Homogeneous Catalytic Hydroformylation of Styrene-Butadiene Copolymers in the Presence of HRh(CO)(PPh3)3

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ABSTRACT: Homogeneous catalytic hydroformylation of unsaturated polymers offers a useful method of producing reactive polymers. Such reactive polymers may serve as substrates for grafting, cross-linking, or further modification reactions. A study of the homogeneous hydroformylation of a styrene-butadiene AB block copolymer (SBR) using the catalyst HRh(CO)(PPh3)3 is presented. The product polymer, which has been characterized using IR and ^{1}H and ^{13}C NMR, is shown to contain an internal aldehyde product as well as an anti-Markovnikov aldehyde product. No hydrogenation of the polymer was observed under hydroformylation conditions. Although the product has limited stability, gel permeation chromatography showed that no unwanted side reactions occurred during the hydroformylation process. Differential scanning calorimetry suggests a cross-linked product results upon precipitation of the product polymer from the reaction solution. Kinetic and spectral studies of the hydroformylation of SBR suggest that the active catalytic species is probably HRh(CO)2(PPh3)2. Although no attempt was made at deriving a stringent rate law in this investigation, the kinetic data were found to be useful for optimization of the reaction rate and product distribution. An increased selectivity of the catalyst toward the anti-Markovnikov product is also possible. The nature of the reaction solvent was found to have an effect on the reaction rate and degree of conversion.

Introduction

Chemical modification of polymers is a postpolymerization process which is useful in altering the reactivity and/or stability of polymers. The introduction of reactive functional groups onto the polymer backbone produces a reactive polymer which can subsequently be used for grafting, cross-linking, or further modification reactions. The catalytic hydroformylation of unsaturated polymers is one such example of the production of a reactive polymer. Chemical modification is a necessary means of introducing aldehyde groups onto the polymer backbone since polymerization of a monomer containing this functionality would result in a cross-linked product.

The introduction of an aldehyde functionality yields a versatile polymer as aldehydes can be easily oxidized or reduced producing useful functionalities for subsequent grafting reactions. Polymers containing the formyl group have been used to immobilize enzymes.[1]

The first report of the hydroformylation of polymers employed the catalyst dicobalt octacarbonyl, Co2(CO)8.[2] In order to accomplish hydroformylation, high temperatures and pressures were used which resulted in substantial gel formation rendering a useless product. Upon the development of hydridocarbonyltris(triphenylphosphine)rhodium(I), HRh(CO)(PPh3)3, by Wilkinson,[3] reaction conditions could be dramatically modified and the hydroformylation of polymers accomplished with the elimination of gel formation.[4] Subsequent to this, a series of derivatives produced from hydroformylated polymers was reported which include nitrile, alcohol, acetate, and amine functionalities.[4-6] Applications for hydroformylated polymers have appeared in the patent literature and include protective coatings,[7-10] smooth, wrinkle-free films,[11] and sizings for glass fibers.[12] In addition to the hydroformylation of unsaturated hydrocarbon polymers there are reports of the hydroformylation of unsaturated polyesters for possible use as membranes.[6,13]

Due to the versatility of the product polymer it is surprising that the hydroformylation of polymers has not been further studied. Although the hydroformylation of small molecules has been extensively studied,[14] there appears to be little information available for polymers and extrapolation of the results obtained for small molecules cannot be assumed since chain length, electronic, and neighboring group effects may affect the product distribution, kinetics, and mechanism of the reaction. Previously, the synthesis and characterization of hydroformylated polybutadiene (PBD)[15] was reported. Recently, Tremont et al. have presented results on a reaction kinetic study involving the HRh(CO)(PPh3)3-catalyzed hydroformylation of low molecular weight polybutadienes to polyaldehydes.[16] A preliminary spectroscopic study on the catalytic hydroformylation and hydroxymethylation of styrene-butadiene copolymers (SBR) has also been reported.[17] Reported in the present paper is the first indepth study of the hydroformylation of a styrene-butadiene copolymer using HRh(CO)(PPh3)3. Despite the complexity of the system, an understanding of the organometallic species present in solution was obtained which leads to the postulation of a reaction mechanism for the process. The product polymer was spectroscopically characterized using IR, ^{1}H and ^{13}C NMR, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC).

Experimental Section

Materials. The polymer used in this study was a styrene-butadiene AB block copolymer (Solprene 308) with an 82 mol % butadiene content, 10 mol % vinyl content, and a weight-average molecular weight of 160 000.

Hydridocarbonyltris(triphenylphosphine)rhodium(I) was prepared from RhCl3·3H2O (Englehard) according to the method described in the literature.[18] The product had a melting point of 124-126 °C, and the infrared showed the characteristic absorptions for ν(RhH) at 2020 cm^{-1} and ν(CO) at 1982 cm^{-1} as reported in the literature.[18]

Analytical-grade toluene (BDH) was used as the solvent for the hydroformylation experiments. The solvent was degassed by a freeze-thaw method immediately prior to the hydroformylation reaction. High-purity synthesis gas (H2:CO = 1:1; Linde) was used as received. A H2:CO ratio of 50:50 (±1.5 mol %) was maintained at all times (confirmed by GC monitoring during the reaction).

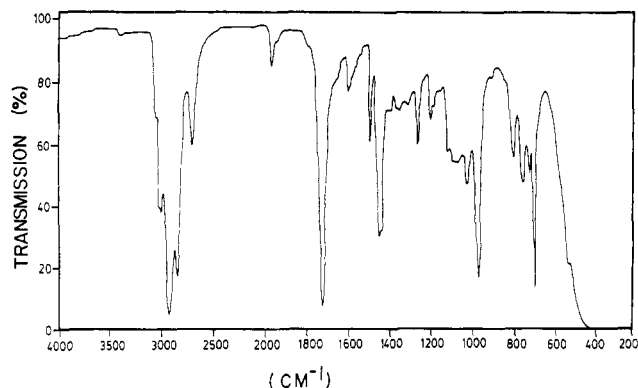All monomers were obtained from Aldrich (with the exception of 1-phenyl-3-hexene) and purified to remove peroxides.[19]

Figure 1. Representative gas uptake curve for the hydroformylation of Solprene 308 using $HRh(CO)(PPh_3)_3$; $[HRh(CO)(PPh_3)_3]_0 = 2.08$ mM, $[C=C]_0 = 444$ mM, pressure $H_2/CO = 68.9$ cmHg, $H_2:CO = 1:1$, $[PPh_3]_0 = 0$, temperature $= 51$ °C, toluene $= 15$ mL.

The Wittig reaction was used to synthesize 1-phenyl-3-hexene. The following three-step synthesis was used.

To a solution of 14.4 g (0.055 mol) of PPh_3 in 15 mL of $CHCl_3$ was added 5 mL (0.055 mol) of n-propyl bromide. The resulting solution was refluxed for 9 h. If on cooling there was no precipitate a small amount of anhydrous ether was added. The white crystals were filtered, washed with ether, and dried in vacuo overnight. The yield of the Wittig salt was 21.0 g (95–99%).

To a solution of 27.8 g (0.072 mol) of Wittig salt in 200 mL of dry degassed toluene was added 50 mL (0.08 mol) of 1.6 M n-butyllithium (n-BuLi) in hexane. The solution immediately turned bright orange. A nitrogen atmosphere was maintained due to the air and moisture sensitivity of n-BuLi. The reaction mixture was stirred for 2 h at room temperature.

After 2 h the bright orange solution was cooled in a dry ice/acetone bath and then 9.5 mL (0.072 mol) of hydrocinnamaldehyde was injected. The solution was stirred for 1 h and then gently warmed to room temperature, at which point the solution turns from a bright orange to a dirty, orange–brown. The solution was stirred for a further 20 h at room temperature.

After 20 h the solution was filtered to remove any precipitates. The toluene was then vacuum distilled from the filtrate. The mother liquor was eluted through a 20-cm column of silica gel 60 (0.2–0.5 mm) using a 9:1 mixture of hexane/ethyl acetate. Thin-layer chromatography was used to monitor the fractions for the product. The fractions containing product were then collected together and the solvents evaporated to obtain the product as a pure, clear, yellow liquid. The yield was 6.3 g (50%), and the product was extremely pungent. The resulting monomer was used immediately as a hydroformylation substrate. (^{1}H NMR: δ 0.8 (t), 1.9 (dq), 2.3 (dt), 2.6 (t), 5.3 (dt), 7.1 (m)).

Kinetic Studies. The kinetic studies were carried out using a computer-automated batch reactor that has been designed to accurately monitor gas consumption while maintaining constant pressure. A detailed description of the apparatus is presented elsewhere.[20] The reactor was calibrated using a bubble flow meter in order to obtain a calibration factor for the moles of gas consumed for a given voltage difference observed by the transducer. In a typical hydroformylation experiment the polymer is accurately weighed and added to a known amount of solvent in a two-necked flask. Upon dissolution a known amount of catalyst is added to the catalyst addition bucket which is suspended above the polymer solution. The solution is then degassed using the typical freeze–thaw technique. Synthesis gas is then added to the reaction flask. When the pressure and temperature have equilibrated, the catalyst is dropped into the solution. Gas uptake begins, and the computer program is then started for data collection. Pressure is maintained constant until the reaction has been completed. A representative gas uptake curve obtained for the hydroformylation of the styrene–butadiene copolymer in the presence of $HRh(CO)(PPh_3)_3$ is shown in Figure 1.

Gas Chromatographic Analysis. A Perkin-Elmer Sigma 2000 gas chromatograph equipped with a 10-ft Haysep A packed column was used to separate the synthesis gas mixtures. The oven temperature was maintained at 30 °C with the injector temperature at 100 °C. The carrier gas was helium, and the flow rate of the carrier and reference gases was maintained at 20 mL/min. A thermal conductivity detector was used and maintained at a temperature of 180 °C.

The system was calibrated for CO, as the accurate detection of H_2 was more difficult. Only two peaks were obtained (with the exception of a small air peak for which the appropriate correction was made); thus, from calibrating for CO the remainder of the injection volume was assumed to be H_2.

Infrared Spectral Analysis. All infrared (IR) spectra were obtained using a Perkin-Elmer 1330 infrared spectrophotometer. Polymer spectra were obtained by solvent-casting the polymer solution onto a NaCl plate and allowing the solvent to evaporate. Catalyst spectra were obtained as a Nujol mull.

NMR Spectral Analysis. Polymers were precipitated in a nitrogen atmosphere with degassed isopropyl alcohol and then dissolved in $CDCl_3$ or C_6D_6. NMR spectra were obtained using a Bruker AM 250-MHz NMR spectrometer. The degree of hydroformylation can be calculated by a comparison of the unsaturated proton integrations for the modified polymer to that of the starting polymer or by the aldehyde proton integration if the degree of hydroformylation is large enough to allow for an accurate estimate. NMR served as a confirmation of the degree of hydroformylation obtained from the automated gas uptake reactor.

Molecular Weight Determinations. A Waters Associates gel permeation chromatograph (GPC) was used to obtain the molecular weight distribution for the starting and modified polymers. Three Waters PL gel columns (10^2, 10^3, and 10^5 Å) were arranged in series and maintained at a temperature of 25.0 °C. Doubly distilled tetrahydrofuran was used as the eluting solvent. A Waters DR R401 differential refractometer and a Waters UV 441 ultraviolet detector were used to detect the eluting polymer.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer DSC-4 to determine the glass transition temperatures of starting and modified polymers. Approximately 20 mg of sample was placed in a sample pan, and the spectrum was scanned from −100 to +150 °C at 40 °C/min.

Results and Discussion

Product Identification. Since Solprene 308 contains both 1,4- and 1,2-butadiene monomeric units, there are three possible hydroformylation products:

Internal addition (a) may occur, and hydroformylation of

Figure 2. IR spectrum of partially hydroformylated Solprene 308.

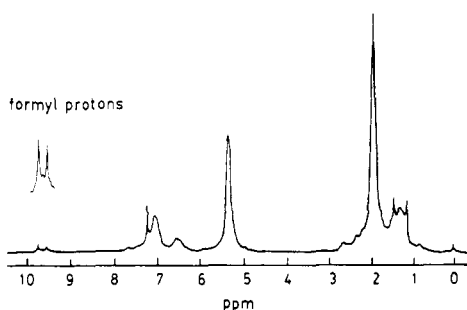**Figure 3.** ^{1}H NMR spectrum of partially hydroformylated Solprene 308.

Figure 4. ^{1}H NMR spectrum of partially hydroformylated 1,4-polybutadiene.

the pendant vinyl groups may occur by either an anti-Markovnikov (b) or Markovnikov (c) addition.

Solprene 308 has been hydroformylated to a maximum of 30% of the available double bonds despite the fact that it initially contained only a 9.5% pendant double-bond content. This suggests that either the molecular weight is changing (via chain degradation resulting in more terminal double bonds), hydrogenation of toluene or aldehyde is occurring, or both internal and pendant double bonds are being hydroformylated. The possibility of three types of aldehyde groups as well as the possibility of undesirable side reactions in the modified polymer complicates the product characterization.

(i) Infrared Spectroscopic Studies. Examination of the IR spectrum for the hydroformylated polymer (Figure 2) shows the introduction of three new stretches. Two of these stretches can be attributed to the introduction of the aldehyde functionality into the polymer. The (CO)–H stretch occurs at 2700 cm^{-1}, and the carbonyl stretch occurs at 1730 cm^{-1}. The new stretch introduced at 1970 cm^{-1} can be attributed to the decomposition product of the catalyst, [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$. The catalyst is still present in the product polymer, as the IR samples were made directly from the polymer reaction solutions. No OH stretch at 3500 cm^{-1} was observed, indicating that there was no detectable hydrogenation of the aldehyde occurring during the intended hydroformylation process.

(ii) ^{1}H NMR Spectroscopic Studies. The proton NMR spectrum of hydroformylated Solprene 308 (Figure 3) shows two broad unresolved aldehyde peaks at 9.5 and 9.7 ppm. These two aldehyde peaks appeared at as low a conversion as 5%. Due to the lack of splitting it was not possible to distinguish between the three possible aldehyde products, and therefore some model compounds were examined to assist with the product elucidation.

Examination of the ^{1}H NMR spectrum of partially hydroformylated 95% 1,4-polybutadiene shown in Figure 4 led to a possible assignment of the aldehyde peaks. The
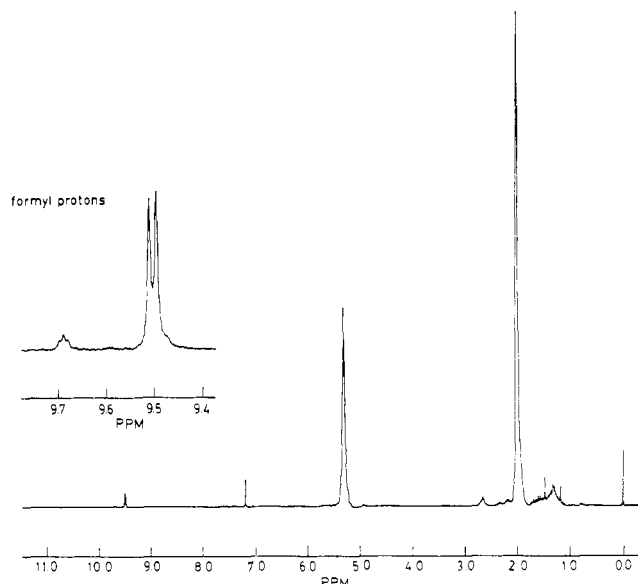
^{1}H NMR spectrum of partially hydroformylated 1,4-polybutadiene shows a doublet at 9.5 ppm and a small triplet at 9.7 ppm. The doublet can be attributed to either the internal addition hydroformylation product or the Markovnikov addition product. The triplet can be attributed to the anti-Markovnikov hydroformylation product of the residual 1,2-butadiene monomeric units. Confirmation of these assignments was obtained by the examination of the proton NMR spectra for partially hydroformylated 1-hexene (9.5 (d), 9.7 (t)) and 3-hexene (9.5 (d)). Work carried out by Wilkinson and co-workers[21] suggests that the doublet is not due to isomerization to the more stable internal alkene before hydroformylation, since in an atmosphere of H$_2$ and CO, the catalyst does not function as an isomerization catalyst. Since the doublet for internal hydroformylation and Markovnikov hydroformylation both occur at 9.5 ppm, it was not possible to distinguish between the two products by ^{1}H NMR. Fortunately it was possible to safely eliminate the Markovnikov product as an SBR hydroformylation product as discussed below. The ^{1}H NMR spectrum for high 1,2-addition of PBD shows only one aldehyde peak at 9.7 ppm, which has been attributed to the anti-Markovnikov product.[15] There is no Markovnikov addition product seen at as high a conversion as 20% in 1,2-PBD. This seems to suggest that the steric hindrance in polymers is too great to favor the Markovnikov product, thereby forcing the reaction to the anti-Markovnikov addition product. Further evidence for this was obtained from an experiment in which SBR was hydroformylated in the presence of added PPh$_3$ in an attempt to eliminate the second aldehyde peak. There was no change in the ratios of the aldehyde peaks at 9.5 and 9.7 ppm, indicating that the added PPh$_3$ was not increasing the selectivity of the catalyst as observed in the case of terminal alkenes.[22] The NMR results coupled with the lack of increased selectivity in the presence of added PPh$_3$ suggest that there was no significant production of the Markovnikov product and that the two aldehyde peaks observed in the ^{1}H NMR spectrum of Solprene 308 were due to the internal product and the anti-Markovnikov product.

^{1}H NMR spectra for 5% and 20% hydroformylated Solprene 308 showed that at 5% conversion both types of hydroformylation products were being produced. At a conversion greater than 10% the peaks which can be
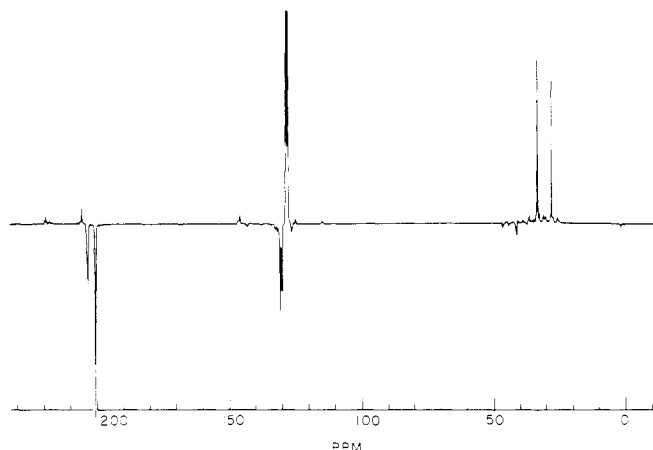
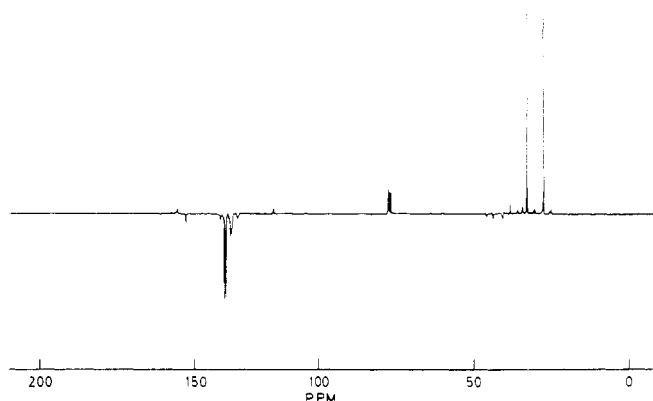**Figure 5.** *J*-modulated ^{13}C NMR spectrum of 5% hydroformylated Solprene 308.

Figure 6. *J*-modulated ^{13}C NMR spectrum of Solprene 308.

attributed to the vinyl protons virtually disappeared. Although both products were initially produced, this suggests an increased specificity of the catalyst toward the pendant double bonds, which can be easily explained by their greater accessibility.

(iii) Carbon-13 Labeling Experiments. In order to obtain a strong ^{13}C NMR spectrum of the carbonyl region, carbon-13 labeling of CO gas was employed. Hydroformylation of Solprene 308 was carried out under the usual initial conditions of 1 atm of synthesis gas at 50 °C using 99% pure ^{13}CO. The reaction vessel was pressurized to 0.5 atm of ^{13}CO and then filled to 1 atm with H_2, and the hydroformylation reaction was allowed to consume the available gas. The extent of the reaction was estimated at 5% using IR spectroscopy. The concentrations of the reactants were maintained at $[C=C]_0$ = 445 mM, [HRh-$(CO)(PPh_3)_3]_0$ = 2.08 mM, and $[PPh_3]_0$ = 0. The reaction was run in 5 mL of benzene-d_6 and the NMR spectrum run directly without precipitation. The resulting *J*-modulated spin-echo ^{13}C NMR spectrum (effective in determining multiplicity) was obtained as shown in Figure 5. Compared to the spectrum of the starting material (Figure 6), several new peaks appear in the carbonyl region (200–220 ppm). Since assignments for SBR appear in the literature,[23] only assignments of the peaks in the carbonyl region are reported here. The negative peak at 200.5 ppm is due to the anti-Markovnikov product. It is important to note that this is the largest peak and in the greatest concentration, again showing the increased specificity of HRh(CO)(PPh$_3$)$_3$ toward terminal unsaturation. The negative peak at 203.3 ppm is assigned to the internal addition product. The small positive peaks at 206 and 222 ppm have been attributed to the rhodium carbonyls by comparison to the ^{13}CO-enhanced ^{13}C NMR spectrum

Table I
Gas Composition during the Hydroformylation Reaction

time, min	% double bond convn	% H$_2$
0	0	51.0
20	5	51.5
40	10	51.7
64	13	52.5
85	15	54.4
170	22	51.5
300	25	51.6
360	28	52.4

of the catalyst run in C_6D_6 (224 (q), 206 (s), 201 (small br s), and 191 (small s)).

Additional information was obtained from the IR spectra of ^{13}CO-hydroformylated Solprene 308. The IR spectrum shows a lower carbonyl stretch of the formyl group (1690 cm^{-1}) and a lower rhodium carbonyl stretch (1930 cm^{-1}). The translation of these IR stretches confirms that they are both carbonyl stretches and can be explained by the high abundance of ^{13}CO present.

(iv) Hydrogenation under Hydroformylation Conditions. Hydroformylation of Solprene 308 has been accomplished to 30% of the available double bonds despite only a 9.5% pendant double bond content. Even though there has been shown to be internal hydroformylation, the possibility of the hydrogenation of carbon–carbon double bonds cannot be neglected. Since hydroformylation has been reported to be 25 times slower for internal double bonds than pendant double bonds[22] and HRh-(CO)(PPh$_3$)$_3$ is a known hydrogenation catalyst[24] (albeit only for terminal double bonds), it is important to determine if any of the gas consumed is associated with hydrogenation of the polymer. An experiment was run in which gas chromatography was used to monitor the gas mixture above the solution. Under standard reaction conditions a gas sample was taken periodically and injected into the GC. The results are given in Table I.

A decrease in the H_2 concentration would indicate an increased consumption of hydrogen. Calculations indicate that at 30% double bond conversion, if 5% hydrogenation had occurred, the concentration of hydrogen in the reactor head space would be 44%. The concentration of H_2 above the solution remains essentially constant, and therefore there appears to be very little if any hydrogenation of alkene or carbonyl occurring. This was confirmed by IR spectroscopy.

(v) Model Studies. It is surprising that at as low a conversion as 5% of the reaction internal hydroformylation had occurred at approximately the same rate as pendant hydroformylation, since HRh(CO)(PPh$_3$)$_3$ is reported to be more specific to terminal double bonds. In order to gain further insight into the hydroformylation of SBR copolymers, some model compounds were studied.

The monomers were purified to eliminate any peroxides that may have formed on standing, and hydroformylation of all the model compounds was carried out under the following conditions: $[C=C]_0$ = 444 mM, [HRh(CO)-$(PPh_3)_3]_0$ = 2.06 mM, temperature = 50 °C, pressure H_2/CO = 68.9 cmHg, H_2:CO = 1:1, toluene = 15 mL, and $[PPh_3]_0$ = 0 mM.

Table II shows the rates of hydroformylation for the various model compounds studied. The rate of hydroformylation of 1-hexene was more than a hundredfold faster than *trans*-3-hexene, showing the steric effect on hydroformylation of internal unsaturation. Cyclohexene (used to model *cis*-3-hexene) was hydroformylated 3 times as fast as *trans*-3-hexene, showing the steric effect of *trans* compounds.

Table II
Rate of Hydroformylation of Model Compounds

monomer	$-d[C=C]/dt$, mM/s
1-hexene	1.35×10^{-1}
trans-3-hexene	1.20×10^{-3}
cyclohexene	3.73×10^{-3}
styrene	1.26×10^{-1}
α-methylstyrene	1.47×10^{-3}
trans-β-methylstyrene	3.16×10^{-3}
1-phenyl-3-hexene	1.78×10^{-3}
1,4-PBD (>95%)	9.28×10^{-3}
1,2-PBD (>90%)	8.48×10^{-2}
Solprene 308	2.18×10^{-2}

Table III
Rate of Hydroformylation of Various SBR Copolymers

copolymer	microstructure	$-d[C=C]/dt$, mM/s	max carbonyl loading, %
Solprene 308	AB block	2.18×10^{-2}	30.0
Solprene 1205	AB block	2.07×10^{-2}	30.6
Finaprene 410	AB block	1.86×10^{-2}	35.3
Kraton 1184	ABA block	2.03×10^{-2}	32.2
Finaprene 414	radial	1.86×10^{-2}	29.6
Finaprene 411	radial	2.40×10^{-2}	29.9
Stereon 840	random	1.88×10^{-2}	30.7

A series of unsaturated phenyl compounds were studied to determine if the phenyl ring would influence the rate of hydroformylation. It was found that the rate is unaffected by the phenyl ring since the phenylalkenes had essentially the same rate as their alkyl derivatives. It also seems that molecular weight did not dramatically affect the rate of hydroformylation in polymers as the rates are essentially those expected from a composite of small-molecule reaction rates.

The following reactivity scheme was observed:

terminal $\gg$ cis internal > trans internal >
disubstituted compounds

where the phenyl ring and molecular weight had little effect.

It appears then that in polymer systems internal double bonds may be consumed and that this may be attributed to their relatively high concentration.

(vi) Other SBR Copolymers. Several other SBR copolymers have been studied in addition to Solprene 308. These include other AB block, ABA block, radial block, and random block copolymers. They were studied in order to examine the effect that copolymer structure had on the rate of reaction. All reactions were carried out under identical reaction conditions: $[C=C]_0 = 444$ mM, $[HRh(CO)(PPh_3)_3]_0 = 2.06$ mM, temperature = 50 °C, pressure $H_2/CO = 68.9$ cmHg, H_2:CO = 1:1, toluene = 15 mL, and $[PPh_3]_0 = 0$ mM. The results are presented in Table III.

All of the copolymers have essentially the same reaction rate and maximum carbonyl loading. This supports the previous conclusion that states that the styrene content, position of the double bonds, and molecular weight have no effect on the rate of reaction. If the phenyl ring were inductive, one would expect the reaction rate to be much higher for the random copolymers, which is not the case. It is also interesting that the maximum carbonyl loading in all the copolymers is approximately 30%. This could be related to coiling of the polymer chain, preventing the exposure of the double bonds to the catalyst and the entrapment of the catalyst at high conversions due to coiling on the consumption of double bonds.

(vii) Gel Permeation Chromatography. In Figure 7 a comparison of the molecular weight distributions obtained for Solprene 308 and 30% hydroformylated Sol-
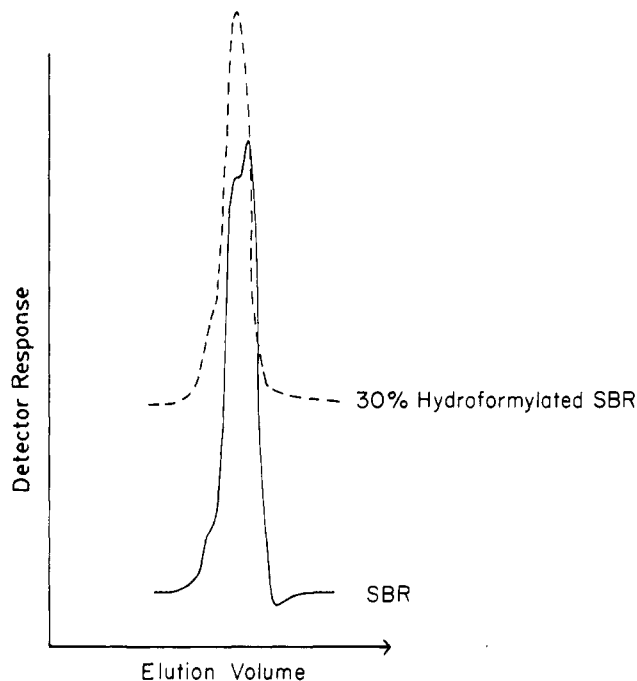

Figure 7. Molecular weight distributions of Solprene 308 and 30% hydroformylated Solprene 308.
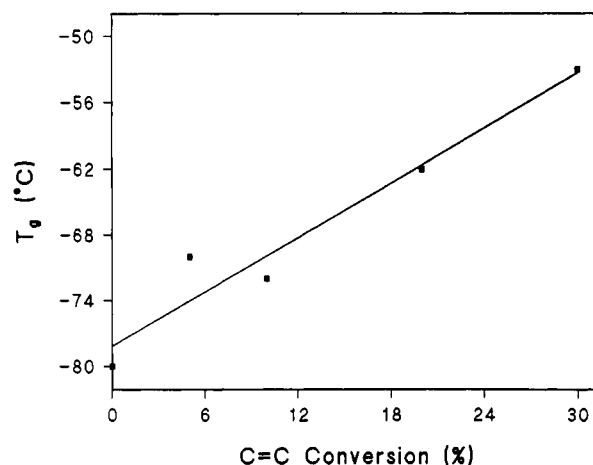

Figure 8. Glass transition temperatures of partially hydroformylated Solprene 308.

prene 308 is presented. Identical distributions to the 30% hydroformylated Solprene 308 were obtained for 5%, 10%, and 20% hydroformylated Solprene 308. The distributions were obtained immediately following the hydroformylation reaction. It was found that microgel formation occurred on standing even if kept in a cold, dark, inert atmosphere. This was especially prevalent at high carbonyl loadings. The distributions obtained immediately following the reaction showed no high or low molecular weight shoulders, indicating that no unwanted side reactions had occurred during the hydroformylation process itself.

(viii) Glass Transition Temperatures. Upon precipitation of the hydroformylated polymers an insoluble product is formed unless great care is taken in preventing exposure to the atmosphere. If great care is taken, a sparingly soluble product is formed although it is only stable for approximately 1 day, even if kept in a cold, dark, inert atmosphere. Glass transition temperatures have been obtained and correspond to the butadiene block. By examination of the glass transition temperatures at various levels of conversion (Figure 8) it can be seen that a linear increase in T_g is consistent with a lightly cross-
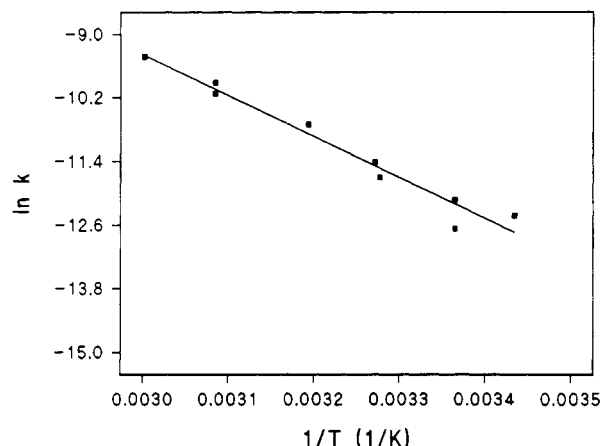
Figure 9. Arrhenius plot for the hydroformylation of Solprene 308 using HRh(CO)(PPh₃)₃.

linked product which accounts for this insolubility. This cross-linking could be the result of aldehyde polymerization, interchain acetal formation, or aldol formation as reported by Ramp and co-workers.[2]

The preceding discussion on the solubility and stability of the product polymer indicates that any further modification reactions involving hydroformylated polymers should be done in situ with a minimum exposure to O_2 and immediately following hydroformylation in order to prevent the production of high molecular weight products. This has been shown to be useful in the production of hydroxymethylated PBD.[15,17]

Kinetic Studies. Hydroformylation kinetic measurements were carried out using Solprene 308. Since only the first 5% of the reaction was found to be first order with respect to carbon–carbon unsaturation, an initial rate method was used to obtain relevant kinetic information.

Kinetic studies of the hydroformylated process are complicated due to the presence of two gases having different solubilities in the chosen solvent. Furthermore, the SBR copolymer contains different types of C=C unsaturation having varying activity as already shown. Nevertheless, the effects of [HRh(CO)(PPh₃)₃], [C=C], [CO], [H₂], [CO + H₂], [PPh₃], solvent, and temperature on the initial rate of the reaction and product distribution were studied. The product distribution was determined using ¹H NMR at 10% hydroformylation.

(i) Effect of Temperature. The effect of temperature on the reaction rate has been studied over the range of 18–60 °C. The following conditions were maintained throughout: [C=C]₀ = 444 mM, [HRh(CO)(PPh₃)₃]₀ = 2.08 mM, [PPh₃]₀ = 0, H₂:CO = 1:1, and total gas pressure = 68.9 cmHg. The apparent activation energy for this range of temperature has been estimated at 64.3 kJ/mol from the Arrhenius plot shown in Figure 9. This value is in the region of chemical reaction control where the diffusion of the reactants does not appear to be the controlling factor governing the reaction.

(ii) Effect of C=C Concentration. Figure 10 shows a plot of the change in the reaction rate with respect to double bond concentration. The temperature was maintained at 51 °C and the total gas pressure at 68.9 cmHg with a 1:1 synthesis gas mixture. The catalyst concentration was maintained at 2.08 mM, and no PPh₃ was added. The effect of C=C concentration on the reaction rate was studied from 27 to 1136 mM. The resultant plot is first order up to approximately 800 mM, at which point the reaction tends toward zero order. Note that the rate of hydrogenation is much lower, also suggesting a lack of hydrogenation under hydroformylation conditions.
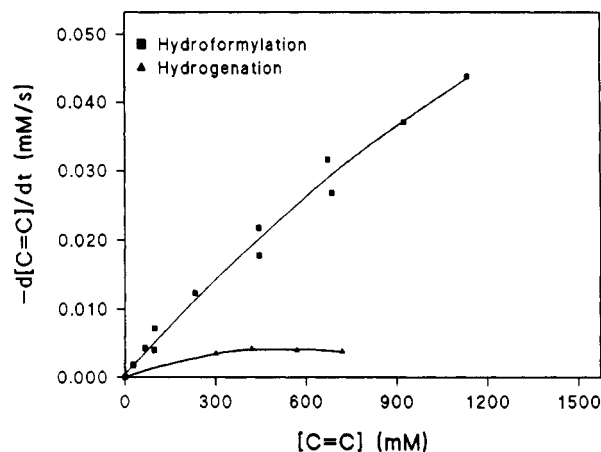

Figure 10. Effect of polymer concentration on the rate of hydroformylation of Solprene 308 using HRh(CO)(PPh₃)₃; [HRh(CO)(PPh₃)₃]₀ = 2.06 mM, pressure H_2/CO = 68.9 cmHg, H_2:CO = 1:1, [PPh₃]₀ = 0, temperature = 51 °C, toluene = 15 mL.

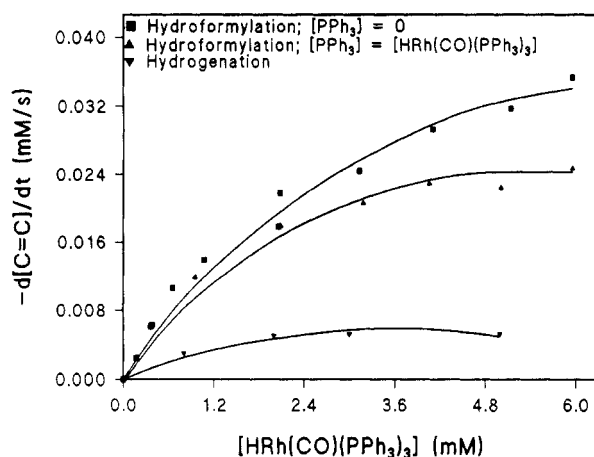**Figure 11.** Effect of catalyst concentration on the rate of hydroformylation of Solprene 308 using HRh(CO)(PPh₃)₃; [C=C]₀ = 444 mM, pressure H_2/CO = 68.9 cmHg, H_2:CO = 1:1, [PPh₃]₀ = 0, temperature = 51 °C, toluene = 15 mL.

(iii) Effect of Catalyst Concentration. The effect of catalyst concentration on the rate of the reaction is shown in Figure 11. The temperature was kept constant at 51 °C, total gas pressure at 68.9 cmHg, [C=C]₀ at 445 mM, and [PPh₃]₀ at 0 mM, and a synthesis gas mixture of 1:1 was used. The catalyst concentration was studied from 0.17 to 5.96 mM. Also included in this plot is the effect of catalyst concentration on the rate of reaction in the presence of an equimolar concentration of PPh₃. The reaction is first order in catalyst concentration up to 1 mM at which point the reaction tends to become zero order. Added PPh₃ inhibits the rate of reaction and forces the reaction to a lower zero-order reaction rate. Again note the low rate of hydrogenation.

(iv) Effect of Added PPh₃. The effect of added PPh₃ on the rate of reaction is shown in Figure 12. The temperature was maintained at 51 °C, the total gas pressure at 68.9 cmHg, [C=C]₀ at 445 mM, and [HRh(CO)(PPh₃)₃]₀ at 2.08 mM, and a synthesis gas mixture of 1:1 was used. The total added concentration of PPh₃ was studied from 0 to 17.2 mM. The rate is inverse first order with respect to added PPh₃. This clearly shows the inhibiting effect of PPh₃, suggesting that a rhodium complex in which at least one PPh₃ ligand had dissociated is responsible for the catalysis.

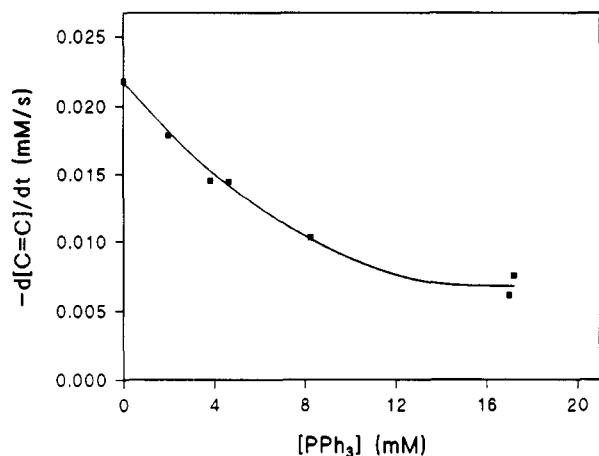Added PPh₃ had no effect on the product distribution. As previously explained this led to the conclusion

Figure 12. Effect of added PPh$_3$ on the rate of hydroformylation of Solprene 308 using HRh(CO)(PPh$_3$)$_3$; [C=C]$_0$ = 444 mM, pressure H$_2$/CO = 68.9 cmHg, H$_2$:CO = 1:1, [HRh(CO)-(PPh$_3$)$_3$]$_0$ = 2.06 mM, temperature = 51 °C, toluene = 15 mL.
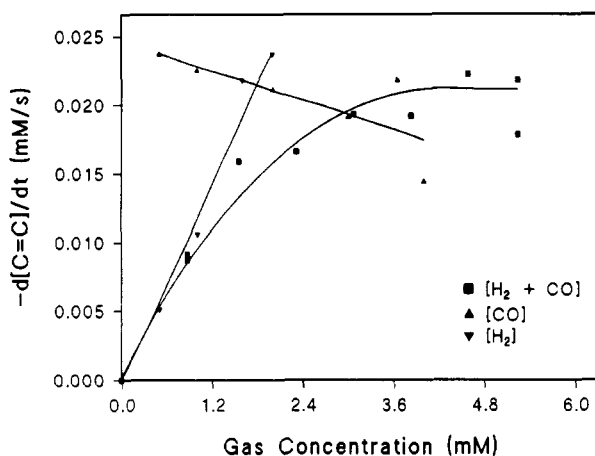
Figure 13. Effect of gas concentration on the rate of hydroformylation of Solprene 308 using HRh(CO)(PPh$_3$)$_3$; [C=C]$_0$ = 444 mM, [HRh(CO)(PPh$_3$)$_3$]$_0$ = 2.06 mM, [PPh$_3$]$_0$ = 0 mM temperature = 51 °C, toluene = 15 mL.

that no Markovnikov addition product was formed. A second conclusion may now be drawn. It is possible that dissociation of a second PPh$_3$ ligand may have occurred and that the monophosphine complex was responsible for catalysis. As there was no change in the product distribution with added PPh$_3$, this also suggests that the monophosphine species is not formed. This may be understood in terms of steric hinderance. Formation of the internal aldehyde is more sterically hindered than the anti-Markovnikov addition product. Therefore, if added PPh$_3$ were preventing the dissociation of a second PPh$_3$ ligand to the less sterically hindered monophosphine complex, then an increase in the anti-Markovnikov product might be expected. This does not appear to occur and therefore leads to the suggestion that it is the diphosphine complex that is responsible for the catalysis.

(v) Effect of Synthesis Gas Concentration. The effect of synthesis gas concentration on the reaction rate can be seen in Figure 13. The temperature was maintained at 51 °C, [C=C]$_0$ at 445 mM, [HRh(CO)(PPh$_3$)$_3$]$_0$ at 2.08 mM, and [PPh$_3$]$_0$ at 0 mM, and a synthesis gas mixture of 1:1 was used. The total synthesis gas concentration was studied from 0.87 to 5.24 mM (20.4–68.9 cmHg). It can be seen that the reaction is first order to zero order with respect to the total synthesis gas concentration.

Also included in Figure 13 are the effect of the [CO] at constant [H$_2$] and the effect of the [H$_2$] at constant [CO].
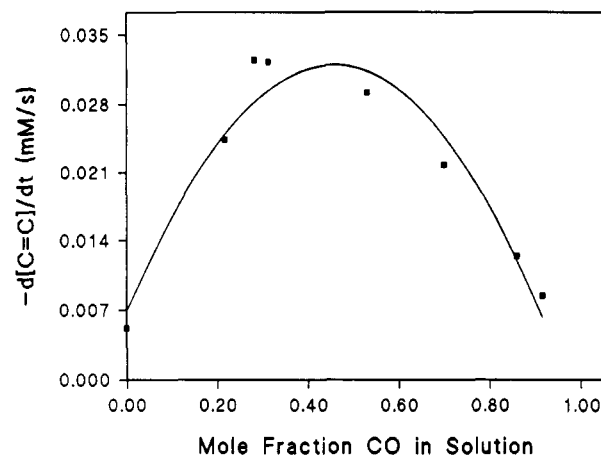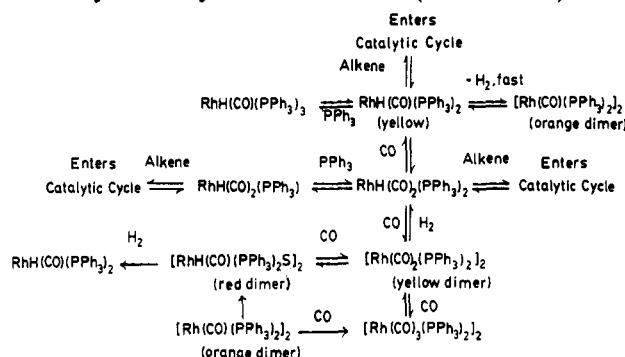

Figure 14. Effect of CO concentration on the rate of hydroformylation of Solprene 308 using HRh(CO)(PPh$_3$)$_3$; [C=C]$_0$ = 444 mM, pressure H$_2$/CO = 68.9 cmHg, [HRh(CO)(PPh$_3$)$_3$]$_0$ = 2.06 mM, [PPh$_3$]$_0$ = 0, temperature = 51 °C, toluene = 15 mL.

Scheme I
Possible Rhodium Species in Solution under Hydroformylation Conditions (S = Solvent)

The reaction rate has a first-order dependence on [H$_2$] and an inverse dependence on [CO].

(vi) Effect of CO Concentration. Figure 14 shows the effect of the mole fraction of CO on the rate of the reaction. The mole fraction of CO was studied from 0 to 0.916. It is of interest to note that the reaction rate reaches a maximum at about 0.3 mole fraction of CO. At a mole fraction below 0.3 there is a decrease in the reaction rate which can be explained by a concentration dependence on CO present in solution for the hydroformylation reaction as well as competing hydrogenation (which has a much lower reaction rate, as can be seen from Figures 10 and 11). At a mole fraction of CO equal to zero (i.e., mole fraction of H$_2$ = 1) the catalyst functions as a hydrogenation catalyst.

It is initially surprising that the reaction rate is not at a maximum at a 0.5 mole fraction of CO. One might expect that below a 0.5 mole fraction of CO, hydrogenation would become dominant and the reaction rate would decrease. This can be explained by examination of the proposed species in solution (Scheme I). Under an atmosphere of hydrogen the formation of HRh(CO)$_2$(PPh$_3$)$_2$ is favored and this has been proposed as the active catalytic species. Below a 0.5 mole fraction of CO the formation of several inactive species is also favored. These inactive species include [Rh(CO)(PPh$_3$)$_2$]$_2$, [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$, and the dicarbonyl species that can form during the catalytic cycle, Rh(COR)(CO)$_2$(PPh$_3$)$_2$. These conclusions are supported by experimental observations as outlined below.

HRh(CO)$_2$(PPh$_3$)$_2$ has previously been reported as the active catalytic species for the hydroformylation of olefins and is the rhodium complex of greatest concentration
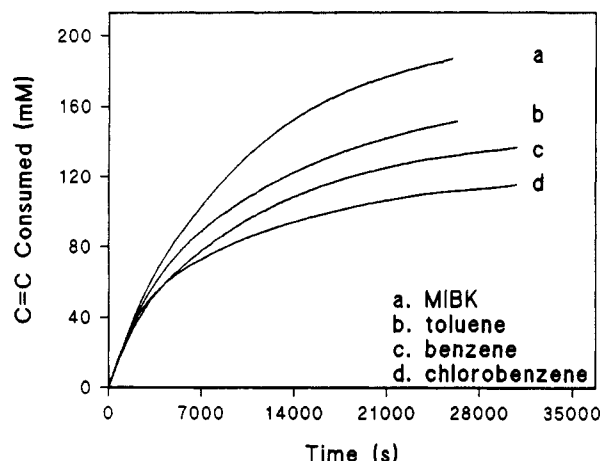
Figure 15. Effect of solvent on the rate of hydroformylation of Solprene 308 using HRh(CO)(PPh₃)₃; [C=C]₀ = 444 mM, pressure H₂/CO = 68.9 cmHg, H₂:CO = 1:1, [HRh(CO)(PPh₃)₃]₀ = 2.06 mM, [PPh₃]₀ = 0, temperature = 51 °C, toluene = 15 mL.

even at $H_2:CO = 6:1$.[22] This has been confirmed experimentally by the addition of the precursor catalyst, HRh-(CO)(PPh₃)₃, to a solution of toluene under an atmosphere of 1:1 synthesis gas. An equimolar gas consumption occurred (0.95–0.99 mol), indicating that a dicarbonyl species is present. As already discussed, the diphosphine complex is present and therefore HRh(CO)₂(PPh₃)₂ appears to be the active catalytic species in polymeric systems.

Under an atmosphere of 1:1 synthesis gas, at the end of the hydroformylation reaction an orange solution results, indicating that some of the catalyst had been converted to the orange dimer. This is supported by IR spectroscopy. The hydride stretch disappears, and the carbonyl stretch shifts to 1970 cm⁻¹. This is consistent with Wilkinson's observations as they proposed that the new band is due to the formation of the orange dimer.[25]

In a CO-rich atmosphere the solution is golden yellow to orange. This can be attributed to the formation of the yellow, orange, and red dimers, as well as Rh(CO)₃(PPh₃)₂. This series of inactive dimers is produced under a CO-rich atmosphere (i.e., mole fraction of CO > 0.5) and accounts for the decreased rates of reaction observed.

Under an atmosphere of relatively high partial pressure of H₂ (i.e., mole fraction of CO < 0.3) the solution turns bright yellow. This can be accounted for by the prevention of the formation of the orange dimer, and the increased rate of reaction can be accounted for by the increased concentration of the catalytically active species, HRh-(CO)₂(PPh₃)₂, in solution.

(vii) Effect of Solvent. Four different solvent systems were studied to see the effect solvent had on the rate of hydroformylation of SBR copolymers. The solvents used were toluene, benzene, chlorobenzene, and methyl isobutyl ketone (MIBK). Figure 15 shows the gas uptake profiles for the hydroformylation of Solprene 308 while using these various solvents. Toluene, benzene, and chlorobenzene had almost identical gas uptake profiles, whereas MIBK had a very different gas uptake profile. When using MIBK, the polymer can be hydroformylated to almost 50% while the aromatic solvents accomplished only 30% conversion. This is an interesting result, suggesting better accessibility of the double bonds. MIBK must be a better solvent for SBR, allowing the polymer molecule to uncoil further and therefore exposing more double bonds. This also prevents entrapment of the catalyst in the polymer coils, allowing for the better transport of the catalyst in solution.

At 10% conversion while using MIBK there was a 1:1 product distribution of the internal addition product and

the anti-Markovnikov addition product as was seen when toluene was used as the solvent. This suggests that the observed change in the gas uptake profile was not a function of a change in the mechanism.

(viii) Product Distribution. The product distribution was also studied under the various reaction conditions described above, and the following variations in the product distribution were observed.

(a) As the temperature was increased from 24 to 60 °C there was a 2-fold increase in the anti-Markovnikov product, indicating an increased specificity toward pendant unsaturation at higher temperatures.

(b) As the polymer concentration was doubled there was a 20% increase in the anti-Markovnikov product, perhaps due to a decreased accessibility of the internal double bonds at high polymer loadings.

(c) As the catalyst concentration was doubled there was a 20% decrease in the production of the anti-Markovnikov product.

(d) At high partial pressures of CO there is an increase in the production of the anti-Markovnikov product. At high total gas pressures the same result is seen, which is also related to the increased CO concentration.

(e) Added PPh₃ had no effect on the product distribution.

Conclusions

Since hydroformylation involves a two-gas system and because of the complex number of rhodium species in solution, no attempt at developing a rate law was made. However, the kinetic data accumulated were useful in providing a better understanding of the active catalytic species which leads to the postulation of a feasible mechanism. Optimization of the reaction rate and product distribution can also be determined.

From Figures 11 and 12, the inhibition of PPh₃ can be seen. As discussed, this and an understanding of the product distribution obtained led to the conclusion that it is a diphosphine complex that is responsible for catalysis. When HRh(CO)(PPh₃)₃ is mixed in a solution of toluene at 51 °C containing no polymer and under 1 atm of synthesis gas, there was 0.95–0.99 mol of gas consumed for every mole of catalyst added. In an atmosphere of H₂ no gas was consumed by the catalyst and therefore the gas consumed must be CO producing the dicarbonyl species, HRh(CO)₂(PPh₃)₂. By altering the gas ratios the inhibiting effect of CO and accelerating effect of H₂ was seen. As discussed this coupled with experimental observations led to the conclusion that HRh(CO)₂(PPh₃)₂ is the active catalytic species. Using this information, the mechanism of hydroformylation of SBR using HRh(CO)(PPh₃)₃ is shown in Scheme II, similar to that proposed for small molecules.[21]

Under the hydroformylation conditions used there were only two of the three possible products observed. This can be explained by the steric hindrance in terminal unsaturation forcing the reaction to anti-Markovnikov addition and, although steric hindrance is present in internal unsaturation, the high concentration of internal double bonds accounts for internal hydroformylation. From the reactivity scheme presented earlier it is probable that cis internal double bonds would be consumed before trans internal double bonds.

As the product sought for further modification or grafting reactions would be the least sterically hindered (or anti-Markovnikov product), optimization of this product is sought. From the study of the product distributions obtained under the various reaction conditions it is clear

Scheme II
Mechanism of Hydroformylation of SBR Using
HRh(CO)(PPh₃)₃

that this may be achieved by running the reaction under the following conditions: temperature = 60 °C, [HRh-(CO)(PPh₃)₃]₀ = 2 mM, [CO + H₂] = 0.005 mM, [C=C]₀ = 1 mM, [PPh₃]₀ = 0 mM, H₂:CO = 1:1, and toluene = 15 mL.

The reaction rate can be optimized by running at 1 atm total pressure at a high partial pressure of H₂. No PPh₃ should be added, as the only function this serves is to decrease the reaction rate, not increase the selectivity. The catalyst concentration should be maintained at 2 mM, as above this concentration there is very little increase in reaction rate (i.e., not cost effective above 2 mM). A high concentration of polymer and a high temperature both serve to increase the reaction rate. From the study of solvent effects it is clear that MIBK and a high partial pressure of H₂ speed up the reaction, but there is no kinetic or product distribution data available and extrapolation of the data obtained for toluene at H₂:CO = 1:1 cannot be assumed. Conveniently the reaction conditions with the exception of a high partial pressure of H₂, coincide with those of the optimization of the product distribution, and therefore the reaction conditions presented above will serve to optimize both the product distribution and reaction rate.

From the study of the hydroformylation of SBR it is evident that the product polymer may be easily characterized using IR and NMR. Small-molecule studies suggest that the phenyl ring and molecular weight do not affect the rate of the reaction, and there was found to be no hydrogenation under typical hydroformylation conditions. Although unstable, the product formed was not cross-linked as observed from GPC studies and will serve as a suitable substrate for further modification reactions.

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