

Characterization of hydroxyl-terminated polybutadiene

V. Structure of polymers produced by thermal and photochemical hydrogen peroxide decomposition

W. D. Vilar^{1,*}, M. T. M. Moutinho², S. M. C. Menezes³, F. M. B. Coutinho⁴

¹ Instituto Militar de Engenharia, Rio de Janeiro 22290-270, RJ, Brazil

² Petroflex/Coperbo, Duque de Caxias, RJ, Brazil

³ Centro de Pesquisas da Petrobrás (CENPES), Rio de Janeiro, Brazil

⁴ Instituto de Macromoléculas Professora Eloisa Mano/UFRJ, P.O. Box 68525, Rio de Janeiro 21945-970, RJ, Brazil

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ABSTRACT

The structures of hydroxyl terminated polybutadienes (HTPB) obtained by free radical polymerization of butadiene in ethanol medium initiated by thermal and photochemical hydrogen peroxide decomposition were studied. The incorporation of alcohol in the polymer chain ends was evidenced by ¹H and ¹³C NMR spectroscopy.

INTRODUCTION

Liquid rubbers have assumed an increasing importance in the world of elastomers market. These polymers are defined as fluid at room temperature but may be converted to a solid network by chemical reactions in such a way that their properties may be compared to those of solid rubber vulcanizates. Liquid rubbers containing reactive groups at the polymer chain ends may be produced by free radical or anionic polymerization. The processes used by the two main producers of liquid polybutadienes by free radical method (Petroflex and Atochem) are based on thermal decomposition of hydrogen peroxide in alcoholic medium giving a hydroxyl terminated polybutadiene (HTPB). The synthesis of HTPB using hydrogen peroxide as initiator requires the homolysis of peroxide bond. The energy required for that is usually supplied by heating hydrogen peroxide at 90°C or at higher temperatures. Another source of energy which may be used to decompose the peroxide bond is ultraviolet radiation. Such process allows the synthesis of HTPB at room temperature. Pinazzi and coworkers¹ related the use of UV radiation ($\lambda=254$ nm) to initiate polymerization of apolar monomers by hydrogen peroxide decomposition. The present authors studied the polymerization of butadiene and other monomers at room temperature using a series of compatibilizing agents, mainly alcohols. The characteristics of HTPBs are dependent on the processes and raw materials employed.

The characterization of HTPB has been the subject of published papers²⁻⁴. The structural features of these telechelic products, especially functionality and types of hydroxyls, dictate the rate of the curing reactions and the ultimate properties⁵ of the materials derived from them, mostly polyurethanes. Molecular weight, functionality 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, and thin layer chromatography. Structure and the nature of hydroxyl end groups were studied by ¹H and ¹³C NMR spectroscopy.

We have synthesized two types of HTPBs using hydrogen peroxide as initiator and ethanol as compatibilizing agent. The first is a low molecular weight HTPB (LMW-

* Corresponding author

HTPB) prepared by thermal decomposition of hydrogen peroxide. The second was prepared by photochemical decomposition of hydrogen peroxide (UV-HTPB). This paper deals with the molecular characterization of these products and makes a comparison with Liquiflex H, a commercial HTPB produced by Petroflex using hydrogen peroxide as initiator and ethanol as compatibilizing agent⁶. In this paper we discuss the assignments of the three main alcoholic functions and of the lower intensity peaks found in ¹H and ¹³C NMR spectra obtained with different HPTBs. The NMR assignment related to three main alcoholic functions in HTPB has aroused some discussion in the literature^{2,4,7-16} and is considered further in the present paper.

EXPERIMENTAL PART

HTPB - Liquiflex H (LIQ-H) was obtained from Petroflex. **LMW-HTPB** was synthesized⁶, at 100°C, using a mixture of 49, 36 and 16 parts w/w of butadiene, ethanol and hydrogen peroxide (50% w/w) respectively. **UV-HTPB** was prepared¹⁷ by recirculating a mixture of 30, 50 and 12 parts w/w of butadiene, ethanol and hydrogen peroxide (50% w/w) respectively, at room temperature, during 8 hours in an annular reactor equipped with an UV lamp emitting 25 Watts of radiation at 254 nm. **GPC** - Gel permeation chromatography was performed using an HPLC SEC LDC Analytica apparatus. THF flow at 1.0 ml/min was used at 40°C with a sample concentration of 0.5 % w/v. Three 3 Styragel columns were used; two PLGEL mixt. bed D, and one 100 Å.GPC calibration was performed using polypropylene glycol standards. **VISCOMETRY** - Viscosity measurements were performed using a Brookfield Synchroelectric RVF, at 25 ± 0,1°C. **FUNCTIONALITY**- The number and weight average functionality (\bar{f}_n and \bar{f}_w) were determined from the product of \bar{M}_n or \bar{M}_w (obtained from GPC data), and hydroxyl content (eq/g). **HYDROXYL CONTENT** - The hydroxyl groups were acetylated by excess acetic anhydride in pyridine (3h, 100°C). The anhydride excess was hydrolyzed with water (1h, 100°C) and acid was back titrated with alcoholic KOH using phenolphthalein as indicator. **NMR** - Nuclear magnetic resonance was performed using a VXR-3000 Varian apparatus, 300 MHz, using 5 mm tubes. For ¹H (300 MHz frequency) the samples were dissolved in CDCl₃ (1%). The spectra were obtained using a 30° pulse 1000 transients and 75°C. For ¹³C (frequency of 75.4 MHz) the concentration was 20-30% in CDCl₃. It was used 45 ° pulses and 12.0 s between pulses. The decoupler mode was gated to avoid NOE and about 1800 pulses were accumulated at room temperature. **CALCULATION OF NMR SPECTRUM LINE VALUES** - Simulated spectra were made using SPECINFO data base from STN (Scientific and Technical Network) data bank¹⁸.

RESULTS AND DISCUSSION

Table 1 shows HTPB characterization data.

Table 1 - HTPB characterization data

HTPB	OH content (meq/g)	GPC					Viscosity (cP) at 25°
		\bar{M}_w	\bar{M}_n	D	\bar{f}_w	\bar{f}_n	
LIQ. H	0.83	4950	2980	1.66	4.10	2.49	5800
LMW	1.61	2860	1520	1.83	4.61	2.45	2300
UV	2.53	1180	890	1.33	3.00	2.26	1050

Table 1 shows that UV-HTPB has higher values of hydroxyl content and lower values of molecular weight, viscosity, functionality and polydispersion. The higher hydroxyl content and lower molecular weight and viscosity are explained by the higher initiator/monomer ratio used in the polymerization. The higher values of functionality and polydispersion observed in LIQ-H and LMW-HTPB are probably due to branching and crosslinking reactions which were enhanced by the higher temperature employed in the polymerization.

Figures 1A and 1B show the ^1H NMR spectra of LIQ-H (1A), UV-HTPB (1B) and Figures 1C and 1D show the ^{13}C NMR spectra of LIQ-H (1C), and UV-HTPB (1D) respectively.

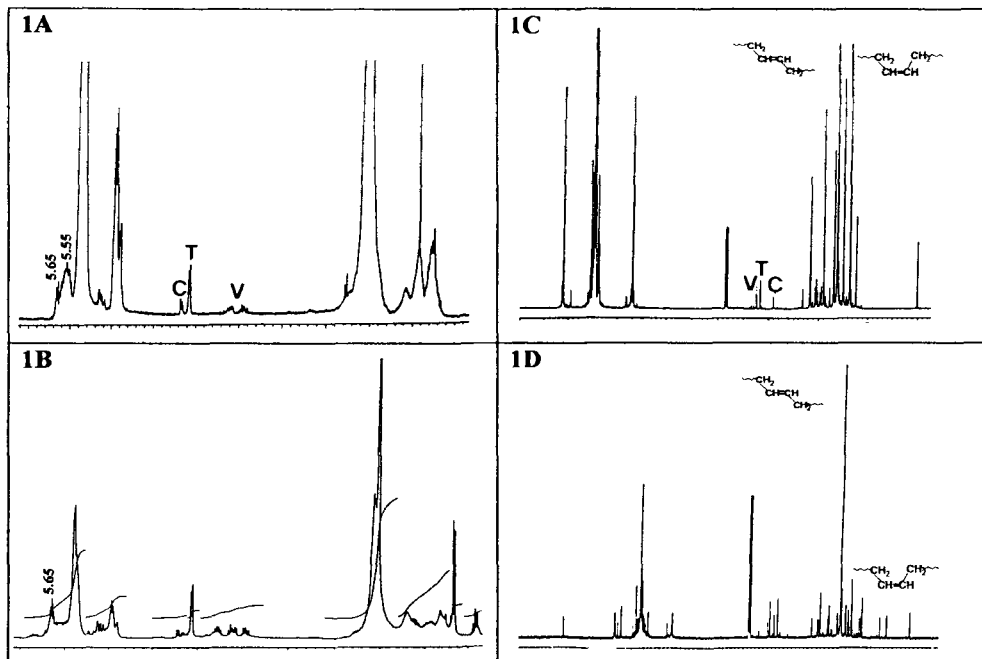


Figure 1 - ^1H NMR spectra of LIQ-H (A), UV-HTPB (B) and ^{13}C NMR spectra of LIQ-H (C), and UV-HTPB (D)

Figures 2A, 2B and 2C show the 3.2 to 4.2 ppm region of ^1H NMR spectra of Liquiflex H (2A), LMW-HTPB (2B) and UV-HTPB (2C) and Figures 2D, 2E and 2F show the 54 to 74 ppm region of the ^{13}C NMR spectra of Liquiflex H (2A), LMW-HTPB (2B) and UV-HTPB (2C), respectively.

Quantitative characterization data for HTPBs are presented in Tables 2 and 3. The results concerning microstructure (Table 2) were calculated from ^1H and ^{13}C NMR spectra according to the literature⁹. The assignments of the three main alcoholic functions relative to the hydroxylated end groups at the vicinity of vinyl ("V"), trans ("T") and cis ("C") repeating units were discussed in previous papers^{2,4}.

From Table 2 it can be seen that UV-HTPB, which was prepared at room temperature, has lower proportions of double bond 1,4-cis structure than LIQ-H and LMW-HTPB which were prepared at higher temperatures. The small proportions of hydroxylated end groups at the vicinity of cis units ("C" structure), in UV-HTPB was taken as an evidence that the "C" structure is the correct assignment in the HTPB NMR spectra and not the "G" structure proposed by Pham and coworkers⁹⁻¹⁶.

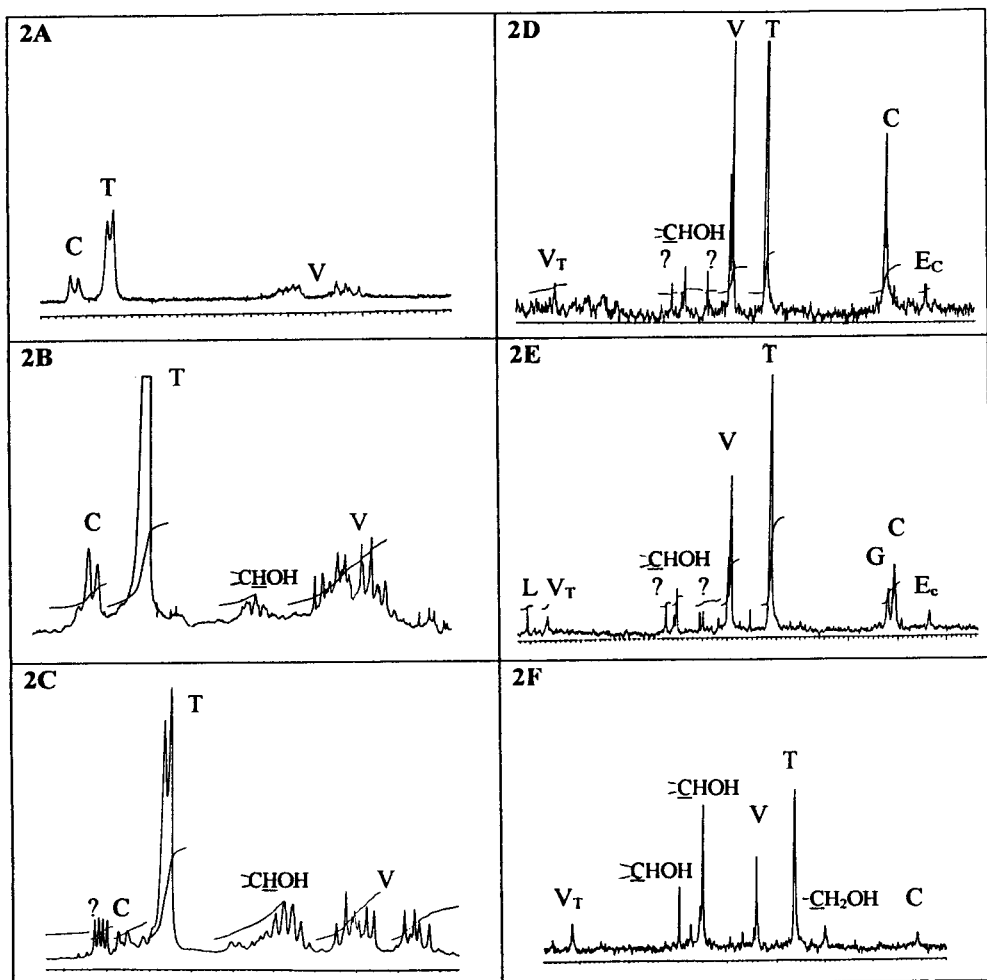


Figure 2 - 3.2 to 4.2 ppm region of ^1H NMR spectra of LIQ-H (A), LMW-HTPB (B) and UV-HTPB (C) and 54 to 74 ppm region of ^{13}C NMR spectra of LIQ-H (D), LMW-HTPB (E) and UV-HTPB (F), respectively

Table 2 - Microstructure and hydroxyl types of HTPBs, from ^1H and ^{13}C NMR data

Structure	LIQ. H	LMW	UV
Double bond 1,2 (vinyl)	20.6	21.9	27.4
Double bond 1,4 (trans)	57.0	56.5	62.2
Double bond 1,4 (cis)	22.3	21.6	10.4
Double bond 1,4 (total)	79.3	78.1	72.6
"T"	52.7	42.1	36.7
"C"	14.0	11.8	6.5
"V"	33.2	35.5	32.2
$\sim\text{CH}_2\text{C}(\text{CH}_3)\text{HOH}$ (OH 2°)	-	10.5	24.6

In trans-2-hexene-1-ol or in trans-2-penten-1-ol the protons attached to olefinic carbons have resonances at $\delta=5.65$ ppm by ^1H MNR spectroscopy and those protons attached to hydroxylated carbons have resonances at $\delta=4.05$ ppm, respectively. In cis-2-hexene-1-ol or in cis-2-penten-1-ol the protons attached to olefinic carbons have resonances at $\delta=5.55$ ppm and those protons attached to hydroxylated carbons have resonance at $\delta=4.20$ ppm by ^1H NMR, respectively¹⁹.

In the COSY pulse sequence spectrum for LIQ-H it was observed that these resonances at $\delta=5.55$ ppm and at $\delta=5.65$ ppm have couplings with those at $\delta=4.20$ ppm (assigned as "C" structure) and $\delta=4.05$ ppm (assigned as "T" structure), respectively²⁰.

The resonances at $\delta=5.55$ ppm and at $\delta=5.65$ ppm are observed in the ^1H NMR spectrum of LIQ-H (Figure 1A), however, only the resonance at $\delta=5.65$ ppm is observed in the ^1H NMR spectrum of UV-HTPB (Figure 1C), which has low proportions of 1,4-cis-structure in the polymer backbone and low proportions of "C" units. This was taken as further evidence that the "C" and "T" structures are the correct assignments not "G" and "H" structures as proposed by Pham and coworkers⁹⁻¹⁶.

Table 2 shows that LMW-HTPB and UV-HTPB samples, which were prepared with higher ethanol/butadiene ratio, have significant proportions of secondary hydroxyl groups. Reaction with solvent during the HTPB synthesis was discussed in previous papers^{3,4}.

Table 3 presents a quantitative evaluation of the structural characteristics of LIQ-H, LMW-HTPB and UV-HTPB, based on their ^{13}C NMR spectra. The assignments of the peaks were discussed in our previous papers^{2,4}.

Table 3 - HTPB structural characterization - ^{13}C NMR data

Structure %	δ (ppm)	Liquiflex H	LMW-HTPB	UV-HTPB
$\begin{array}{c} \sim\text{CH}-\text{CH}_2\text{OH} \\ \\ \text{CH}=\text{CH}_2 \end{array}$ (V)	64.8	25.2	22.2	18.6
$\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{CH}_2\text{OH} \end{array}$ (T)	63.2	48.6	42.1	31.2
$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ \quad \\ \quad \text{CH}_2\text{OH} \end{array}$ (C)	58.1	16.5	11.3	7.1
$\begin{array}{c} \sim\text{CH}_2-\text{C} \sim \\ \\ \text{CH}-\text{CH}_2\text{OH} \end{array}$ (G)	58.6	-	7.2	-
$\sim\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}$ (OH 1°)	62.0	-	-	7.1
non identified	66.0	1.9	3.2	-
$\sim\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{OH}$ (OH 2°)	67.0	2.0	4.7	29.2
non identified	67.5	1.0	1.5	-
$\sim\text{CH}(\text{CH}=\text{CH}_2)\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ (OH 2°)	68.0	-	-	5.8
$\begin{array}{c} \sim\text{CH}_2-\text{CHOH} \\ \\ \text{CH}=\text{CH}_2 \end{array}$ (V _T)	72.4	1.9	3.1	1.0
$\begin{array}{c} \text{OH} \\ \\ \sim\text{CH}_2-\text{C} \sim \\ \\ \text{CH}=\text{CH}_2 \end{array}$ (L)	73.7	-	1.6	-
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \sim\text{HC}-\text{CH} \sim \end{array}$ (E _o)	56.5	2.8	3.1	-

The data in Table 3 show that the main differences between LIQ-H and LMW-HTPB in comparison with UV-HTPB are related to "C", "G", "L", and "E_c" structures, as well as to primary and secondary hydroxyl groups.

LIQ-H, LMW-HTPB and UV-HTPB were produced at 120°C, 100°C and room temperature respectively, employing ethanol/butadiene and hydrogen peroxide/butadiene ratios respectively low, high and very high.

The lower proportion of "C" structure and the fact that the "G", "L" and "E_c" are not observed in ¹³C NMR spectrum of UV-HTPB can be explained by lower temperature employed in its polymerization.

The high ethanol/butadiene ratio employed in UV-HTPB polymerization is responsible for the high amounts of secondary and also for the small amounts of primary hydroxyl groups detected by the ¹³C NMR.

The mechanism of the reaction with ethanol during HTPB polymerization was previously discussed^{3,4}.

The assignments of the resonances at $\delta=67.5$ ppm, $\delta=68.0$ ppm and $\delta=62.0$ ppm to those structures in Table 3 were based on our simulations¹⁸ with model compounds that produced the results in Table 4.

Table 4 - Results of simulated spectra with model compounds

Structure (OH type)	Assignment (ppm)
CH ₃ CH=CH-CH ₂ CH ₂ CH ₂ OH (primary)	62.1
CH ₃ CH=CHCH ₂ CH(CH ₃)OH (secondary)	67.4
CH ₃ CH(CH=CH ₂)CH ₂ CH(CH ₃)OH (secondary)	68.2

Peaks at $\delta=62.20$ ppm attributed to -CH₂OH at $\delta=66.95$ ppm and at $\delta=68.13$ ppm attributed to -CH(CH₃)OH were related in literature¹⁹ for 4-penten-1-ol, 4-penten-2-ol and 2-decanol, respectively. Those results are in agreement with our data obtained by simulation (Table 4).

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