

Determination of the Hydrogenation Degree of Telechelic Polybutadiene by ^1H NMR

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Abstract: *The liquid hydroxyl terminated polybutadiene (HTPB) was hydrogenated to improve its thermal and oxidative resistance. Hydrogenation was carried out using cyclohexane as solvent and a soluble catalyst system consisting of diisobutylaluminum hydride (DIBAL-H) and Co^{III} acetylacetonate, at a molar ratio of 6:1. Hydrogenation was only possible after esterification of hydroxyl groups due to interactions with the catalyst system. ^1H NMR technique was used to confirm the esterification and hydrogenation of the polymeric material. This method can be also used to determine the degree of hydrogenation in different reaction times.*

Introduction

Hydroxyl terminated polybutadiene (HTPB) has a wide variety of applications, including adhesives, sealants, coatings and binder for propellants.¹⁻⁴ Nevertheless, because of unsaturations in the backbone of the polymer, it is subject to thermal and oxidative degradations. To enhance the material resistance to these degradations, it is necessary to remove carbon-carbon unsaturation, which can be done through a hydrogenation process. However, the relatively high cost of this process is a limiting factor for broader applications. Using different techniques and employing low cost catalysts make it possible to decrease the overall cost of the process and improve feasibility.

In this respect, homogeneous catalysts has attracted much interest because of the high degree of selectivity and activity of some catalysts in the reduction of double bonds even in the presence of other functional groups. Previous authors have already tested homogeneous catalytic systems with partial and total yield in HTPB hydrogenation.⁵⁻¹²

In the present work, an ester modified HTPB was hydrogenated using a homogenous catalyst to improve the thermal and oxidative properties of the polymer.

Experimental

HTPB was used as collected from Petroflex industrial area ($M_w = 2900$, $\nu = 5500$ cPs at 25°C , $[\text{OH}] = 0,81$ meq/g). Acetic anhydride was used as received. Cyclohexane was received from Petroflex industrial area, already purified by molecular sieve absorption followed by distillation. A 5% w/w solution of diisobutylaluminum hydride in cyclohexane was prepared and stored in sealed bottles under dry nitrogen. Cobalt^{III} acetylacetonate (acac) was used as received. Catalyst synthesis was done into sealed bottles under dry nitrogen. Hydrogenation reactions were carried out in a 3.7 L Parr reactor.

Esterification

200 g of HTPB was refluxed at 100°C for 2 hours with 46.8 g of acetic anhydride (487.5 meq) and then dried under vacuum at 100°C

for 35 minutes. An ester modified HTPB, a transparent viscous liquid (yield 100%), was obtained.

IR (irtran, cm^{-1}) 1745, 1238; NMR (CDCl_3) δ : 4.6-4.7 ($\text{HC}=\text{CH}(\text{cis})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$); 4.6-4.5 ($\text{HC}=\text{CH}(\text{trans})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$); 4.15-4.0 ($\text{H}_2\text{C}=\text{CH}(\text{vinyl})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$).

Catalyst synthesis

In a dried and sealed bottle filled with dry nitrogen, 0.5 g of Co^{III} acetylacetonate was added to 71.3 g of cyclohexane. Afterwards, 23.9 g of a 5% DIBAL-H cyclohexane solution was added drop wise. A brownish homogeneous solution was obtained. The bottle was then stored under refrigeration.

Ester modified HTPB hydrogenation

In a Parr reactor (3.7 L of capacity) under 1.1 kg/cm^2 nitrogen pressure, 100 g of the ester modified HTPB (1851.85 meq of unsaturation) was dissolved in 900 ml cyclohexane. 101.49 ml of the catalyst solution was added with a syringe (catalyst unsaturation molar ratio of 1:1250). Temperature was risen to 90°C , and, hydrogen pressure was set to 10 kg/cm^2 . IR (Irtran, cm^{-1}) 2920, 2850, 1745, 1463; NMR (CDCl_3) δ : 4.0441 (s, CH_x-OH $x=1,2$), 2.0452 (s, CH), 1.2462 (s, CH_2), 0.8713 (s, CH_3),

Results and discussion

Different catalyst unsaturation molar ratios were tested, starting from 1:500 up to 1:1250, but for all molar ratios, hydrogenation of the unsaturated compounds were observed. We found that hydrogenation with a soluble catalyst system in cyclohexane, with diisobutylaluminum hydride and Co^{III}

acetylacetonate, at a molar ratio of 6:1, was only possible, after HTPB esterification of hydroxyl groups. In fact, as noted in other previous experiments with different catalysts, such as titanocenes, the presence of polar groups, such as hydroxyls, inhibits hydrogenation. The protection of the polar group by esterification with acetic anhydride was effective, once a 100 % conversion from hydroxyls - OH - to esters - OR was obtained. This result was confirmed by IR spectra: carbonyls stretching at 1745 cm^{-1} and CO bending at 1238 cm^{-1} , and also confirmed by NMR spectra, which shows the group - $\text{HC}=\text{CH}(\text{cis})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$, at 4.6-4.5 ppm, - $\text{HC}=\text{CH}(\text{trans})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$ and at 4.15-4.0 ppm, the group - $\text{H}_2\text{C}=\text{CH}(\text{vinyl})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$ at 4.6-4.7 ppm.

The hydrogenation degree of conversion was also determined using the two techniques, IR and ^1H (^1H NMR). For IR, the gradual reduction of absorbance peaks of 1,2-*vinyl* (910 cm^{-1}) and 1,4-*trans* (966 cm^{-1}) indicate the hydrogenation degree of the sample. The assignment of ^1H NMR spectra of hydroxyl and carboxylic groups is shown in the structures in Table 1, which confirm hydrogenation. To determine polybutadiene microstructures the assignments of ^1H NMR spectra in the region of 6.2 to 5.25 ppm to configurations 1,4-*cis/trans* and 5.05 to 4.8 ppm to configurations 1,2-*vinyl* were made. In the hydrogenated material the unsaturations were almost completely converted.^{13,14} The samples were dissolved in CDCl_3 , which was used as internal reference for chemical shifts.

An analytical method was developed to determine HTPB esterification, as well as the hydrogenation reaction evolution of the material after esterification.

Table 1 presents the results of the assignment of ^1H NMR of the materials shown in Figures 1 to 6: initial HTPB (sample 1), the material after esterification (sample 2) and the material after esterification and hydrogenation (sample 3). Table 1 shows the chemical environment of the hydrogens of group CH_2 bound to oxygen of sample 1 in relation to sample 2, decreasing

the shield magnetic field, independent of stereochemistry, after esterification. Sterification did not change the material microstructure. According to ^1H NMR spectra, hydrogenation was complete, and the IR spectrum ($\text{C}=\text{O}$ 1745 cm^{-1}), shows the presence of the protecting group.

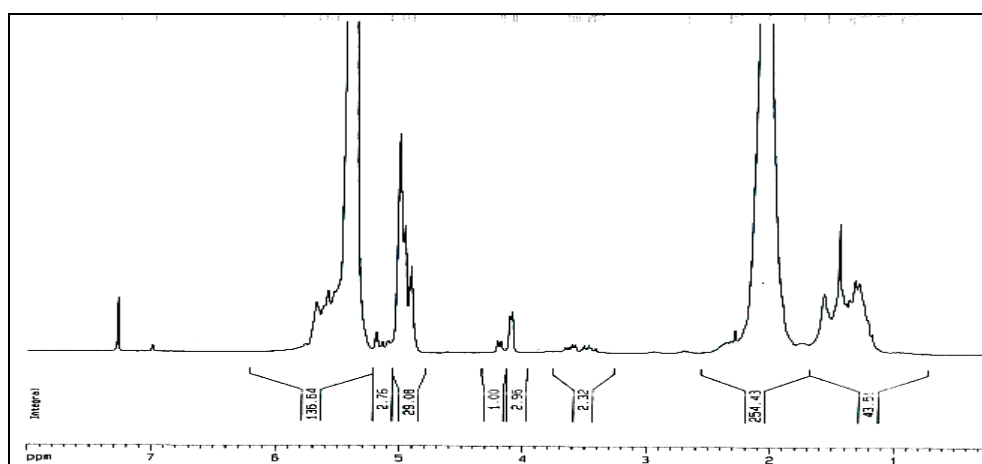


Figure 1. ^1H NMR spectrum of HTPB (sample 1)

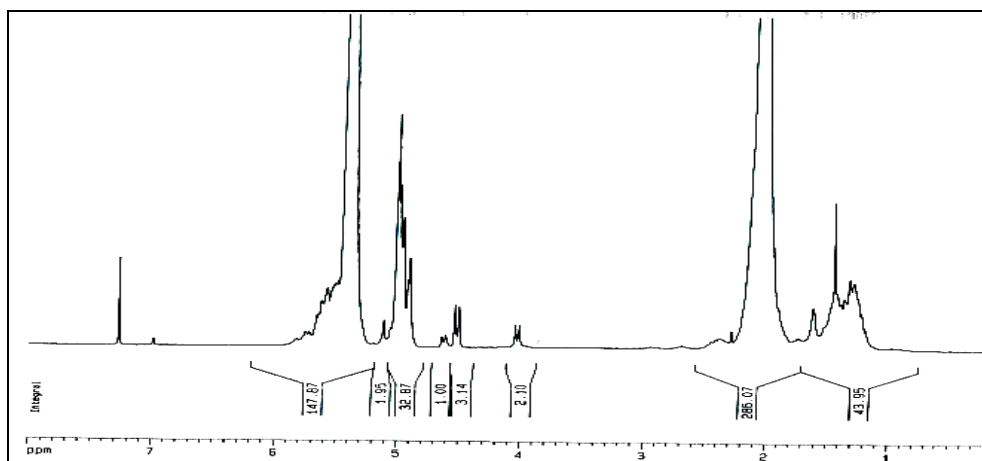


Figure 2. ^1H NMR spectrum of HTPB after esterification (sample 2)

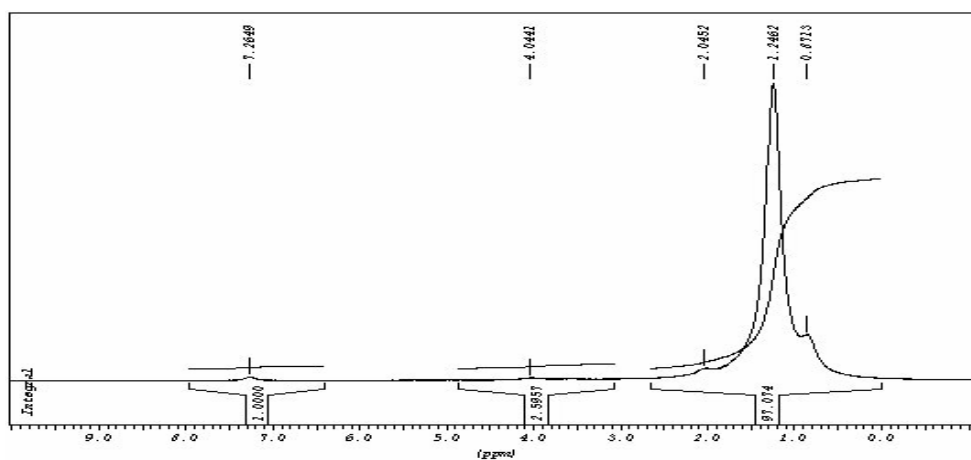


Figure 3. ^1H NMR spectrum of HTPB after esterification and hydrogenation (sample 3)

Table 1. Structures, assignments and molar %, samples 1, 2 and 3

Structures	Assignment (ppm)	Sample 1 (%molar)	Sample 2 (%molar)	Sample 3 (%molar)
$\text{HC}=\text{CH}(\text{cis})-\text{CH}_2\text{OH}$	4.3-4.15	15.9	0	0
$\text{HC}=\text{CH}(\text{trans})-\text{CH}_2\text{OH}$	4.15-3.95	47.1	0	0
$\text{H}_2\text{C}=\text{CH}(\text{vinyl})-\text{CH}_2\text{OH}$	3.8-3.3	36.9	0	0
$\text{HC}=\text{CH}(\text{cis})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$	4.7-4.6	-	16.0	na
$\text{HC}=\text{CH}(\text{trans})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$	4.6-4.5	-	50.3	na
$\text{H}_2\text{C}=\text{CH}(\text{vinyl})-\text{CH}_2\text{O}-(\text{CO})-\text{R}$	4.15-4.0	-	33.7	na
$\text{H}-\text{C}=\text{C}-\text{H}(\text{cis and trans}) + \text{H}-\text{C}=\text{C}$ vinyl	6.2-5.25	80.8 (<i>cis+trans</i>)	80.0 (<i>cis+trans</i>)	0
$\text{H}_2-\text{C}=\text{C}$ vinyl	5.05-4.8	19.2	20.0	0

na – not available

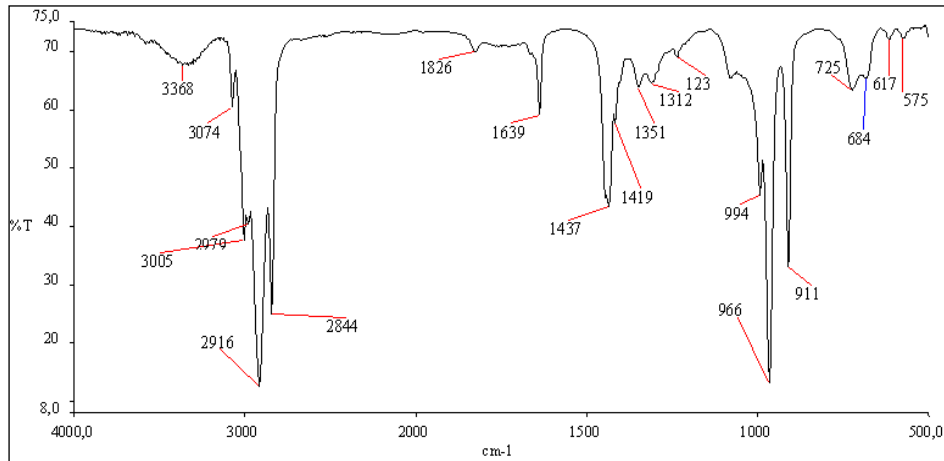


Figure 4. IR spectrum of HTPB (sample 1)

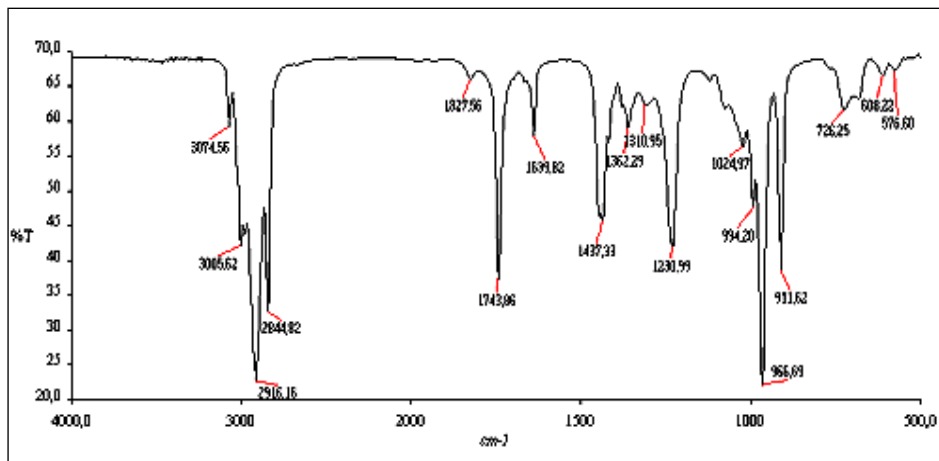


Figure 5. IR of HTPB after esterification (sample 2)

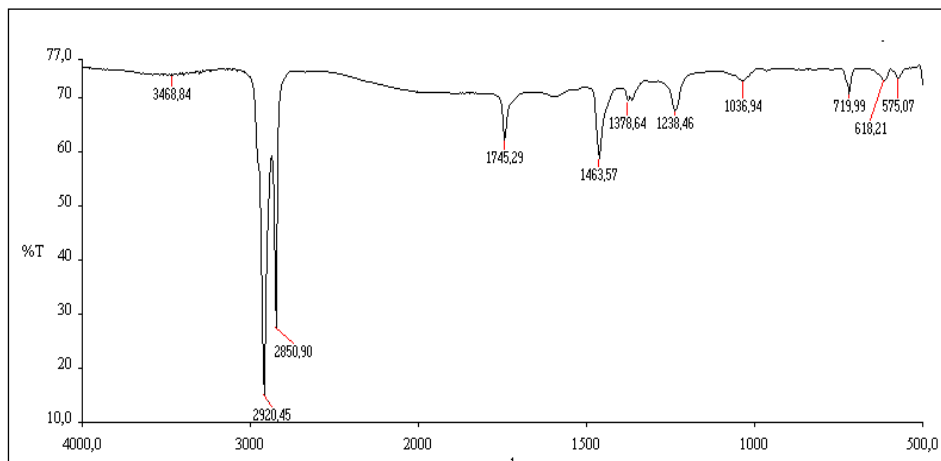


Figure 6. IR spectrum of HTPB after esterification and hydrogenation (sample 3)

Conclusions

Our results OR Our experimental data show that it is possible to produce the ester of HTPB followed by its hydrogenation_using a Co Ziegler-Natta catalyst in a mild hydrogenation condition. If the target is to obtain hydrogenated HTBP, it will be necessary to remove hydroxyl protection in another synthesis step. These results also show that ^1H NMR is an analytical method capable of confirming the esterification and hydrogenation of the polymeric material. it is possible to use this method to evaluate the degree of hydrogenation in different reaction times.

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