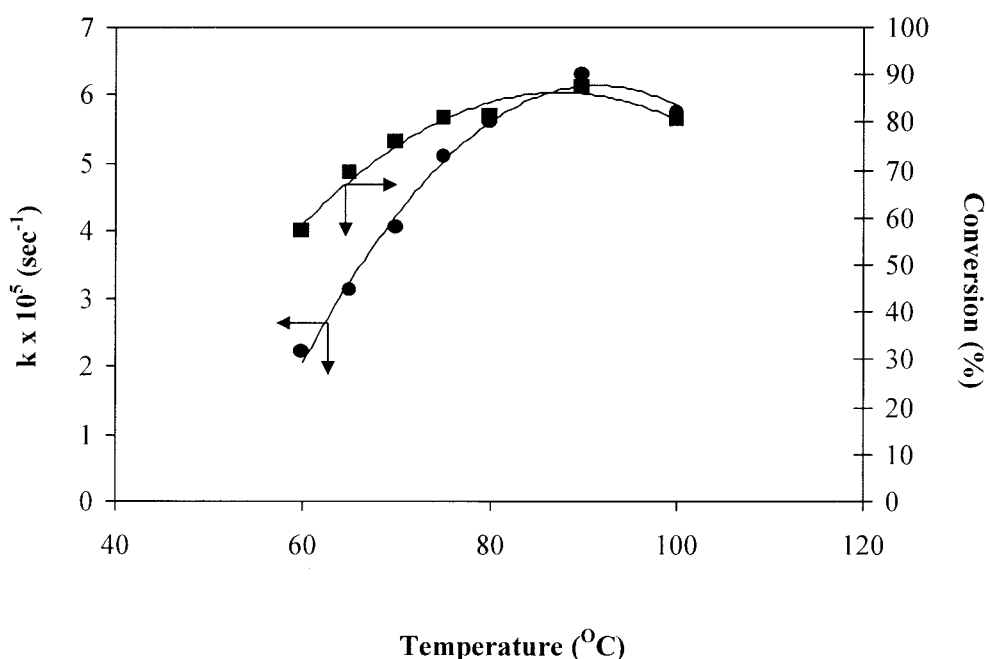


Figure 8 Effect of the temperature on (●) k and (■) the conversion at 10 h ($[\text{C}=\text{C}] = 370 \text{ mM}$; $[\text{Rh}] = 326 \text{ }\mu\text{M}$; H_2/CO pressure = 55.1 bar; $\text{H}_2/\text{CO} = 1:1$).

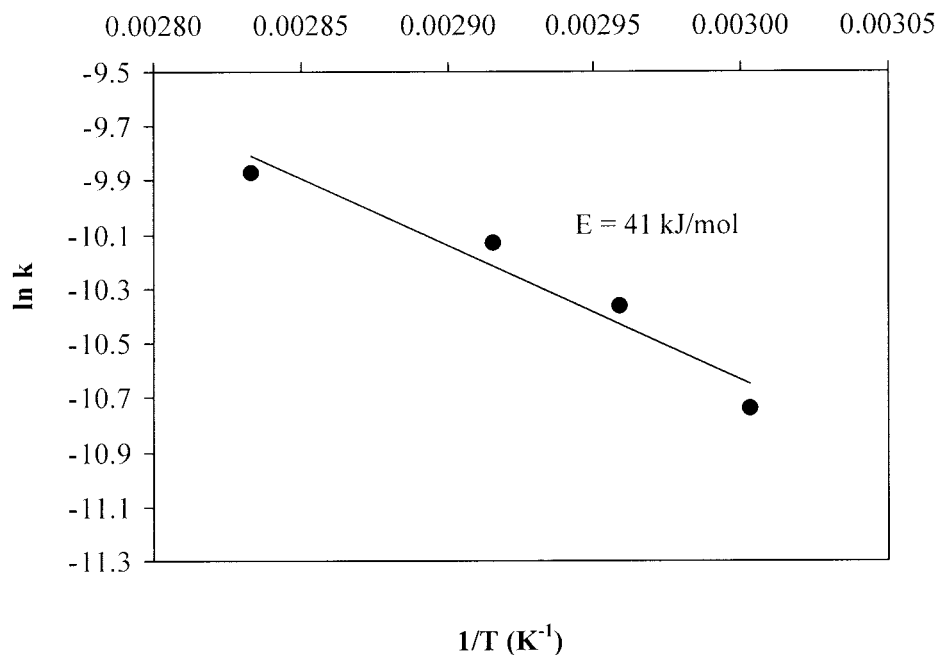


Figure 9 Arrhenius plot for the hydroformylation of PBD.

cycle. This agreed with the observation by Scott and Rempel⁵ for the hydroformylation of SBR with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.

Reaction mechanism and rate law

Scott and Rempel⁵ suggested a mechanism for the $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ -catalyzed hydroformylation of

SBR that is consistent with the IR spectroscopy observation of the hydride stretch and carbonyl stretch shifting. This proposed mechanism can be used to describe the hydroformylation of PBD in this work, as shown in Scheme 2.

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is dissociated to form $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ as the first species in the catalytic cycle, and this reaction can be reversed:

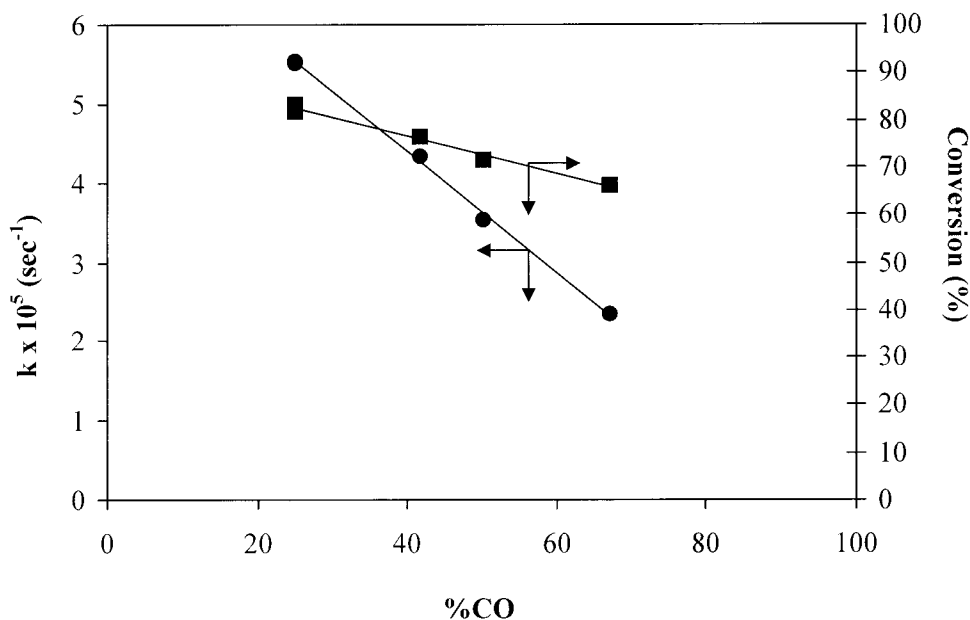
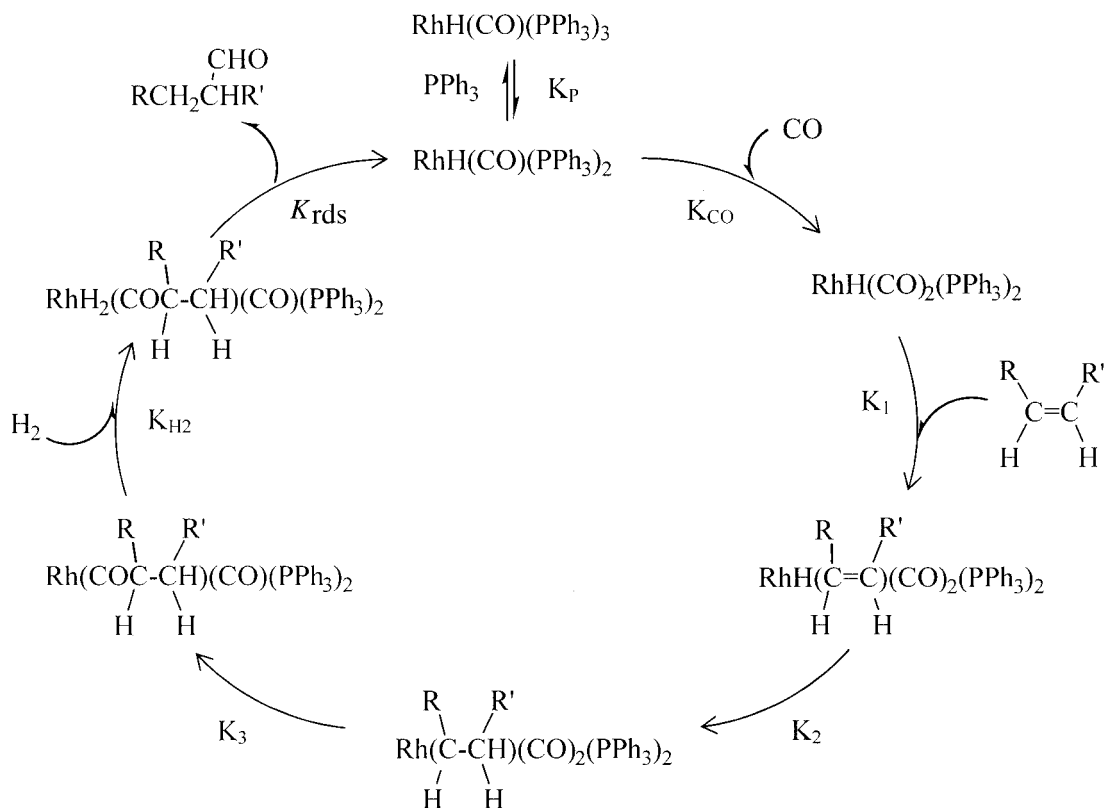


Figure 10 Effect of the CO percentage in the synthesis gas on (●) k and (■) the conversion at 10 h ($[\text{C}=\text{C}] = 370 \text{ mM}$; $[\text{Rh}] = 326 \text{ } \mu\text{M}$; H_2/CO pressure = 41.3 bar; temperature = 70°C).



Scheme 1 Possible rhodium species in solution under hydroformylation conditions (S = solvent).

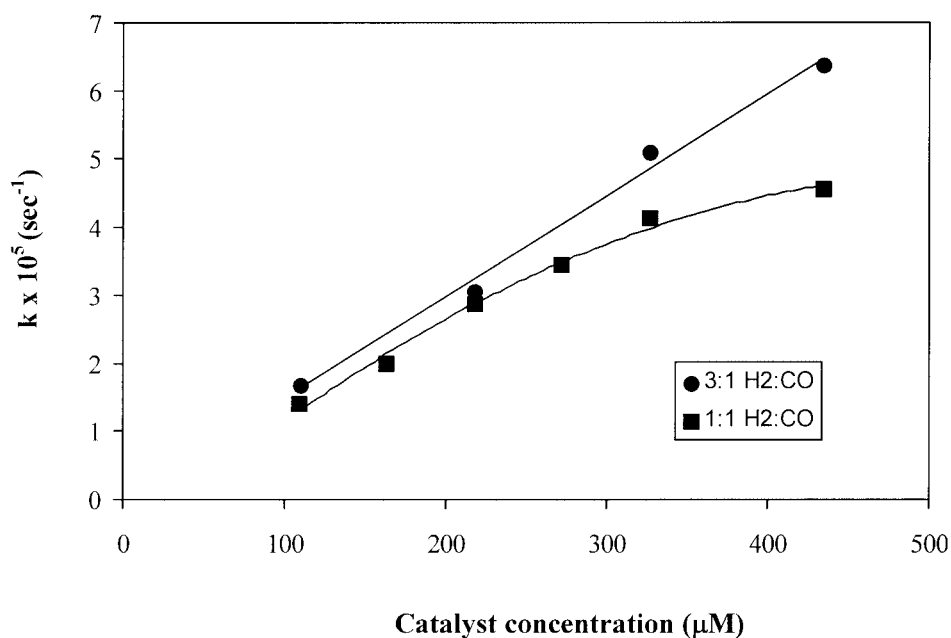


Figure 11 Effect of the catalyst concentration on k at $\text{H}_2/\text{CO} = (\bullet) 3:1$ and $(\blacksquare) 1:1$ ($[\text{C}=\text{C}] = 370 \text{ mM}$; H_2/CO pressure = 41.3 bar; temperature = 70°C).

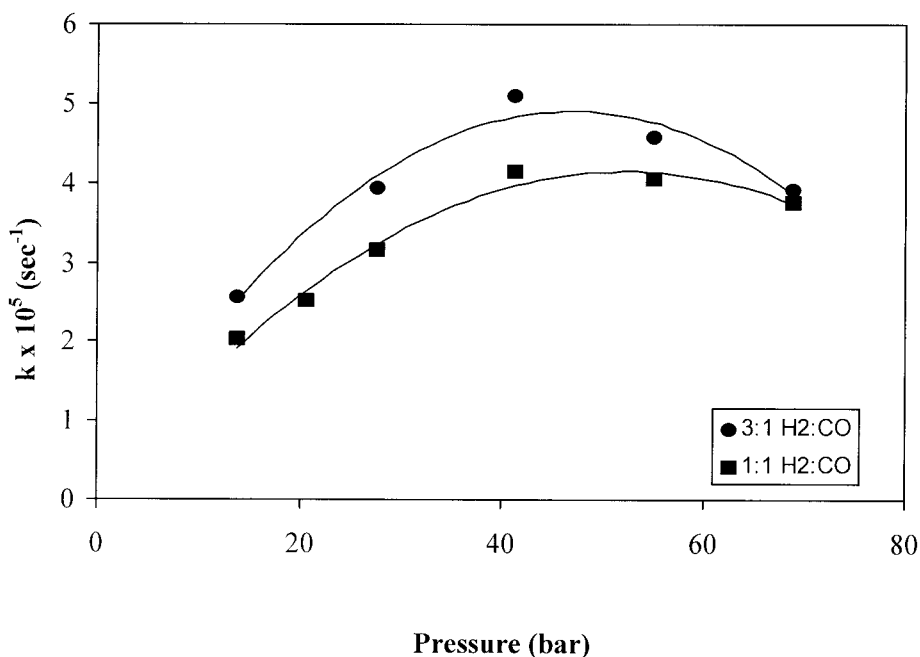
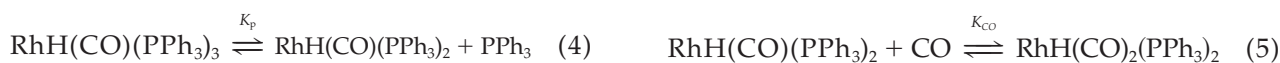


Figure 12 Effect of the total pressure on k at $H_2/CO =$ (●) 3:1 and (■) 1:1 ($[C=C] = 370 \text{ mM}$; $[Rh] = 326 \text{ }\mu\text{M}$; $H_2/CO = 1:1$; temperature = 70°C).



During hydroformylation, the dicarbonyl complex, $RhH(CO)_2(PPh_3)_2$, can be formed through the reaction of $RhH(CO)(PPh_3)_2$ with CO as follows:

The dicarbonyl complex interacts with the carbon-carbon double bonds to form the olefin complex:

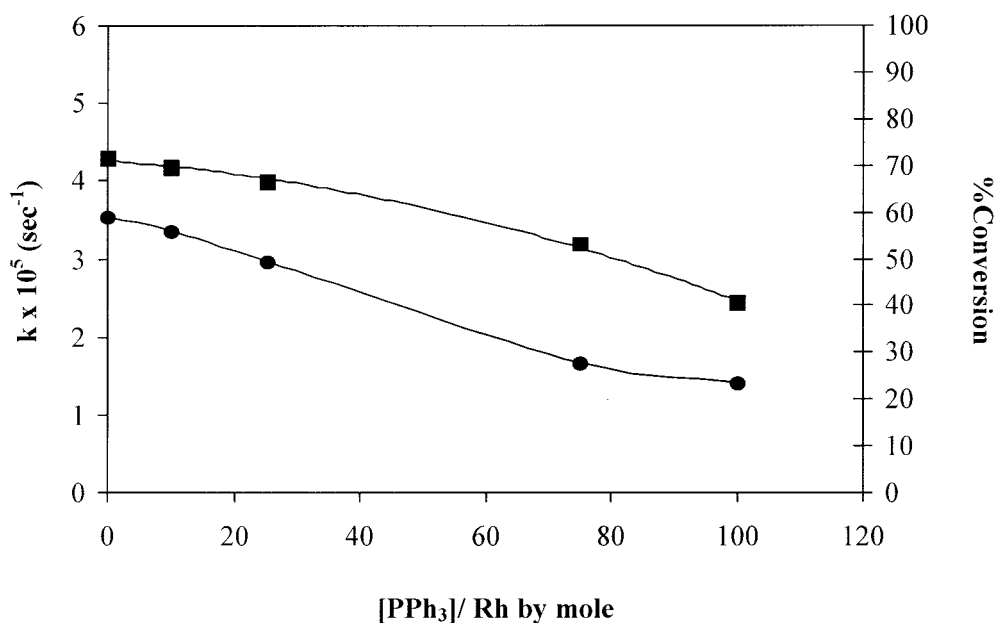
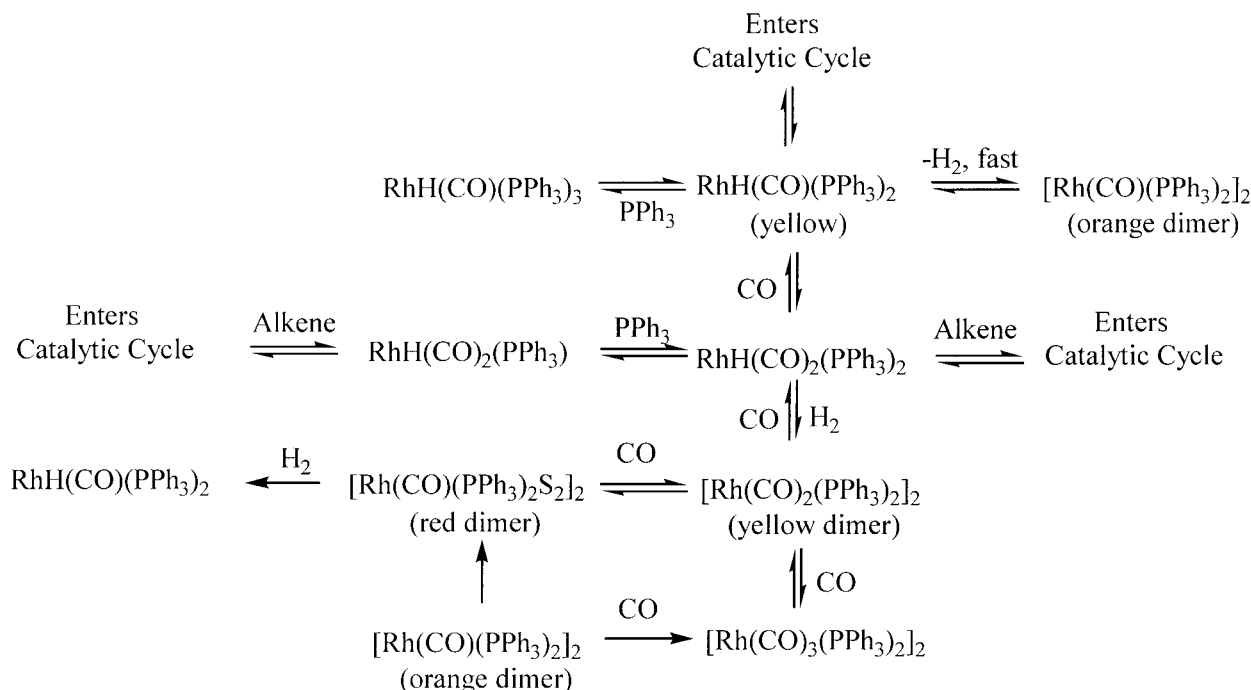
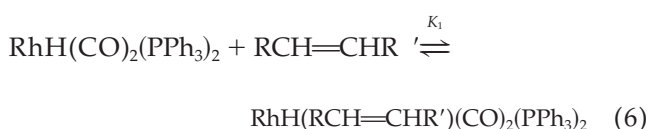


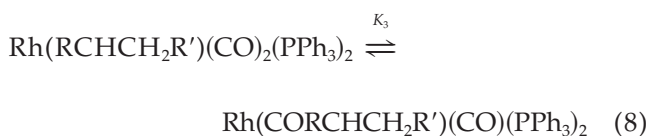
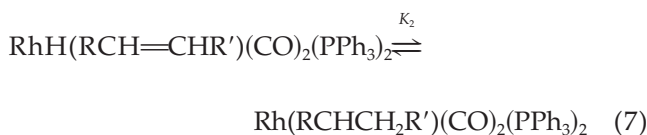
Figure 13 Effect of added triphenyl phosphine on (●) k and (■) the conversion at 10 h ($[C=C] = 370 \text{ mM}$; $[Rh] = 326 \text{ }\mu\text{M}$; H_2/CO pressure = 41.3 bar; $H_2/CO = 1:1$; temperature = 70°C).



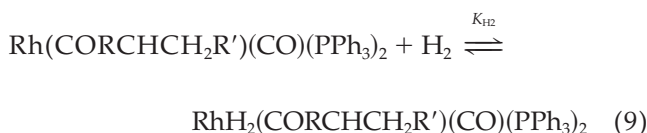
Scheme 2 Mechanism behind the hydroformylation of PBD with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.



Afterward, the complex is reformed through the substitution of the double bond with H_2 surrounding the Rh species to obtain $\text{Rh}(\text{RCHCH}_2\text{R}')(\text{CO})_2(\text{PPh}_3)_2$ [eq.(7)]. Furthermore, the dicarbonyl species is reduced into monocarbonyl species, and the carbonyl group is formed in the olefin molecule on the rhodium complex [eq. (8)]:



The hydrogen molecule is added to coordinate with $\text{Rh}(\text{CORCHCH}_2\text{R}')(\text{CO})(\text{PPh}_3)_2$ to give $\text{RhH}_2(\text{CORCHCH}_2\text{R}')(\text{CO})(\text{PPh}_3)_2$:



According to the catalytic cycle for the hydroformylation reaction, the rate expression can be written as follows:

$$-\frac{d[\text{C}=\text{C}]}{dt} = k_{\text{rds}}[\text{RhH}_2(\text{CORCHCH}_2\text{R}')(\text{CO})(\text{PPh}_3)_2] \quad (10)$$

For the system at equilibrium, a material balance on the rhodium charged to the system can be described as follows:

$$\begin{aligned} [\text{Rh}]_T &= [\text{RhH}(\text{CO})(\text{PPh}_3)_3] + [\text{RhH}(\text{CO})(\text{PPh}_3)_2] \\ &\quad + [\text{RhH}(\text{CO})_2(\text{PPh}_3)_2] + [\text{RhH}(\text{RCH}=\text{CHR}') \\ &\quad \times (\text{CO})_2(\text{PPh}_3)_2] + [\text{Rh}(\text{RCHCH}_2\text{R}')(\text{CO})_2(\text{PPh}_3)_2] \\ &\quad + [\text{Rh}(\text{CORCHCH}_2\text{R}')(\text{CO})(\text{PPh}_3)_2] \\ &\quad + [\text{RhH}_2(\text{CORCHCH}_2\text{R}')(\text{CO})(\text{PPh}_3)_2] \quad (11) \end{aligned}$$

With the results from the application of the equilibrium relation of each reaction step [eqs. (4)–(9)], $\text{RhH}_2(\text{CORCHCH}_2\text{R}')(\text{CO})(\text{PPh}_3)_2$ can be substituted into eq. (11). Thus, the rate law for hydroformylation can be rearranged as follows:

$$-\frac{d[\text{C}=\text{C}]}{dt} = \frac{[\text{Rh}]_T K_1 K_2 K_3 K_{H_2} K_{\text{CO}} K_P [\text{H}_2][\text{CO}][\text{C}=\text{C}]}{\alpha} \quad (12)$$

where α is equal to $[PPh_3] + K_P(1 + K_{CO}[CO]) + K_1K_{CO}K_P[C=C](1 + K_2) + K_1K_2K_3K_{CO}K_P[CO][C=C](1 + K_{H_2}[H_2])$.

According to the proposed mechanism, the rate expression is consistent with the observed kinetic data. From the kinetic study, the reaction rate is first-order with respect to the C=C and catalyst concentrations, and this agrees with eq. (12). In the experiments, the first-order behavior with respect to the total pressure was observed from 13.8 to 41.3 bar. This can be explained by eq. (12): if $K_1K_2K_3K_{CO}K_P[CO][C=C](1 + K_{H_2}[H_2])$ is small with respect to the others in the dominator, the reaction rate is first-order with respect to $[H_2]$. Above the total pressure of 41.3 bar, the reaction rate becomes zero-order with respect to the total pressure as a result of the predominant term, $K_1K_2K_3K_{CO}K_P[CO][C=C](1 + K_{H_2}[H_2])$, of eq. 12. Also, the triphenyl phosphine concentration is inversely proportional to the reaction rate, and this is consistent with the results of kinetic studies.

CONCLUSIONS

The catalytic hydroformylation of high-molecular-weight *cis*-1,4-PBD was achieved with $HRh(CO)(PPh_3)_3$ in monochlorobenzene at a conversion of nearly 80% under high pressures and at moderate temperatures. The hydroformylated product showed some selectivity toward 1,2-PBD, the concentration of which was about 2% in the substrates, as shown by FTIR and 1H -NMR analysis. The 2^4 -factorial experimental design was used to determine the significant parameters for the hydroformylation reaction. The resultant normal probability plot clearly indicated that the temperature, catalyst concentration, and total pressure of the synthesis gas were important factors. Kinetic studies showed that the reaction rate was first-

order with respect to the catalyst and carbon-carbon double-bond concentration and the total pressure of the synthesis gas. Also, the inverse first-order rate with respect to the triphenyl phosphine concentration and CO percentage in the synthesis gas mixture was found. The apparent activation energy was estimated to be 41 kJ/mol from 60 to 80°C.

References

- McManus, N. T.; Rempel, G. L. *J Macromol Sci Rev Macromol Chem Phys* 1995, 35, 239.
- Ramp, F. L.; Dewitt, E. J.; Trapasso, L. E. *J Polym Sci* 1966, 4, 2267.
- Sanui, K.; MacKnight, W. J.; Lenz, R. W. *Macromolecules* 1974, 7, 952.
- Tremont, S.; Remsen, E. E. *Macromolecules* 1990, 23, 1984.
- Scott, P. J.; Rempel, G. L. *Macromolecules* 1992, 25, 2811.
- Azuma, C.; Mituboshi, T.; Sanui, K.; Ogata, N. *J Polym Sci Polym Chem Ed* 1980, 4, 2267.
- McGrath, M. P.; Sall, E. D.; Forster, D.; Tremont, S. J.; Sendjarevic, A.; Promer, D.; Jiang, J.; Iyer, K.; Klemperer, D.; Frisch, K. C. *J Appl Polym Sci* 1995, 56, 533.
- Mohammadi, N. A. Ph.D. Thesis, University of Waterloo, 1987.
- Sibtain, F.; Rempel, G. L. *J Polym Sci Part A: Polym Chem* 1991, 23, 1984.
- Chen, J.; Ajjou, A. N.; Chanthateyanonth, R.; Alper, H. *Macromolecules* 1997, 30, 2897.
- Trzeciak, A. M.; Ziolkowski, J. J. *Coord Chem Rev* 1999, 190, 883.
- Mertzweiler, J. K.; Cull, N. L. U.S. Pat. 3,318,972 (1967).
- Cull, N. L.; Mertzweiler, J. K. U.S. Pat. 3,337,489 (1967).
- Mertzweiler, J. K.; Segura, M. A.; Cull, N. L. U.S. Pat. 3,365,411 (1968).
- Cull, N. L. U.S. Pat. 3,314,911 (1967).
- Mertzweiler, J. K.; Cull, N. L.; Hawley, R. S. U.S. Pat. 3,425,895 (1969).
- Verdol, J. A.; Ryan, P. W. U.S. Pat. 3,427,366 (1969).
- Ahmad, N.; Robinson, S. D.; Uttley, M. F. *Inorg Synth* 1974, 15, 45.
- Montgomery, D. C. *Design and Analysis of Experiments*; Wiley: New York, 1997; Chapter 7.
- Evan, D.; Yagupsky, G.; Wilkinson, G. *J Chem Soc A* 1968, 2660.