

Article

Hydrogenation of Styrene-Butadiene Rubber Catalyzed by Tris(triisopropylphosphine)hydridorhodium(I)

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Abstract: The hydrogenation of C=C bonds in styrene–butadiene rubber (SBR), catalyzed by RhH(P(i-Pr)₃)₃, was experimentally investigated. Tris(triisopropylphosphine)hydridorhodium(I), RhH(P(i-Pr)₃)₃ (i-Pr=CH(CH₃)₂) was prepared by using rhodium chloride (RhCl₃), tetrahydrofuran (THF), triisopropylphosphine (P(i-Pr)₃) and a sodium mercury amalgam. The effect of catalyst/polymer ratio, reaction temperature, and hydrogen pressure on the reactivity of the catalytic system has been studied. The optimal experimental condition was obtained. The hydrogenated styrene-butadiene rubber (HSBR) was analyzed by FT-IR and ¹H-NMR. In the absence of any additives, the conversion of C=C bonds in SBR could easily reach 95% in a short period of time, and no obvious cross-linking was observed. The dynamic properties of SBR did not change after the hydrogenation of the unsaturated C=C bonds. A preliminary reaction mechanism was also proposed. This study provides a new route, not only for the chemical modification of SBR by using a rhodium complex but also for the hydrogenation of other unsaturated polymers, such as diene-based rubbers.

Keywords: styrene-butadiene rubber; hydrogenation; hydrido rhodium complex; triisopropylphosphine



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1. Introduction

Styrene Butadiene Rubber (SBR) is one of the most widely used synthetic rubbers in the world. This copolymer has good strength, outstanding resilience, and high elongation at break [1]. It has been used in various industrial applications, including the manufacture of tires, wire and cable insulation, shoe soles, adhesives, membranes, belts and hoses, toys, and surgical and sanitary products [2]. However, SBR has poor aging properties due to the presence of unsaturated carbon-carbon double bonds (C=Cs) in its butadiene segment [3]. An improved material can be obtained by hydrogenating the double bonds present in SBR [4]. Hydrogenated styrene butadiene rubber (HSBR) exhibits improved thermal, oxidation, ozone, and UV (ultraviolet) resistance [5]. These properties allow HSBR to be used in extended applications, which include the abovementioned applications as well as other applications that require weather and temperature resistance [6–10].

Recently, several catalysts have been reported to be effective in the hydrogenation of SBR [11,12]. Barrios et al. utilized a Ziegler-Natta-type catalyst made from a reaction between NiAcAc and n-BuLi to selectively hydrogenate 1,2-vinyl and 1,4-trans bonds in a styrene-butadiene copolymer [13]. He Y. et al. prepared diimide and used it in the hydrogenation of SBR to obtain HSBR with a degree of hydrogenation of more than 90%; however,

in contrast to the $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ -catalyzed hydrogenation, this hydrogenation process produces a number of side-reactions and even promotes cross-linking of the polymer, which affects the elastomer processing properties [5]. Guo et al. synthesized a $\text{Pd}/\text{g-C}_3\text{N}_4$ catalyst and performed a non-homogeneous catalytic hydrogenation reaction of SBR under mild conditions, and the results showed that the HD of HSBR could reach up to 95% when the addition of Pd NPs was 1.0%. It was found that the unique nanostructure of $\text{g-C}_3\text{N}_4$ in this catalyst could enhance its catalytic activity [14]. Menossi et al. obtained hydrogenated PBs with 86~100% hydrogenation degree by hydrogenation of polybutadiene (PB) using Wilkinson/triphenylphosphine as a homogeneous catalyst/co-catalyst. Fourier infrared spectroscopy revealed that the 1,2-vinyl double bond on the PB molecular chain was more reactive than the 1,4-trans bond during the hydrogenation process due to the smaller spatial site resistance. In addition, they found that the process of hydrogenation of PB using the homogeneous catalyst $\text{RhCl}(\text{PPh}_3)_3/\text{PPh}_3$ at high pressure has some drawbacks, i.e., it leads to excision as well as cross-linking reactions of the molecular chains, which broaden the molecular weight distribution of the polymer [15]. Holleben et al. proposed a way to hydrogenate SBR using a Pd/C catalyst with limonene as a hydrogen source [16]. Jamanek et al. provided a hydrogenation process using monocyclopentadienyl titanium (IV) [6]. He et al. claimed that group VII metal carboxylates with one or more aluminum alkyls are useful hydrogenation catalysts [5]; whereas Dath et al. favored a catalyst with at least one group Ia, Ib, IIb, VIb, VIIb, or VIII metal on the support of an alkaline earth metal silicate [17]. In addition to SBR, the $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ catalyst can also be used in other diene-based rubbers, such as NBR. In our past research, we found that $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ can not only reduce the $\text{C}=\text{C}$ double bond in NBR but also reduce nitrile to primary amine, and the nitrile content can be reduced from 40% to less than 10% in 5 h at 60 °C and 500 psig H_2 [18].

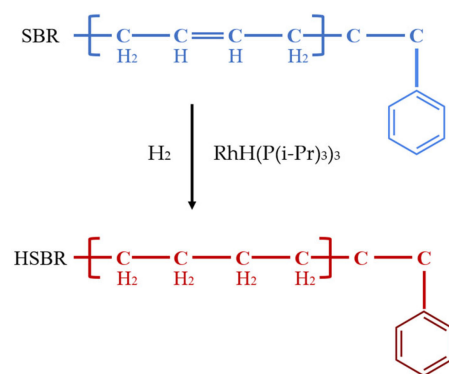
Some of the main concerns in the hydrogenation of SBR are minimizing the amount of catalyst metal residue left in the products [19] as well as preventing cross-linking [4]. The presence of metal residue might give rise to product contamination and limit its use [20]. Ko et al. described a process to remove the metal catalyst from the hydrogenated polymer solution from around 200 ppm to 5–10 ppm [19]. Yet, metal residue removal is a costly process. The removal requires expensive processes due to the corrosive nature of the compound consisting of the catalyst or formation of acid salts in the process and may involve multiple stages or further treatment [20]. Hence, it is essential to use an efficient catalyst that can be used in a small amount to hydrogenate SBR in a reasonable time such that removal of the metal catalyst becomes unnecessary.

In this communication, the possibility of utilizing Tris(triisopropylphosphine) Hydrido Rhodium (I) for the hydrogenation of SBR at a low catalyst concentration under mild reaction conditions, which has not yet been reported in the open literature, is carefully examined. Various experimental conditions have been thoroughly investigated and an optimal condition has been obtained for the hydrogenation. $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ has proved to be a very active and versatile catalyst in many areas, such as the water gas shift reaction (WGS) [21,22] and the photochemical dehydrogenation of alcohols [23,24], etc. The solvent used in this research is tetrahydrofuran as a very common solvent for styrene polymerization and SBR production.

2. Results and Discussion

2.1. Analysis of HSBR (Hydrogenated SBR)

The dynamic properties of SBR did not change after the hydrogenation of unsaturated $\text{C}=\text{C}$ bonds. The Molecular Weight increases from 250,000 Dalton to 280,000 Dalton MW when 94% conversion is achieved; meanwhile, the hydrodynamic radius (R_H) remains at 19–20 nm and the viscosity increases slightly from circa 15 cP to 25 cP. There is no gel formation observed during and after the hydrogenation process. The structural sketch of SBR before and after hydrogenation is shown in Scheme 1.



Scheme 1. Catalytic hydrogenation of SBR.

Fourier Transform Infrared (FT-IR) was employed to determine the Degree of Hydrogenation (conversion of carbon-carbon double bonds). The FT-IR spectra of SBR and HSBR are shown in Figure 1. The spectrum of SBR indicates peaks at 699 cm^{-1} due to the styrene unit, 757 cm^{-1} due to 1,4-cis, 910 cm^{-1} due to 1,2-vinyl, and 967 cm^{-1} due to 1,4-trans unsaturated units. As the level of hydrogenation increases, the peak at 910 cm^{-1} (attributed to vinyl $-CH_2-$) and the peaks at 967 and 994 cm^{-1} (assigned to $-CH-$ trans units) have disappeared in Figure 1b compared to Figure 1a, and the peak at 1450 cm^{-1} due to the $-CH_2-$ deformation vibration increases. The disappearance of all characteristic absorbencies of $C=C$ suggests nearly quantitative hydrogenation of the $C=C$ bonds. A new peak at 723 cm^{-1} for cis-1,4 saturated units appears in the spectra of the hydrogenated SBR (HSBR) samples, which has been significantly overlapped by the peak at 699 cm^{-1} for styrene. The disappearance of all characteristic peaks of $C=C$ (757 cm^{-1} due to 1,4-cis, 910 cm^{-1} due to 1,2-vinyl, 967 cm^{-1} due to 1,4-trans unsaturated unit) also proved that the hydrogenation degree of SBR(HSBR) reached 100%. A peak at 1374 cm^{-1} due to the deformation vibration of the $-CH_3$ group is also clear in the spectra of HSBR due to the reduction of the pendent vinyl group. Two peaks at 2852 cm^{-1} and 2925 cm^{-1} due to the $-CH-$ stretching vibration of the $-CH_2-$ group (methylene) increase with an increase in the level of hydrogenation. The absorption peak at 699 cm^{-1} shows no change in intensity, reflecting that the aromatic ring of the styrene unit is not reduced under the given hydrogenation conditions. The retention of the same intensity of the characteristic absorbance for the aromatic rings at 699 , 1450 , and 1493 cm^{-1} indicates that the hydrogenation is highly selective toward olefinic bonds.

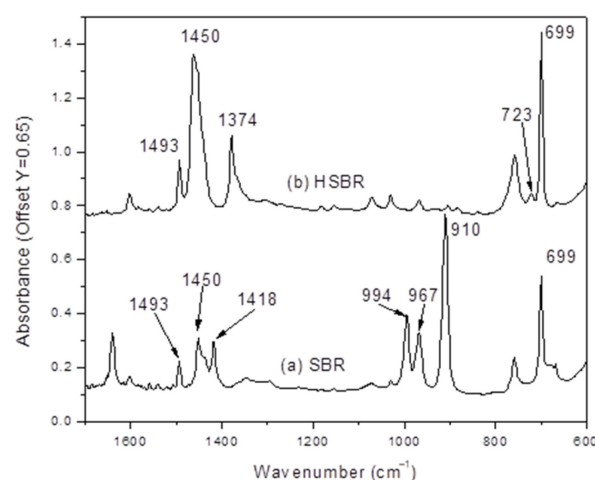


Figure 1. IR Spectra of SBR (a) and HSBR (b).

Figure 2 shows a representative ^1H -NMR spectrum of non-hydrogenated SBR and partially hydrogenated SBR. Major peaks are observed in the aliphatic (0.5–2.8 ppm) and olefinic (4.6–5.8 ppm) regions. Aromatic protons show peaks in the region of 6.8–7.2 ppm. Detailed assignments of typical NMR peaks for SBR can be found in many publications [25]. There is no change in the intensity of the peaks due to styrene, reflecting the stability of the aromatic ring toward hydrogenation. With the progress of hydrogenation, the olefinic peak area decreases considerably. Concurrently, a peak at 1.25 ppm assigned to the methylene sequence increases with the increase in the hydrogenation of the double bonds. The peak at 4.99 ppm due to the 1,2-butadiene unit is almost absent from the spectrum of hydrogenated SBR, indicating that 1,2-butadiene units are more rapidly hydrogenated than 1,4 units. The characteristic peaks in the olefin (4.6–5.8 ppm) region before hydrogenation in Figure 2b almost completely disappeared, indicating that the SBR has been completely hydrogenated with a 100% hydrogenation degree; this is in accordance with the IR results discussed above.

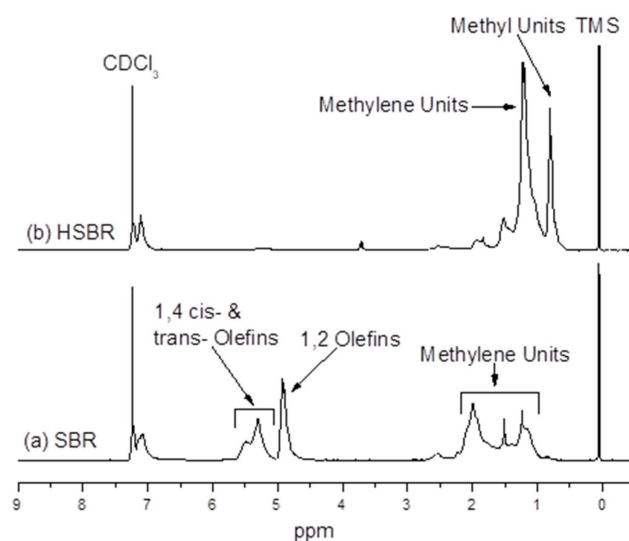


Figure 2. ^1H -NMR spectra of SBR (a) and HSBR (b).

2.2. Activity Testing

In Figure 3, the effect of temperature on the hydrogenation of SBR is clearly shown (Entry 1 to 5 in Table 1). From 60 °C to 120 °C, since there is more energy for molecules to move faster, the final hydrogenation degree of C=C increases from 60% to 92% after reacting for 5 h. However, a further increase in temperature does not improve the performance. Instead, when the temperature is as high as 140 °C or higher, the reactivity of the catalyst does not increase much or even drops to a lower level. There are two possible causes for this: firstly, the high temperature causes the rubber solution to become unstable. According to the published literature regarding SBR hydrogenation, the highest temperature reported is 160 °C; there is some coagulation of SBR observed when the temperature is higher than 120 °C. Secondly, the catalyst being used is not very stable under high temperatures, such as 140 °C or higher. $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ might be deactivated at such a high temperature, as reported by Yoshida et al. [26,27].

Table 1. Summary of Results of SBR Hydrogenation.

Entry	[Rh] (mmol)	Rh (wt%)	Temperature (°C)	Pressure (psig)	Hydrogenation Degree (mol%)
1	0.1	4.63	60	500	88
2	0.1	4.63	80	500	90
3	0.1	4.63	100	500	92
4	0.1	4.63	120	500	92

Table 1. Cont.

Entry	[Rh] (mmol)	Rh (wt%)	Temperature (°C)	Pressure (psig)	Hydrogenation Degree (mol%)
5	0.1	4.63	140	500	63
6	0.025	1.16	100	500	71
7	0.05	2.315	100	500	73
8	0.075	3.47	100	500	92
9	0.1	4.63	100	500	92
10	0.125	5.79	100	500	92
11	0.15	6.95	100	500	94
12	0.175	8.10	100	500	95
13	0.2	9.26	100	500	95
14	0.1	4.63	100	100	87
15	0.1	4.63	100	300	90
16	0.1	4.63	100	500	94
17	0.1	4.63	100	700	94
18	0.1	4.63	100	900	91
19	0.1	4.63	100	1100	91

Commercial SBR, 2.5 wt% in THF, total volume = 100 mL, reaction time = 5 h; The error was within 5%.

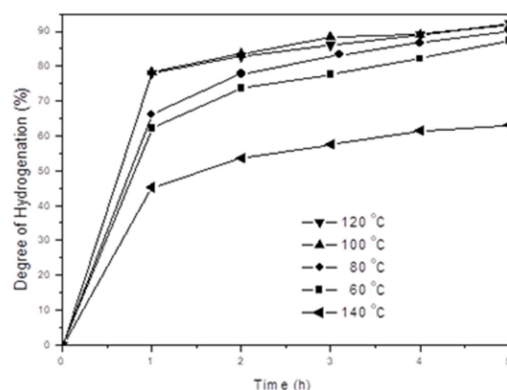


Figure 3. Effect of temperature on the hydrogenation of SBR (0.06 g catalyst (0.1 mmol Rh), 100 mL 2.5 wt% SBR in THF, 500 psig).

Figure 4 clearly shows that the reaction occurs faster by increasing the amount of catalyst added from 0.025 mmol to 0.125 mmol (Entry 6 to 10 in Table 1), especially from 0.05 mmol to 0.075 mmol. This can be explained that there are more C=C bonds at the surface of the SBR particle and they are the easiest to be hydrogenated; more catalysts will remove those unsaturated bonds on the surface much faster. When 0.125 mmol catalyst was added, the degree of hydrogenation was almost 95% within 4 h. However, on adding a greater amount of catalyst into the system (Entry 11 to 13 in Table 1), the hydrogenation process did not proceed any faster, which probably can be explained in that it is harder or impossible for excess catalyst to be transported into the SBR particles. It was worth noting that a high Rh/rubber ratio (rhodium amount > 0.2 mmol) may cause rubber coagulation during the experiment, which could be caused by excessive rhodium salt. Singha [28], reported that $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ caused gel formation when it was added to an NBR latex at 75 °C and 1 atmosphere of N_2 , which is confirmed by previous work in our group [29].

The influence of hydrogen pressure on the SBR hydrogenation reaction was also examined (Entry 14 to 19 in Table 1). Figure 5 shows that the degree of hydrogenation decreases as the hydrogen pressure decreased. It seems that H_2 pressure does have some effect on the hydrogenation of carbon-carbon double bonds in SBR using this rhodium hydrido complex because the higher H_2 pressure results in a higher concentration of H_2 in the aqueous phase and makes hydrogenation of carbon-carbon double bonds easier. However, it is worthwhile to mention that the hydrogenation degree only varies from 90% to 95% when the hydrogenation pressure is between 300 psig and 1100 psig; therefore, it

may be concluded that the hydrogenation rate is mainly controlled by the catalyst mass transfer within the SBR particles.

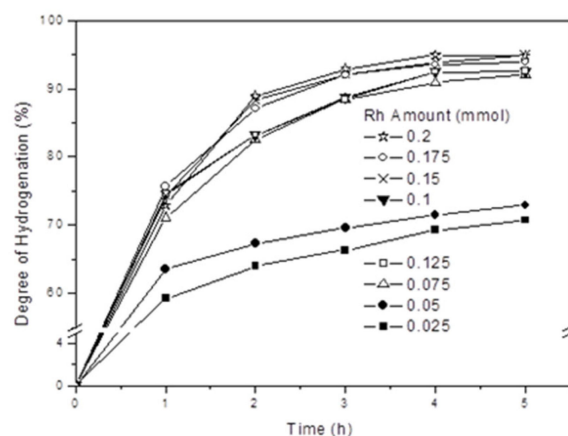


Figure 4. Effect of catalyst loading on the hydrogenation of SBR (100 mL SBR in THF (2.5 wt%), 100 °C, 500 psig, 250 rpm).

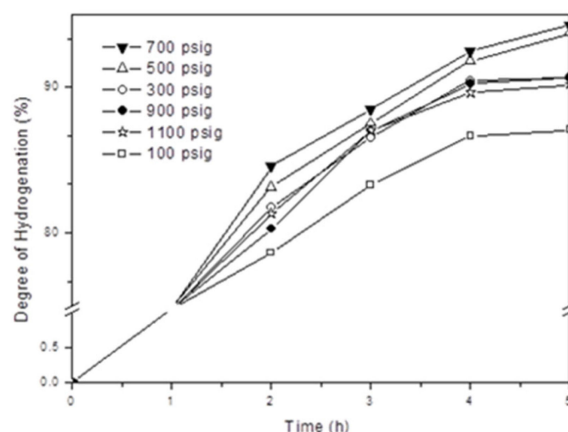


Figure 5. Effect of hydrogen pressure on the hydrogenation of SBR (0.06 g catalyst (0.1 mmol Rh), 100 mL SBR in THF (2.5 wt%), 100 °C).

2.3. Preliminary Study of Proposed Mechanism

A possible reaction mechanism using $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ shown in Figure 6 is proposed for the hydrogenation of C=C in styrene butadiene rubber (SBR). The reaction commences with the $\text{P}(\text{i-Pr})_3$ ligand dissociation of the $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ catalytic species [30]. This intermediate readily reacts with H_2 to form the species $\text{RhH}(\text{H}_2)(\text{P}(\text{i-Pr})_3)_2$ [31]. It is proposed that when SBR is in the presence of this catalytic species, the species will bond with SBR across the carbon-carbon double bond similar to the mechanism. Nelson et al. [30] reported the hydrogenation of alkenes using Wilkinson's catalyst. The reaction undergoes alkene migratory insertion during the hydrogenation process, and then reductive elimination of the hydrogenated SBR. The original $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ catalytic species can be reproduced with the addition of $\text{P}(\text{i-Pr})_3$.

The technology of hydrogenation of SBR has been widely studied and thoroughly understood. Singha et al. [28] reported a similar mechanism taking place using a ruthenium-based Wilkinson-type catalyst whose structure is very similar to that of $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$, the catalyst being used in this study. The family of RhClPR_3 and RhHPR_3 , where R represents different ligands, has been widely studied [28,32]. The most well-known of these is Wilkinson's Catalyst ($\text{R} = \text{P}(\text{i-Pr})_3$). It has been theorized that all catalysts of this type react in the same way to hydrogenate olefins in both small molecules and polymers.

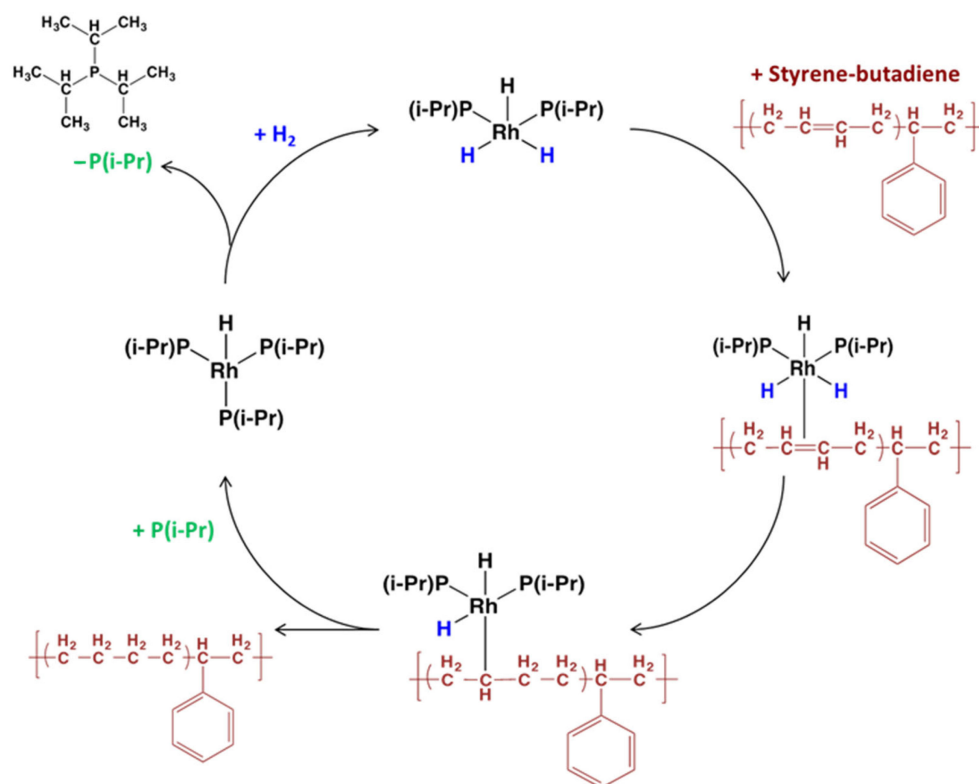


Figure 6. Possible mechanism for the hydrogenation of SBR using $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$.

3. Materials and Methods

3.1. Materials

The catalyst used, $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$, was prepared according to the reported recipe [33] with all the chemicals being purchased from Fisher Scientific (Thermo Fisher Scientific Waltham, MA, USA) or Sigma-Aldrich (Sigma-Aldrich, Inc. St. Louis, MO, USA). The hydrogen gas utilized in this investigation was oxygen-free (less than 1 ppm) with a purity of 99.999% obtained from Praxair Canada (Mississauga, CA). Reagent-grade tetrahydrofuran was obtained from Caledon Laboratory Chemicals (Georgetown, ON, Canada). Styrene butadiene rubber (SBR) was provided by Lanxess Inc., (Elmira, ON, Canada) containing 50 wt% vinyl content and 25 wt% styrene content, with a density of 0.94 g/cm³.

3.2. Apparatus

Hydrogenation experiments were carried out in a 300 mL autoclave manufactured by Parr Instruments (Parr Instrument Company, Moline, IL, USA). The precursor catalyst was added to a small glass drum (drum wall thickness less than 0.2 mm) and then carefully placed in the catalyst addition device at the head of the reactor. The head of the reactor must always be kept straight to prevent the drum (containing the catalyst) from falling or spilling. In most cases, the total volume of NBR latex is 100 mL. The mixed solution is degassed with nitrogen or argon for at least 30 min and then heated to reaction temperature. The catalyst is then injected into the mixture with hydrogen (100 psig) and the hydrogen pressure is increased to the pressure required for the reaction (500–1000 psig). The hydrogen pressure and reaction temperature were kept constant throughout the experiment [18].

A Thermo Nicolet 6700 Fourier Transform Infrared Spectroscopy (Thermo Fisher Scientific Inc. Waltham, MA, USA) was operated using OMNIC 8.2 software; a Thermo HAAKE MARS II Rheometer operated (Thermo Fisher Scientific Inc. Waltham, MA, USA) with RheoWin4 Software and equipped with cone/plate sensors and Pressure Sensor D400/300 (with PZ38b Rotor) was used for viscosity measurement; A Malvern Viscotek GPCmax VE 2001 (Malvern Instruments Ltd, Malvern, UK) Gel Permeation Chromatography (GPC) with a TDA 305 Triple Detector Array (Malvern Instruments Ltd, Malvern, UK) and UV

detector 2500 was used for molecular weight determination. A column set was employed consisting of three 300 × 8 mm columns filled with a PL (polyhydroxyl) gel with an average particle size of 10 µm; A Bruker 300 MHz Nuclear Magnetic Resonance (NMR) (Bruker Corporation, Billerica, MA, USA) equipped with a QNP Probe device was employed for chemical structure analyses.

3.3. Hydrogenation Procedure

Solutions of SBR (2.5 wt%) in tetrahydrofuran (THF) were initially prepared and placed on a shaker for one day to allow for the complete dissolution of the rubber. Hydrogenation of SBR was performed in a Parr 4560 Mini Bench Top Reactor (300 mL) (Parr Instrument Company, Moline, IL, USA) equipped with a Parr 4842 Controller (Parr Instrument Company, Moline, IL, USA). A designated amount of the desired rubber solution was added to the reaction vessel. The reactor was then bolted shut after assembling all parts and tested for leaks with 100 psig H₂ gas. Once the reactor was assembled and tested for leaks, the vessel was degassed using H₂ gas. To degas the reactor, the reaction vessel was placed in an ice/water mixture and the gas output valve was connected to a hose placed in a bucket of water. With all valves closed the reactor was turned on to rotate at 250 rpm. The H₂ inlet valve was opened and the reactor vessel was filled with 100 psig H₂ gas, then the hydrogen inlet valve was closed and then the gas output valve was opened to allow H₂ to slowly leak out of the output hose causing a trail of small bubbles in the bucket of water.

Once the pressure in the reactor was at 0 psig and bubbles stopped flowing, the H₂ input valve was opened slightly while the output valve into the water bucket was fully opened. The reactor was kept this way for at least 30 min as H₂ was allowed to flow in and out of the reaction vessel. Once the time was up, both valves were quickly closed, the ice/water mixture was removed and the vessel was dried. The heating mantle for the reactor was placed around the vessel and the heater was adjusted to set the reaction temperature.

While the reaction vessel was reaching the desired temperature, a designated amount of catalyst was prepared in a glove box. The catalyst was obtained using a gas-tight syringe under an argon atmosphere. Once the desired temperature was reached the gas exhaust valve was quickly opened to release pressure built up during heating. The catalyst was quickly taken from the argon environment and inserted into the reactor through a valve. All valves were closed, the temperature was increased if desired and the pressure was increased to a certain value, usually 500–1000 psig H₂. Samples were taken normally every hour for 5 to 6 h and measured on sodium chloride disks via FT-IR.

For each experiment, many repeats were conducted to confirm consistency and accuracy, that the results matched very well, and the error was within 5%.

3.4. Determination of the Degree of Hydrogenation

In order to determine the Degree of Hydrogenation (conversion of carbon-carbon double bonds) in the hydrogenation reaction, samples were taken at certain time intervals during the experiments. A Thermo Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) was used for Fourier Transform Infrared (FT-IR) analysis of the samples. The degree of hydrogenation was calculated based on the method developed by Marshall et al. [34–36] and modified by De Sarkar et al. [37,38]. A₉₆₇, A₉₀₉, and A₆₉₉ represent the absorbance values of trans, vinyl, cis, and styrene units at 967, 909, and 699 cm^{−1}, respectively. As the aromatic ring of the styrene unit is unaffected during hydrogenation, the 699 cm^{−1} peak serves here as the internal standard. The detailed calculation is listed below:

$$A_{699} = \text{absorbance at } 699 \text{ cm}^{-1}$$

$$A_{910} = \text{absorbance at } 910 \text{ cm}^{-1}$$

$$A_{967} = \text{absorbance at } 967 \text{ cm}^{-1}$$

$$A(910) = A_{910}/A_{699} \text{ and } A(967) = A_{967}/A_{699}$$

$K(910) = 1.7635$, a constant specific to this peak

$K(967) = 0.4717$, a constant specific to this peak

$$\text{Degree of Hydrogenation (mol \%)} = 1 - (A(910) \times 50\%/K(910) + A(967) \times 50\%/K(967)) \times 100\% \quad (1)$$

3.5. Synthetic Procedure of $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$

A mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.98 g, 4 mmol) and $\text{P}(\text{i-Pr})_3$ (1.6 mL, 8 mmol) was stirred in 35 mL of THF for 20 h and then concentrated under vacuum to give a solid product. THF (35 mL), $\text{P}(\text{i-Pr})_3$ (1.0 mL, 5 mmol), and 1% Na/Hg (40 g) were sequentially added to the solid product and stirred at room temperature for 20 h. The reaction solution was filtered and dried under a vacuum (0.001 mm Hg). The solid was recrystallized from pentane (0.5 mL) containing free $\text{P}(\text{i-Pr})_3$ to give yellow crystals of $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ (1.4 g, 60%) [18].

3.6. Cross-Linking or Gel Formation Determination

Gel formation (gelling or gelation) was determined by checking if the resultant HNBR was totally soluble in MCB(monochlorobenzene), MEK(methylethylketone) or THF(tetrahydrofuran) at room temperature by the naked eye. It can be also confirmed via viscosity using a Thermo HAAKE MARS II Modular Advanced Rheometer System (Thermo Fisher Scientific Inc. Waltham, MA, USA) equipped with Pressure Sensor D400/300 (with PZ38b Rotor) (Thermo Fisher Scientific Inc., Waltham, MA, USA). Once the gel was found, the gel content can be checked for some samples according to the ASTM D3616-95 method (A weighed sample is allowed to stand 16 to 20 h in a suitable solvent. The sol, or soluble portion, is removed from the rubber mixture and the viscosity and gel is determined on this solution).

4. Conclusions

An effective catalytic system for the hydrogenation of carbon-carbon double bonds in SBR was successfully developed. In the absence of any additives, the C=C bonds in SBR were hydrogenated by using $\text{RhH}(\text{P}(\text{i-Pr})_3)_3$ to more than 95% in a relatively short period of time and no obvious cross-linking was observed. This is the first time such a versatile and convenient catalyst has been applied for polymer hydrogenation. Optimization of the experimental conditions has been carried out for eco-friendly and energy-saving purposes. The dynamic properties of SBR did not change after the hydrogenation of the unsaturated C=C bonds. This study provides a new route not only for the chemical modification of SBR by using a rhodium complex but also for the hydrogenation of other unsaturated polymers such as diene-based rubbers.

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Conflicts of Interest: The authors hereby declare no conflict of interest.

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