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NMR Characterization of a Hydrogenated Hydroxytelechelic Polyisoprene

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The microstructure of a hydrogenated hydroxytelechelic polyisoprene was investigated by ^1H - and ^{13}C NMR spectroscopy. The hydroxyl average functionality ($\overline{f_{\text{noH}}} \sim 2.2 \pm 0.1$) and the hydrogenation rate ($\sim 95\%$) of this low molar mass polyol were calculated. ^{13}C NMR signals arising from 1,4-, 1,2-, and 3,4-units were assigned, as well as head-to-head and tail-to-tail linkages of the 1,4-units. Four main primary alcoholic end groups were identified and the presence of tertiary alcohol was confirmed.

Keywords: Hydrogenated polyisoprene; Microstructure; ^1H and ^{13}C NMR

Low-molecular-weight hydroxy-terminated polyolefins are inert polyols that can be used to prepare high-molecular-weight polyurethanes. The inertness of these soft segments contributes to the enhancement of solvent resistance and mechanical properties of the resulting polymers as compared to the corresponding unsaturated homologues^[1–4], and the polymers exhibit very good thermal stability for electrical insulating

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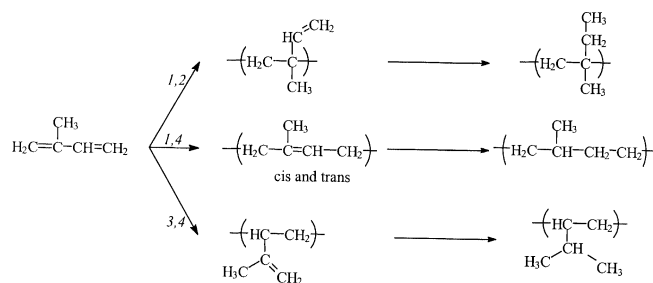
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applications^[5]. Moreover, good transparency of the final product is linked to the content of lateral alkyl groups, e.g., ethyl in hydroxytelechelic hydrogenated polybutadiene^[6].

In previous work, we investigated the microstructure of a hydroxy-terminated polyisoprene (PIHT)^[7]. Sequence distribution of the 1,2-, 3,4-, and 1,4-units, arrangement of head and tail linkages, and the different kinds of alcoholic end groups were discussed. In this work, the microstructure of the corresponding hydrogenated polyisoprene, H-PIHT, was determined using nuclear magnetic resonance (NMR) techniques. According to the sequence distribution of PIHT (Table I) from which it proceeds, H-PIHT should exhibit methyl, ethyl, and isopropyl pendant groups (Scheme 1) and therefore should also lead to colorless products with good transparency. Moreover, in order to prepare polyurethane materials it will be important to identify the different kinds of alcoholic groups on the polymer backbone, each one having its own reactivity and therefore affecting reaction kinetics. Furthermore, because of the incomplete hydrogenation step, the remaining vinyl double bonds could be used for specific grafting reactions^[8].

TABLE I Microstructure and functionality of PIHT^[7]

Microstructure				Average hydroxyl functionality
<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	3,4	
0.32	0.56	0.06	0.06	2.0



SCHEME 1 Repeating units in H-PIHT after hydrogenation.

EXPERIMENTAL

Materials

The low-molar-mass hydroxytelechelic hydrogenated polyisoprene (H-PIHT) used in this work is a commercial polymer EPOL^{®[9]}, kindly supplied by Atofina. Its main characteristics, given by the supplier, are an average molar mass $M_n = 2600$ ($I = 2.2$) and a hydroxyl functionality $f_{nOH} = 2.34$.

Measurements

All NMR experiments were performed in $CDCl_3$ solvent at a controlled temperature of 298 K on a Bruker AVANCE DMX 500 spectrometer, equipped with a 5 mm QXI (1H , ^{13}C , ^{15}N , ^{31}P) probe.

Recording of 1H -1D NMR spectrum between 0 and 10 ppm required the use of a 6009.62 Hz spectral window that was digitized with 32k points. The ^{13}C -1D NMR spectra, J-modulated spin echo (J-mod), and inverse gated 1H -decoupling were recorded between 0 and 200 ppm, using a 30,300 Hz spectral window digitized into 64k points. About 600 transients were accumulated using a pulse width of 9 μs for a 90° flip angle and a relaxation delay of 20 and 40 s for the ^{13}C J-mod and inverse gated 1H -decoupling spectra, respectively. Broad band proton decoupling was employed in order to remove ^{13}C - 1H coupling in all spectra.

The heteronuclear single quantum correlation (HSQC) spectrum was measured using 512 increments of 16 scans of 2048 complex points each, with the spectral widths in f_1 and f_2 of 22,637 and 5000 Hz, respectively, and a relaxation delay of 2 s. The HSQC spectrum used time-proportional phase incrementation (TPPI)-phase cycling to provide quadrature detection in f_1 and was displayed in a phase-sensitive mode. All two-dimensional NMR data matrices were zero-filled in the f_1 dimension. Prior to the Fourier transformation, a phase-shifted sine-bell filter function was applied. Processing of NMR data was performed on an SGI Indigo2, using Bruker program's Xwinnmr 2.1.

RESULTS AND DISCUSSION

H-PIHT was analyzed by 1H , ^{13}C , and 2-D NMR techniques. The 1H NMR spectrum (Figure 1) exhibits three distinct regions, A, B, and C, corresponding to the ethylenic (5.4–4.8 ppm), alcoholic (3.8–3.3 ppm), and aliphatic protons, respectively.

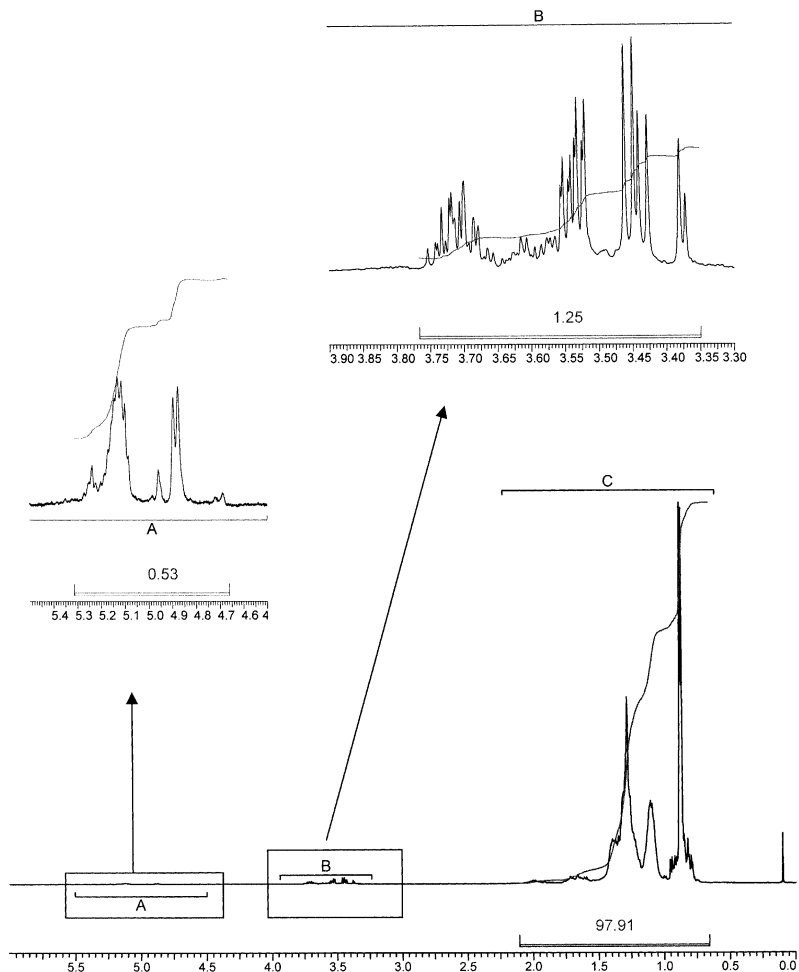


FIGURE 1 ^1H NMR 500 MHz spectrum of H-PIHT in CDCl_3 .

Ethylenic Region

Signals in this region clearly show that the hydrogenation step is incomplete. By comparison with the PIHT spectrum, the remaining unsaturations do not correspond to the classical polyisoprene units but probably to structural defects, already present in PIHT, but hidden or in too small an amount to be observed (Figure 2). In the ^1H - ^1H correlated spectroscopy (COSY) experiment, the main peaks (4.8–

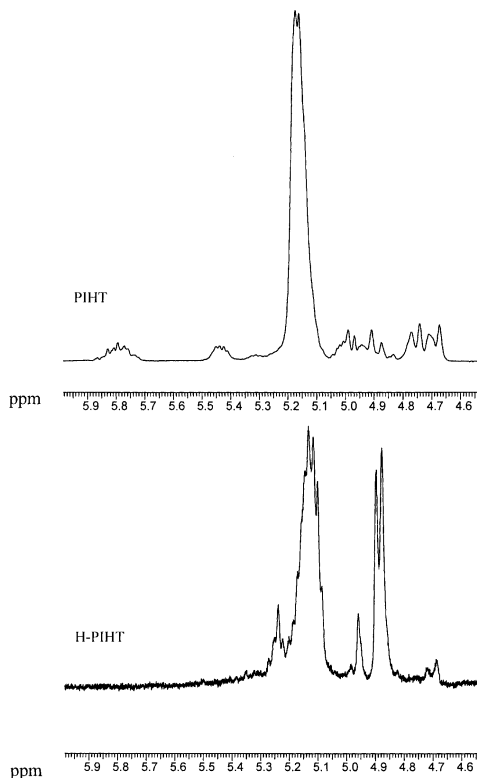


FIGURE 2 ^1H NMR 500 MHz spectra of PIHT and H-PIHT in the ethylenic region.

5.2 ppm) do not exhibit any off-diagonal correlation. Therefore, the main defects were assumed to come from $\text{RR}'\text{C}=\text{CH}_2$ or $\text{RR}'\text{C}=\text{CHR}''$ structures, Figure 3(a). Moreover, because no significant signals under 120 ppm owing to structures $\text{C}=\text{CH}_2$ are observed (Figure 4) on the ^{13}C J-mod NMR spectrum, the main ethylenic signals were attributed to trisubstituted double bonds. According to the H-PIHT polydispersity, these defects may arise from transfer reactions occurring in the polymerization step, which lead to specific structures that are difficult to hydrogenate. If so, these defects may inhibit further grafting reactions. However, these unsaturations should be affected less by degradation reactions and contribute to the chemical inertness of the final product.

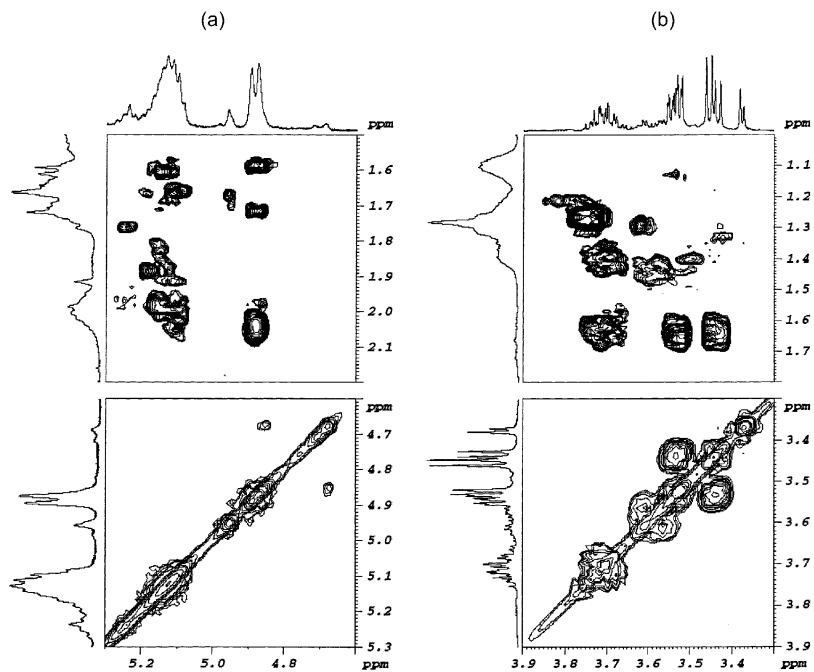


FIGURE 3 ^1H - ^1H NMR 500 MHz COSY spectrum: ethylenic (a) and alcoholic (b) regions.

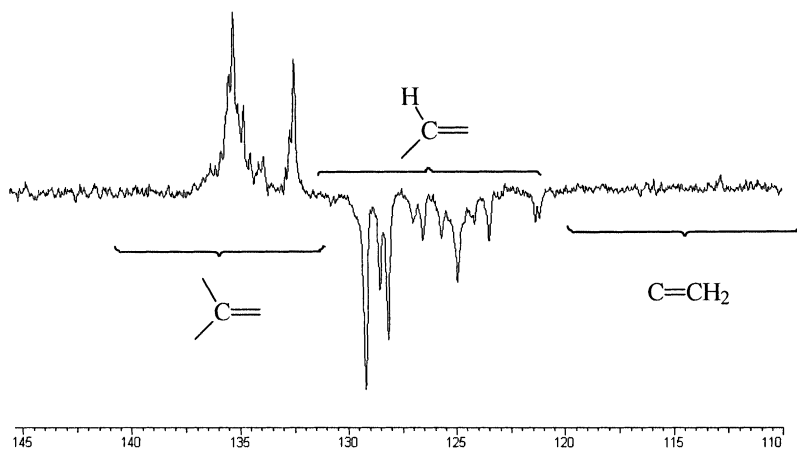
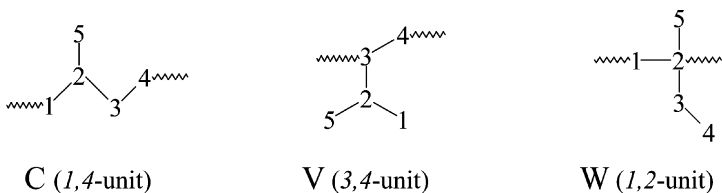


FIGURE 4 H-PIHT ^{13}C NMR spectrum: ethylenic region (110–145 ppm).

Aliphatic Region

Hydrogenated polyisoprenes containing 1,4-, 1,2-, and 3,4-units exhibit complicated ^{13}C NMR resonances arising from different types of linkages (Figure 5). According to the PIHT microstructure, the polymer is highly 1,4 constituted, having 1,2-, and 3,4-units randomly distributed along the polymer backbone^[7]. The following notation was used:



The expected triads are the three different units surrounded by 1,4-units: C-C-C, C-V-C, and C-W-C.

Each signal was further identified according to literature^[10] and model compounds, e.g., squalane for 1,4-units. Moreover the chemical shift of each carbon atom in the hydrogenated polymer can be predicted using the empirical equations for branched and linear alkanes proposed by Paul and Grant^[11] or Lindeman and Adams^[12].

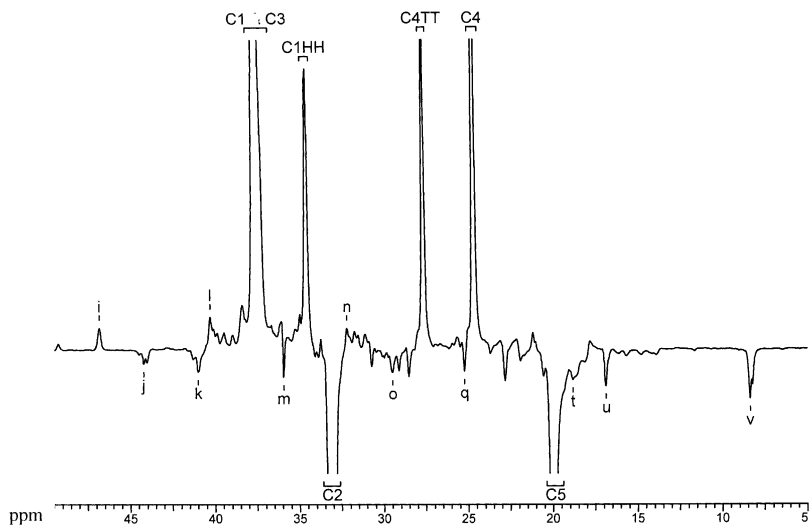


FIGURE 5 H-PIHT ^{13}C NMR spectrum: aliphatic region (5–50 ppm).

V4 and W2 signals could be predicted but not identified because of the numerous neighboring peaks. Considering the assignments given in Table II, one can notice that the predicted shifts are very close to the experimental ones. Only C-atoms of the 3,4-unit exhibit large differences between the observed and calculated chemical shift values. According to Tanaka et al.^[13], this result arises from the steric effect of the pendant isopropyl group of this kind of unit. Other specific isolated signals (i, k, m, u, v) were also assigned using calculated chemical shift values and model compounds.

The signals around 28, 33, and 34.5 ppm are due to irregular addition occurring during the polymerization step, i.e., head-to-head (*HH*) and tail-to-tail (*TT*) linkages^[10,14] (Table III). The ¹³C NMR spectrum of squalane was investigated because it exhibits a signal at 27.78 ppm due to the central methylene carbon, which has a chemical environment similar to that of the C4 carbon in the 1,4-4,1 linkage, leading therefore to the identification of *C4TT*. The two other signals (*C1HH* and *C2HH*) were identified according to the literature^[10,14].

TABLE II Calculated and observed ¹³C NMR chemical shifts of H-PIHT (aliphatic region)

Signal	Attribution	Squalane	PI ^[10]	δ Calc.	δ Obs.	$\Delta\delta$ ppm
C1	1,4-C1-1,4	37.52	37.47	37.5	37.50	0
C3	1,4-C3-1,4					
C2	1,4-C2-1,4	32.87	32.84	32.1	33.1	1
C4	1,4-C4-1,4	24.89	24.51	25.3	24.68	0.62
C5	1,4-C5-1,4	19.80	19.83	20	19.96	0.04
j	1,4-V3-1,4		44.39	41.9	44.01	2.11
o	1,4-V2-1,4		29.32	30.1	29.49	0.61
t	1,4-V1-1,4		19.34	20.1	18.81	1.29
	1,4-V5-1,4					
l	1,4-W1-1,4		—	40.0	40.29	0.29
n	1,4-W3-1,4		—	32.8	32.19	0.61
v	1,4-W4-1,4		—	9.4	8.36	1.04
q	1,4-W5-1,4		—	25	25.22	0.22
k	1,4-V3-3,4		41.43	39.7	41.00	1.3
i	1,2-C1-1,4		—	46.20	46.81	0.61
2mP^a						
m	1,4-C2-OH	35.63		34.7	35.95	1.65
u	1,4-C5-OH	16.65		17.2	16.9	0.3

^a2-methyl-1-pentanol.

TABLE III Distribution of 1,4-linkages in H-PIHT: comparison to PIHT and radical PI values

Linkage	Signal	δ (ppm)	Squalane (ppm)	PI ^[10] (ppm)	H-PIHT (%)	PIHT ^[7] (%)	PI ^[10] (%)
1,4-1,4 (tail-to-head)	C1, C3	37.50	—	37.47	57.9	56	60
$\begin{array}{c} \text{C} \\ \\ \text{---C}_1\text{---C}_2\text{---C}_3\text{---C}_4\text{---C}_1\text{---C}_2\text{---C}_3\text{---C}_4\text{---} \\ \\ \text{C} \end{array}$ 1,4-4,1 (tail-to-tail)	C4	24.68					
$\begin{array}{c} \text{C} \\ \\ \text{---C}_1\text{---C}_2\text{---C}_3\text{---C}_4\text{---C}_3\text{---C}_2\text{---C}_1\text{---} \\ \\ \text{C} \end{array}$ 4,1-1,4 (head-to-head)	C4 <i>TT</i>	27.66	27.78	27.42	14.6	16.5	14
$\begin{array}{c} \text{C} \\ \\ \text{---C}_4\text{---C}_3\text{---C}_2\text{---C}_1\text{---C}_2\text{---C}_3\text{---C}_4\text{---} \\ \\ \text{C} \end{array}$	C1 <i>HH</i>	34.60	—	34.41	15.4	15.5	14
$\begin{array}{c} \text{C} \\ \\ \text{---C}_4\text{---C}_3\text{---C}_2\text{---C}_1\text{---C}_2\text{---C}_3\text{---C}_4\text{---} \\ \\ \text{C} \end{array}$	C1 <i>HH</i>	33.26		33.25			

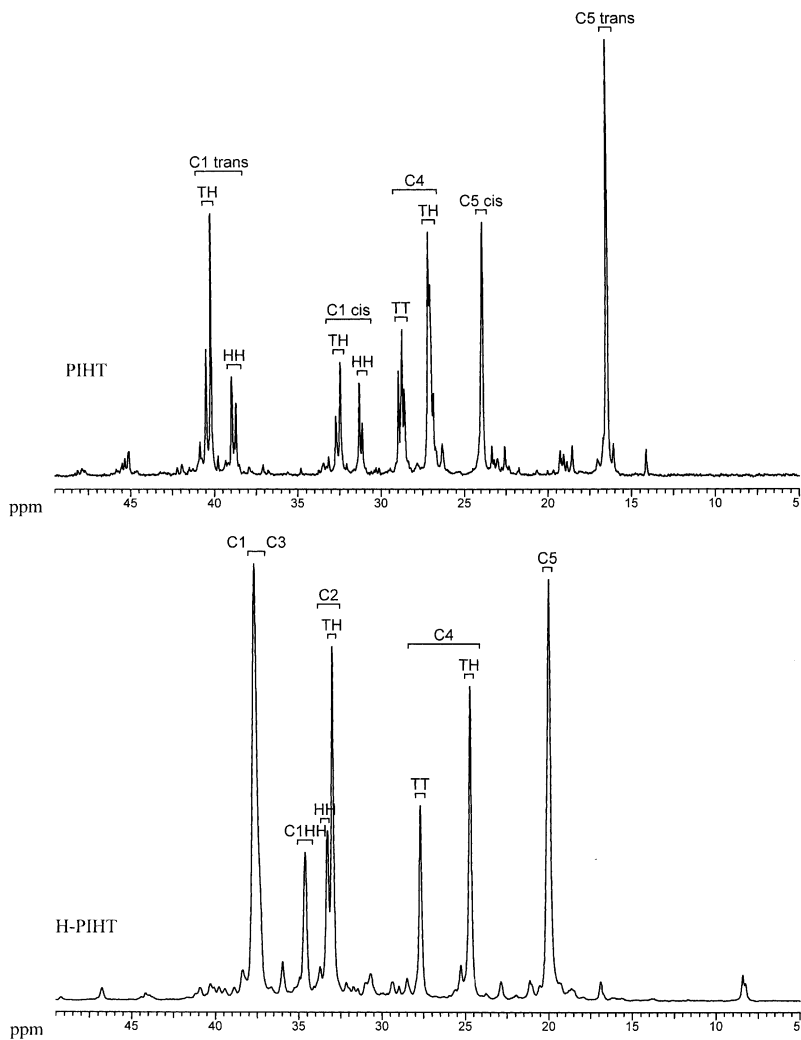


FIGURE 6 ¹H NMR 500 MHz spectra of PIHT and H-PIHT in the aliphatic region.

The sequence distribution of the 1,4-units could then be determined using the following equations:

$$1,4-1,4 = (C4/\Sigma)\%1,4$$

$$1,4-4,1 = (C4TT/2\Sigma)\%1,4$$

$$4,1-1,4 = (C1HH/2\Sigma)\%1,4$$

with $\Sigma = C4 + C4TT/2 + C1HH/2$, and $\%1,4 = 88\%$ (Table I)^[7].

Our results, which are consistent with those obtained for the PIHT precursor (Table III), are close to the sequence distribution of the 1,4-units in radically prepared polyisoprene (PI). These results also confirm that no degradation had occurred during the catalytic hydrogenation step. This last point was confirmed by size exclusion chromatography (SEC) measurements.

Roberts et al.^[15] reported that a double bond in a mono-olefin had an influence on the chemical shift of the α and β neighboring aliphatic C-atoms. The magnitude of influence, i.e., shift factor, was estimated by comparing the chemical shift of a carbon atom in PIHT^[7] with that of the corresponding one in H-PIHT (Figure 6). The shift factors determined in this work (Table IV) are close to those obtained by Roberts et al., using trisubstituted and 1,1-disubstituted ethylene, and Sato et al.^[16], using hydrogenated and non-hydrogenated polyisoprene.

Alcoholic Region

After hydrogenation, the six different alcoholic end groups identified on PIHT should give four new hydroxyl ends (Scheme 2), here called 1,4-OH, 4,1-OH, 1,2-OH, and 4,3-OH.

We have isolated five main regions on the H-PIHT ¹H NMR correlated to five different C atoms according to the 2-D NMR ¹H-¹³C COSY spectrum (Figure 7). In order to easily distinguish the quaternary and secondary C atoms from tertiary and primary C atoms, a J-mod ¹³C NMR was performed. All the signals correspond to even C atoms. By comparing the insensitive nuclei enhancement by polarization transfer (INEPT) ¹³C NMR spectrum, one can easily identify quaternary C atoms a and b and then c to g that come from the primary alcohol structures listed in Scheme 2.

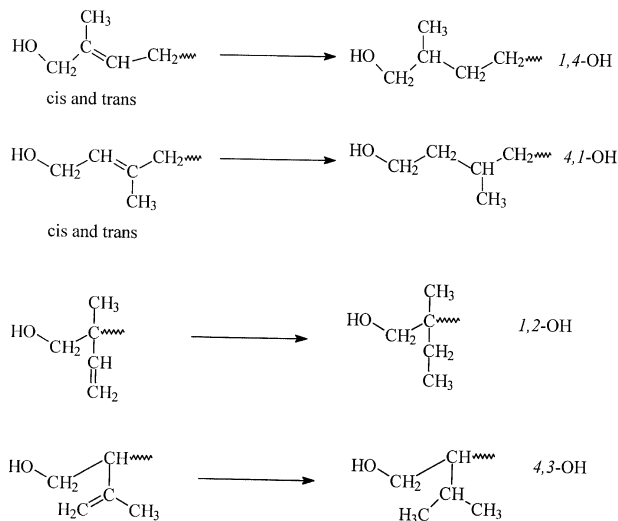
The 1,2-OH end units were primarily assigned to (c, B4) in agreement with the ¹H-¹H COSY spectrum, Figure 3(b), which did not exhibit any off-diagonal correlation for the B4 signal.

¹³C NMR spectra of model compounds were performed to attribute the other hydroxyl end units. On one hand, 2-methyl-1-pentanol led to the unambiguous identification of the 1,4-OH extremity (d, B3). On the other hand, 3-methyl-1-pentanol and 3,7-dimethyl-1-octanol were chosen for the 4,1-OH end unit (g, B1) attribution. Finally 2-isopropyl-5-methyl-1-hexanol was used to identify the 4,3-OH extremity (f, B2) (Table V).

As noted for different hydroxytelechelic polymers, the nature of the penultimate unit has a great influence on the chemical shift of the end unit. In the case of alcohol end-cap polydienes, a multiplicity of the chemical shift is generally observed for the vinylic units^[7,16]. This

TABLE IV Shift factors for PIHT

Structure	Chemical shift (ppm)				Shift factor (ppm)	
	Carbon	H-PIHT	Peak	PIHT	Sato ^[16]	Dorman ^[14]
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C=CH---CH}_2\text{---} \\ \begin{array}{cccc} 1 & 2 & 3 & 4 \end{array} \end{array} $	1	37.52	C1	<i>cis</i>	-5.02	-5.39
				<i>trans</i>	+2.78	+2.23
		34.60	C1HH	<i>cis</i>	-3.45	
				<i>trans</i>	+4.20	
	4	24.89	C4	<i>cis</i>	+2.13	+1.85
				<i>trans</i>	+2.24	+2.18
		27.66	C4TT	<i>cis</i>	+1.04	
				<i>trans</i>	+1.04	
	5	19.80	C5	<i>cis</i>	+4.08	+3.42
				<i>trans</i>	-3.16	-4.07



SCHEME 2 Expected end units in H-PIHT.

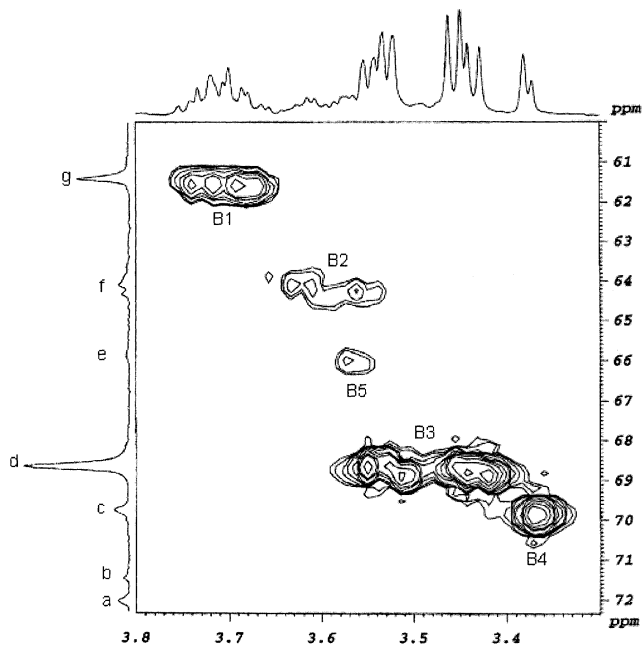
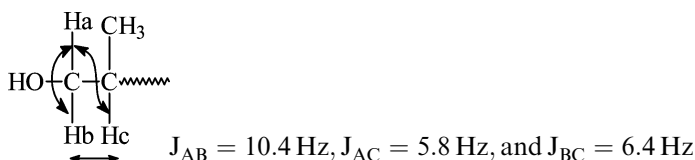
FIGURE 7 ^1H - ^{13}C 2-D NMR spectrum: alcoholic region.

TABLE V ^1H and ^{13}C NMR chemical shifts of the alcohol end units

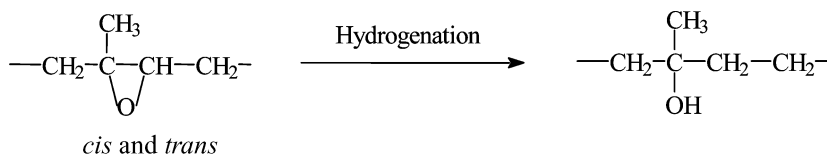
Hydroxyl	Signal	^1H (ppm)	Signal	^{13}C (ppm)
1,4-OH	B3	3.45–3.55	d	68.29
4,1-OH	B1	3.68–3.76	g	61.06
1,2-OH	B4	3.38	c	69.38
4,3-OH	B2	3.56–3.64	f	63–64
Tertiary alcohols	—	—	a and b	71.10 and 71.64

multiplicity is also observed here, after the hydrogenation step, for the 1,2-OH and 4,3-OH extremities, which still exhibit duplicated signals.

On the other side, the multiplicity of the 1,4-OH signal comes from the presence of the chiral C-atom, and the coupling constants were determined.



Finally, a and b signals (Figure 7) could correspond to tertiary alcoholic functions coming from the hydrogenation of the 1,4-epoxydized units present in the PIHT precursor^[7]:



Even if the hydrogenation step could also lead to secondary alcoholic functions, no characteristic signal corresponding to this kind of structure was found in this study.

By using the alcoholic region B and aliphatic region C (Figure 1) in the ^1H NMR spectrum, the average hydroxyl functionality ($\overline{f_{\text{noH}}}$) was estimated as follows:

$$\overline{f_{\text{noH}}} = \frac{\frac{B}{2}}{\frac{C}{10} + \frac{B}{2}} \frac{\overline{Mn}}{70} = 2.1$$

This value is greater than two, whereas the chain ends have been taken into account. It is thus probable that the additional primary alcohol functions, resulting from transfer reactions on the macromolecular chain,

correspond to the (B5,e) signal on Figure 7. Moreover, this value, slightly higher than for the measured PIHT value, does not take into account the presence of tertiary alcohol in the chain. One can thus expect the real functionality would be higher. This last was estimated by ^{13}C NMR:

$$\overline{f_{\text{noH}}} = 2.1 \frac{a + b + c + d + e + f + c}{c + d + e + f + g} = 2.24$$

The resulting hydroxyl functionality is slightly lower than the value given by the supplier (2.34), this last being classically determined by titration.

According to these assumptions, the hydrogenation rate (H%) was calculated:

$$\text{H}\% = 100 \left(1 - \frac{A}{\frac{C-7A-8B/2}{10} + A + B/2} \right) = 94.7\%$$

CONCLUSION

The microstructure and functionality of H-PIHT were determined by NMR spectroscopy. The four main identified hydroxyl ends are all primary alcoholic functions. Tertiary alcoholic functions were identified. From the sequence distribution and SEC analysis, no degradation was observed for the hydrogenation step. This last step was incomplete, and about 5% of double bonds were still present on the polymer backbone. This unsaturation arose from transfer reactions and they are probably inert owing to their steric hindrance. With an average hydroxy functionality greater than two, H-PIHT is a good candidate to prepare polyurethane materials with desirable optical, chemical, and thermal properties.

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