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Hydroxyl-terminated polybutadiene

IV. NMR assignments of three main hydroxylated end groups

W. D. Vilar[1,*], S. M. C. Menezes[2], P. R. Seidl[3]

[1] Instituto Militar de Engenharia, Rio de Janeiro 22290-270, RJ, Brazil
[2] Petrobrás Research Center (CENPES), Rio de Janeiro, Brazil
[3] Escola de Química, Universidade Federal do Rio de Janeiro, Brazil

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SUMMARY

Liquiflex-H is commercially available hydroxyl terminated polybutadiene (HTPB) produced by Petroflex. It was analyzed by ^{1}H and ^{13}C NMR spectroscopy with regard to three main hydroxylated end groups. The NMR assignments related to three main alcoholic functions has raised some controversy in the literature and is considered further in our discussion. HETCOR and COSY pulse sequence NMR techniques were used in this work to solve this question.

INTRODUCTION

In our previous papers[1-3] concerning HTPB characterization, the three main alcoholic functions were identified and quantitatively determined and a mechanistic approach for the polymerization was presented.

We have shown by ^{1}H and ^{13}C NMR spectroscopy that the original interpretation of Ramey[4] and Bresler[5] was essentially correct. Spectral data for carbon and hydrogen groups of the three main hydroxylated end groups are best accounted for by effects due to the vicinity of vinyl "V", trans "T" and cis "C" units (Table 1). These observations were rationalized by proposing mechanisms for the polymerization reaction that would lead to the formation of the species that were identified.

Nevertheless, according to Pham and coworkers[6-13], absorption of the three main primary alcohol function were attributed to "V", "H" and "G" structures (Table 1). The "G" group (similar to geraniol) is a short branch originating from a chain transfer process.[13]

Commercial HTPBs are produced by free radical polymerization of butadiene using hydrogen peroxide as initiator and an alcohol as a solvent. Liquiflex H and P are produced by Petroflex using ethanol[14] and R-45HT and R-45M are produced by Atochem using isopropanol[15] as solvents.

In the HTPB polymerization the hydrogen peroxide molecule is thermally dissociated into two hydroxyl radicals (HO•). This free radical initiates the polymerization of butadiene. The principal termination path in HTPBs polymerization is macroradical coupling which explains its functionality of near by two[2,3].

Studies of HTPB functionality distribution made by Inagaki[16] and Ninan[17] showed that HTPBs with functionality greater than two have high molecular weights. This was taken as an indication that HTPB with functionality greater than two were formed by branching and crosslinking reactions. This means that HTPBs with high molecular weight and high functionality have hydroxylated end groups ("C", "T" or "V" structures), instead of hydroxyl groups randomly distributed along the chains, like in "G" structures proposed by Pham and coworkers.

The assignment of HTPB in NMR spectra to "C" or "G" structures implies macromolecules of different geometries. These different polyol species result in HTPB

* Corresponding author

based polyurethanes with different properties, so, the assignment of the correct structure ("C" or "G") is very important for understanding the relationships between structure and property in HTPB based polyurethanes.[18]

This paper presents a discussion of the assignments of the three main alcoholic functions found in ^{1}H and ^{13}C NMR spectra of HTPB.

EXPERIMENTAL PART

Material

HTPB (commercial sample) was a conventional Liquiflex H produced by Petroflex.

NMR spectra

Nuclear magnetic resonance was performed using a VXR-300 Varian apparatus, using 5 mm tubes. For ^{1}H (300 MHz frequency) the samples were dissolved in $CDCl_3$ at a concentration of 1%. The spectra were obtained using a 30° pulse 16 transients and ambient temperature. For ^{13}C (75.4 MHz) the concentration was 20-30% in $CDCl_3$. We have used 45 ° pulses and a delay of 12.0 s between pulses. The decoupler mode was gated to avoid NOE and about 1800 pulses were accumulated at ambient temperature. All the chemical shifts were refered to TMS (dissolved in the $CDCl_3$ solvent)

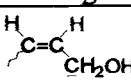
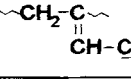
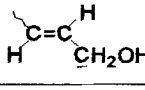
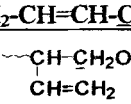
The **HETCOR** spectrum was obtained in $CDCl_3$ using 1.0 s of delay between pulses, ambient temperature, 192 repetitions and 192 increments. A line broadening of 3.0 Hz was used before transforming the spectrum.

The **COSY** spectrum was acquired also using $CDCl_3$ as solvent, ambient temperature, 16 repetitions and 256 increments. The acquisition time was 0.22 s.

RESULTS AND DISCUSSION

Table 1 summarizes different assignments for the three main alcoholic functions found in the literature.

Table 1. NMR assignments for the three main hydroxylated structures in HTPB

	Author (reference)			
Structures assigned	Bresler	Ramey	Pham	Our assignment
 (C)	5	4	-	1-3
 (G)	-	-	6-13	
 (T)	5	4	1-3	-
^^CH_2-CH=CH-CH_2OH (H)	-	-	6-13	-
 (V)	5	4	6-13	1-3

Figures 1A and 1B show the ^{1}H and ^{13}C NMR spectra of Liquiflex H and figures 1C and 1D correspond respectively to expansion of 3.2 to 4.2 and 54 to 74 ppm regions.

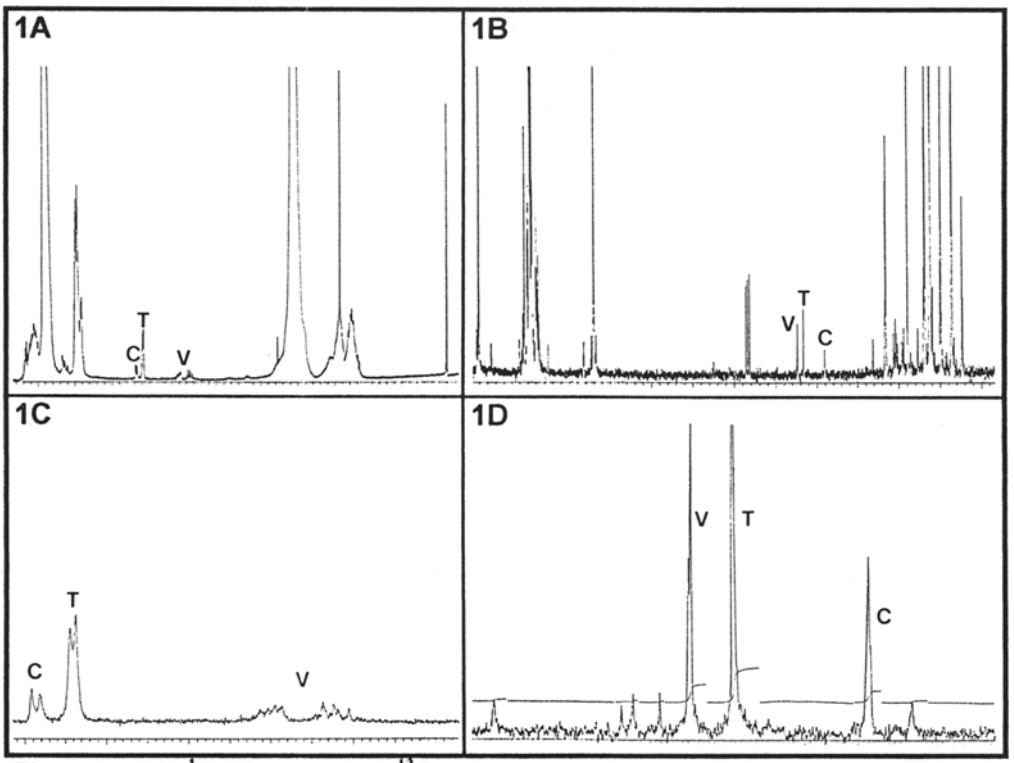


Figure 1 - (1A) ^{1}H NMR and (1B) ^{13}C NMR spectra of HTPB, (1C) 3.2 to 4.2 ppm region of ^{1}H NMR and (1D) 54 to 74 ppm region of ^{13}C NMR of HTPB

Figures 1A/1C (^{1}H) and 1B/1D (^{13}C) show that HTPB has resonances at δ=3.51 ppm, δ=4.08 ppm and δ=4.18 ppm (^{1}H), and δ=64.96 ppm, δ=63.45 ppm and δ=58.30 ppm (^{13}C). The resonances in these regions are attributed to the carbons and hydrogens in the neighborhood of the hydroxyl group[1-13]

Table 2 shows NMR resonances of selected model compounds.[19]

Table 2. NMR chemical shifts of model compounds[19]

Model compounds	^{1}H (δ/ppm)			^{13}C (δ/ppm)
	$-\underline{CH_2}OH$	$-\underline{CH}=\underline{CH}-CH_2OH$	$-CR=\underline{CH}-CH_2OH$	$-\underline{C}H_2OH$
cis-2-hexen-1-ol	4.20	5.55	-	58.46
cis-2-penten-1-ol	4.20	5.55	-	58.35
trans-1-hexen-1-ol	4.05	5.65	-	63.62
trans-2-penten-1-ol	4.05	5.65	-	63.56
geraniol	4.15	-	5.40	59.30

Figure 2 shows the HETCOR pulse sequence spectrum for Liquiflex H, revealing that resonances at δ=3.51 ppm, δ=4.08 ppm and δ=4.18 ppm in the ^{1}H spectrum are coupled to those at δ=64.96 ppm, δ=63.45 ppm and δ=58.30 ppm in the ^{13}C spectrum. This fact is consistent with the assignment to structures, "V", "T" and "C" respectively.

Figure 3 shows the COSY pulse sequence spectrum for Liquiflex-H.

Figure 4 shows the 5.2 to 5.7 ppm region of the ^{1}H spectrum of Liquiflex H.

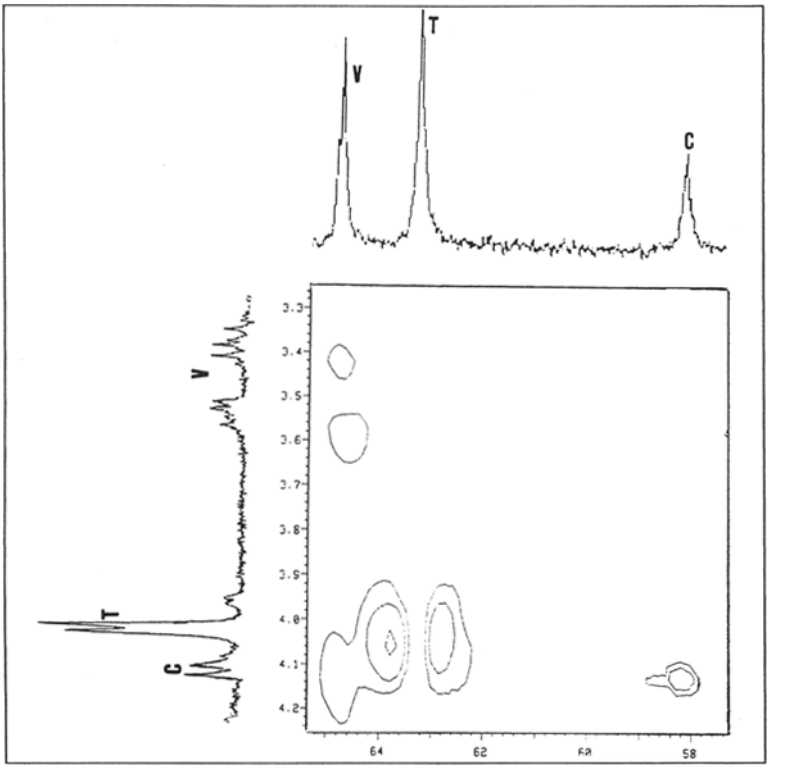


Figure 2 - HETCOR pulse sequence spectrum for HTPB.

In Figure 3 we can see the coupling of the resonance at δ=4.18 ppm ("C" structure) with another at δ=5.55 ppm and the coupling of the resonance at δ=4.08 ppm ("T" structure) with another at δ=5.65 ppm, respectively.

There are two main points to be clarified between the alternatives proposed in the earlier literature[4,5] and our recent assignments[1-3] and the systematic investigations of Pham and coworkers[6-13].

The first is related to group "H" of Table 1. Since no stereochemistry relative to the double bond is indicated in reference 13, it is implicit that the structures designated as cis ("C") or trans ("T") would display similar chemical shifts.

Reasonable models for the respective polymer structures may be proposed by adding alkyl groups to the respective "C" and "T" units that contain a CH_2OH group vicinal to a double bond, such as cis and trans-2-penten-1-ol or cis and trans 2-hexen-1-ol, for example. As can be observed from Table 2, cis and trans isomers reveal distinct carbon and hydrogen chemical shifts and the size of the respective substituent has a rather small influence on these shifts. Thus group "H" would lead to two peaks if both cis and trans forms were present.

The ^1H spectrum[19] of trans-2-hexen-1-ol shows a methylene doublet at 4.05 ppm and the olefinic protons appear very close together, around 5.65 ppm, corresponding a calculated difference in chemical shifts of 1.60 ppm. In Figure 3 we can see the coupling of the resonance at δ=4.08 ppm ("T" or "H" structure) with another at δ=5.65 ppm, corresponding a calculated difference in chemical shift of 1.57 ppm. Thus it is clear that the "H" group of references 6-13 corresponds to the "T" structure of Table 1.

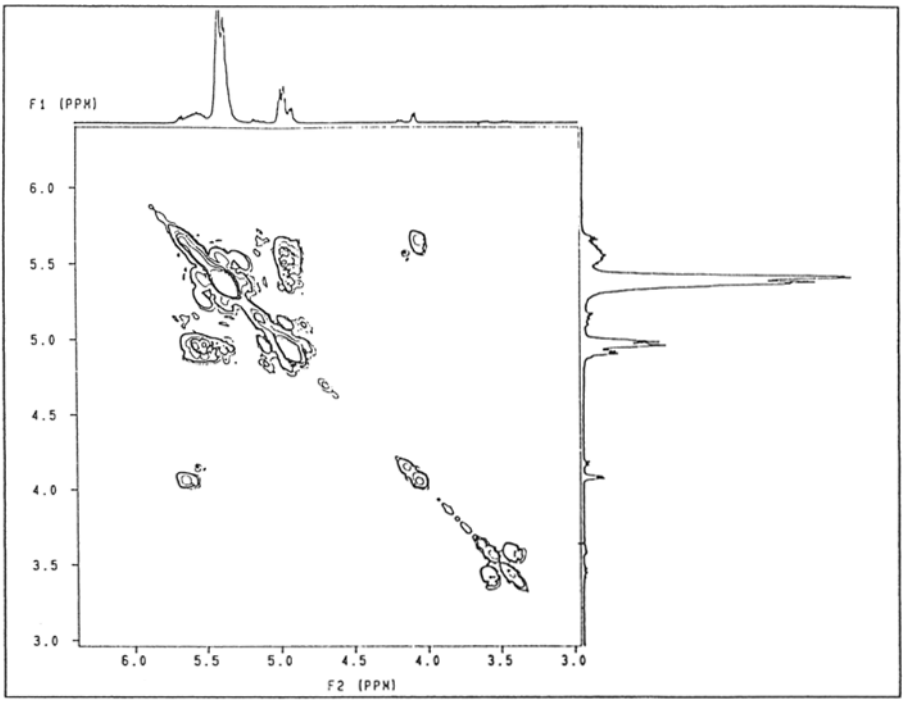


Figure 3 - COSY pulse sequence spectrum for HTPB.

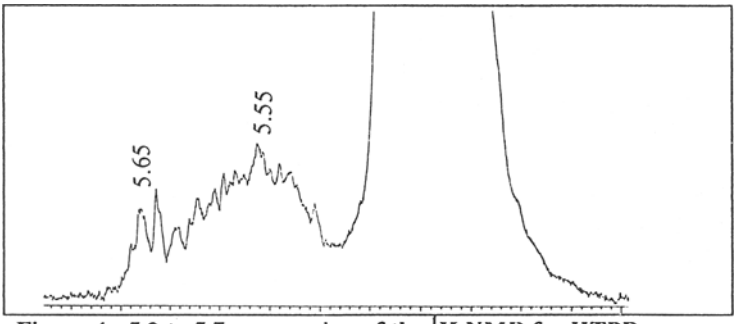


Figure 4 - 5.2 to 5.7 ppm region of the ^{1}H NMR for HTPB.

The second point is whether the peak appearing around 4.2 ppm on the ^{1}H spectrum of HTPB corresponds to a "C" or "G" unit.

A comparison of ^{1}H spectra of model coumpounds[19] show that a "G" group would contain a doublet at 4.15 ppm which corresponds to the two protons that are bonded to the carbon atom bearing the hydroxyl group and is coupled to a triplet at 5.4 ppm which corresponds to the olefinic proton vicinal to the methylene protons. It leads to a calculated chemical shift difference of 1.25 ppm. On the other hand, cis-2-hexen-1-ol would display the methylene doublet at 4.20 ppm and the olefinic protons would appear very close together, around 5.55 ppm, corresponding a calculated difference in chemical shift of 1.35 ppm. In Figure 3 we can see the coupling of the resonance at δ=4.20 ppm ("C" structure) with another at δ=5.55 ppm, corresponding a calculated difference in chemical shift of 1.35 ppm.

In situations in which differences in conditions in which spectra are run make it difficult to base interpretations on absolute chemical shifts, ^{13}C chemical shift differences may be used to assign respective peaks.[20]

Using this criterion for deciding between the two alternatives, the evidence points to the "C" group since the observed difference in chemical shifts is 5.15 ppm between "T" and "C" units identified respectively at δ=63.45 ppm and δ=58.30 ppm from the HETCOR spectrum (Figure 2) whereas the difference calculated for "G" from geraniol[19] and "T" from trans-2-hexene-1-ol[19] is 4.32 ppm while the calculated difference for "C" from cis-2-hexene-1-ol[19] and "T" from trans-2-hexene-1-ol is 5.14 ppm.

It should be pointed out that our spectra were run in $CDCl_3$ as was the case of model compounds[19] used. In our previous work[1] as well as in Pham's book[12] the ^{13}C NMR spectra of HTPB were also run in $CDCl_3$ and the chemical shift differences between "T" ("H") and "C"("G") units is also on the order of 5.1 ppm. Thus it is clear that the "G" group of references 6-13 corresponds to "C" structure of Table 1.

This was taken as a demonstration that the assignments of the "C" and "T" are the correct units that are found in NMR spectra of HTPB.

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