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# Characterization of hydroxyl-terminated polybutadiene

## I. NMR analysis of hydroxylated end groups

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## ABSTRACT

Commercial samples of hydroxyl terminated polybutadienes (HTPB) were analysed by $^1$H and $^{13}$C NMR spectroscopy, in regard to hydroxylated end groups. The results were discussed and compared with those reported so far.

## INTRODUCTION

There are two industrial processes for the synthesis of HTPB using hydrogen peroxide as initiator. The first is American and is employed by Atochem and the commercial products are R45M and R45HT. This process uses isopropanol as solvent [1]. The second process is Brazilian, and it was developed by Petrobras and is employed by Petroflex. The latter HTPB is commercialized under the tradenames of Liquiflex P and Liquiflex H. This process uses ethanol as solvent[2].

The characterization of HTPB has been extensively explored in the literature. The structural features of these telechelic products specially functionality and types of hydroxyls dictate the rate of curing reactions and the ultimate properties of the materials produced from them, mostly polyurethanes. Molecular weight, funcionality and the relations between molecular weight distribution and functionality distribution have been investigated by means of conventional techniques, such as end groups analysis, vapor pressure osmometry, gel permeation chromatography, thin layer chromatography. Structure and the nature of hydroxyl end groups were studied by $^1$H and $^{13}$C NMR spectroscopy. Undoubtedly the major contribution to NMR characterization of HTPB is due to Pham, who published a series of papers on the suject[3-9].

This paper presents the results obtained with R45M, R45HT, Liquiflex H and Liquiflex P by $^1$H and $^{13}$C NMR studies, focusing on the nature of the terminal hydroxyl groups. This subject has aroused some argument in the literature [10-11] and is considered further in our discussion.

## EXPERIMENTAL

HTPB - Commercial samples are Atochem products R45M & R45HT, and Petroflex products Liquiflex P & Liquiflex H. NMR - VRX-300 Varian apparatus, 300 MHz ($^1$H frequency), 5 mm tubes. $^1$H - The samples were dissolved in $C_6D_6$ at a concentration of 1%. The spectra were obtained using a 30$^0$ pulse, 1000 transients and 75$^0$C. $^{13}$C - (frequency of 75.4 MHz). The concentration was 20-30% in $CDCl_3$. We have used 45$^0$ pulse and 12.0 s between pulses. The decoupler mode was gated to avoid NOE and about 1800 pulses were accumulated at ambient temperature.

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## RESULTS AND DISCUSSION

Figures 1 and 2 show the hydroxyl region of the $^1H$ and $^{13}C$ NMR spectra of Liquiflex H samples.

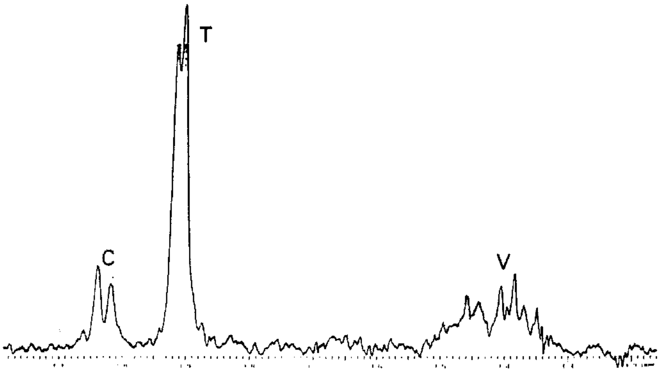


Figure 1 - 3.2 to 4.2 ppm region of the $^1H$ NMR (300 MHz) for Liquiflex H.

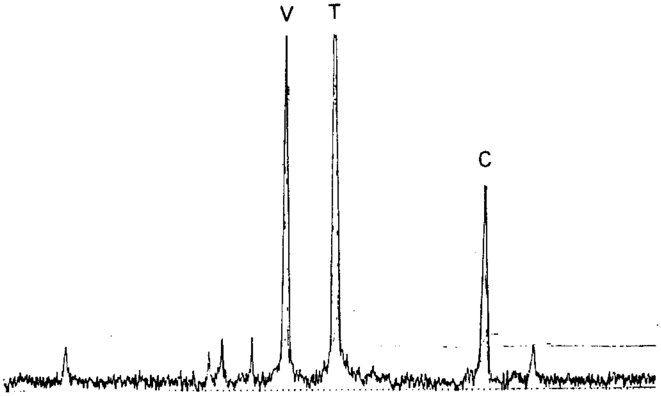


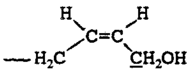
Figure 2 - 54 to 74 ppm region of the $^{13}C$ NMR (75.4 MHz) for Liquiflex H.

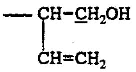
The assigments of olefinic and $CH_2$ resonances in HTPB NMR spectra are well established [3,10,11]. In addition to these olefinic and $CH_2$ resonances, the NMR spectra of HTPB yielded other peaks related to three main alcoholic funnctions. These peaks were assigned differently in the literature[3-11] (Table 1).

**TABLE 1**

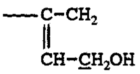
NMR assignments for the three main alcoholic fucntions in HTPB and model compounds

| Resonance δ (ppm) | | Structures Assigned | Author |
|---|---|---|---|
| $^1H$ | $^{13}C$ | | |
| 4.00 | 58.1 | "C" | Ramey [10] |
| 4.05 | - | "C" | Brasler [11] |
| 4.05 | 58.1 | "G" | Pham [3-9] |
| 4.03 | 58.1 | "C" | This work |
| 3.90 | 62.89 | "T" | Ramey [10] |
| 3.95 | - | "T" | Bresler [11] |
| 3.95 | 63.2 | "H" | Pham [3-9] |
| 3.91 | 63.2 | "T" | This work |
| 3.40 | 64.83 | "V" | Ramey [18] |
| 3.37 | - | "V" | Bresler [11] |
| 3.3 - 3.5 | 64.8 | "V" | Pham [3-9] |
| 3.42 | 64.8 | "V" | This work |

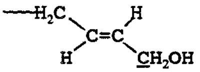

"C"


$-CH(-\underline{C}H_2OH)-CH=CH_2$

"V"


$-C(-CH_2)=CH-\underline{C}H_2OH$

"G"


"T"

$-CH_2-CH=CH-\underline{C}H_2OH$ "H"

Table 1 summarizes the reported results so far, and it can be seen that our results as well as Bresler's[11] agree with Ramey's[10] assignments. The latter was the first to use NMR spectroscopy to elucidate the nature of OH groups in HTPB. He showed that these hydroxyls are predominantly primary and allylic, based on the fact that when the OH groups of HTPB reacted with $CF_3COOH$, one single resonance relative to $-CH_2OOCCF_3$ was seen in the $^{19}F$ NMR spectrum. As the derivatives from primary and secondary alcohols show resonances within a difference of about 0.5 ppm, it was concluded that the predominance of primary alcohols was greater than 95%. As a matter of fact it was found (see Part II of this series) that a significant amount of higher alcoholic functions are present. Ramey's assignments were substantiated by the chemical shifts of cis and trans 3-methyl allyl alcohols. The cis and trans 3-methyl allyl isomers resonate at $\delta = 57.9$ ppm and $\delta = 62.9$ ppm respectively[14], which were correlated to $\delta = 58.1$ ppm and $\delta = 62.89$ ppm resonances in the $^{13}C$ NMR spectra of HTPB. The polymer peak at $\delta = 64.83$ ppm was assigned to the vinyl hydroxyls, based on the fact that saturated alcohols show a peak aproximately at $\delta = 62$ ppm, and the vinylic double bond in the vicinity should shift this resonance downfield[10].

Pham[3-9] did not distinguish between "C" and "T" structures, assuming that both forms should have the same peaks at $\delta = 63.2$ ppm (called "H" structure). He agrees with the assignment at $\delta = 64.8$ ppm for the vinyl hydroxyls (called "V" structure) and assigned the $\delta = 58.1$ ppm to the structure called "G" by correlating with the resonance of geraniol, as the $-\underline{C}H_2OH$ of this compound shows a peak at $\delta = 58.6$ ppm[12].

Most of the work done by Bresler[11] et al. was done at 270 MHz $^1H$ NMR, and our work is based mostly on $^{13}C$ NMR. In this work, we used cis and trans-butene-2-ol-1 and cis and trans-hexene-2-ol-1 as model compounds. The $^{13}C$ NMR spectra of these model compounds were obtained by using the SPECINFO data base from STN (Scientific and Technical Network) data bank. It has in its memory NMR data from the literature (as cis and trans-butene-2-ol-1 and trans-hexene-2-ol-1) and unpublished (as cis-hexene-2-ol-1) [13]. We found for cis-butene-2-ol-1 a peak at $\delta$ = 57.90 ppm and for cis-hexene-2-ol-1 another at $\delta$ = 58.12 ppm. For trans-butene-2-ol-1 the chemical shifts varied according to the references, and were located at $\delta$ = 63.22 ppm, $\delta$ = 63.00 ppm, $\delta$ = 62.90 ppm and $\delta$ = 61.60 ppm. For trans-hexene-2-ol-1 a peak was found at $\delta$ = 63.20 ppm. All these peaks were assigned to the -$CH_2OH$ resonance, leading us to attribute the resonances at $\delta$ = 58.1 ppm and $\delta$ = 63.2 ppm in the HTPB spectrum to structures "C" and "T" respectively, as Ramey and Bresler did, and not to "G" or "H" as Pham (Table 3).

Our assignment is further supported by the following reasoning: results from fractionation of HTPB by preparative GPC, and subjected to polarity-controlled adsorption thin-layer chromatography to determine the functionality distribution of each fraction, showed that: the low molecular weight fractions (400 < Mn < 2000) of R45M and R45HT are composed mainly by di- and monofuncional species; the intermediate (2000 < Mn < 7000) by difunctional species; and the high molecular weight fractions (7000 < Mn < 30000) by polyfunctional species[15]. This was taken as an indication that the higher functionalities of HTPB were due to branching and crosslinking reactions, and not by the presence of hydroxyl groups randomly distributed along the chains. On the other hand, it was shown by Pham[6] that fractions of R45M with 3000 < Mn < 30000 and functionality (fn) between 1.9 and 3.5 had pratically the same amount of "G" structures. Taking into account that "G" structure corresponds to a hydroxyl group in the middle of the chain[3], this finding is in contradiction with the functionality increase with molecular weight and indicates that probaly the resonance observed at $\delta$ = 58,1 ppm is "C" structure and not "G". This however does not discard the possibility of the existence of small amounts of "G" structure in HTPB.

Tables 2 ($^{1}$H) and 3 ($^{13}$C) show the corresponding quantitative data for microstructure and types of hydroxyl end groups of HTPB's samples. The microstructure results were calculated from the $^{1}$H and $^{13}$C NMR spectra according to the literature[3].

**TABLE 2**

$^{1}$H NMR data for HTPB samples

| Structures % | R45M | R45HT | Liq.P | Liq.H |
|---|---|---|---|---|
| Double bond 1,2 (vinyl)[a] | 21.6 | 21.3 | 21.1 | 20.6 |
| Double bond 1,4 (trans)[a] | 57.8 | 56.7 | 57.9 | 57.0 |
| Double bond 1,4 (cis)[a] | 20.7 | 22.0 | 21.0 | 22.3 |
| Double bond 1,4 (total)[a] | 78.5 | 78.7 | 78.9 | 79.3 |
| "T" | 52.3 | 51.1 | 53.4 | 52.7 |
| "C" | 14.3 | 14.1 | 13.6 | 14.0 |
| "V" | 33.4 | 34.7 | 32.9 | 33.2 |
| Functionality $f_n$ [a] | 1.6 | 2.0 | 1.7 | 2.0 |

[a] calculated according to ref. 3

**TABLE 3**

Hydroxyl end groups in HTPB - $^{13}$C NMR data

| Structures % | $\delta$ (ppm) | R45M | R45HT | Liq.P | Liq.H |
|---|---|---|---|---|---|
| "V" | 64.8 | 24.3 | 24.2 | 26.2 | 25.2 |
| "T" | 63.2 | 45.3 | 45.8 | 48.5 | 48.6 |
| "C" | 58.1 | 17.5 | 18.1 | 16.0 | 16.6 |

From Tables 2 and 3 it can be seen that regarding to microstructure, Liquiflex and R45 samples have comparable amounts of cis, trans and vinyl components. These samples have also comparable amounts of the three main hydroxylated end group functions, namely "C", "T" and "V", which are in the vicinity of the cis, trans and vinyl groups of the monomeric units. R45M and

Liquiflex P have lower functionalities and are products used for rocket fuel binders. The functionality values reported here were calculated by a NMR based method which takes into account only the primary hydroxyl groups[3] and are somewhat lower than the true ones (see Part II of this series).

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