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Catalytic Hydroformylation of Styrene−Butadiene Copolymers

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ABSTRACT: Homogeneous catalytic hydroformylation of styrene−butadiene copolymers was examined with five rhodium catalyst precursors. Under a total pressure of 800 psi H_2 and CO at 40 °C, $[Rh(COD)_2]BF_4$ and $[Rh(COD)Cl]_2$ are more active than $HRh(CO)(PPh_3)_3$, $[Rh(COD)dppb]BF_4$, or $[Rh(COD)]BPh_4$. The hydride $HRh(CO)(PPh_3)_3$ is the most effective of the catalysts at 200 psi and 40 °C. Full conversion of polyolefin could be achieved using $[Rh(COD)_2]BF_4$ or $[Rh(COD)Cl]_2$ as the hydroformylation catalyst. The polyaldehydes, characterized using IR and ^1H and ^{13}C NMR spectroscopy as well as gel permeation chromatography, are stable under the synthesis gas conditions and formed gels in the presence of air.

Introduction

The synthesis of functionalized polymers is of value when there is control of both the degree of functional group addition and the molecular weight distribution of the resulting polymer.[1] However, the polymerization of functionalized monomers has potential problems.[1] Therefore, the selective catalytic chemical modification of polymers has received increasing attention in recent years.[1−9] The metal-catalyzed carbonylation of unsaturated substrates has been widely studied as a method to synthesize carbonyl-containing compounds.[10] Some catalytic reactions are highly *regio*- and *stereo*selective[11] and have been used successfully for the functionalization of polymers.[12] One of the most interesting methods for the catalytic functionalization of polybutadiene and styrene−butadiene copolymers (SBR) is by hydroformylation using cobalt or rhodium catalysts, since polymers containing the reactive aldehydic unit are useful for further transformations.[1−9] The cobalt-catalyzed hydroformylation of polybutadiene was carried out under relatively severe conditions.[1] Also, it suffers from a lack of specificity due to the potential reduction of the aldehyde groups to alcohols and isomerization or hydrogenation of the residual unsaturation in the substrates. These undesirable side reactions gave high-M_w, gelled materials.[1] The rhodium catalyst, $HRh(CO)(PPh_3)_3$, has been used for the hydroformylation of polybutadiene and SBR in high selectivity at low−moderate conversion.[2−6] However, cross-linking occurred when there was a higher conversion of vinyl groups into aldehydes.[2,3] So far, most of the reported catalytic hydroformylation reactions have involved polymers having M_w less than 200 000.[2,6] To our knowledge, the hydroformylation of polybutadiene or SBR with M_w over 200 000 has not been reported to give formyl loading higher than 50%.

Most of the catalytic hydroformylation reactions of polybutadiene and SBR used $HRh(CO)(PPh_3)_3$ as the catalyst precursor under moderate conditions.[2−6] Recently, $Rh(acac)(CO)_2$ (acac = acetyl acetonate) has been reported to be a highly reactive catalyst for the hydroformylation of a low molecular weight ethylene propylene diene monomer polymer. However, deactivation of $Rh(acac)(CO)_2$ in the catalytic hydroformylation of polybutadiene has been reported,[3] and a full conversion of C═C to aldehyde cannot be achieved using $HRh(CO)(PPh_3)_3$ as the hydroformylation catalyst due to the steric hindrance of the polymer coils.[2,4] Thus far, literature reports on the rhodium-catalyzed hydroformylation of the olefinic units in polymers showed incomplete conversion to the aldehydes. One of us has developed a number of selective catalytic hydroformylation processes,[11a,b] as well as highly selective catalytic hydrocarboxylation of polybutadiene with palladium catalysts.[12] We now wish to report the highly selective hydroformylation of SBR affording up to 98% loading of formyl groups without unwanted side reactions using $[Rh(COD)_2]BF_4$, where COD is *cis,cis*-1,5-cyclooctadiene, as the catalyst.

Experimental Section

Polymers. The styrene−butadiene copolymers (SBR) investigated were Duradene 707 and Duradene 709, supplied by Firestone Synthetic Rubber & Latex Co., without further treatment. These polymers are slightly branched, random solution polymerized copolymers of butadiene and styrene. The amount of bound styrene in Duradene 707 is 23.5 wt %, of which <1% exists as a block styrene with M of 222 800 and polydispersity of 2.88. Duradene 709 contains 35 wt% of bound styrene, of which 5% exists as block styrene with M_w of 252 300 and polydispersity of 2.61. The microstructure of these polymers consists of 10% 1,2-vinyl-, 40% 1,4-*cis*-, and 50% 1,4-*trans*-polybutadiene. The NMR spectrum shows a broad signal at 7.2−7.0 ppm for the phenyl groups, CH_2═C gives a signal at 5.0−4.8 ppm, and protons associated with CH═CH and CH═CH_2 fall in the range 5.6−5.2 ppm in the ^1H NMR spectra. The allylic and benzylic protons appeared at 2.0 and 2.5 ppm, respectively.

$HRh(CO)(PPh_3)_3$, $[Rh(COD)Cl]_2$, and $[Rh(COD)]BPh_4$ were prepared according to literature methods.[13] $[Rh(COD)dppb]BF_4$, $[Rh(COD)_2]BF_4$, and solvents were purchased from Aldrich and were used as received. The solvents were purified using standard procedures.

All solution ^1H and ^{13}C NMR spectra were recorded on either a Varian XL-300 or a Gemini-200 NMR spectrometer using $CDCl_3$ as the solvent and Me_4Si (TMS) as the internal standard. Solutions of polyaldehyde for NMR experiments were prepared by replacing THF with $CDCl_3$ under a nitrogen atmosphere: an aliquot (2 mL) of produced polyaldehyde was removed immediately from the autoclave after reaction. This solution was concentrated to less than 0.1 mL by passing N_2 through the solution at room temperature, and then 1 mL of $CDCl_3$ was added to dissolve the polymer. This was repeated three times to prepare the $CDCl_3$ solution for NMR experiments due to the instability of polyaldehyde if solvent is completely removed.[6]

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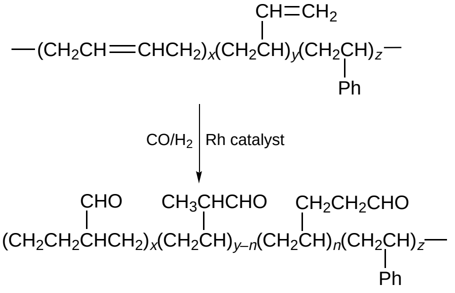
Infrared data were collected on a Bomem MB-100 FT-IR spectrometer using a thin mull of polymer coated on a KBr plate. Gel permeation chromatography (GPC) was run using a Waters 510 HPLC pump operating on a 1 mL/min flow rate with three consecutive Styragel HT columns effective from 5×10^2 to 4×10^6 and detected using a Waters 410 differential refractometer detector. HPLC-grade THF was used as eluant. The molecular weight for the polymers are based on calibration with polybutadiene standards. The polyaldehyde solution for GPC analysis was prepared immediately following the hydroformylation reaction by dilution with the eluant to a concentration of 0.8 mg of the polyaldehyde in 1 mL of THF.

All reactions unless otherwise specified were carried out in a glass liner placed in a 45 mL stainless steel autoclave.

General Procedure for the Hydroformylation Reactions. A glass liner containing a solution of SBR (130 mg) and a rhodium catalyst (1 mol %) in THF (10 mL) was placed in a 45 mL autoclave equipped with a magnetic stirring rod. The autoclave was flushed three times with CO and then pressurized to the desired level. The hydrogen line was attached to the autoclave, and then the pressure was gradually increased to the desired level. The autoclave was placed in an oil bath on a heater stirrer preset to the reaction temperature. After the appropriate reaction time, the autoclave was cooled to room temperature, the excess H_2/CO gas was released, and the resulting polymer was immediately analyzed using GPC, ^1H and ^{13}C NMR, and IR under a N_2 atmosphere.

Results and Discussion

Treatment of SBR with synthesis gas (1:1 CO/H_2) and a catalytic amount of a rhodium catalyst gave hydroformylated products (eq 1). Three different types of



$$-(\mathrm{CH_2CH{=}CHCH_2})_x(\mathrm{CH_2}\overset{\mathrm{CH{=}CH_2}}{\mathrm{CH}})_y(\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}})_z- \xrightarrow[\text{Rh catalyst}]{\mathrm{CO/H_2}} -(\mathrm{CH_2CH_2}\overset{\mathrm{CHO}}{\mathrm{C}}\mathrm{HCH_2})_x(\mathrm{CH_2}\overset{\mathrm{CH_3CHCHO}}{\mathrm{CH}})_{y-n}(\mathrm{CH_2}\overset{\mathrm{CH_2CH_2CHO}}{\mathrm{CH}})_n(\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}})_z- \quad (1)$$

formyl groups may be produced according to the microstructure of SBR which contains 10% 1,2-vinyl- and 90% 1,4-polybutadiene. These polyaldehydes were characterized using IR and NMR (^1H, ^{13}C) spectroscopy, and GPC. The infrared spectra showed two new bands, an intense absorption at 1724 cm^{-1} and a band of medium strength at 2711 cm^{-1}, as well as a decrease in the intensity of 968 and 911 cm^{-1} absorption bands. These four characteristic absorptions are attributed to $\nu_{C=O}$ and ν_{C-H} of the CHO groups and δ_{C-H} of CH= and CH_2=, respectively. Comparing the ^1H NMR spectrum of the starting polymer with that of polyaldehyde, the signals at 5.6−5.2 ppm (C*H*=C*H* and C*H*=CH_2) and 5.0−4.8 (CH_2=) either decreased appreciably in intensity or completely disappeared, depending on the extent of conversion. Meanwhile, the polyaldehyde showed two new signals, corresponding to internal and terminal CHO groups, respectively, in both the ^1H and ^{13}C NMR spectra. The chemical shift of 9.7 ppm in the ^1H NMR, and the corresponding signal at 202.3 ppm in the ^{13}C NMR, is assigned to the anti-Markovnikov addition product. All the formyl groups grafted on the backbone and the Markovnikov addition product of the terminal vinyl groups in SBR gave a broad signal at 9.5 ppm in the ^1H NMR spectrum and at 204.8 ppm in the ^{13}C NMR spectrum. Due to the lack of splitting and signal broadening, the branched aldehyde and the internal aldehyde cannot be distinguished in this manner. These results are consistent with the literature values of 9.7 and 9.5 ppm in the ^1H NMR as well as 202.1 and 204.7 ppm in the ^{13}C NMR for aldehyde-grafted SBR.[2,4a]

Table 1. Catalytic Hydroformylation of SBR

polymer no.	catalyst[a]	conditions[b]	yield (%)	conversion (%)
Duradene 707				
1	HRh(CO)(PPh$_3$)$_3$	1/1, 40, 19	28	27
2	[Rh(COD)Cl]$_2$	1/1, 40, 19	5	6
3	[Rh(COD)$_2$]BF$_4$	1/1, 40, 22	15	16
4	[Rh(COD)dppb]BF$_4$	1/1, 40, 19	6	6
5	[Rh(COD)]BPh$_4$	1/1, 40, 18	3	3
Duradene 709				
6	HRh(CO)(PPh$_3$)$_3$	1/1, 40, 16	23	22
7	HRh(CO)(PPh$_3$)$_3$	1/1, 40, 36	58	60
8	[Rh(COD)dppb]BF$_4$	4/4, 40, 20	13	13
9	[Rh(COD)dppb]BF$_4$	4/4, 40, 46	38	36
10	[Rh(COD)$_2$]BF$_4$[c]	2/1, 25, 15	17	17
11	[Rh(COD)$_2$]BF$_4$[c]	4/4, 40, 44	98	100
12	[Rh(COD)Cl]$_2$	4/4, 40, 44	87	100
13	[Rh(COD)Cl]$_2$	4/4, 40, 19	30	45
14	HRh(CO)(PPh$_3$)$_3$	4/4, 40, 72	81	80
15	HRh(CO)(PPh$_3$)$_3$	4/4, 40, 36	55	53
16	[Rh(COD)$_2$]BF$_4$	4/4, 40, 36	85	87
17	[Rh(COD)Cl]$_2$	4/4, 40, 72	81	100

[a] 1 mol % of rhodium to vinyl groups. [b] Conditions: P_{H_2}/P_{CO} (100 psi), temp (°C), time (h). [c] 1.78 mol % of rhodium to vinyl groups.

It has been reported that the selectivity for the hydroformylation of polybutadiene and SBR can be calculated from gas consumption and IR experiments.[2,4a] The signal for the phenyl protons at 7.0−7.2 ppm remains unchanged in the ^1H NMR spectrum of the polyaldehyde compared to SBR. The resonances for the CHO groups appeared at 9.7−9.5 ppm, while that for C*H*= of the reactant occurred at 5.6−5.2 ppm. These signals are very well resolved, and thus the signal for the phenyl protons can be used as the internal standard to determine the selectivity for catalytic hydroformylation using THF as the reaction solvent.

Studies show HRh(CO)(PPh$_3$)$_3$ is a highly selective hydroformylation catalyst for SBR and polybutadiene, with no hydrogenation and unwanted side reactions observed for up to 50% conversion.[2] Therefore, the accuracy of the measurement for hydroformylation selectivity using NMR integration was tested in the hydroformylation reaction using HRh(CO)(PPh$_3$)$_3$ as the catalyst. Table 1 compares the results calculated using the signal for the phenyl protons as the internal standard against those assuming that all of the olefin consumed afforded aldehyde. It is seen that the conversion of olefin and yield of aldehyde using HRh(CO)(PPh$_3$)$_3$ give essentially the same result. These results, as expected, show that the selectivity for aldehyde is 100% using HRh(CO)(PPh$_3$)$_3$ as the catalyst. At optimized conditions, there is 80% conversion of double bond units to aldehydes. However, efforts to improve the conversion failed (maximum of 44% of available double bonds for Duradene 707 and 80% conversion for Duradene 709) possibly because of steric hinderance.[2,4a] It has been shown that the active rhodium catalyst does not remain attached to any polymer chain for an extended time period.[4] Small rhodium complexes would be expected to penetrate the polymer coils to give higher double-bond conversion into aldehyde. Hence, several rhodium complexes, [Rh(COD)Cl]$_2$, [Rh(COD)$_2$]BF$_4$, [Rh(COD)dppb]BF$_4$, and [Rh(COD)]BPh$_4$ (Rh^{zwt}), widely used as precursors for catalytic hydroformylation of

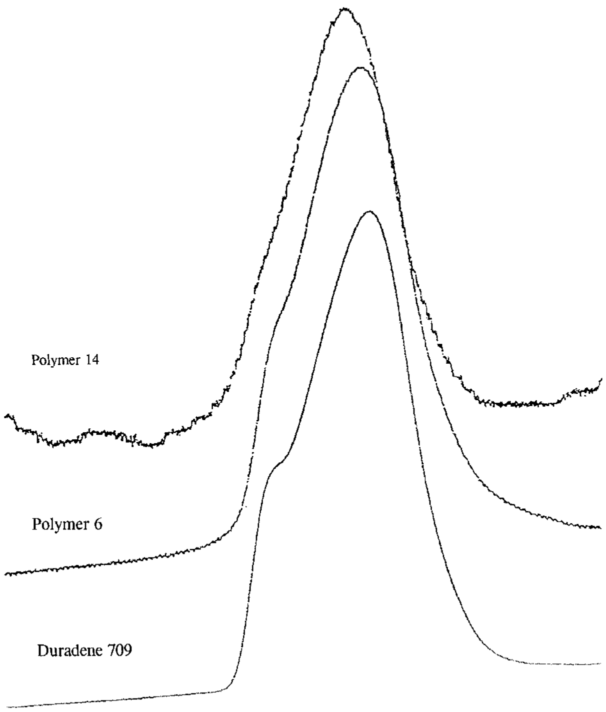


Figure 1. Comparison of the molecular weight distribution of Duradene 709 with its 23% and 80% hydroformylated polymers.

monomeric unsaturated compounds, have been examined as the hydroformylation catalyst for SBR (Table 1). Both Duradene 707 and 709 can be catalytically hydroformylated using all of the four rhodium complexes under mild reaction conditions. The results suggest that $HRh(CO)(PPh_3)_3$ is the most active catalyst for the hydroformylation reaction at pressures of 200 psi H_2/CO (1/1) at 40 °C.

The dimer of chloro(1,5-cyclooctadiene)rhodium complex is appreciably less active than $HRh(CO)(PPh_3)_3$ for the hydroformylation of SBR (Table 1, entries 1 and 2) at 200 psi of syngas and 40 °C. Studies have shown that $[Rh(COD)Cl]_2$ is a more active hydroformylation catalyst under higher pressures.[14] Therefore, a pressure of 800 psi for syngas with 1:1 of H_2/CO was used for the hydroformylation of SBR. The complete conversion of double bonds in SBR resulted in 44 h at 40 °C. However, the selectivity for hydroformylation was 87%, with 13% being assumed with double-bond hydrogenation. The catalytic hydroformylation of SBR by $[Rh(COD)_2]BF_4$ is superior to that by $[Rh(COD)Cl]_2$ at 200 psi CO/H_2 pressure. However, complete conversion of the polyolefin cannot be achieved under the reaction conditions. The hydroformylation activity of $[Rh(COD)_2]BF_4$ was enhanced at 800 psi syngas (Table 1, entries 10 and 11). Importantly, 98% selectivity for the hydroformylation of SBR with the complete conversion of available double bonds has been achieved using $[Rh(COD)_2]BF_4$ (Table 1, entry 11). These results (Table 1) suggest that both $[Rh(COD)Cl]_2$ and $[Rh(COD)_2]BF_4$ show higher reactivity for the catalytic hydroformylation of SBR than $HRh(CO)(PPh_3)_3$.

A comparison of the molecular weight distribution of polyaldehyde and Duradene 709 is shown in Figure 1. Identical distributions were obtained for 80% and 23% of hydroformylated Duradene 709, using $HRh(CO)(PPh_3)_3$ as the catalyst. Similar GPC molecular weight distributions were observed using $[Rh(COD)Cl]_2$, $[Rh(COD)_2]BF_4$, and $[Rh(COD)dppb]BF_4$ as the catalysts for the hydroformylation of Duradene 707 and Duradene 709. These distributions were obtained immediately following the hydroformylation reaction which showed no high or low molecular weight shoulders, and the results are given in Table 2. An increase in the molecular weight average is expected for polyaldehydes since the addition of aldehyde functionality will increase the molecular weight of each butadiene unit from 54.1 to 84.1 g/mol. A theoretical calculation of M_w could be obtained based on the conversion and is compared in Table 2 with the experimental results. As expected, for different percentages of formyl group loadings, the measured M_w are in accord with the calculated molecular weights except for polymer 11. These results indicate that no gross cross-linking or chain scission occurred during the hydroformylation process. Polymer 11 (98% formyl loading), giving much higher values of the polydispersity and M_w than the anticipated value, is likely cross-linked. We found that the hydroformylation reaction solutions of SBR, which were exposed to air for 30 min after reaction, could not be filtered through a 0.25 μm filter. Also, a diluted solution of polymer 11 could not be filtered after exposure to air for 2 h. Because polyaldehydes with >80% of formyl loading did not form gels (polymers 14, 17, 16, and 12) and an immediately diluted solution of polymer 11 can be filtered and analyzed with GPC (data in Table 2), the formation of gels should not be related to the hydroformylation process. Since the undiluted polyaldehyde reaction solutions form gels in less than 30 min after exposure to air, cross-linking should not be the aggregation of individual polymer molecules in the dilute solution. Therefore, it can be safely assumed that the gel formation of polyaldehyde was caused by polyacetal formation both intramolecularly to give a macroring and intermolecularly to give cross-linked polymer. This is confirmed by the ^{13}C NMR spectrum for the gel which shows a broad signal of acetal at 110−117 ppm and by the infrared spectrum showing a new absorption band at 1165 cm^{-1}.

Table 2. Molecular Weight Averages for Duradene 709 and Hydroformylated Products

polymer no.	−CHO loading (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	calcd $M_w \times 10^{-3}$
Duradene 709	0	96.8	252.3	2.61	
8	13	91.5	260.1	2.84	264.1
6	23	90.8	252.0	2.78	273.2
9	38	93.0	268.8	2.89	286.9
7	58	105.4	386.5	3.67	305.1
14	81	101.8	302.7	2.97	326.1
17	81	56.4	331.0	5.80	326.1
16	85	72.3	361.8	5.00	329.7
12	87	68.9	318.5	4.62	331.5
11	98	112.9	720.6	6.38	341.5

Since the polyaldehydes are stable under synthesis gas conditions, gel formation of polyaldehydes must be related to the exposure of the polyaldehyde solutions to air following the hydroformylation reaction. Therefore, GPC analysis of dilute solutions of polyaldehydes was performed after various interval times of polyaldehyde solutions exposed to air. The results are illustrated in Figure 2. It is seen that the 81% hydroformylated Duradene 709 gave higher M_w and polydispersity (Table 3) after exposure of the polymer solution to air. The same results have been observed in a 44% hydroformylated Duradene 707 (Figure 3) and other polyaldehydes. This suggests that O_2 accelerates the formation of acetal. As seen in Table 3, a smaller increase in M_w and polydispersity was observed in a low

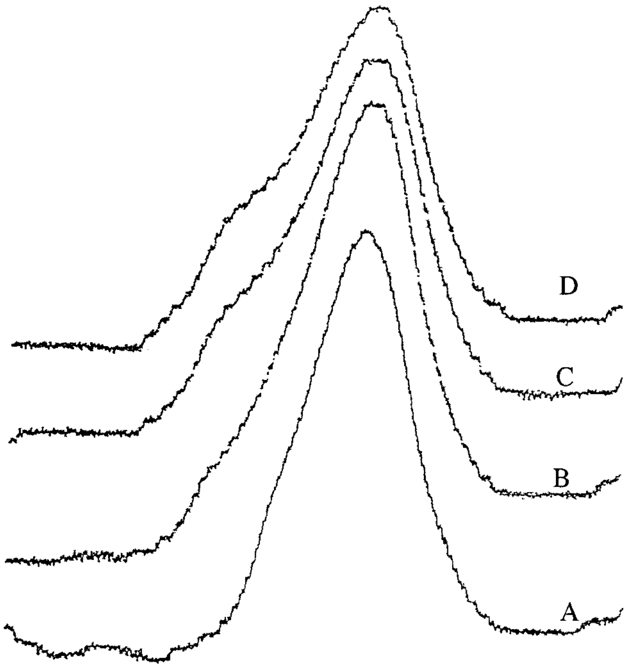


Figure 2. Comparison of the molecular weight distribution of polymer 14 before and after exposure to air for different time intervals: (A) polymer 14; (B) exposure to air for 45 min; (C) 105 min; (D) 150 min.

Table 3. Comparison of Molecular Weight Averages of Polyaldehydes after Exposure to Air

polymer no.	−CHO loading (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
Duradene 709	0	96.8	252.3	2.61
6	23	90.8	252.0	2.78
6a[a]		90.4	363.1	4.02
14	81	101.8	302.7	2.97
14a		108.1	614.5	5.68
14b[b]		109.5	1079.5	9.86
14c[c]	98	116.1	1453.2	12.51
11		112.9	720.6	6.38
11a		128.1	1419.7	11.08

[a] 45 min after the polymer was exposed to air at room temperature (in 0.8 mg/mL of THF solution). [b] 105 min after exposure to air. [c] 150 min after exposure to air.

hydroformylated polymer, after it was exposed for the same period of time as a highly hydroformylated polymer. This observation is consistent with the results that polymers with higher concentrations of aldehyde loading form gels easier than a polymer with a lower concentration of aldehyde.[2,4] The above discussion indicates that gel formation for a polyaldehyde is not related to the hydroformylation process under the reaction conditions. The slightly higher M_w and polydispersity for polymer 11 must be caused by the more facile formation of acetal because the complete conversion of polyolefin produces a considerably greater concentration of aldehydic groups.

The zwitterionic Rh complex, [(COD)Rh-η^6-$C_6H_5BPh_3$] (Rh^{zwt}), can also catalyze the conversion of up to 80% of the double bonds of SBR to hydroformylated products under 1200 psi pressure of syngas and at 150 °C for 18 h. Chain degradation of the polymer occurs under the severe reaction conditions, suggesting that it is a less reactive hydroformylation catalyst. Rh^{zwt} has been used for the highly *regio*- and *stereo*selective catalytic hydroformylation of unsaturated compounds.[11a,b] Unfortunately, the expected selectivity for the Markovnikov product was not observed as was found in simple molecules. This may be due to the steric effect of the polymer chain coils which block the accessibility of Rh^{zwt}.

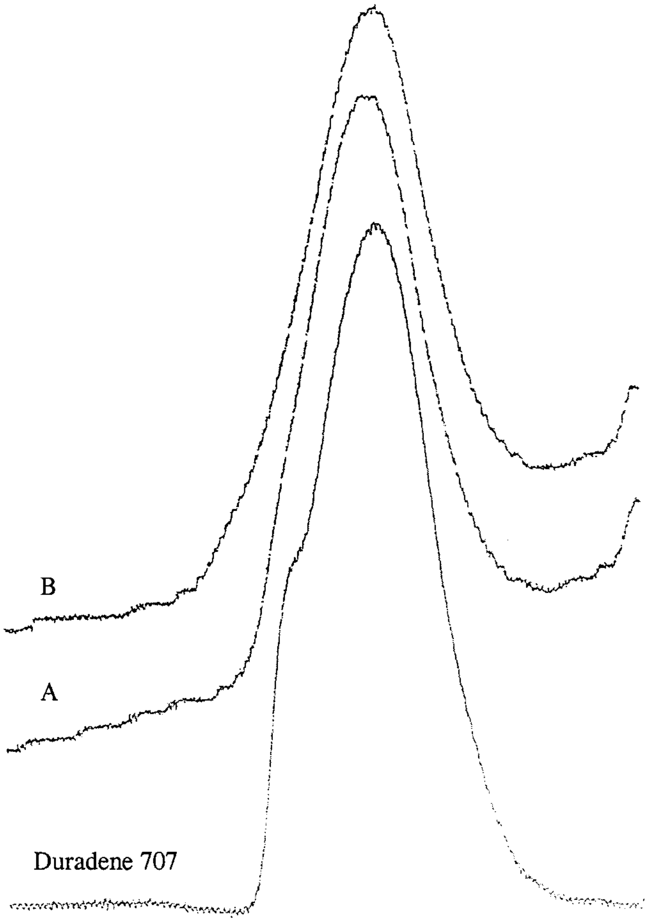


Figure 3. Comparison of the molecular weight distribution of Duradene 707 to a 44% hydroformylated polymer before (A) and after (B) it was exposed to air for 45 min.

Conclusion

The highly selective and reactive hydroformylation of SBR using $[Rh(COD)_2]BF_4$ as the catalyst, to afford complete conversion of olefin to aldehyde, was achieved at 40 °C and 800 psi syngas; use of $[Rh(COD)Cl]_2$ as the catalyst precursor gave complete conversion with 13% of hydrogenation. The polyaldehydes were not cross-linked during the hydroformylation process using any of the five rhodium complexes as the catalyst precursors. Gel formation of polyaldehyde was caused by the formation of acetal which was accelerated by the presence of O_2.

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