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Hydrogenation of styrene-butadiene rubber by hydrogen transfer from limonene

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ABSTRACT:

The heterogeneous catalytic transfer hydrogenation of styrene-butadiene rubber (SBR) by the use of limonene as hydrogen source and as solvent in the presence of Pd/C as catalyst has been studied. The influence of the heating time on the reduction and on the structure of the donor was studied. Partial hydrogenations of the olefinic bonds of SBR are obtained when a mixture of limonene, SBR and 10% Pd/C is refluxed with vigorous stirring for 50-200 minutes.

INTRODUCTION:

The hydrogenation of carbon-carbon double bonds in polymeric systems, usually polymers of 1,3-butadiene and isoprene has been used to prepare elastomers wich exhibit improved thermal and oxidative stability when compared to their parent polymers. Among the available methods leading to hydrogenation is worth mentioning heterogeneous catalytic hydrogenation, homogeneous catalytic hydrogenation and the reaction with diimide. Howewer, these methods require special apparatus and hydrogen, the synthesis and handling of transition metal complexes, long reaction time and besides they give low yields and chain degradation[1,2].

It has been reported that the carbon-carbon double bond of low molecular weight olefins can be hydrogenated with Pd/C using limonene, a terpene, as hydrogen source[3], whose efficiency in the catalytic transfer hydrogenation (CTH) is known[3-6]. This procedure was employed to reduce unsaturated units in hydroxylated polybutadiene (PBLH)[4], but no other reports of its use with polymers have appeared so far. Because of the simple apparatus and technique required for CTH, it seems that such reductions could be very useful for modifying polymers. We therefore studied the reduction of SBR to determine favorable reaction conditions[5] and to evaluate the influence of the reaction time in polymer modification.

EXPERIMENTAL

1 - Materials

Commercial samples of SBR 1502 (Petroflex S/A) were purified by dissolution in toluene, filtration, followed by precipitation of the polymer into ethanol. The polymer was then washed with ethanol and dried at room temperature under vacuum for 24h. Limonene (Dieberger Oleos Essenciais), hexane, ethanol and toluene (Grupo Química) were used without further purification. The 10% Pd/C and the Celite were produced by Merck.

2- Method

The general procedure for CTH was to introduce 0.059 g of 10% Pd/C, 19 mL of limonene and 0.8 g of SBR in a two necked round-bottom flask equipped with a reflux condenser and a thermometer. The mixture was refluxed in an oil bath with vigorous magnetic stirring for 50-200 min. After the reaction, the mixture was filtered through Celite to remove the catalyst. The polymer was then precipitated in ethanol.

3- Characterization

The SBR and the reduced SBR ^{1}H NMR data were recorded by a Varian VL 200 nuclear magnetic resonance spectrometer, using CCl_4 as solvent and Me_4Si and D_2O as internal standards. The reaction residues were analyzed by gas chromatography in a CG 3537D equipment with a Carbowax 20M capillary column (50 x 0.25 x 0.3µm) with injector temperature of 180°C, detector temperature of 240°C and column temperature of 180-200°C (4°C/min).

The percent hydrogenation of carbon-carbon double bond was evaluated by ^{1}H NMR spectroscopy, according to equation 1:

$$\% \text{ hydrogenation} = 100 - 100 \times Q / Q' \qquad (1)$$

where, Q is the ratio between the number of vinylic and aromatic protons obtained from the ^{1}H NMR spectrum of the hydrogenated polymer and Q' is that for the purified SBR ^{1}H NMR spectrum.

The filtrate obtained after the separation of the catalyst and the hydrogenated polymer was analyzed by gas chromatography and its composition was determined by comparison with standards.

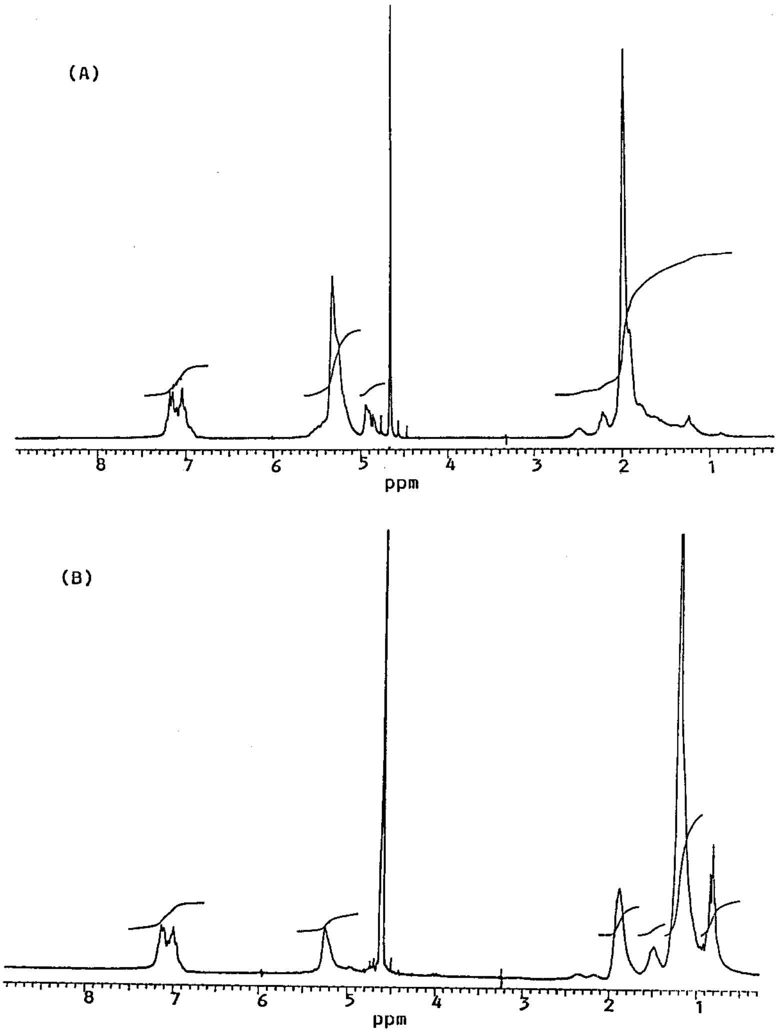


Figure 1 - (A) ^1H nmr spectrum of purified SBR
(B) ^1H NMR spectrum of reduced SBR after 150 minutes of reaction.

RESULTS AND DISCUSSION

The ^1H NMR spectrum (Figure 1A) shows that the sample contains 75% 1,2-units. This material was refluxed for varying times with limonene and 10% Pd/C, as optimized in a previous study[5]. The hydrogenated polymers were analyzed by ^1H NMR, as shown in Figure 1B, which shows the spectrum of the polymer after 150 minutes of refluxing..

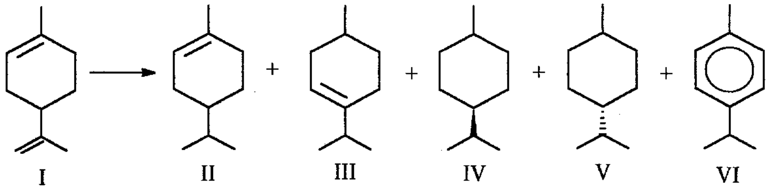
The percent hydrogenation was evaluated by equation 1 and the results are shown in Table 1 (averages of three experiments for each reaction time).

Table 1
Percentage of Reduction with Reaction Time[a]

Sample	Reaction Time (min)	(Q)	Reduction (%)
BCTH 1	50	1.29	51.14
BCTH 2	100	1.07	59.47
BCTH 3	150	0.79	70.08
BCTH 4	200	0.78	70.95

a. The reaction ratio Q' obtained by ^1H NMR analyses of purified SBR was 2.64.

The increase in the reduction of the polymer allows different products to be obtained from SBR by varying the reaction time. After 200 minutes of reflux, the degree of hydrogenation is not very different from the one obtained after 150 minutes. This can be explained by the presence of only trans(IV) and cis(V) p-menthanes and p-cymene(VI) in the mixture after 150 minutes of reaction. These structures shown below are products of limonene disproportionation and are not good hydrogen donors[3].



As demonstrated in a previous study[6], the disproportionation of limonene is competitive with hydrogen transfer to the substrate. Furthermore, the efficiency of the hydrogenation is related to the presence of hydrogen donor in the reaction media. So, the analysis of the final filtrate for each CTH reaction was made to check the degree of disproportionation of limonene.

Table 2
Disproportionation of Limonene

Sample	Reaction time(min)	I	II	III	IV	V	VI
BCTH 1	50	+	+	+	-	-	+
BCTH 2	100	+	+	+	-	-	+
BCTH 3	150	-	-	-	+	+	+
BCTH 4	200	-	-	-	+	+	+

(+) presence of the substance, (-) absence of the substance
I : limonene, II: Δ^1-p-menthene, III: Δ^3-p-menthene, IV: trans-p-menthane, V: cis-p-menthane, VI: p-cymene

Comparing the results in Table 1 with those in Table 2 one can see that the polymer hydrogenation is linked to the presence of limonene (I) and/or the presence of the intermediates II and/or III. Similar behaviour has been observed for the reduction of the carbon-carbon double bonds in isophorone. It this case, hydrogenation occurs even in the absence of limonene (I), provided the Δ^1 and Δ^3-p-menthenes (II and III) are present[9].

By comparing the maximum hydrogenation achieved with SBR (70%, 150 minutes) with that obtained with PBLH (50%, 50h)[4] under the same experimental conditions, one is led to believe that the presence of an hydroxyl and/or a phenyl group might affect the efficiency of the process.

CONCLUSION

CTH using limonene as hydrogen source is a simple and useful alternative for the hydrogenation of styrene-butadiene rubber. Besides efficiency and short reaction time this method presents safe and easy handling. Polymer crosslinking degradation was not observed[7]. Studies on the influence of functional groups in the efficiency of this process are under way.

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