

Influence of 1,2 Units Content on the Hydrogenation of Polydienes by TSH

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ABSTRACT: The influence of 1,2 vinyl content on hydrogenation of SBR and BR rubbers with high molecular weight by a noncatalytic method using *p*-toluenesulfonylhydrazide (TSH) as reagent was investigated. Results show an increase of hydrogenation percentage with molar ratio of the reagents, temperature, and reaction time. The degree of hydrogenation depends strongly on the microstructure of the rubber mainly on the amount of 1,2 content. Infrared spectroscopy (FTIR) was used to confirm the microstructural characteristics of the hydrogenated rubbers. The degree of hydrogenation was determined by io-

dometry method and ¹H-NMR analysis. The change in the thermal behavior of hydrogenated rubbers was followed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), which showed a difference in flexibility chain and thermal stability. The kinetic studies demonstrate that the diimide reduction follows a first-order reaction with respect to olefin substrate. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1195–1203, 2011

Key words: noncatalytic hydrogenation; polydienes; 1,2 content, *p*-toluenesulfonylhydrazide

INTRODUCTION

Hydrogenation is a synthetic way of obtaining polymers with a certain degree of unsaturation, resulting in new materials with different properties. The literature^{1–3} reports that hydrogenation improves weathering, thermo-oxidative resistance; decreases gas permeability, and in some cases, improve the mechanical properties. There are many methods to hydrogenate polydienes which involve catalytic and noncatalytic processes.^{3–7} Catalytic hydrogenation has been the conventional process to hydrogenate polydienes, but some problems are reported, such as high cost of equipment and catalyst, as well as low efficiencies resulting from limited solubility.¹ Hence, some studies investigated the noncatalytic procedure as an alternative to substitute catalytic hydrogenation in unsaturated polymers.^{2,3,6–8} Generally high concentrations of the TSH reagent are used, making the noncatalytic method expensive due to the high price

of TSH reagent. Furthermore, no broad investigation is reported in the literature, especially involving BR and SBR rubbers with different microstructures and high molecular weight using mild reaction conditions. Schultz and Turner⁹ report that through the hydrogenation of polybutadiene and poly(styrene-*co*-butadiene) rubbers, materials can be formed that resemble low density polyethylene and poly(styrene-*co*-butylene) as illustrated in Figure 1, depending on the microstructure of the primary polymer chain. The purpose of this study was to determine the best conditions for a controlled hydrogenation of high molecular weight butadiene rubber (BR) and poly(styrene-*co*-butadiene) rubber (SBR) with different microstructures, mainly with different amount of 1,2 unit towards hydrogenation using diimide generated *in situ* by thermolysis of *p*-toluenesulfonylhydrazide (TSH). The reaction is homogeneous and generally performed under nitrogen gas at atmospheric pressure. A small molar ratio TSH/C=C like 0.5/1 and temperature at 112°C were used.

The modification was qualitatively monitored by fourier transform infrared (FTIR) analysis and the degree of hydrogenation was determined by iodometry method and hydrogen nuclear magnetic resonance spectroscopy (¹H-NMR) analysis. The thermal behavior of the hydrogenated products was monitored by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

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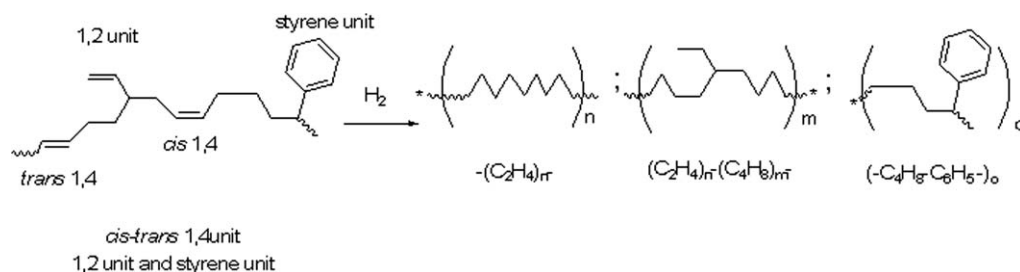


Figure 1 Schematic representation of *cis* and *trans* BR 1,4 units, 1,2 units and styrene unit and the structures formed behind the hydrogenation process.

EXPERIMENTAL

Material

The rubbers used in this study were: *cis*BR (4% of 1,2 unit, $M_w = 527,000$); BR47 (47% 1,2 unit; $M_w = 475,680$); BR70 (70% 1,2 unit, $M_w = 496,360$); SBR32 (32% 1,2 unit; 25% styrene unit, $M_w = 206,600$); SBR62 (62% 1,2 unit; 21% styrene unit; $M_w = 214,800$). The rubbers were supplied by Lanxess AG and used without further purification. The molecular weight was determined by chromatography analysis using PS as standard. P-toluenesulfonylhydrazide (TSH) (97%, mp 108–110°C), *o*-xylene, chlorobenzene obtained from Aldrich Chemical were used as purchased. The hydrogenation samples were designated H_*cis*BR, H_BR47, H_BR70, H_SBR32, and H_SBR62 where inscription H represents the hydrogenation process. The degree of hydrogenation is written between parentheses at the end, for instance, H_*cis*BR(58) is a *cis*BR with a degree of hydrogenation equal to 58% sample.

Hydrogenation procedure

Hydrogenation was carried out in *o*-xylene, using TSH as diimide promoter, the hydrogenation agent, under a nitrogen atmosphere, magnetic stirring, reflux and temperature at 112°C ± 1°C. The molar ratio TSH/C=C varied between 0.15 and 2.00. Samples were removed at different reaction times and precipitated in methanol. The hydrogenated rubbers were purified by dissolution in an appropriate solvent, reprecipitated and dried under vacuum at 40°C.

Characterization

Infrared spectroscopy

The chemical structure of the primary and hydrogenated samples was monitored by FTIR^{2,3,10} using an FTIR Instrument (Model Nicolet 60-Nexus). The FTIR spectra were obtained on films casted from toluene on NaCl plates using a resolution of 4 cm⁻¹ and 32 scans.^{7,11}

Degree of hydrogenation

The degree of hydrogenation was determined by ¹H-NMR and by the iodometry method, using xylene as solvent, as described in the literature.^{10–15} The ¹H-NMR analysis was performed in an NMR Spectrometer (Varian 300 MHz) in CDCl₃ solution. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS).

Thermal analysis

Thermal stability was investigated by thermogravimetric analysis, TGA (Hi-Res TGA 2950 Thermogravimetric analyzer-TA Instruments), at 10°C/min, under N₂ atmosphere, from room temperature to 600°C. The maximum decomposition temperature (T_{max}) of each sample was obtained from the peak maxima of the DTG curve. The thermal behavior was monitored by differential scanning calorimetry, DSC (Modulated DSC 2920-TA Instruments) at a heating rate of 10°C/min under N₂ atmosphere in aluminum pans. The temperature interval used for the analysis was appropriate to the chemical nature of the rubber, as well as the degree of hydrogenation of the sample. The glass transition (T_g) and melting (T_m) temperatures were determined from the second scan. By-products formed by the TSH decomposition were controlled by FTIR and ¹H-NMR analysis.^{11,16}

RESULTS AND DISCUSSION

FTIR analysis

Depending on the degree of hydrogenation and the primary microstructure of the polymer chain, materials resembling polyethylene or similar products can be formed by hydrogenation. The FTIR spectra of nonhydrogenated and hydrogenated *cis*BR samples are illustrated in Figure 2(a). The bands at 1640 cm⁻¹ attributed to C=C bonds, as well the band at 735 cm⁻¹, which corresponds to the stretching vibration of the *cis*-1,4 unit, gradually disappear as the hydrogenation proceeds. H_*cis*BR samples initially show an absorbance around 720 cm⁻¹, corresponding to the $(-CH_2-)_{n \geq 4}$ rocking vibration for amorphous

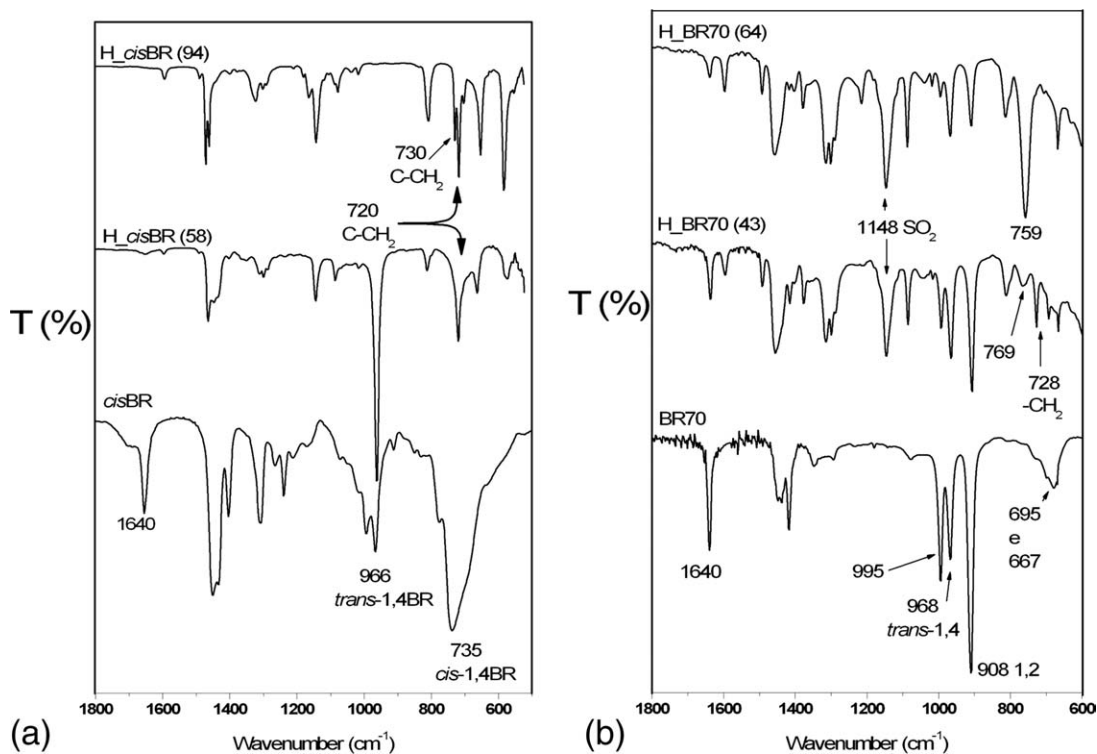


Figure 2 (a) FTIR spectra of *cis*BR and H_*cis*BR samples. (b) FTIR spectra of BR70 and H_BR70 samples.

state polymer chains^{12,15} and for high degrees of hydrogenation [H_*cis*BR (94)] another band around 730 cm⁻¹, associated with (-CH₂-)_{n>4} rocking vibration for the crystalline state is detected.

The BR47 as well as the BR70, Figure 2(b), with the hydrogenation, show a gradual decrease of the bands at 968 cm⁻¹, due to *trans*-1,4 unit present in the BR, as well as at 995 cm⁻¹ and 908 cm⁻¹, due to

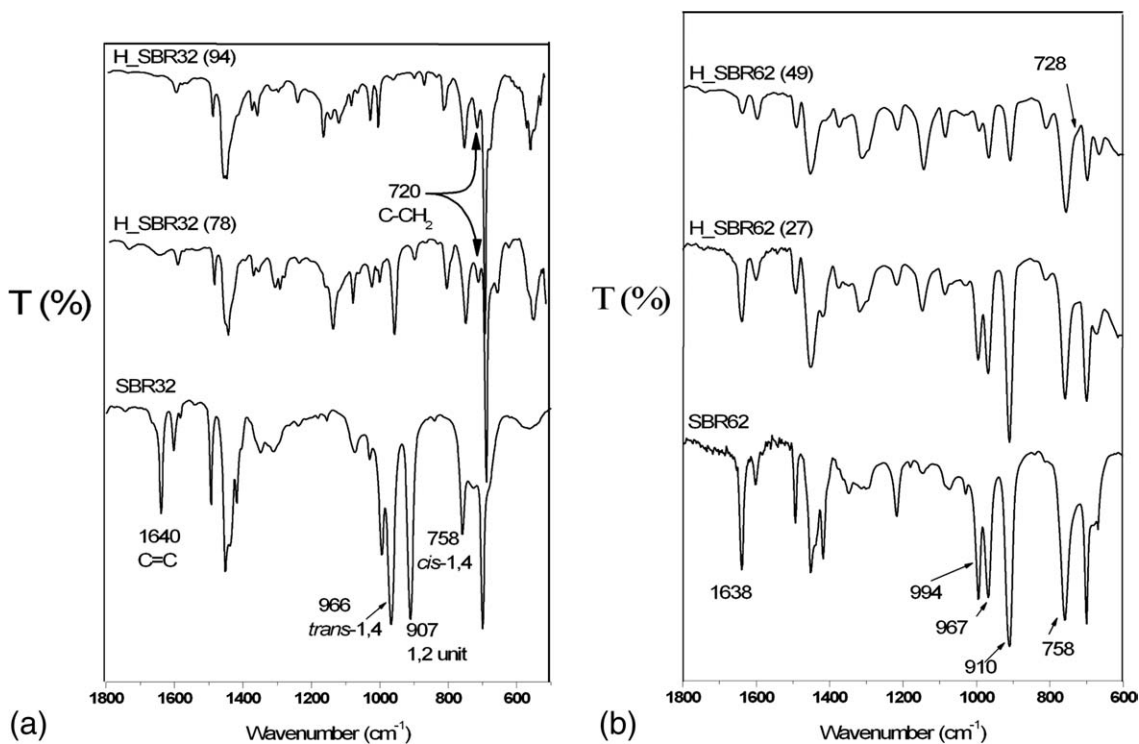


Figure 3 (a) FTIR spectra of SBR32 and H_SBR32 samples. (b) FTIR spectra of SBR62 and H_SBR62 samples.

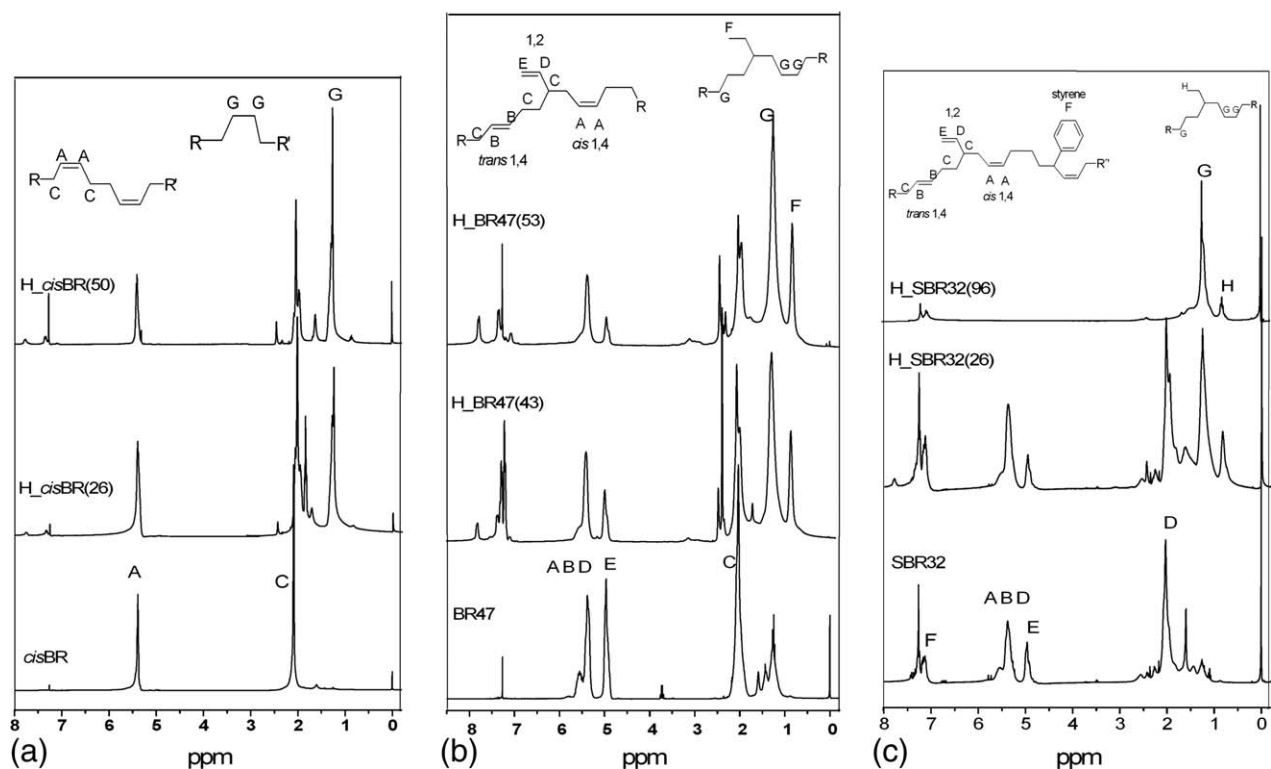


Figure 4 (a) $^1\text{H-NMR}$ spectra of *cis*BR and H_{cis}BR with 26 and 50% hydrogenation degree. (b) $^1\text{H-NMR}$ spectra of BR47 and H_{BR47} with 43 and 53% hydrogenation degree. (c) $^1\text{H-NMR}$ spectra of SBR32 and H_{SBR32} with 26 and 96% hydrogenation degree.

1,2 butadiene unit. At about 40% hydrogenation a new band, around 728 cm^{-1} , can be observed. It is associated with vibration of the $-\text{CH}_2$ segment formed, but at higher degrees of hydrogenation this band shifted to 759 cm^{-1} .

FTIR spectra of SBR32 and SBR62 and their partially hydrogenated samples, Figure 3(a,b) show a gradual decrease in the intensity of the bands at 966 cm^{-1} , attributed to *trans*-1,4, and of the bands at 994 cm^{-1} and at 910 cm^{-1} , attributed to 1,2 vinyl double bonds in the butadiene segment. These disappear completely at a high degree of hydrogenation, as can be observed in $\text{H}_{SBR}(94)$ sample. At the same time it is observed that the appearance and gradual increase of the band at $720\text{--}728\text{ cm}^{-1}$, correspond to rocking vibration of the $-\text{CH}_2$ segments.⁴ The band at 730 cm^{-1} is not observed in these samples, probably because the length of the polyethylene sequences formed by hydrogenation are not enough to form the arrangement for the crystalline phase.

Nuclear magnetic resonance spectroscopy

$^1\text{H-NMR}$ spectra of *cis*BR, BR47, SBR32 and their corresponding hydrogenated samples are showed in Figure 4(a–c). The decreased intensity of the peaks in the olefinic region at 5.2–5.4 ppm, assigned to the hydrogens adjacent to double bonds of the *cis* and

trans-1,4 units and at 4.8–5.0 ppm for olefinic hydrogens of 1,2 units, if present, can be seen. At the same time, new peaks appear at 0.8 and 1–1.5 ppm, related to methyl, methine and methylene hydrogens of the saturated unit confirming the hydrogenation.

Table I shows the degree of hydrogenation determined by $^1\text{H-NMR}$ and by the iodometry method. The results show a good correlation between the values determined independently by both methods of analysis. The discrepancy between the values of the *cis*BR ($\sim 50\%$ hydrogenated) is probably due to the

TABLE I
Degree of Hydrogenation Determined by $^1\text{H-NMR}$ and by the Iodometry Method

Samples	Degree of hydrogenation (%)	
	Iodometry method	$^1\text{H-NMR}$
<i>cis</i> BR	38	33
	51	41 ^a
	71	68
BR70	45	43
	61	64
BR47	43	43
	55	52
SBR32	53	50
	77	79
	78	78

^a Sample only partially soluble in CDCl_3 at 20°C .

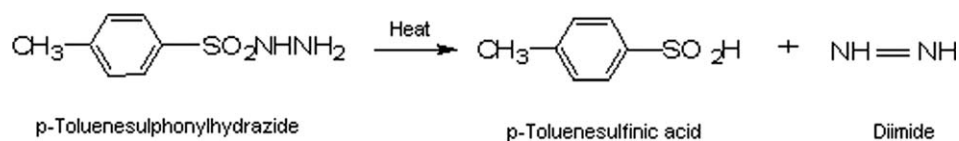


Figure 5 Thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) generating diimide and *p*-toluenesulfonic acid.

fact that the sample is partially crystallized¹⁷ and does not completely soluble in CDCl_3 . However, in iodometry, hot xylene was used and it was completely solubilized. In this way the result obtained by iodometry should be more significant.

Thermal decomposition of TSH (by products)

As can be seen in Figure 5, the decomposition of *p*-toluenesulfonylhydrazide (TSH) generates the diimide, the hydrogenation agent, and a byproduct, the *p*-toluenesulfonic acid.

This product can undergo an ionic or radical addition to yield sulfones and sulfides or, still, it can react with the double bond of pendant vinyl groups or unsaturated bonds along the polymer structure.^{5,10,18,19} Their presence can be monitored by FTIR and $^1\text{H-NMR}$ analysis.^{10,18,20,21} Typical bands in FTIR analysis are visualized at 1318 cm^{-1} and 1145 cm^{-1} , corresponding to the asymmetric and symmetric stretching of the SO_2 group, at 811 cm^{-1} associated with C–H rocking vibration, and at 1020 cm^{-1} , attributed to the *p*-tolyl aromatic ring. Peaks are detected at 2.4 ppm by $^1\text{H-NMR}$, due to the methyl group attached to an aromatic ring, and at 7.70 ppm due to the hydrogens from the aromatic ring of the *p*-toluenesulfonic group.

In our work, we observed that the presence of byproducts depends on the microstructure of the primary polymer and on the reaction conditions. In FTIR analyses of the H_BR70 and H_SBR62, Figures 2(b) and 3(b), a strong band at 1148 cm^{-1} , typical for SO_2 groups is observed. Its presence is confirmed by $^1\text{H-NMR}$ analysis. We attributed this fact a high amount of 1,2 units which must be favorable to the addition of the byproduct. Comparing the $^1\text{H-NMR}$ spectra of H_cisBR(47) and H_BR70 (51) sample, 4% and 70% of 1,2 content, respectively, Figure 6, it is easy to find the characteristic peaks attributed to fragments of *p*-toluenesulfonic acid at 2.4 and 7.7 ppm in H_BR70(51) sample. Further evidence is the broad resonance at 3.0 ppm involving methylene units adjacent to TSH fragments. To certify if the byproducts was bonded as a pendant group or merely an impurities of the rubber hydrogenated sample, H_BR70 and H_SBR62 samples with different degree of hydrogenation were redissolved, coagulated and subsequently extracted in acetone or ethanol, non solvents for the polymer, but very good solvent for the byproduct.

The samples were newly analyzed by FTIR and $^1\text{H-NMR}$, but similar results were obtained, confirming that the fragments of the *p*-toluenesulfonic acid were bonded to the polymer chain, preferentially to 1,2 units, probably favored by steric reasons.

Influence of microstructure

In a previous work¹¹ it was showed that, depending on the reaction conditions, *cis*BR and SBR32, reach a high degree of hydrogenation (ca. 70–90%) in relatively short reaction times (2 h). In subsequent studies, we observed that it is possible to perform hydrogenation using mild reaction conditions, TSH/C=C 0.5/1 and temperature of 112°C , favoring a good controlled reaction. Under these conditions, the reaction rate is lower, so the influence of the polydienes

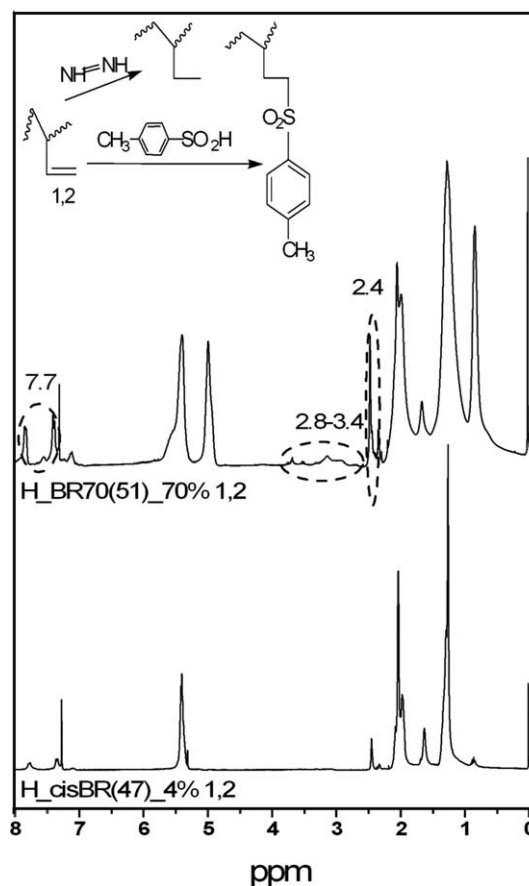


Figure 6 $^1\text{H-NMR}$ spectra of H_cisBR(47) and H_BR70(51) with 4 and 70% 1,2 content, respectively.

microstructure can more easily monitored. On the other hand, a low amount of TSH is required, and consequently, a smaller amount of byproduct is formed. Thus, the purification process is easier and a more homogeneous polymer is obtained. Besides, the process becomes more feasible economically.

Therefore, BR samples (*cis*BR, BR47, BR70) and SBR samples (SBR32, SBR62) with different amount of 1,2 unit were hydrogenated under mild conditions, TSH/C=C 0.5/1 at 112°C, Figures 7 and 8, respectively. The results show that the sample with high 1,2 content presents the highest conversion of double bond (C=C). This allow us to conclude that the reactivity of 1,2 units, present in BR and SBR under analysis, is higher than the 1,4 units. This was also observed by Mango et al.³ who applied non catalytic hydrogenation to low molecular weight BR and SBR as well as by Parker et al.²² who studied the catalytic hydrogenation of BR and SBR latex with a low 1,2 content (ca 13 wt %).

In our study, no influence of the presence of styrene in the SBR rubbers (21% to SBR62 and 24% to SBR32 styrene units) could be observed.

Differential scanning calorimetry

In a previous study,¹¹ the influence of hydrogenation on *cis*BR chain flexibility was discussed and a significant shift in T_g as well as an appearance of an endothermic peak assigned as melting point (T_m) associated with the presence of crystalline structure was observed. This effect corroborate the FTIR analysis where bands related to $-\text{CH}_2$ groups of saturated segments of the polymer chain associated with the presence of amorphous and crystalline domains were detected.

In these studies, using mild reaction conditions and depending on the degree of hydrogenation, a tendency to form crystallites could also be observed. Samples between 30 and 40% degrees of hydrogenation exhibit a glass transition temperature (T_g) and a melting point (T_m). On the other hand, the sample with 41% of hydrogenation showed only one T_m peak. As hydrogenation proceeds two T_m peaks could be visualized, which are better defined as the degree of hydrogenation increased. We attributed this fact to the formation of different-sized crystallites, as a consequence of different segments of polyethylene formed. It was observed that the region around 40–48% degree of hydrogenation is the threshold between a pure amorphous rubber like polymer and the appearance of a crystalline phase.

In the case of BR47 and BR70 samples a gradual increase in T_g with ongoing hydrogenation was also observed. H_BR47(54) shows an increase of 39°C, whereas and H_BR70(58) shows an increase of 50°C,

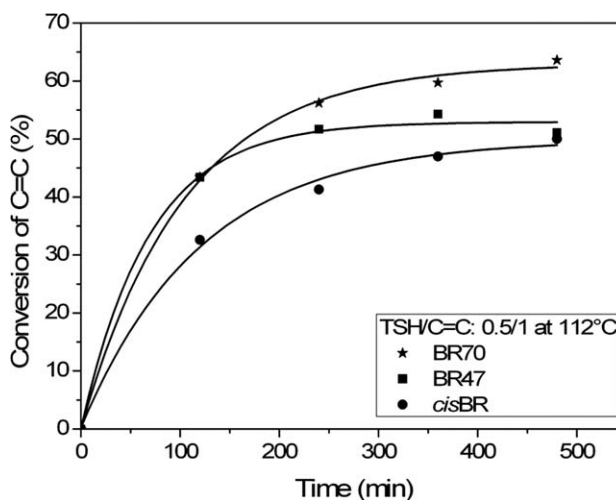


Figure 7 Conversion of double bonds as function of reaction time of H_BR samples with 4, 47, and 70% 1,2 content, respectively. Molar ratio TSH/C=C 0.5/1; T: 112°C.

always related to the T_g of the primary polymer. Hence, samples with higher 1,2 content need more energy to move their polymeric segments. No evidence of the crystallization phenomena was detected in the H_BR47 and H_BR70, probably due to a greater amount of 1,2 units that prevented the crystallization of the material, even to high modification levels. In the case of SBR samples, besides the 1,2 units, the presence of styrene groups, randomly distributed along the polymer chain prevents the formation of crystallites.²³ H_SBR32 and H_SBR62, with 25% and 21% of styrene, respectively, show a similar linear increase in its T_g value and no crystallization could be observed. Table II shows the T_g and T_m values as a function of degree of hydrogenation for all the samples under study.

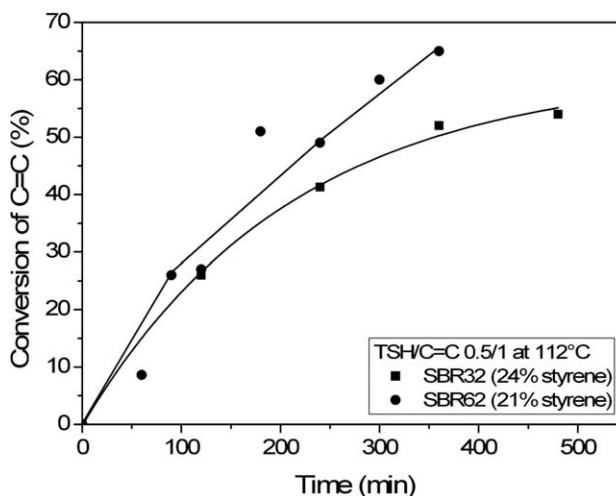


Figure 8 Conversion of double bonds as function of reaction time to SBR32 and SBR62 samples. Molar ratio TSH/C=C 0.5/1; T: 112°C.

TABLE II
Variation of T_g According to the Degree of Hydrogenation of *cis*BR, BR47, BR70, SBR32, and SBR62 Samples. Rate 10°C/min

	1,2 unit (%)	Styrene (%)	Degree of hydrogenation (%)	T_g (°C)	T_m (°C)
<i>cis</i> BR	4	0	0	-108	
			33	-77	24
			54	-	26
BR 47	47	0	0	-58	-
			27	-47	-
			54	-19	-
BR70	70	0	0	-42	-
			45	-21	-
			58	12	-
SBR32	32	24	0	-48	-
			26	-35	-
			54	-14	-
SBR62	62	21	0	-24	-
			27	-13	-
			49	6	-

Stability of hydrogenation rubbers

According to the literature,^{1,15} thermal stability increases with the amount of saturated segments. This property was investigated by thermogravimetric analysis (TGA). Until a certain degree of hydrogenation, H_BR47, H_BR70, H_SBR32 and H_SBR62 samples showed increased thermal stability. However, the opposite behavior was observed at higher degrees of hydrogenation. This must be a consequence of the presence of fragments of *p*-toluenesulfonic acid linked to polymer chain, which were detected as described previously in FTIR and ¹H-NMR analysis, promoting an acceleration of the degradation process. The detailed investigation of this phenomenon is described in a previous article recently published by the authors.¹⁷

Kinetic studies^{6,19,22}

The overall reaction of double bond hydrogenation of the polydienes rubbers by TSH involves two steps: the TSH decomposition to generate diimide, Figure 5, and, subsequently, the hydrogenation of double bonds (C=C). Diimide is an active intermediate that coordinates with the double bond, and releases two hydrogen atoms. The rate law of the reaction can be expressed as

$$v_{\text{Hidrog}} = k[\text{polymer}][\text{TSH}] \quad (1)$$

Assuming that $[\text{TSH}] = [\text{N}_2\text{H}_2]$, it is possible to write

$$\frac{d[\text{C}=\text{C}]}{dt} = -k[\text{C}=\text{C}][\text{N}_2\text{H}_2] \quad (2)$$

where $[\text{C}=\text{C}]$ is the double bond concentration

Supposing that hydrogenation follows a first order reaction related to double bonds, the conversion rate can be expressed as

$$\ln \frac{1}{(1-X)} = k_{\text{app}} \cdot t \quad (3)$$

where $k_{\text{app}} = k \cdot [\text{N}_2\text{H}_2]$

The apparent rate constant (k_{app}) can be calculated from the slope of the linear plot of $\ln 1/(1-X)$ as a function of time according to eq. (3), where X is the fraction of hydrogenated double bonds. The mathematical evaluation was applied to the data of *cis*BR, BR47, BR70 samples, Figure 7, and SBR32 and SBR62, Figure 8, under the reaction conditions TSH/C=C 0.5/1 at 112°C. The linearity of the graphics for SBR samples, Figure 9, confirms that the reaction followed a first order reaction related to double

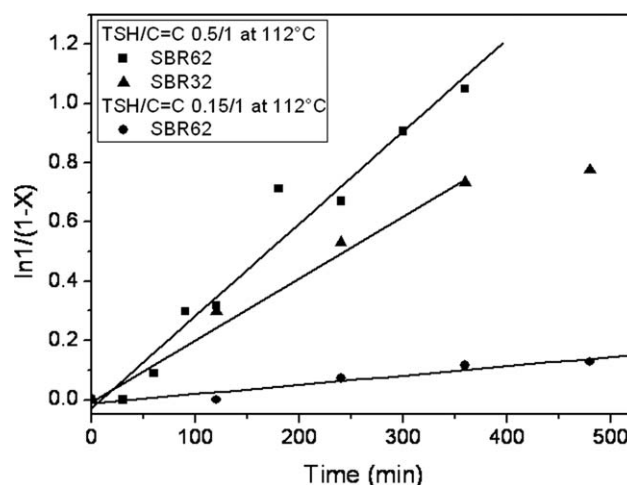


Figure 9 First-order fitting of the hydrogenation of SBR32 and SBR62 as function of time.

bonds. The apparent constant values are presented in Table III. Comparing the SBR62 sample produced with different molar relations TSH/C=C 0.15/1 and 0.5/1, both at 112°C, we observed a significant increase (10 times) in the reaction rate when the molar ratio TSH/C=C is increased from 0.15 to 0.5. The [C=C] is the same in both experiments. The low reaction rate of SBR62 0.15/1 can be attributed to the very small amount of TSH used.

The behavior of the *cis*BR, BR47 and BR70 samples is shown in Figure 10. The lack of experimental data during the first 2 hours does not allow us to calculate the apparent constant rate in this range. However, qualitatively, it is easy to see that until 2 hours of reaction the conversion is high with a sharp inclination of the linear fit. A significant difference in the behavior between *cis*BR and BR47 samples was observed, which may be related to the amount of 1,2 units present in the samples. For longer reaction times a new behavior was detected, also linear, but with a moderate and practically equal slope ($\sim 4.10^{-4} \text{ seg}^{-1}$) for all the samples.

The results confirm a higher reactivity of 1,2 units compared to 1,4 units under hydrogenation. This was also noted by Mango and Lenz³ and Harwood et al.¹⁹ using a similar system to hydrogenated unsaturated substrates.

CONCLUSIONS

Noncatalytic hydrogenation using TSH as a reagent is fast and efficient. In this work it could be demonstrated that hydrogenation can be performed under mild conditions as TSH/C=C 0.5/1 and temperature of 112°C. The process can be controlled to achieve different degrees of hydrogenation and lead us to variable materials with properties and specific characteristics. Furthermore, the use of a small amount of TSH is economically favorable and the end products are easier to purify. The degree of hydrogenation depends on the reaction conditions, molar ratio of TSH/C=C, temperature, time and microstructure of primary polymer. The hydrogenation process, as well as the presence of byproducts can be monitored by FTIR and ¹H-NMR analysis. The hydrogenation of high *cis*BR is fast and the H_*cis*BR(94) showed thermal properties similar to PE. Crystalline domains were detected through the

TABLE III
The Apparent First Order Reactions Rates (k_{app})
Calculated for SBR62 and SBR32 Samples

Sample	TSH/C=C (mol/mol)	k_{app} (seg ⁻¹)
SBR62	0.15/1 at 112°C	0.52×10^{-5}
SBR32	0.5/1 at 112°C	3.70×10^{-5}
SBR62	0.5/1 at 112°C	5.18×10^{-5}

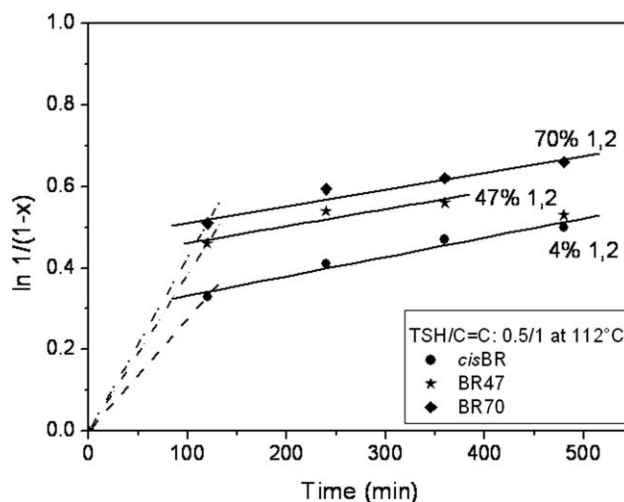


Figure 10 First-order fitting of the hydrogenation course of *cis*BR, BR47, BR70 samples.

rocking vibration of $-\text{CH}_2$ segments in FTIR analysis and a typical T_m point in DSC analysis. On the other hand, H_BR47, H_BR70, H_SBR32, and H_SBR62 did not show the crystallization phenomena. This can be associated with the amount of 1,2 units present in these samples, which inhibits the crystallization of these structures. Careful monitoring showed the presence of fragments of *p*-toluenesulfonic acid attached to the polymer chain, especially found in the samples with a high amount of 1,2 units. The kinetic study showed a higher reactivity for the 1,2 units than for the *cis-trans* 1,4 units. The styrene group apparently not affected the degree of hydrogenation achieved.

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