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Characterization of hydroxyl-terminated polybutadiene

II. Determination of hydroxylated structures and a mechanistic approach for the polymerization

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ABSTRACT

Liquiflex is a commercial hydroxyl terminated polybutadiene (HTPB) produced by Brazilian technology. It was characterized with respect to molecular weight, functionality, microstructure and hydroxyl group types. The results were compared with those obtained for R45M and R45TH Atochem products. A mechanistic approach for the polymerization reaction is presented.

INTRODUCTION

HTPB is a telechelic liquid rubber obtained by hydrogen peroxide initiated polymerization of butadiene. It is produced by Atochem (R45M and R45HT) in a process which employs isopropanol as solvent[1], and by Petroflex (Liquiflex P and Liquiflex H), using ethanol as solvent[2]. The two HTPBs differ to a certain extent. Liquiflex P and R45M have lower functionality and are used as rocket fuel binders.

The characterization of R45M and R45HT has been published in the literature as to molecular weight, functionality and their distributions, determined by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC)[3-9]. Microstructure has been studied by means of nuclear magnetic resonance (^{1}H and ^{13}C NMR)[10-17]. In these works the <u>cis</u>- and <u>trans</u>- (1,4 enchainment) and <u>vinyl</u>- (1,2 enchainment) structures were quantified and the relative quantity of the three main alcoholic functions determined. The NMR assignments were discussed in our previous paper[17].

This paper presents the molecular characterization of Liquiflex P and Liquiflex H in comparison to R45M and R45HT. Assignments of the lower intensity peaks found in ^{13}C NMR spectra of these HTPB's are also considered, and a proposal of some mechanistic pathways for the structural features is made.

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EXPERIMENTAL PART

HTPB - Commercial samples of R45M, R45HT, Liquiflex H and Liquiflex P. **GPC** - Waters Chromatograph Ana Prep model, 3 stryragel columns (100, 500 and 1000 Å), THF was used as solvent, in a 1 ml/min flow, 30°C. Calibration by polypropylene glycol standards. **VPO** - Wescan 232A osmometer calibrated with polystyrene standards. HTPB samples were vacuum dried during 24h at 60°C and their purity was checked by NMR. Antioxidant (2,6-di-t-butyl, 4-methylphenol) concentration was determined by ultraviolet spectroscopy and $\bar{M}n$ was calculated taking into account this quantity[9]. **VISCOMETRY** - Brookfield Synchrolectric RVF, 25±0,1°C. **FUNCTIONALITY** - The number and weight average functionalities ($\bar{f}n$ and $\bar{f}w$) were determined by the product of $\bar{M}n$ and $\bar{M}w$ (obtained from VPO and GPC data), and hydroxyl content (in eq/g). **HYDROXYL CONTENT** - The hydroxyl groups were acetylated by excess acetic anhydride in pyridine (3h, 100°C). The excess anhydride was hydrolysed with water (1h, 100°C) and titrated with alcoholic KOH using phenolphthalein as indicator. **NMR** - VXR-300 Varian apparatus, 300 MHz, 5mm tubes. ^{13}C (frequency of 75,4 MHz). The concentration was 20-30% in $CDCl_3$. We have used 45° pulses and 12,0 s between pulses. The decoupler mode was gated to avoid NOE and about 1800 pulses were accumulated at ambient temperature **CALCULATION OF NMR SPECTRUM LINE VALUES** - Simulated spectra were made using SPECINFO data base from STN (Scientific and Technical Network) data bank.

RESULTS AND DISCUSSION

HTPB CHARACTERIZATION

Table 1 shows the results of molecular weight, polydispersion, functionality, hydroxyl content and viscosity.

TABLE 1
Characterization Data of Commercial HTPB

HTPB	Hydroxyl content meq/g	G P C					VPO		Brookfield Viscosity
		$\bar{M}w$	$\bar{M}n$	$\bar{f}w$	$\bar{f}n$	D	$\bar{M}n$	$\bar{f}n$	cP (25°C)
Liq. H	0.83	4950	2980	4.10	2.49	1.86	2710	2.25	5800
R45HT	0.86	5180	2910	4.45	2.50	1.78	2630	2.26	7100
Liq. P	0.75	4980	3190	3.70	2.39	1.56	2920	2.19	6000
R45M	0.76	5040	3090	3.83	2.35	1.63	2790	2.12	6900

$D = \bar{M}_w / \bar{M}_n$

The data show that Liquiflex samples have lower values for viscosity, polydispersion and weight average functionality. It was found[6,8] that fractions of higher molecular weight contain most of the polyfunctional molecules. This fact allows us to suppose that Liquiflex samples might have smaller amounts of polyfunctional molecules than the correspondent Atochem products.

Figures 1 and 2 show portions of the ^{13}C NMR spectra of Liquiflex H and R45M

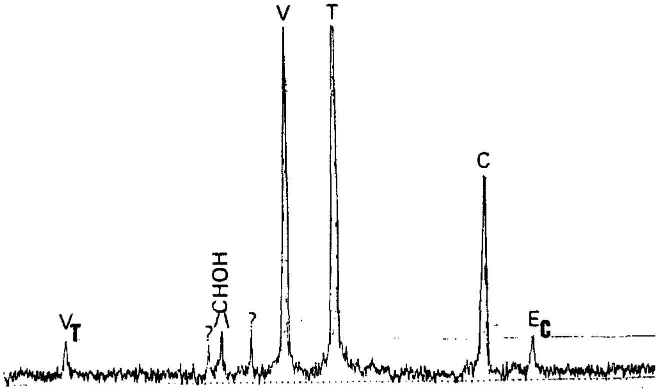


Figure 1 - 54 to 74 ppm region of the ^{13}C NMR (75.4 MHz) spectrum of Liquiflex H.

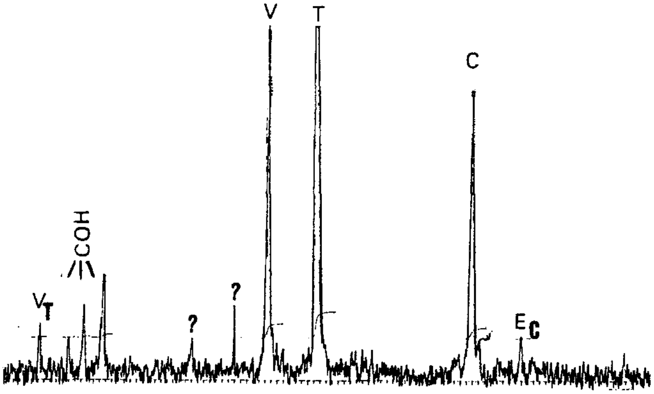


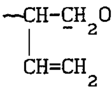
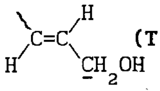
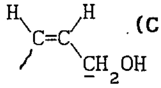
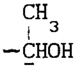
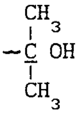
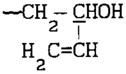
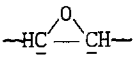
Figure 2 - 54 to 74 ppm region of the ^{13}C NMR (75.4 MHz) spectrum of R45M

The assignments of the lower intensity peaks found in ^{13}C spectra were made based on the different hydroxyl structures possibly formed during the polymerization reaction by free radical mechanism. These assignments were made by comparison with spectra of model compounds simulated using SPECINFO data base from STN (Scientific and technical Network) data bank.

The assignments of the three main alcoholic functions, relative to the hydroxylated end groups in the vicinity of vinyl (V), trans (T) and cis (C) units, were discussed in our previous paper[17].

Table 2 shows ^{13}C NMR data of HTPBs.

Table 2
HTPB Structural Characterization - ^{13}C NMR Data

Structures %	δ (ppm)	R45M	R45HT	Liq. P	Liq. H
 $-\underset{CH=CH_2}{\underline{C}H}-\underline{C}H_2OH$ (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
non identified	66.0	1.6	1.9	1.8	1.9
 $-\overset{CH_3}{\underline{C}HOH}$ (OH 2°)	67.0	-	-	3.1	2.0
non identified	67.5	1.6	1.0	1.5	1.0
 $-\overset{CH_3}{\underset{CH_3}{\underline{C}}}\ OH$ (OH 3°)	70-72	6.6	4.6	-	-
 $-CH_2-\underset{H_2C=CH}{\underline{C}HOH}$ (V_T)	72.4	1.5	2.0	1.6	1.9
 (E_c)	56.5	1.5	2.5	1.2	2.8

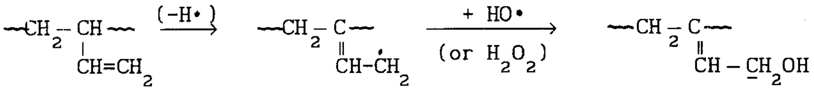
MECHANISM

Based on the ^{13}C NMR assignments some mechanistic routes are proposed for the polymerization of butadiene by a free radical mechanism, using hydrogen peroxide as initiator and alcohol as solvent.

less likely to occur. Nevertheless, simulations performed with SPECINFO lead us to assign the resonance found at $\delta = 72,4$ ppm to the species (V_T) formed in path (8) which contains one secondary allylic hydroxyl group. This indicates that although less probable, path (8) occurs to a certain extent.

4 - Sequential Reations with HO• (or H_2O_2)

The formation of "G" structure proposed by Pham[10-14], and assigned to the resonance at $\delta = 58.1$ ppm as discussed previously[17], can occur by abstraction of a hydrogen, followed by reaction with HO• (or H2O2). This reaction is also less likely to occur due to the two phases already mentioned.



$$\text{—}CH_2\text{–}\underset{\substack{|\\ CH=CH_2}}{CH}\text{—} \xrightarrow{(-H\bullet)} \text{—}CH_2\text{–}\underset{\substack{\| \\ CH\text{–}\dot{C}H_2}}{C}\text{—} \xrightarrow[\text{(or } H_2O_2)]{+\ HO\bullet} \text{—}CH_2\text{–}\underset{\substack{\| \\ CH-\underline{C}H_2OH}}{C}\text{—}$$

(G) **(9)**

5. Reaction with solvent

As it can be seen from the data in Table 2, R45 samples have a significant amount of tertiary hydroxyl structures (6.6% for R45M and 4.6% for R45HT) assigned to the resonance at δ = 70-72 ppm. This is not seen in Liquiflex products but instead a peak at $\delta = 67,0$ ppm is observed, which was assigned to secondary hydroxyl groups. Simulation with the following model compounds yielded:

Structure		Assignment (ppm)
$CH_3-CH=CH-CH_2-\underline{C}(CH_3)HOH$	**(OH 2°)**	67.4
$CH_3-CH=CH-CH-\underline{C}(CH_3)_2OH$	**(OH 3°)**	70.0
$CH_3-CH(CH=CH_2)-CH_2-\underline{C}(CH_3)_2OH$	**(OH 3°)**	71.0

Reactions with solvent have already been mentioned in the literature for this system[16] and in our case would explain the appearance of secondary and tertiary hydroxyl groups according to the scheme:

$$HOC(CH_3)_2H + \bullet OH \text{ (or } \bullet Bd_nOH) \longrightarrow HO\dot{C}(CH_3)_2 + H_2O \text{ (or } HBd_nOH) \qquad \textbf{(10)}$$

$$HOCH_2CH_3 + \bullet OH \text{ (or } \bullet Bd_nOH) \longrightarrow HO\dot{C}HCH_3 + H_2O \text{ (or } HBd_nOH) \qquad \textbf{(11)}$$

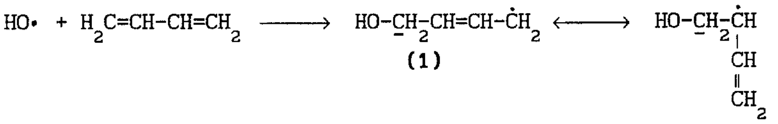
$$HO\dot{C}(CH_3)_2 \xrightarrow[\text{(or } +\ \bullet Bd_nOH)]{+nBd\ +\ \bullet OH} HOC(CH_3)_2Bd_nOH \qquad \textbf{(12)}$$

$$HO\dot{C}HCH_3 \xrightarrow[\text{(or } +\ \bullet Bd_nOH)]{+nBd\ +\ \bullet OH} HOCH(CH_3)Bd_nOH \qquad \textbf{(13)}$$

The greater stability of form (10) relative to (11) would explain the greater tertiary hydroxyl group content in R45 compared to secondary hydroxyls in Liquiflex.

1. Initiation

This step occurs by the reation between HO• radicals and butadiene molecules.



$$HO\bullet + H_2C{=}CH{-}CH{=}CH_2 \longrightarrow \underset{(1)}{HO{-}CH_2{-}CH{=}CH{-}\dot{C}H_2} \longleftrightarrow HO{-}CH_2{-}\dot{C}H(CH{=}CH_2) \quad (2)$$

Addition of a new monomer to the active centers (1) and (2) produce "T", "C" and "V" species (Table 2) in which the CH_2 groups attached to OH are observed in ^{13}C NMR at δ = 63.2 ppm, δ = 58.1 ppm and δ = 64.8 ppm respectively[17].

2. Propagation

This step can be presented as:

$$\left.\begin{array}{l} T\bullet \\ C\bullet \\ V\bullet \end{array}\right. + nBd \longrightarrow \begin{array}{l} TBd_n\bullet \\ CBd_n\bullet \\ VBd_n\bullet \end{array} \qquad (3)$$

were **T·** , **C·** and **V·** stand for T, C, and V radicals and Bd stands for the monomer.

3. Termination

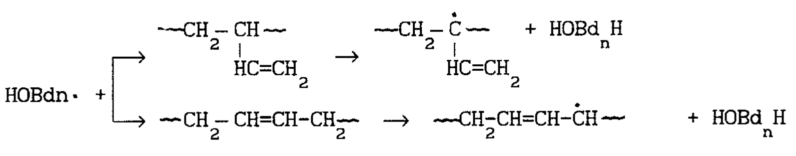
3.1 - Radical Coupling

$$\begin{array}{c}(T\cdot + T\cdot),(T\cdot + C\cdot),\ (T\cdot + V\cdot),\ (C\cdot + C\cdot),\ (C\bullet + V\cdot) \text{ and } (V\bullet + V\bullet) \\ \downarrow \\ \text{linear HTPB} \end{array} \qquad (4)$$

This kind of termination is the most probable, due to the high concentration of free radicals existing in this type of polymerization. The chains are linear and hydroxyl groups are of "T", "C" and "V" type.

3.2 - Chain Transfer

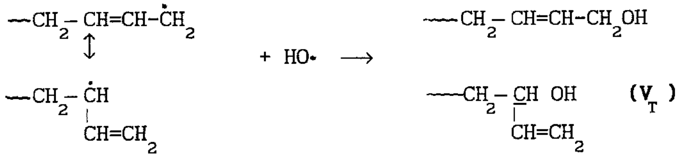
These reactions give rise to mono- and polyfunctional molecules (5 and 6).



$$HOBd_n\bullet + {-}CH_2{-}CH(HC{=}CH_2){-} \rightarrow {-}CH_2{-}\dot{C}(HC{=}CH_2){-} + HOBd_nH \qquad (5)$$

$$HOBd_n\bullet + {-}CH_2{-}CH{=}CH{-}CH_2{-} \longrightarrow {-}CH_2{-}CH{=}CH{-}\dot{C}H{-} + HOBd_nH \qquad (6)$$

3.3 - Reaction With Initiator Radicals (or H_2O_2)



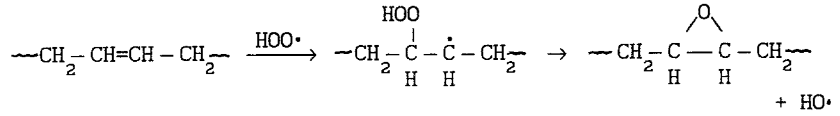
$$\left.\begin{array}{c} {-}CH_2{-}CH{=}CH{-}\dot{C}H_2 \\ \updownarrow \\ {-}CH_2{-}\dot{C}H(CH{=}CH_2) \end{array}\right. + HO\bullet \longrightarrow \begin{array}{ll} {-}CH_2{-}CH{=}CH{-}CH_2OH & (7) \\ {-}CH_2{-}CH(OH)(CH{=}CH_2) \quad (V_T) & (8) \end{array}$$

Since in this particular free radical process the polymer and the solvent are in two separate phases, and the initiator is present in the latter, this kind of termination is

6. Epoxy Formation

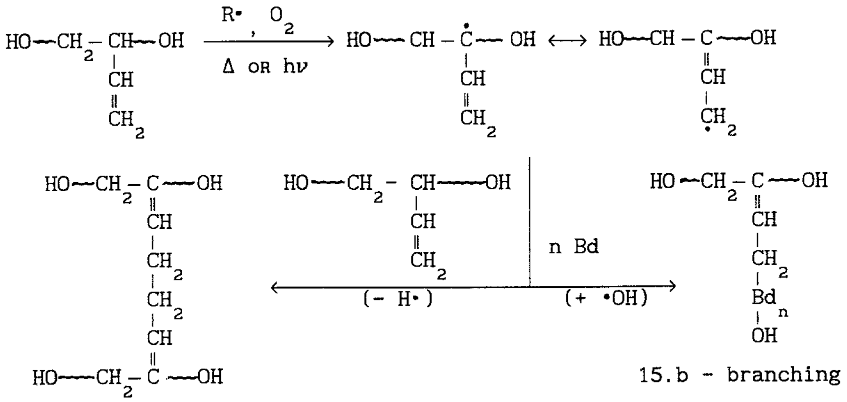
The peak found at δ = 56.5 ppm in the ^{13}C NMR spectrum was assigned to cis epoxy groups (Ec)[18-19]. It was detected in all HTPB samples and at higher concentrations in R45HT and Liquiflex H, both produced at a higher temperature than R45M and Liquiflex P. The trans epoxy group (ET) appears at δ = 58.5 ppm[18-19] close to "C" (δ = 58,1 ppm) and "G" (δ = 58,6 ppm) structures. It was not detected in any spectra of HTPB, but this does not eliminate the possibility of the existence of small amounts of this structure. The origin of these groups could be explained as follows:

$$HOOH + {\cdot}OH \longrightarrow HOO{\cdot} + H_2O \qquad \textbf{(14)}$$



7. Branching and Cross Linking Reactions

These reactions can occur during the polymerization, processing or storage of the liquid rubbers. They are favored by higher temperatures and by the presence of free radicals, and can be detected by the increasing viscosity or broadening of the GPC peak in the higher molecular weight region, by increasing polydispersity[1-2].



15.a - crosslinking

15.b - branching

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