# Characterization of hydroxyl-terminated polybutadiene

## III. Comparison between conventional and low molecular weight products

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## ABSTRACT

A comparison between the molecular structure of conventional and low molecular weight hydroxyl terminated polybutadienes (HTPBs) is presented. The conventional HTPB samples were R45M, R45HT (Atochem), Liquiflex P and H (Petroflex, Brazil), and the low molecular weight ones were R20LM (Atochem) and two laboratory synthesized materials. The structural differences found were attributed to dissimilarities in fabrication processes for each type of HTPB. Some mechanistic pathways for the polymerization are suggested.

## INTRODUCTION

Synthetic rubbers were initially developed as a substitute for natural rubber, leading to the production of solid elastomers, such that existing compounding and molding technology could be applied. Solid rubber as a raw material presents some disadvantages, such as high equipment cost, high energy consumption and difficulties in processing automation. These factors hindered the tendency of elastomers to follow the tremendous growth of plastics in the last decades. Aiming to overcome these difficulties, liquid rubbers were developed. Although these rubbers have a higher manufacturing cost, their great versatility in processing makes their production profitable.

The most important liquid rubber produced so far is hydroxyl terminated polybutadiene (HTPB) which is available in two commercial grades with number average molecular weights of 1200 or 2800. These materials are prepared by the free radical polymerization of butadiene, using hydrogen peroxide as initiator and an alcohol as solvent. The higher molecular weight HTPBs are produced by Atochem (R45M and R45HT) using isopropanol as solvent[1], and by Petroflex in Brazil (Liquiflex P and Liquiflex H) using ethanol as solvent[2]. The structural differences between these products were discussed in previous papers[3,4]. A further low molecular weight HTPB (LM-HTPB), is commercialized by Atochem[5] (R20LM).

Higher molecular weight grades of HTPB are conventional products with a wide range of applications and are consumed on a greater scale compared to LM-HTPB. Nevertheless the latter presents some advantages over conventional HTPB in polyurethane manufacturing, such as a lower viscosity which facilitates casting or RIM molding, a higher compatibility with other polyols, and better mechanical properties[5-7].

Besides molecular weight, the two kinds of HTPB exhibit some differences in regard to molecular structure, due to dissimilarities in fabrication. The molecular characterization of LM-HTPB cannot be found in the literature. A comparison between the mechanical

properties of polyurethanes derived from laboratory prepared LM-HTPB and from R45M and R45HT has been reported[6].

We synthesized two types of LM-HTPBs using hydrogen peroxide as initiator and ethanol (HTPB-LM1) or methanol (HTPB-LM2) as solvent[7]. This paper presents the molecular characterization of this products in comparison with R20-LM and four commercial samples of conventional HTPBs, namely R45M, R45HT, Liquiflex H and Liquiflex P, taking into account functionality, molecular weight, microstructure and hydroxyl types. Based on the characterization data some mechanistic pathways are suggested for the polymerization.

## EXPERIMENTAL PART

**HTPB** - R20LM was obtained form Atochem. HTPB-LM1 and HTPB-LM2 were synthesized using ethanol and methanol as solvent respectively[7]. **GPC** - Gel permeation chromatography was performed using an HPLC SEC LDC Analytica apparatus. THF solvent 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 $\overset{o}{A}$.GPC calibration was performed using polypropylene glycol standards. **VPO** - Vapor pressure osmometry was done using a Wescan 232A osmometer which calibrated with polystyrene standards. HTPB samples were vacuum dried for 24h at 60°C and their purity was checked by NMR. **VISCOMETRY** - Viscosity measurements were performed using a Brookfield Synchrolectric RVF, at a temperature of $25 \pm 0,1°C$. **FUNCTIONALITY**- The number and weight average functionality ($\overline{f}_n$ and $\overline{f}_w$) were determined from the product of $\overline{M}_n$ or $\overline{M}_w$ (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 hydrolyzed with water (1h, 100°C) and titrated with alcoholic KOH using phenolphtalein 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 $C_6D_6$ at a concentration of 1%. The spectra were obtained using a 30° pulse 1000 transients and 75°C. For $^{13}C$ (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[8].

## RESULTS AND DISCUSSION

Table 1 shows the results concerning molecular weight, polydispersity, functionality, hydroxyl content and Brookfield viscosity for conventional and low molecular weight HTPBs. Table 1 shows that LM-HTPBs have lower molecular weights and viscosities, and higher hydroxyl contents than conventional HTPBs, as expected. No great difference between LM and conventional HTPBs products was found for number average ($\overline{f}_n$) and weight average ($\overline{f}_w$) functionality, and in polydispersities.

Quantitative characterization data of conventional and LM-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 literature[9]. The assignments of the three main alcoholic functions relative to the hydroxyl end groups in the vicinity of vinyl ('V'), trans ('T') and cis ('C') units were discussed in our previous paper[3].

**Table 1 - HTPB Characterization data for conventional and low molecular weight products.**

| HTPB | Hydrox. content meq/g | GPC | | | | | VPO | | Brook. Visc. cP (25°C) |
| | | $\overline{M}_w$ | $\overline{M}_n$ | $\overline{f}_w$ | $\overline{f}_n$ | D | $\overline{M}_n$ | $\overline{f}_n$ | |
|---|---|---|---|---|---|---|---|---|---|
| LIQ.P | 0.75 | 4980 | 3190 | 3.70 | 2.39 | 1.56 | 2920 | 2.19 | 6000 |
| LIQ.H | 0.83 | 4950 | 2980 | 4.10 | 2.49 | 1.66 | 2710 | 2.25 | 5800 |
| R45HT | 0.86 | 5180 | 2910 | 4.45 | 2.50 | 1.78 | 2630 | 2.26 | 7100 |
| R45M | 0.76 | 5040 | 3090 | 3.83 | 2.35 | 1.63 | 2790 | 2.12 | 6900 |
| LM1 | 1.61 | 2860 | 1520 | 4.61 | 2.45 | 1.83 | 1340 | 2.16 | 2300 |
| LM2 | 1.81 | 2770 | 1320 | 5.02 | 2.39 | 2.10 | 1160 | 2.10 | 2100 |
| R20LM | 1.77 | 2900 | 1480 | 5.13 | 2.62 | 1.96 | 1240 | 2.19 | 2500 |

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

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

| Structures | R45M | R45HT | LIQ.P | LIQ.H | LM1 | LM2 | R20LM |
|---|---|---|---|---|---|---|---|
| Double bond 1,2 (vinyl)* | 21.6 | 21.3 | 21.1 | 20.6 | 21.9 | 23.7 | 22.9 |
| Double bond 1,4 (trans)* | 57.8 | 56.7 | 57.9 | 57.0 | 56.5 | 55.0 | 55.1 |
| Double bond 1,4 (cis)* | 20.7 | 22.0 | 21.0 | 22.3 | 21.6 | 21.3 | 22.0 |
| Double bond 1,4 (total)* | 78.5 | 78.7 | 78.9 | 79.3 | 21.6 | 21.3 | 22.0 |
| 'T' | 52.3 | 51.1 | 53.4 | 52.7 | 47.0 | 41.8 | 47.8 |
| 'C' | 14.3 | 14.1 | 13.6 | 14.0 | 13.2 | 11.4 | 13.6 |
| 'V' | 33.4 | 34.7 | 32,9 | 33.2 | 39.8 | 46.8 | 38.6 |

* calculated according to ref. 9

From Table 2 it can be seen that with respect to microstructure, all LM-HTPB samples contain comparable amounts of cis, trans and vinyl enchainments. These samples have also comparable concentrations of the three main hydroxylated end group functions, namely 'C', 'T' and 'V'.

Table 3 presents a tabulation of the structural features of conventional and LM-HTPBs, based on $^{13}$C NMR spectra. The assignment of the low intensity peaks were based on assumptions for the different structures possibly formed during free radical polymerization. These peaks were compared with those of the corresponding simulated model compounds[8].

Figure 1 shows the 54 to 74 ppm region of the $^{13}$C NMR spectra of R20LM (A), HTPB-LM1 (B), HTPB-LM2 (C), which are low molecular weight products and of Liquiflex H (D), a conventional HTPB.

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

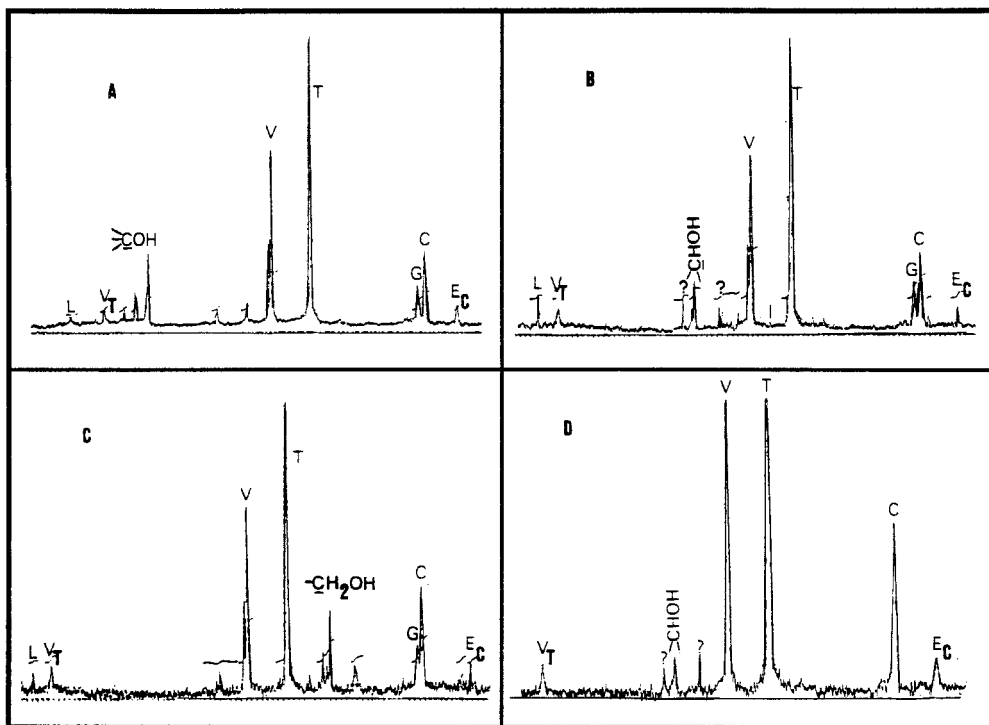| Structure (%) | δ (ppm) | R45M | R45HT | LIQ.P | LIQ.H | R20LM | LM-1 | LM-2 |
|---|---|---|---|---|---|---|---|---|
| ～CH–CH$_2$OH / CH=CH$_2$ (V) | 64.8 | 24.3 | 24.2 | 26.2 | 25.2 | 19.8 | 22.2 | 19.7 |
| C=C with H, CH$_2$OH (T) | 63.2 | 45.3 | 45.8 | 48.5 | 48.6 | 38.2 | 42.1 | 42.2 |
| C=C with H, H, CH$_2$OH (C) | 58.1 | 17.5 | 18.1 | 16.0 | 16.5 | 9.8 | 11.3 | 9.0 |
| ～CH$_2$–C～ / CH–CH$_2$OH (G) | 58.6 | - | - | - | - | 6.7 | 7.2 | 8.6 |
| ～CH$_2$OH (OH 1°) | 60-62 | - | - | - | - | - | - | 12.4 |
| unidentified | 66.0 | 1.6 | 1.9 | 1.8 | 1.9 | 2.6 | 3.2 | 0.9 |
| CH$_3$ / ～CHOH (OH 2°) | 67,0 | - | - | 3,1 | 2,0 | - | 4.7 | - |
| unidentified | 67,5 | 1.6 | 1.0 | 1.5 | 1.0 | 2.5 | 1.5 | - |
| CH$_3$ / ～C–OH (OH 3°) / CH$_3$ | 70-72 | 6.6 | 4.6 | | | 13.7 | - | - |
| ～CH$_2$–CHOH / CH=CH$_2$ (V$_T$) | 72.4 | 1.5 | 2.0 | 1.6 | 1.9 | 3.5 | 3.1 | 3.0 |
| OH / ～CH$_2$–C～ / CH=CH$_2$ (L) | 73.7 | - | - | - | - | 0.9 | 1.6 | 1.8 |
| ～HC—CH～ (E$_C$) (epoxide O) | 56.5 | 1.5 | 2.5 | 1.2 | 2.8 | 2.4 | 3.1 | 2.5 |

**Figure 1 - 54 to 74 ppm region of the $^{13}$C NMR (75.4 MHz) for R20LM (A), HTPB-LM1 (B), HTPB-LM2 (C) and Liquiflex H (D).`**
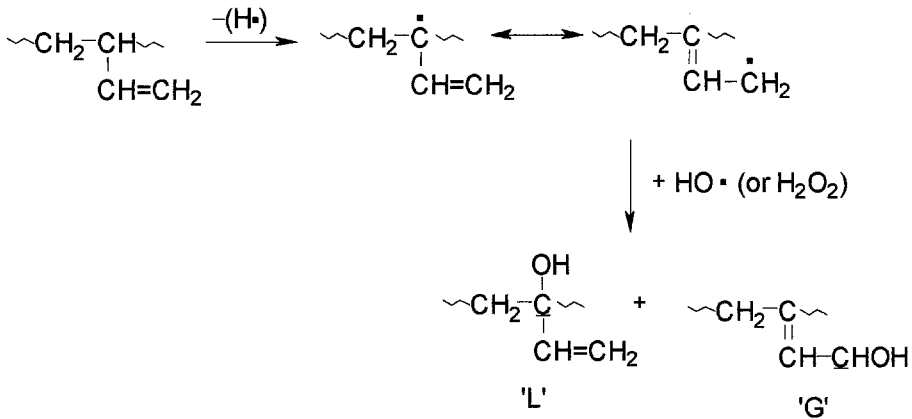
The data in Table 3 show that the main differences between conventional and low molecular weight HTPBs are related to 'G', 'L' and 'V$_T$' structures, as well as to primary, secondary and tertiary hydroxyl groups. These findings are discussed below.

**Mechanism**

Based on the $^{13}$C NMR results, described above, some mechanistic pathways are proposed for the synthesis of LM-HTPBs by a free radical polymerization using hydrogen peroxide as initiator and an alcohol as solvent. The steps related to the initiation, propagation and termination are similar to those presented previously[4] for conventional HTPBs.
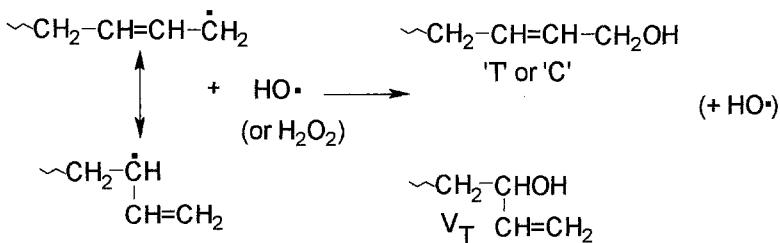
**1- Sequential reactions with HO• radicals (or H$_2$O$_2$)**

The 'G' structure was proposed by Pham who assigned it the δ=58.1 ppm resonance[9,10]. That structure can be formed by the abstraction of an hydrogen atom from a carbon atom linked to 1,2 double bond group followed by reaction with a HO• radical (or H$_2$O$_2$):

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~CH₂-CH~ —(H·)→ ~CH₂-C·~ ⟷ ~CH₂-C~
  |                  |              ‖
  CH=CH₂         CH=CH₂        CH-CH₂·

|  + HO · (or H₂O₂)
▼

        OH
        |
~CH₂-C~      +     ~CH₂-C~
     |                   ‖
     CH=CH₂           CH-CHOH
     'L'                  'G'

The higher amount of 'G' in relation to 'L' may be attributed to the lower steric hindrance found in the formation of 'G' than 'L'. These species are similar to geraniol and linalool which have peaks at δ=58.6 ppm and at δ=73.7 ppm, respectively assigned to their CH₂OH resonance[11]. For conventional HTPBs 'G' and 'L' structures are not observed and this can be explained as follows. In this particular free radical process the polymer and the solvent are in two separate phases, and since the initiator is present in the latter this reaction is less likely to occur. However, very high concentrations of initiator are required to prepare LM-HTPBs to obtain low molecular products, thus increasing the probability of reactions with HO• or H₂O₂. These facts, however, do not exclude the possibility of the presence of a non resolved peak at δ=58.6 ppm overlapped by the peak at δ=58.1 ppm assigned to the 'C' structure in ¹³C NMR spectra of conventional HTPBs (Figure 1D)

## 2- Termination by reaction with initiator radicals (or H₂O₂)

The higher amounts of 'V_T' structures found in LM-HTPBs (3.0% to 3.5%) than in conventional HTPBs (1.5% to 2.0%) is also attributed to the high initiator concentrations required to prepare LM-HTPBs, favoring termination with initiator radicals (or H₂O₂).

~CH₂-CH=CH-C·H₂          ~CH₂-CH=CH-CH₂OH
  ↕        + HO·  →        'T or 'C'
                                              (+ HO·)
~CH₂-C·H     (or H₂O₂)    ~CH₂-CHOH
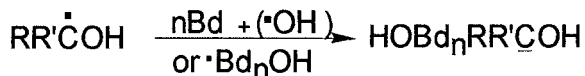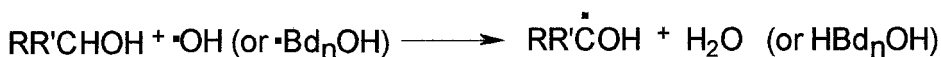  |                          V_T  CH=CH₂
  CH=CH₂

## 3-Reactions with solvent.

As can be seen from Table 3, LM1, LM2 and R20LM samples which were prepared with ethanol, methanol and isopropanol respectively, have significant amounts of secondary primary and tertiary hydroxyl groups. According to our previous results[4] the peak at $\delta=67,0$ ppm was assigned to carbon atoms linked to secondary hydroxyls while the peaks at $70<\delta<72$ ppm were assigned to carbon atoms linked to tertiary hydroxyl groups. The assignment of the resonances at $60<\delta<62$ ppm to carbons linked to primary hydroxyl groups was based on simulations with model compounds which yielded:

| Structure | Assignment (ppm) |
|-----------|------------------|
| $CH_3-CH=CH-CH_2-\underline{C}H_2OH$ | 62.1 |
| $CH_3-CH(CH=CH_2)-CH_2-\underline{C}H_2OH$ | 60.5 |

A peak at $\delta=62.2$ ppm attributed to $-\underline{C}H_2OH$ was reported for 1-decanol[11], which confirms our results obtained by simulation[9].

Reactions with solvent have been discussed in the literature for the preparation of HTPB[12,13], and this could explain the presence of primary, secondary and tertiary hydroxyl groups according to the scheme:

$$RR'CHOH + {}^{\bullet}OH \ (or \ {}^{\bullet}Bd_nOH) \longrightarrow RR'\overset{\bullet}{C}OH + H_2O \ (or \ HBd_nOH)$$

$$RR'\overset{\bullet}{C}OH \ \xrightarrow[\text{or} \cdot Bd_nOH]{nBd \ + (^{\bullet}OH)} HOBd_nRR'\underline{C}OH$$

Where: R=R'=H stands for methanol; R=CH$_3$ and R'=H for ethanol; and R=R'=CH$_3$ for isopropanol

A higher content of hydroxyl groups originating from reactions with solvent was found in LM-HTPB compared to that in conventional HTPBs. This is due to the greater dilution used in low molecular weight process, because of safety reasons.

## 4- Epoxy formation

The peak found at $\delta=56.5$ ppm in the ${}^{13}C$ NMR spectrum was assigned to _cis_ epoxy groups ($E_C$)[14]. It was detected in all LM-HTPB samples in higher concentrations than in conventional HTPBs[4]. The _trans_ epoxy groups ($E_T$) appears at $\delta=58.5$ ppm, close to 'G' ($\delta=58.6$ ppm) structures. It was not detected in the spectra of LM-HTPBs, but this does not exclude the possibility of their existence in small amounts.

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