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Characterization of hydroxyl-terminated polybutadiene

VI. Reactions with solvent during polymerization

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ABSTRACT

^1H and ^{13}C NMR spectra were used to study the structure of hydroxyl-terminated polybutadiene (HTPB) obtained by using hydrogen peroxide as initiator and an alcohol as solvent. This alcohol was introduced into the polymer chain, forming a hydroxylated end group. The subject has aroused some argument in the literature and is considered further in our discussion of reaction mechanisms.

INTRODUCTION

In view of the importance of proper characterization of HTPB's structures in order to assess properties of polyurethanes formed from these compounds, we have undertaken an extensive investigation of the nature of hydroxyl groups in HTPB that were subject to controversies in the literature.[1-15] In our most recent work[2] we have shown that there is no ambiguity relative to the assignment of proton and carbon-13 NMR spectra of hydroxyl end groups and that the early work of Ramey[3] and Bresler[11] is essentially correct.

A question remained, however, as to the nature of products formed by reactions with solvent during HTPB polymerization. Reactions with alcohol used as solvent in the HTPB polymerization initiated by hydrogen peroxide have also been discussed in the literature.[7-15] When methanol,[7,9,11,13] ethanol[8-13] or isopropanol[8,9,11,13] were used as a solvent in HTPB polymerization they were introduced into the polymer chain forming end group structures, mainly, $-CH=CHCH_2CRR'OH$, where: R=R'=H stands for methanol, $R=CH_3$ and R'=H for ethanol and $R=R'=CH_3$ for isopropanol.

In their recent work[15], Pham and co-workers attributed the structures formed by reactions with the solvent in HTPB-C (presumably R20LM from Atochem) to ether functions and not to hydroxyl groups. Their results are based on experiment consisting of the acetylation of the hydroxylated groups of HTPB-C, and the comparison of the ^{13}C NMR spectra of the HTPB-C and of the acetylated HTPB-C. They expected that all hydroxyl groups would be acetylated and $-\underline{C}H_2OH$ absorptions would be shifted to corresponding $-\underline{C}H_2OAc$ chemical shifts. They observed that the peaks at 70.0, 70.5 and 70.9 ppm, in the HTPB-C spectrum, were not shifted and concluded that they are due to ether functions and not to hydroxyl groups. They assigned those peaks to *tert*-butoxy (t-BuO) structures and attributed their formation to the use of a mixture of *tert*-butanol and isopropanol as solvent in HTPB-C polymerization. They proposed a mechanism for the polymerization of HTPB-C initiated or terminated with *tert*-butoxy radicals and formation of ether groups (Scheme 1).

$t\text{-}BuOH + HO\bullet \rightarrow t\text{-}BuO\bullet + H_2O$ (1)
$t\text{-}BuO\bullet + CH_2=CH\text{-}CH=CH_2 \rightarrow t\text{-}BuO\text{-}CH_2\text{-}CH=CH\text{-}CH_2\bullet$,etc.

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These results are in conflict with the following considerations: According to the literature[16-19] the solvent used in the Arco/Atochem process is isopropanol and not a mixture of isopropanol and *tert*-butanol as mentioned by Pham.[15] Tertiary hydroxyl groups, as those present in HTPB-C (R20LM), have very low reactivity. They are not acetylated[13,14] and practically do not react with isocyanate groups.[20] The tertiary hydroxyl groups present in HTPB-C samples probably are not acetylated as Pham and co-workers suppose so the corresponding absorptions are not shifted.

We synthesized a conventional HTPB using hydrogen peroxide as initiator and pure isopropanol (HTPB-A) as solvent[16] and two types of low molecular weight HTPBs (LM-HTPBs) using ethanol (HTPB-LM1) or methanol (HTPB-LM2) as solvent.[21] This paper presents the characterization of products and their comparison with Liquiflex H, R20LM and R45HT proton and carbon-13 NMR spectra. Based on the characterization data, the incorporation of fragments of solvent molecules in the HTPB chain is considered in our discussion.

EXPERIMENTAL PART

HTPB - *R45HT* and *R20LM* are conventional and low molecular weight HTPBs respectively and were obtained from Atochem. *Liquiflex H* is a conventional HTPB produced using ethanol as solvent[21] and was obtained from Petroflex. *HTPB-A* was synthesized using hydrogen peroxide as initiator and pure isopropanol as solvent.[16] *HTPB-LM1* and *HTPB-LM2* were synthesized using hydrogen peroxide as initiator and ethanol and methanol as solvent respectively.[21] 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 (dried under 10^{-3} mm de Hg, at room temperature, during 24 hours) were dissolved in C_6D_6 at a concentration of 5%. 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 - Spectra were simulated using the SPECINFO data base from STN (Scientific and Technical Network) data bank.[22]

RESULTS AND DISCUSSION

Figure 1 shows the 54 to 74 ppm region of the ^{13}C NMR spectra of HTPB-LM1 (A), R20LM (B), HTPB-LM2 (C), which are low molecular weight products; and of HTPB-A (D), Liquiflex H (E) and R45HT (F) which are conventional HTPBs. The assignments of olefinic and CH_2 resonances in HTPB NMR spectra are well established.[6] In addition to these olefinic and CH_2 resonances, the NMR spectra of HTPB yielded other peaks related to three main alcoholic functions (Figure 1). Table 1 summarizes the assignments reported so far. The correct NMR assignments of these peaks were discussed previously, the three main alcoholic functions were attributed to the hydroxylated end groups in the vicinity of vinyl (V), trans (T) and cis (C) units,[1,2] and not to the (G) and (H) structures proposed by Pham and co-workers.[4-7,15] The assignments of the lower intensity peaks found in ^{13}C spectra (Figure 1 and Table 1) were also assigned differently in the literature.[8,9,11,12,15] The ^1H and ^{13}C NMR quantitative characterization data of conventional and low molecular weight HTPBs were presented previously.[9]

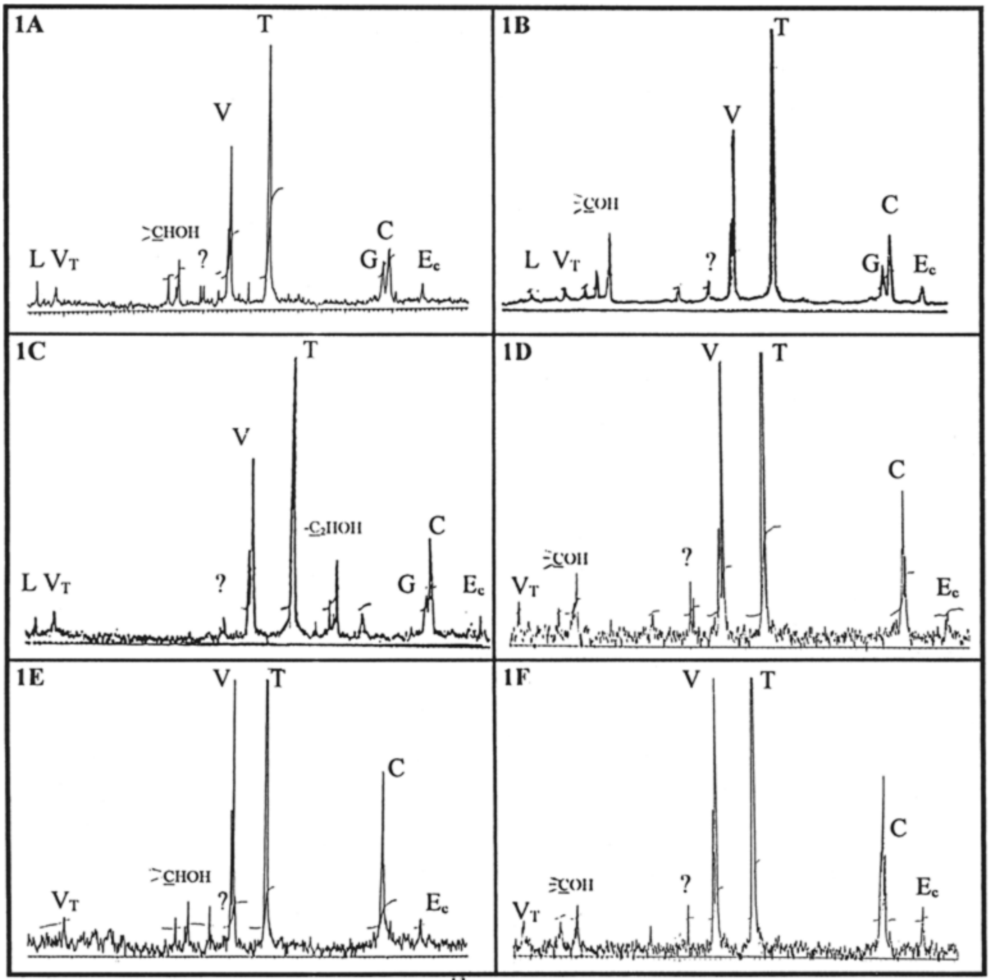


Figure 1 - 54 to 74 ppm region of the ^{13}C NMR (75.4 MHz) for HTPB-LM1 (A), R20LM (B), HTPB-LM2 (C), HTPB-A (D), Liquiflex H (E) and R45HT (F) .

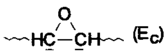
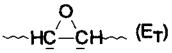
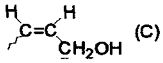
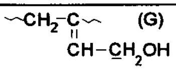
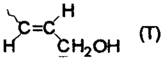
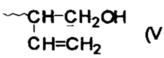
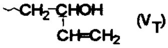
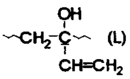
Mechanisms

Based on the ^{1}H and ^{13}C NMR results, some mechanistic pathways are proposed for the synthesis of HTPBs by a free radical polymerization using hydrogen peroxide as initiator and an alcohol as solvent. The steps related to the initiation, propagation, termination, reactions with HO• (or H_2O_2), reactions with solvent, epoxy formation, branching and cross linking reactions were presented presiously.[8,9]

Reaction with solvent

In their recent work[15], Pham and co-workers assigned the absorptions at 70 to 72 ppm in ^{13}C NMR spectra of the HTPB-C (R20LM) to *tert*-butoxy units and proposed the mechanism in scheme (1) for the formation of ether groups attributed to the use of a mixture of isopropanol and *tert*-butanol as solvent in HTPB-C polymerization.

Table 1. NMR assignments for differents structures in HTPB

Structures assigned	Resonance - δ (ppm)		Assignment and reference			
	^{1}H	^{13}C	Bresler	Ramey	Pham	Ours
^^CH=CHCH$_2$CH(C$\underline{H}_3$)OH	1.15	-	-	-	-	This work
^^CH$_2$CH$_2$CH(C$\underline{H}_3$)OH	1.10	-	-	-	-	This work
^^CH$_2$C(C$\underline{H}_3$)$_2$OH	1.20	-	-	-	-	This work
^^CH$_2$OCH(C$\underline{H}_3$)$_2$	1.03	-	-	-	15	-
^^CH$_2$OC(C$\underline{H}_3$)$_3$	1.14	-	-	-	15	-
 (E$_C$)	2.8	56.3 to 56.5	-	-	15	8-9
 (E$_T$)	2.6	58.0 to 58.5	-	-	15	8-9
 (C)	4.00 to 4.08	58.1 to 58.3	16	8	-	1-2
 (G)	4.05	58.1 to 58.6	-	-	4-7, 15	
^^CH$_2\underline{C}$H$_2$OH (prim. OH)	-	60 to 62	-	-	-	9
 (T)	3.95 to 4.15	62.9 to 63.4	16	8		1-2
^^CH$_2$-CH=CH-$\underline{C}$H$_2$OH (H)	3.95	63.2	-	-	4-7, 15	-
 (V)	3.3 to 3.5	64.8 to 65.1	11	8	4-7, 15	1-2
not identified	-	66.0	-	-	-	8-9
^^CH=CH-CH$_2\underline{CH}$(CH$_3$)OH [sec. OH]	3.67 to 3.77	67.0	11	-	-	8-10
^^CH$_2$-CH$_2\underline{C}$H(CH$_3$)OH [sec. OH]	3.79	67.5	-	-	-	This work
^^CH$_2\underline{C}$(CH$_3$)$_2$OH [tert. OH]	-	70 to 72	-	-	-	8-9
^^O$\underline{C}$(CH$_3$) [Ether]	-	70 to 70.9	-	-	15	-
 (V$_T$)	-	72.4 67.2	- -	- -	- 15	8-9 -
 (L)	-	73.7	-	-	-	8-9

There are several points to be clarified:

1) The mechanism in equation (1) proposed by Pham and co-workers[15] can occur with isopropanol, ethanol or methanol.. Chemical shifts for ether model compounds that would be formed according the mechanism in the equation (1), are estimated[22] in Table 2. Yet these chemical shifts are not observed in the ^{13}C NMR spectra of HTPBs prepared with isopropanol, ethanol and methanol (Figure 1 and Table 1).

2) For a mixture of isopropanol and *tert*-butanol according to the mechanism of equation (2) the formation of a tertiary hydroxyl group is more probable.

3) Absorptions at 70 to 72 ppm are present in the ^{13}C NMR spectra of HTPB-A, R20LM and R45HT (Figures 1D, 1B and 1F). Furthermore, absorptions at 70 to 72 ppm in ^{13}C NMR spectra of the of HTPB-A prepared with pure isopropanol as solvent should be due to a ^^CH$_2\underline{C}$(CH$_3$)$_2$OH unit and not a ^^CH$_2$O$\underline{C}$(CH$_3$)$_3$ as Pham reports.[15]

Table 2 - Results of simulated spectra with ether model compounds

Structure	Assignment (ppm)
$\mathrm{CH_3{-}CH{=}CH{-}\underline{C}H_2{-}O{-}\underline{C}H_3}$	70.37 and 57.71
$\mathrm{CH_3{-}CH{=}CH{-}\underline{C}H_2{-}O{-}\underline{C}H_2CH_3}$	69.22 and 65.40
$\mathrm{CH_3{-}CH{=}CH{-}\underline{C}H_2{-}O{-}\underline{C}(CH_3)_2H}$	66.46 and 68.80
$\mathrm{CH_3{-}CH{=}CH{-}\underline{C}H_2{-}O{-}\underline{C}(CH_3)_3}$	63.42 and 71.90
$\mathrm{CH_2{=}CH{-}C(CH_3)H{-}\underline{C}H_2{-}O{-}\underline{C}H_3}$	65.96 and 58.33
$\mathrm{CH_2{=}CH{-}C(CH_3)H{-}\underline{C}H_2{-}O{-}\underline{C}H_2{-}CH_3}$	68.30 and 66.13
$\mathrm{CH_2{=}CH{-}C(CH_3)H{-}\underline{C}H_2{-}O{-}\underline{C}(CH_3)_2H}$	66.84 and 71.56
$\mathrm{CH_2{=}CH{-}C(CH_3)H{-}\underline{C}H_2{-}O{-}\underline{C}(CH_3)_3}$	67.85 and 72.66

The existence of the reactions with solvent during the polymerization of HTPB was proposed in our previous papers.[8,9] This is based on the fact that samples which were prepared with ethanol (HTPB-LM1), methanol (HTPB-LM2) and isopropanol (R20LM), contain significant amounts of secondary, primary and tertiary hydroxyl groups, respectively. Reactions with solvent have been discussed in the literature for the preparation of HTPB[8-14], and this could explain the presence of primary, secondary and tertiary hydroxyl groups according to the scheme:

RR'CHOH + HO• (or HOBd$_n$•) → RR'(OH)C• + H_2O (or HOBd$_n$H) (2)
RR'(OH)C• + n Bd → HOCR'RBd$_n$• ,etc.

Where: R=R'=H stands for methanol; R=CH_3 and R'=H for ethanol; and R=R'=CH_3 for isopropanol

Our assignments (Table 1) of the peaks observed in ^{13}C NMR spectra of HTPBs at $60<\delta<62$ ppm (for HTPB-LM2 produced using methanol as solvent), at $67<\delta<67.5$ ppm (for HTPB-LM1 and Liquiflex H produced using ethanol as solvent) and at $70<\delta<72$ ppm (for HTPB-A, R20LM and R45HT produced using isopropanol as solvent) agree with simulations[22] made by using model alcohol compounds for structures in Table 3. A peak at $\delta=62.2$ ppm attributed to ^^$\mathrm{\underline{C}H_2OH}$ was reported for 1-decanol[23]; peaks at $\delta=67.5$ ppm and $\delta=67.8$ ppm attributed do ^^$\mathrm{\underline{C}(CH_3)HOH}$ were reported for 2-octanol[23] and 2-methyl-1-butanol[24], respectively; and a peak at $\delta=72.2$ ppm attributed to ^^$\mathrm{\underline{C}(CH_3)_2OH}$ was reported for 2-methyl-pentene-4-ol-2. It should be noted that tertiary alcohols formed by reaction with isopropanol according to scheme 2 would contain the quaternary carbon identified by DEPT experiments in the vicinity of 70 ppm[15] while the t-Bu ether predicted from scheme 1 would be deshielded by at least 1 ppm. Otherwise, the resonances for the ^^$\mathrm{\underline{C}H_2OC(CH_3)}$ unit that would be observed with more intensity than those for the ^^$\mathrm{\underline{C}(CH_3)_2OH}$ unit are not

Table 3 - Results of simulated spectra with alcohol model compounds

Structure		Assignment (ppm)
$\mathrm{CH_3{-}CH{=}CH{-}CH_2{-}\underline{C}H_2OH}$	(prim. OH)	62.1
$\mathrm{CH_3{-}CH(CH{=}CH_2){-}CH_2{-}\underline{C}H_2OH}$	(prim. OH)	60.5
$\mathrm{CH_3{-}CH{=}CH{-}CH_2{-}\underline{C}(CH_3)\ HOH}$	(sec. OH)	67.4
$\mathrm{CH_3{-}CH{=}CH{-}CH{-}\underline{C}(CH_3)_2OH}$	(tert.OH)	70.0
$\mathrm{CH_3{-}CH(CH{=}CH_2){-}CH_2{-}\underline{C}(CH_3)_2OH}$	(tert. OH)	71.0

Figure 2 shows the 1.0 to 2.5 ppm region of the ^1H NMR spectra of HTPB-LM2 (2A), Liquiflex H (2B), HTPB-A (2C) and R20LM (2D), respectively.

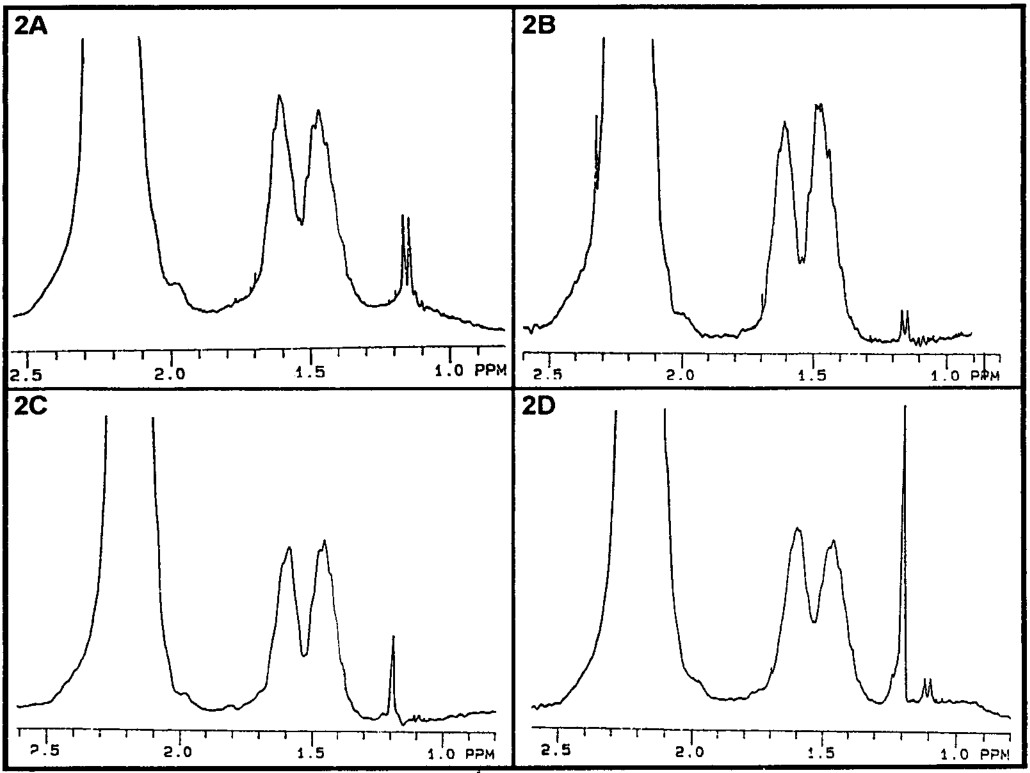


Figure 2 - 1.0 to 2.5 ppm region of the ^{1}H NMR for HTPB-LM1 (A), Liquiflex H (B), HTPB-A (C) and R20LM (D).

Recourse to model compounds helps clarify some other aspects of spectral interpretation. Pham and co-workers[15] assigned the doublet at $\delta=1.03$ ppm and the singlet at $\delta=1.14$ ppm in the ^{1}H NMR spectrum of HTPB-C to ^^$CH_2OCH(C\underline{H}_3)_2$ (isopropoxy) and to ^^$CH_2OC(C\underline{H}_3)_3$ (tert-butoxy) units. They attributed the formation of these ether structures in HTPB-C to the use of a mixture of *tert*-butanol and isopropanol as solvent.

But, as we have pointed out, comparison of ^{13}C NMR spectra of HTPBs prepared with methanol (HTPB-LM2), ethanol (HTPB-LM1 and Liquiflex H) and isopropanol (R20LM, HTPB-A and R45HT) (Figure 1 and Table 1) with simulated[22] chemical shifts shows no correlation with ether model compounds in Table 2 and good agreement with alcohol model compounds in Table 3.

In the ^{13}C NMR (Figures 1A and 1E) and ^{1}H NMR H (Figures 2A and 2B) spectra of HTPB-LM1 and Liquiflex we observe absorptions at $67<\delta<67.5$ ppm attributed to a ^^$CH_2\underline{C}H(CH_3)OH$ unit and a doublet at $\delta=1.15$ ppm due to ^^$CH=CHCH_2CH(C\underline{H}_3)OH$ unit and not a triplet as would be expected for the ^^$CH=CHCH_2OCH_2C\underline{H}_3$ unit. A doublet attributed to a —$CH_2CH(C\underline{H}_3)OH$ unit at $\delta=1.18$ ppm and a absorption at $\delta=67.84$ ppm attributed to a —$CH_2\underline{C}H(CH_3)OH$ unit were reported[23] for 6-methyl-5-hepten-2-ol.

In the ^{13}C NMR (Figures 1B and 1F) and in ^{1}H NMR spectra of R20LM and HTPB-A (Figures 2C and 2D) we observe peaks at $70<\delta<72$ ppm attributed to a ^^$CH_2\underline{C}(CH_3)_2OH$ units and singlet at $\delta=1.2$ ppm due to ^^$C(C\underline{H}_3)_2OH$ unit. A singlet at

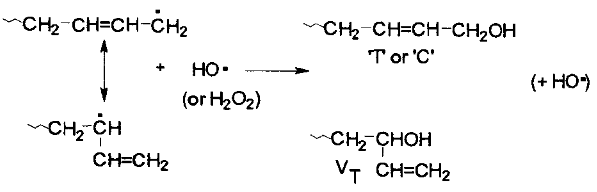
δ=1.20 ppm attributed to a $—CH_2C(C\underline{H}_3)_2OH$ unit and a peak at δ=70.97 ppm attributed to a $—CH_2\underline{C}(CH_3)_2OH$ unit were reported[23] for 2-methyl-2-hexanol

A doublet with low intensity at δ=1.10 ppm is also observed in Figure 2D and is almost imperceptible in Figure 2C and may be attributed to ^^$CH_2CH_2CH(C\underline{H}_3)OH$ or ^^$CH_2OCH(C\underline{H}_3)$ units. The higher intensity peak in R20LM spectra is probably due to the fact that the low molecular weight HTPBs are prepared with very high ratios[26] of hydrogen peroxide/butadiene and isopropanol/butadiene. Absortions at δ=67.5 ppm are also observed with low intensity in ^{13}C NMR spectra of HTPBs prepared in isopropanol as HTPB-A (Figure 1D), R45HT (Figure 1F) and R20LM (Figure 1B). The absortions observed at δ=67.5 ppm in ^{13}C NMR and the doublet at δ=1.10 ppm in ^{1}H NMR spectra of HTPB-A, R45HT and R20LM may be attributed to the absorption of $—CH_2\underline{C}H(CH_3)OH$ and $—CH_2CH(C\underline{H}_3)OH$ units. This structure can be formed by abstraction of one of the six hydrogens atoms of the two $-CH_3$ groups of isopropanol. The resulting free radical would initiate the polymerization forming a HTPB chain with a secondary hydroxyl group. The peak at δ=67.2 ppm in ^{13}C NMR spectra of HTPB-C that according to Pham [15] was shifted after acetylation to δ=70.1 ppm is probably due to the ^^$CH_2\underline{C}H(CH_3)OH$ unit mentioned before. In the HETCOR[15] pulse sequence spectrum for HTPB-C the peak at δ=67.2 ppm shows coupling with another at δ=3.65 ppm. Absorptions at $3.67 \leq \delta \leq 3.77$ ppm attributed to a $—CH_2C\underline{H}(CH_3)OH$ unit were reported for HTPB[8-11] and 2-methyl-2-hexanol[23].

Termination by reaction with initiator radicals (or H_2O_2)

The termination of the HTPB polymerization by reaction with initiator radicals (or H_2O_2) was discussed previously.[8,9].

Pham and co-workers[15] related the peak at δ=67.2 ppm in the ^{13}C NMR spectrum of HTPB-C to "V_T" structure (Table 1). According to our simulation[22] this structure has a peak attributed to ^^$\underline{C}H(CH=CH_2)OH$ at δ=72.4 ppm which were observed in the ^{13}C NMR spectra of all HTPB samples.[9] The peak at δ=72.2 ppm which was observed, but not identified by Pham[15] in the ^{13}C NMR spectra of HTPB-C is the correct absorption of this "V_T" structure.



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