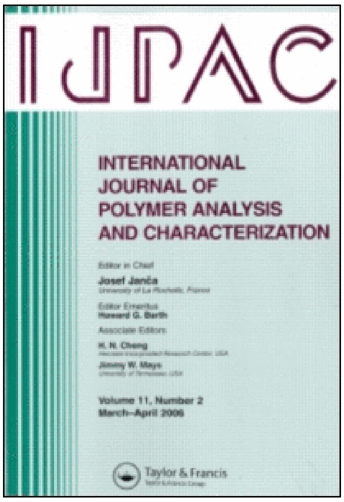


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Microstructural Characterization of Hydrogen Peroxide Initiated Hydroxytelechelic Polyisoprene

F. Burel[a]; H. Oulyadi[b]; C. Bunel[a]
[a] Laboratoire de Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Mont-Saint-Aignan cédex, France [b] Laboratoire de RMN-CNRS UPRES_A 6014, Université de Rouen, Mont-Saint-Aignan cédex, France

To cite this Article Burel, F. , Oulyadi, H. and Bunel, C.(2000) 'Microstructural Characterization of Hydrogen Peroxide Initiated Hydroxytelechelic Polyisoprene', International Journal of Polymer Analysis and Characterization, 6: 1, 193 — 212

To link to this Article: DOI: 10.1080/10236660008034658

URL: http://dx.doi.org/10.1080/10236660008034658

Int. J. Polym. Anal. Charact.,
2000 Vol. 6, pp. 193–212
Reprints available directly from the publisher
Photocopying permitted by license only

Microstructural Characterization of Hydrogen Peroxide Initiated Hydroxytelechelic Polyisoprene*

F. BUREL[a], H. OULYADI[b] and C. BUNEL[a,†]

[a]*Laboratoire de Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Place E. Blondel, B.P.08, 76131 Mont-Saint-Aignan cédex France;*
[b]*Laboratoire de RMN-CNRS UPRES_A 6014, Université de Rouen, 76821 Mont-Saint-Aignan cédex France*

(Received 20 September 1999; In final form 12 December 1999)

The examination of an H_2O_2-initiated hydroxytelechelic polyisoprene by ^1H and ^{13}C NMR allowed the characterization of the microstructure. The hydroxyl functionality ($f_{n_{OH}} \sim 2.0$) and the fraction of the different units were calculated (*trans*-1,4: 56%; *cis*-1,4: 32%; 1,2-vinyl: 6%; 3,4-vinyl: 6%). Five main primary alcoholic groups were identified that clearly show that termination only comes from 1,4-units and initiation process is preferentially due to the 1,2- or 3,4-vinyl units. Signals due to the 1,2-unit were assigned, whereas no clear distinction was made up to now in the literature. The distribution of head-to-head (4,1-1,4), tail-to-tail (1,4-4,1) and head-to-tail linkage was determined.

Keywords: Polyisoprene; Microstructure; ^1H and ^{13}C NMR; End groups

INTRODUCTION

Determination of polyisoprene microstructures has been studied by different techniques. The first and far most used is infrared

---

[*] Presented at the 12th International Symposium on Polymer Analysis and Characterization (ISPAC-12), La Rochelle, France, June 28–30, 1999.
[†] Corresponding author.

spectroscopy.[1-7] To determine the content of different types of unit present in the polymer, the authors used the absorption bands of high intensity at 11 µm and 11.25 µm for the out-of-plane bending vibration of the hydrogen atoms attached to the olefinic structure of the 1,2 and 3,4 units, respectively.[8]

For determining *cis*- and *trans*-1,4 content different ways are given. Richardson and Sacher[1] chose the 12 µm absorption band but, in this case, the values found are strongly affected by the width depending on the nature of the neighboring units. The use by Binder and Ransaw[2] of the 8.84 and 8.68 µm absorption bands of low intensity to calculate the *cis*- and *trans*-1,4 content is altered by the presence of an undetermined interference absorption band at 8.77 µm while the use of the 7.25 and 7.22 µm bands of the methyl group in the 1,4 unit in Ciampelli *et al.*[3] method works well only if no 1,2 structure is present. Moreover, the infrared methods which are based on the assumption that the molar extinction coefficient of a structural unit is always constant independent of the neighboring units, seem inaccurate. This last remark shows the limits of the technique.

Ozonolysis[10,11] or pyrolysis[12,13] can be used to investigate the distribution of the isomeric units in polyisoprene. However, these methods cannot differentiate *cis*- and *trans*-1,4 units because both are converted into the same reaction products.

So far, ^{1}H NMR has been applied for the determination of the isomeric structure of polyisoprene[9,14-16] and ^{13}C NMR spectroscopy has been used to give detailed sequence structure of polybutadienes[17-20] and polyisoprenes.[21-26] Moreover, for most of the studied polyisoprenes, the content 1,2 units was negligibly small and controversy still remains for peak assignments.

Nevertheless, the quantitative determination of the 1,2 unit is of great interest for modification reactions.[27-42] The main advantage in the modification of a preformed polymer is that no changes in the microstructure are expected during the process.

In this work, we report the ^{1}H and ^{13}C NMR study of an H_2O_2-initiated hydroxytelechelic polyisoprene. The distribution of the different units is investigated, as well as the nature of the alcoholic groups on the chain. A series of 2D-NMR techniques permitted the assignment of all relevant peaks.

EXPERIMENTAL

Materials

The low molar mass polyisoprene (PIHT) used in this work (POLY IP®) is a commercial hydroxytelechelic polymer synthesized by radical polymerization and was kindly supplied by Elf Atochem. Its main characteristics are the average molar mass $M_n = 2500$ and the average hydroxyl functionality $f_{n_{OH}} = 2.30$.

Measurements

FTIR spectroscopy was carried out with a Perkin-Elmer Spectrum 2000 system on an IRTRAN window by transmission mode.

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

The recording of ^1H 1D NMR spectrum between 0 and 10 ppm required the use of a 6009.62 Hz spectral window which was digitized with 32 k 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 30300 Hz spectral window digitized into 64 k points. About 6000 transients were accumulated using a pulse width of 9 µs for a 90° flip angle and a relaxation delay of 20 s 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 HSQC spectrum was measured using 512 increments of 16 scans of 2048 complex points each, with spectral widths in f_1 and f_2 of 22637 and 5000 Hz, respectively, and relaxation delay of 2 s. The HMBC spectrum used similar conditions but with 24 transients per increment, and a Δ delay of 70 ms. Both spectra used TPPI phase cycling to provide quadrature detection in f_1; the HSQC spectrum was displayed in a phase sensitive mode and the HMBC in absolute values. All two-dimensional NMR data matrices were zero-filled in the f_1 dimension. Prior to Fourier transformation, a phase shifted sine-bell filter function was applied. Processing NMR data was performed on an SGI Indigo2, using the Bruker program Xwinnmr2.1.

RESULTS AND DISCUSSION

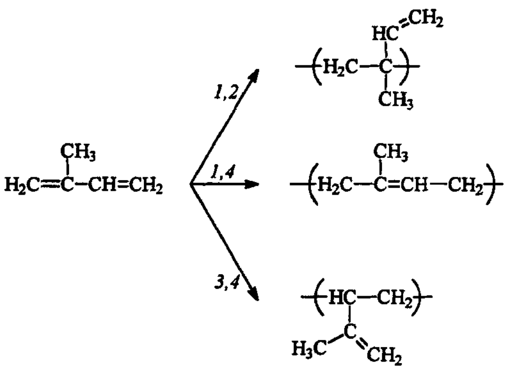
^{1}H-NMR

When polymerizing isoprene, three types of addition are possible, leading to 1,2 and/or 3,4, and/or 1,4 units (Scheme 1), which in our case are clearly evidenced by IR spectroscopy (Fig. 1). The ^{1}H-NMR spectrum (Fig. 2) shows that this polyisoprene is highly 1,4 structured according to the signals at 5.16 ($-C\underline{H}=$), 2.08 and 2.03 ($-C\underline{H}_2-$*trans* and *cis*), 1.72 and 1.63 ppm ($C\underline{H}_3$- *cis* and *trans*). The *trans*/*cis* ratio 1.78 was determined by using the *cis*-CH_3 and *trans*-CH_3 peaks. The other minor signals are linked to the presence of 1,2 and 3,4 structures and to alcohol end groups.

Alcohol End Groups

According to Fages and Pham,[43] the 3.3–4.3 ppm region can be attributed to protons $-C\underline{H}_2OH$ of α-unsaturated primary alcohol (Fig. 2: *F* and *G*) and $-C\underline{H}_nOH$ ($n = 1$ or 2) of α-saturated alcohol (Fig. 2: *H*).

α-unsaturated primary alcohol: Having a highly 1,4-structured polyisoprene, we may assume that α-unsaturated primary alcohol comes mainly from the hydroxylated 1,4-end units. Consequently, four kinds of signals should be found according to the orientation and configuration of the end unit. Firstly, two singlets for the *cis* and *trans*



SCHEME 1 Type of repeating units in polyisoprene chain.

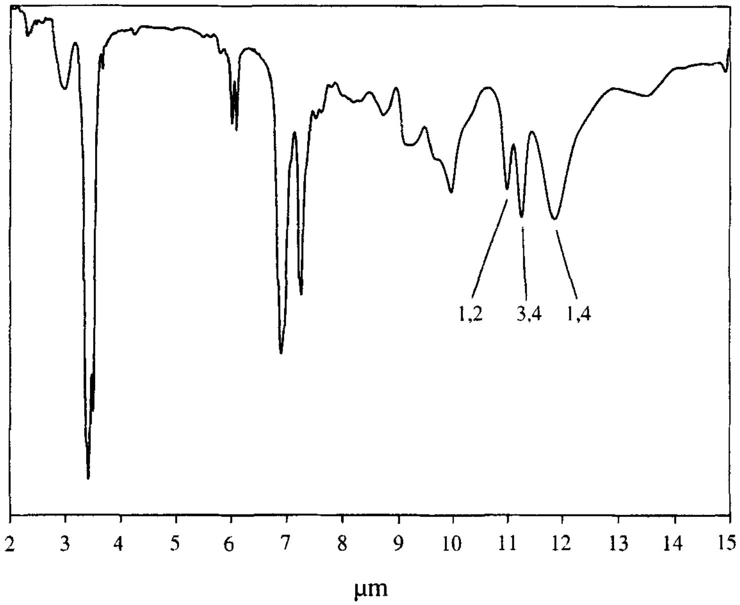


FIGURE 1 FTIR spectrum of polyisoprene.

—CH_2—CH=C(CH_3)C$\underline{H}_2$OH protons and, secondly, two doublets for the *cis* and *trans* —CH_2(CH_3)C=CH—C$\underline{H}_2$—OH ones. Moreover, the multiplicity of the peaks can be greater if the effect of the penultimate unit is observed as mentioned by Pham[44] in the microstructural study of a hydroxytelechelic polybutadiene (PBHT).

Due to the highest content of *trans* 1,4 unit, the *G* undoubtedly corresponds to the *trans* —CH_2—CH=C(CH_3)C$\underline{H}_2$OH protons and shows no penultimate effect. This assignment is confirmed on the COSY spectrum that shows no off-diagonal correlation (Fig. 3).

The *cis* —CH_2—CH=C(CH_3)C$\underline{H}_2$OH protons are more difficult to locate due to overlapping and these protons correspond to the singlet F_2 (Fig. 3), as seen subsequently with the help of ^{13}C NMR.

Therefore, the *F* corresponds to the —CH_2(CH_3)C=CH—C$\underline{H}_2$—OH protons, and will be subsequently correlated with the ethylenic protons. The spectra of nerol and geraniol as models,[45] which are

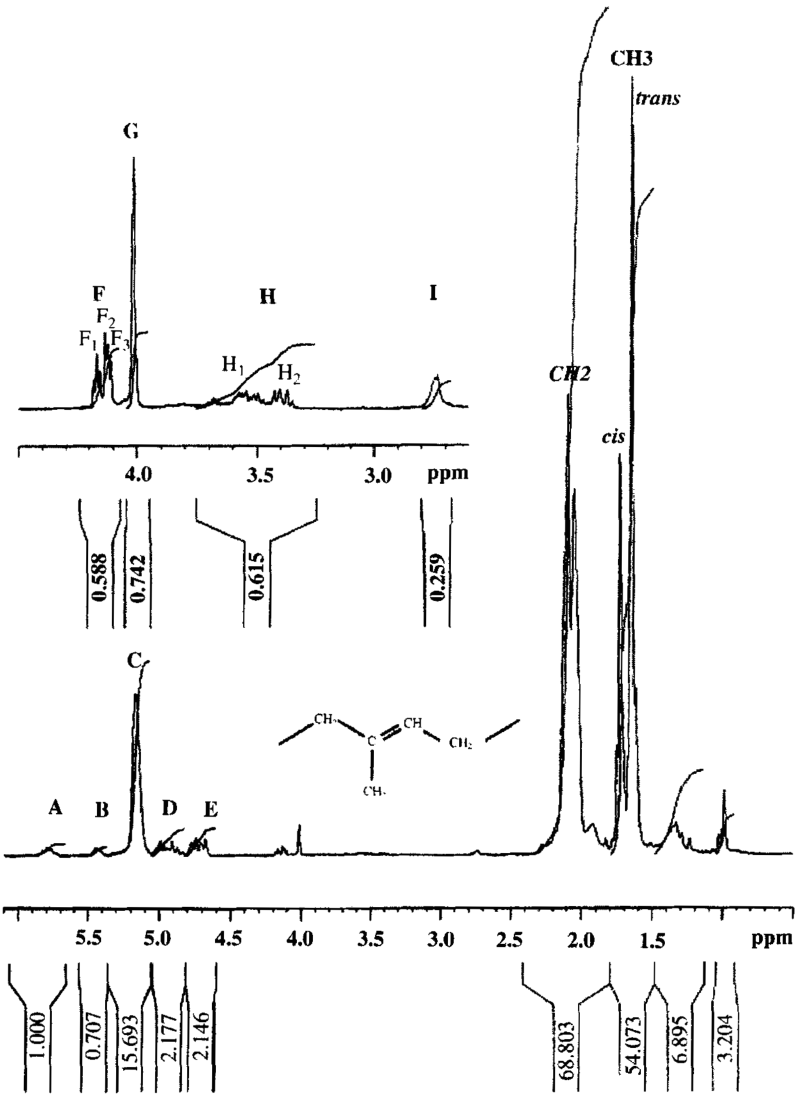


FIGURE 2 ^1H NMR spectrum of polyisoprene.

respectively *cis* and *trans* $(CH_3)_2C{=}CH{-}CH_2CH_2(CH_3)C{=}CH{-}CH_2{-}OH$, clearly show the influence of a *cis*- or *trans*-1,4 configurations on chemical shifts and leads to the identification of F_1 (*cis*) and

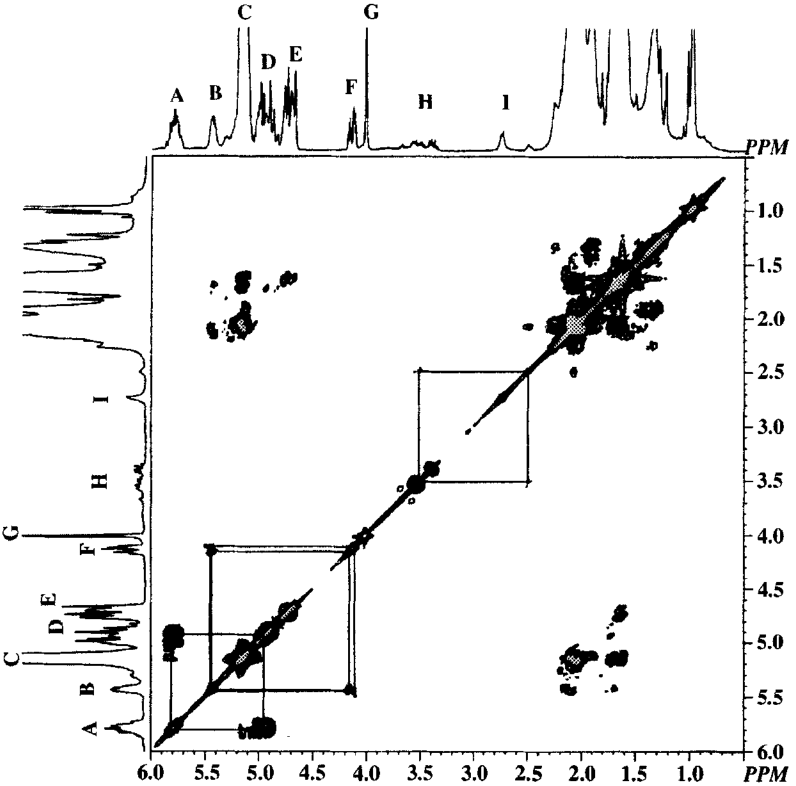


FIGURE 3 ^1H NMR COSY spectrum of the α-unsaturated primary alcohol region.

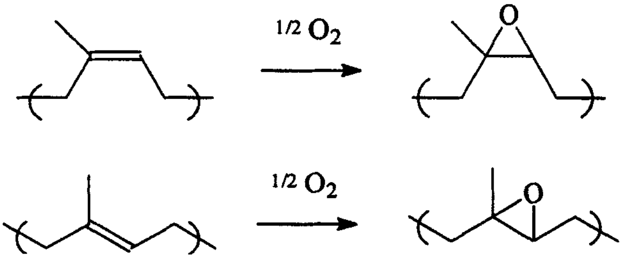
F_3 (*trans*). Nevertheless, we have two complex signals for F_1 and F_3 instead of two predicted doublets. As mentioned above, this can be explained in terms of a penultimate unit effect. Depending on whether or not the penultimate unit is *trans* or *cis*-1,4, two doublets (four peaks) can be expected for each type of proton. In our case, three peaks are observed for F_1 and F_3 which come from the overlapping of two doublets.

α-saturated alcohol: Only primary α-saturated alcohol can be observed in the *H* region (Fig. 2). The H_1 could belong to the $HOC\underline{H_2}C(CH_3)$ protons, because they do not exhibit any off-diagonal correlation in Figure 3. On the contrary, the H_2 exhibits a correlation with the signal at 2.50 ppm and is therefore assigned to the


$HOC\underline{H}_2CH-$ protons of the 3,4-unit. Here again, the multiplicity of H_1 and H_2 can be explained by coupling and the penultimate unit effect.

Epoxide Region

The *I* region exhibits a signal that can be related to the presence of epoxides in the polymer structure.[46,47] These groups can come from side reactions with nascent oxygen during the synthesis of PIHT by analogy with PBHT[48] and according to the following scheme:



1,2 and 3,4 Structures

According to the literature,[9,14–16] the signals in the 4.65–5.05 ppm region can be attributed to $C{=}C\underline{H}_2$ protons of polyisoprene vinyl units, but without a clear distinction between the 1,2 and 3,4-structures. A ^1H-^1H COSY measurement was therefore performed to observe any coupling between ethylenic protons. The Figure 3, shows the resolved off-diagonal correlation signal, leading to the assignment of the vinyl 1,2-unit protons (*A* and *D*) and, consequently, the 4.65–4.80 ppm region (*E*) was attributed to the vinyl proton signal of the 3,4-unit. As mentioned above, there is an off-diagonal correlation between *F* and *B* that shows that a part of *B*, according to the integration, is the $—CH_2(CH_3)C{=}C\underline{H}—CH_2—OH$ proton of the 1,4-end units.

Moreover, the irradiated spectrum (Fig. 4) confirms the correlation between *A* and *D* showing that the signals of the vinyl 1,2 and 3,4-units

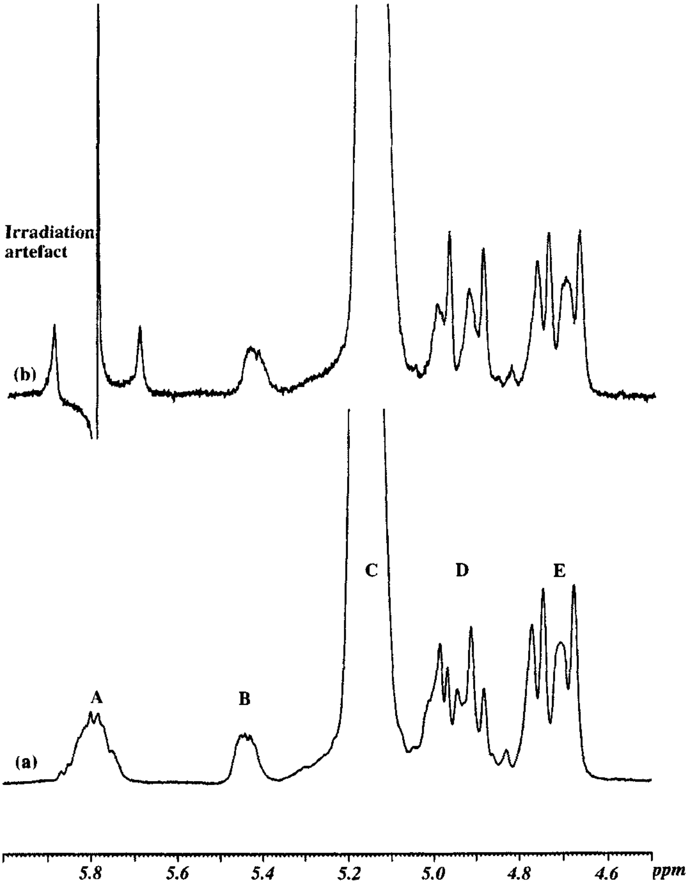


FIGURE 4 ^{1}H NMR spectra of the 1,2- and 3,4-vinylic regions: (a) nonirradiated and (b) irradiated.

(*D* and *E*) are similar leading to the confirmation of similar environment, undoubtedly *cis* and *trans* 1,4 units.

Aliphatic Protons

Finally, two last signals can clearly be attributed to the aliphatic region according to the literature[9, 14–16]: $C\underline{H}_3$ of the 1,2-unit at 0.99 ppm and the $C\underline{H}$ of the 3,4-unit at 2.27 ppm (Tab. I).

TABLE I Chemical shifts of PIHT protons

Proton type	*Unit*	*Shift (ppm)*
$-\underline{H}C{=}CH_2$	1,2	5.8
$>C{=}C\underline{H}-$	1,4	5.16
$-HC{=}C\underline{H}_2$	1,2	4.9
$>C{=}C\underline{H}_2$	3,4	4.7
$>C\underline{H}-\underset{\vert}{C}{=}CH_2$	3,4	2.27
$\underline{H}_2C-\overset{\vert}{C}{=}CH-C\underline{H}_2$	1,4-*trans*	2.08
	1,4-*cis*	2.03
$\underline{H}_3C-C{=}CH-$	1,4-*cis*	1.72
	1.4-*trans*	1.63
$\underline{H}_3C-\underset{\vert}{C}{=}CH_2$	1,2	0.99

Polymer Composition

The fractions of 1,4, 1,2 and 3,4-structures in the polymer could be calculated as follows:

$$\text{Let}\quad S = B + C + \frac{D+E}{2}$$

where B, C, D and E are the integrations of the corresponding peaks,

$$\%_{1,4}(cis\ \text{and}\ trans) = \frac{B+C}{S}\quad \text{with}\quad \frac{\%_{1,4}trans}{\%_{1,4}cis} = 1.78$$

$$\%_{1,2} = \frac{D}{2S}\qquad \%_{3,4} = \frac{E}{2S}$$

The results (Tab. II) are in agreement with those found previously for the polyisoprenes obtained by free-radical polymerisation.[9,34,49–51]

The hydroxyl functionality ($f_{n_{OH}}$) calculated from Figure 2 according to:

$$f_{n_{OH}} = \frac{F+G+H}{2S}\frac{\text{Mn}}{68}$$

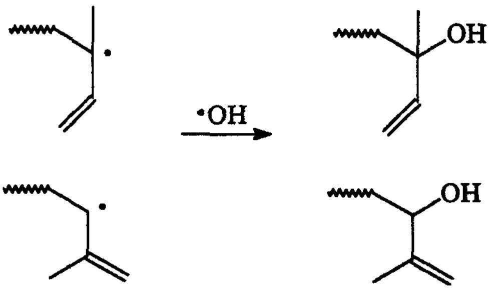
TABLE II Microstructural composition and functionality of PIHT

Microstructure				*Average hydroxyl*
cis-1,4	*trans*-1,4	1,2	3,4	*functionality*
0.32	0.56	0.06	0.06	2.0

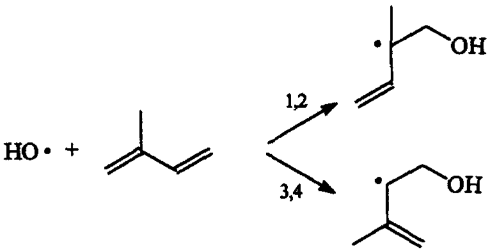
was found close to 2.0. This value is lower than the manufacturer's data. The difference can be due to the fact that the manufacturer's value is determined by back-titration with KOH of the carboxylic functions from the reaction between acetic anhydride in excess and PIHT. Indeed, by this way, the epoxy groups can react and the hydroxyl functionality value is overestimated.

Initiation and Termination Mechanisms

The alcohol formed from the initiation or termination step in the 1,4-polymerization are the most abundant $((F+G)/(F+G+H)=68\%)$. Nevertheless, this ratio is lower than the one of the 1,4-unit in the polymer $(\%_{1,4}(\textit{cis}\text{ and }\textit{trans})=88\%)$. Moreover, in our experimental conditions, no secondary and tertiary alcohol functions were revealed which only involve the termination between 1,4- and OH radicals. As a matter of fact, the termination reaction from 1,2- or 3,4-radicals would lead to secondary or tertiary alcohol functions:



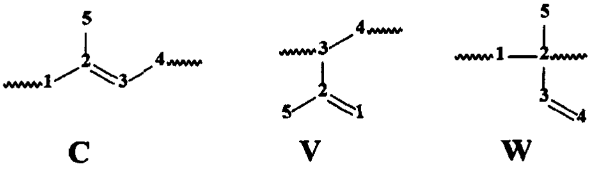
Thus, as 50% of 1,4-units are due to the termination process ($f_{n_{OH}}$ ~ 2.0), only the remaining 18% participate to the initiation step and therefore 32% results from 1,2- or 3,4-units that only lead, in that case, to the primary alcohol according to the following scheme:



The preferential initiation by 1,2- or 3,4-vinyl units was also observed by Pham[44] in the microstructural study of a hydroxytelechelic polybutadiene (PBHT).

^{13}C-NMR

In order to label the position of a particular carbon atom, the *i*th *C* atom of 1,2-(*W*), 3,4-(*V*) and 1,4-(*C*) units is marked by W_i, V_i and C_i, respectively ($i = 1$ to 5) where the carbons are numbered according to the following scheme:



Aliphatic Carbons

The ^{13}C NMR spectrum of the aliphatic region is shown in Figure 5. The peaks were identified according to the literature[21–26] and by HSQC and HMBC experiments (Tab. III).

To confirm the above assignments, we have used a predictive model for the linear saturated hydrocarbons.[52] In this model, the chemical shift δ_i of the *i*th *C*-atom is expressed by the following relationship:

$$\delta_i = B + \sum_l A_l \cdot n_{il} \tag{1}$$

The constant B is almost equal to the chemical shift of methane, -2.5 ppm, n_{il} is the number of carbons in the lth position relative to the ith carbon and A_l is the chemical shift parameter assigned to the lth *C*-atom. The five A_l values: α, β, γ, δ and ε found by the regression analysis of the chemical shifts of linear alkanes and the correction for branching effects, are given in Table IV. The chemical shifts of polyisoprene evaluated only on the basis of these parameters by means of Eq. (1) are far from the experimental values. Dorman *et al.*[53] reported that a double bond in a mono-olefin had influence on the α

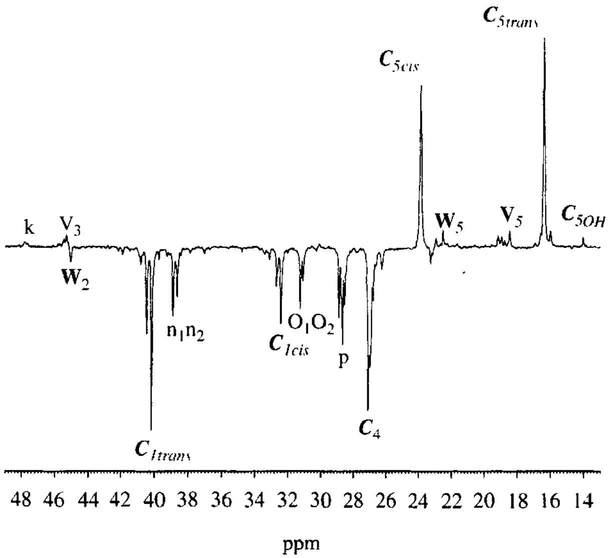


FIGURE 5 J-modulated spin echo ^{13}C NMR spectrum of the aliphatic region.

TABLE III Calculated and observed chemical shifts of PIHT carbons

		^{13}C *Chemical shift (ppm)*		
Signal	*Assignment*	*Calc.*	*Obs.*	*Δppm*
k	V_{3OH}	47.7	47.8	0.1
V_3	$c,t\text{-}V_3\text{-}c,t$	45.2	45.3	0.1
W_2	$c,t\text{-}W_2\text{-}c,t$	–	45.1	–
C_{1trans}	$C_{1T,c}$	39.7	40.46	0.76
	$C_{1T,t}$	39.7	40.18	0.48
n_1	$C_{1T,t}$ (head-to-head)	36.7	38.93	2.23
n_2	$C_{1T,c}$ (head-to-head)	36.7	38.67	1.97
C_{1cis}	$C_{1C,c}$	32.1	32.69	0.59
	$C_{1C,t}$	32.1	32.43	0.33
o_1	$C_{1C,c}$ (head-to-head)	29.0	31.27	2.27
o_2	$C_{1C,t}$ (head-to-head)	29.0	31.1	2.1
p	C_{4c} (tail-to-tail)	29.3	28.70	−0.6
	C_{4t} (tail-to-tail)	29.6	28.70	−0.9
C_4	C_{4trans}	27.0	27.13	0.13
	C_{4cis}	26.7	27.02	0.32
C_{5cis}	C_{5cis}	23.5	23.88	0.38
W_5	$c,t\text{-} W_5\text{-}c,t$	–	22.54	–
V_5	V_5	19.5	18.4/19.2	−1.1/−0.3
C_{5trans}	C_{5trans}	16.0	16.64	0.64
C_{5OH}	t, C_{5OH}	13.1	14.1	1.0

TABLE IV Chemical shift parameters for predictive model

Values for alkanes[52]		*Correlation parameters*[26, 52]	
α	+9.1	C_{1cis}	−5.4
β	+9.4	C_{1trans}	+2.2
γ	−2.5	C_{4cis}	+1.9
δ	+0.3	C_{4trans}	+2.2
ε	+0.1	C_{5cis}	+3.4
1°(3°)	−1.1	C_{5trans}	−4.1
1°(4°)	−3.4	V_3	+3.4
2°(3°)	−2.5	V_4	0.0
2°(4°)	−7.2	V_5	−0.6
3°(2°)	−3.7	Terminal OH_α	+48
3°(3°)	−9.5	Terminal OH_β	+10
4°(1°)	−1.5	Terminal OH_γ	−5
4°(2°)	−8.4	$C_{(OH)}$[a]	−1.6

[a] Determined in this paper.

aliphatic carbon and had little effect on the β aliphatic carbon. As a result, Sato *et al.*[26] determined the shift factor related to the influence of a double bond by comparing the chemical shift of a carbon atom in polyisoprene to the corresponding one in hydrogenated polyisoprene (Tab. IV: correction parameters). Finally, the calculated chemical shifts are in good agreement with the experimental ones (Tab. III). A maximum Δppm ~ 2 is only observed for n_1, n_2 and o_1, o_2 but, in that case, there is no ambiguity for their assignment.

By using C_5 integration, *trans*/*cis* ratio was found to be 1.68, which is 5% lower than the ^{1}H value. The fraction of the different units cannot be calculated by using V_5 and W_5 signals because their integration values are not accurate because of the presence of neighboring peaks. Finally, the distribution of head-to-head, tail-to-tail and head-to-tail linkages was determined (Tab. V) using the following equations:[26]

$$1{,}4\text{-}\underline{1{,}4\,trans} = (C_{1trans}/\Sigma)\%1{,}4$$

$$1{,}4\text{-}\underline{1{,}4\,cis} = (C_{1cis}/\Sigma)\%1{,}4$$

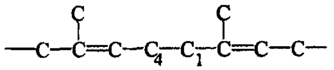
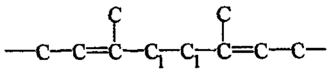
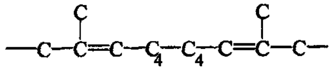
$$4{,}1\text{-}\underline{1{,}4\,trans} = ((n_1 + n_2)/2\Sigma)\%1{,}4$$

$$4{,}1\text{-}\underline{1{,}4\,cis} = ((o_1 + o_2)/2\Sigma)\%1{,}4$$

$$1{,}4\text{-}4{,}1 = (p/2\Sigma)\%1{,}4$$

where $\Sigma = C_{1trans} + C_{1cis} + (n_1 + n_2)/2 + (o_1 + o_2)/2 + p/2$.

TABLE V Distribution of 1,4-linkages in PIHT

Linkage	*Sequence*	*Chemical shift (ppm)*	*% linkage in PIHT*
1,4-1,4 (tail-to-head)			
 $-C-\overset{\overset{C}{\vert}}{C}=C-C_4-C_1-\overset{\overset{C}{\vert}}{C}=C-C-$	*cis – trans* *trans – trans*	40.46 40.18	36.9
	cis – cis *trans – cis*	32.69 32.43	19.1
4,1-1,4 (head-to-head)			
 $-C-C=\overset{\overset{C}{\vert}}{C}-C_1-C_1-\overset{\overset{C}{\vert}}{C}=C-C-$	*trans – trans* *cis – trans*	38.93 38.67	8.9
	trans – cis *cis – cis*	31.10 31.27	6.6
1,4-4,1 (tail-to-tail)			
 $-C-\overset{\overset{C}{\vert}}{C}=C-C_4-C_4-C=\overset{\overset{C}{\vert}}{C}-C-$		28.70	16.5

Epoxy and Alcohol Carbons

The assignment of carbon signals between 55 – 70 ppm was performed by using ^{13}C NMR (Fig. 6) and ^{1}H-^{13}C 2D NMR techniques (Fig. 7).

Partly epoxidized *cis-* and *trans-*1,4 polydiene studies by ^{13}C NMR,[47, 54, 55] indicate characteristic epoxy carbon resonances in the 55 – 65 ppm region leading to the attribution of *c*, *e* and *g* signals (Tab. VI). Good agreement with calculated values can be noticed. No epoxides originating from the 1,2- and 3,4-units were found because these are less reactive[39] and less abundant in the polymer chain.

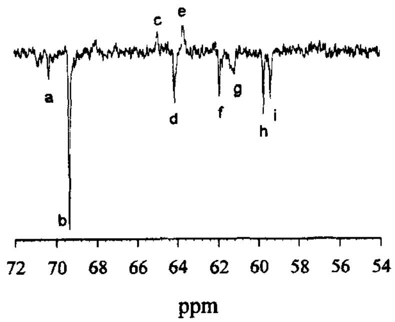


FIGURE 6 J-modulated spin echo ^{13}C NMR spectrum of the epoxy and primary alcohol regions.

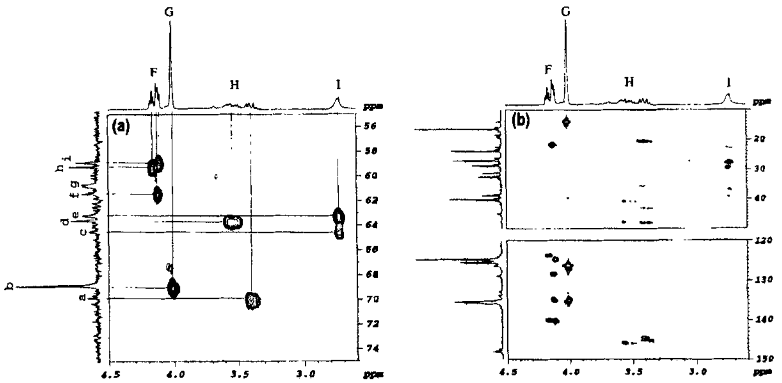
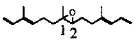
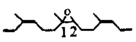
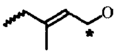
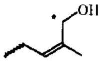
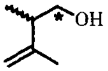
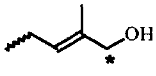
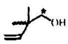


FIGURE 7 ^{1}H-^{13}C 2D NMR spectrum of the epoxy and primary alcohol regions.

TABLE VI Chemical shifts of carbons and protons of epoxy units and alcohol end units

	^{13}C			^1H	
		Shift (ppm)			*Shift*
Structure	*Signal*	*Obs.*	*Calc.*[a]	*Signal*	*(ppm)*
	*e* (2) *g* (1)	63.7 61.3	63.5 60.0	*I*	2.7
	*c* (2) *g* (1)	65.0 61.3	64.5 60.0	*I*	2.7
	*i*	59.4	59.7	F_3	4.12
	*h*	59.8	60.0	F_1	4.17
	*f*	62.0	61.8	F_2	4.13
	*d*	64.1	64.1	H_1	3.5–3.6
	*b*	69.4	69.4	*G*	4.0
	*a*	70.4	71.3	H_2	3.3–3.5

[a] Determined in this paper.

According to our assumptions in the ^{1}H NMR part, Figure 7a should exhibit eight correlations (3 for *F*, 1 for *G*, 2 for *H* and 2 for the *I* region).

Firstly, *b* is correlated with *G* and, therefore, corresponds to *trans*-$CH_2—CH{=}C(CH_3)\underline{C}H_2OH$. Likewise, in the *F* region, F_2 signal is correlated with *f* and has a very close structure to the *G* signal (Fig. 7b). We can then assume that *f* is related to the same kind of end unit as *b* ($—CH_2—CH{=}C(CH_3)\underline{C}H_2OH$) but in a *cis*- configuration. Finally, F_1, F_3, H_1 and H_2 are associated, respectively, to *h*, *i*, *d* and *a*. Calculated and observed chemical shifts are reported in Table VI. In order to obtain the best fit, we have introduced a new parameter $C_{(OH)}$ by taking *b* signal as a basis, which involves a correction on $\underline{C}H_2OH$ of α-unsaturated primary alcohol. This correction parameter was introduced in Table IV.

Olefinic Region

Figure 8 exhibits the ^{13}C NMR spectrum of the olefinic region arising from different types of structures in the polymer. The chemical shifts for the 1,4- (C_2, C_3) and 3,4-units (V_1, V_2) are close to the reported ones [21–26] but still some signals remain undetermined, mainly those corresponding to the 1,2-unit and those of the end units. More details are obtained with the corresponding ^1H-^{13}C HSQC experiment (Fig. 9) which shows clearly that V_1 and W_4 have overlapping chemical shifts (correlation with respectively, *E* and *D*) and that W_3 (correlation with *A*) is strongly affected by its environment leading to two signals. Consequently, by using C_2, C_3, V_2-W_3 and V_1-W_4

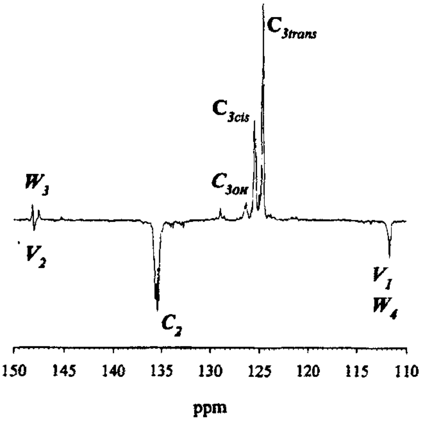


FIGURE 8 J-modulated spin echo ^{13}C NMR spectrum of the olefinic region.

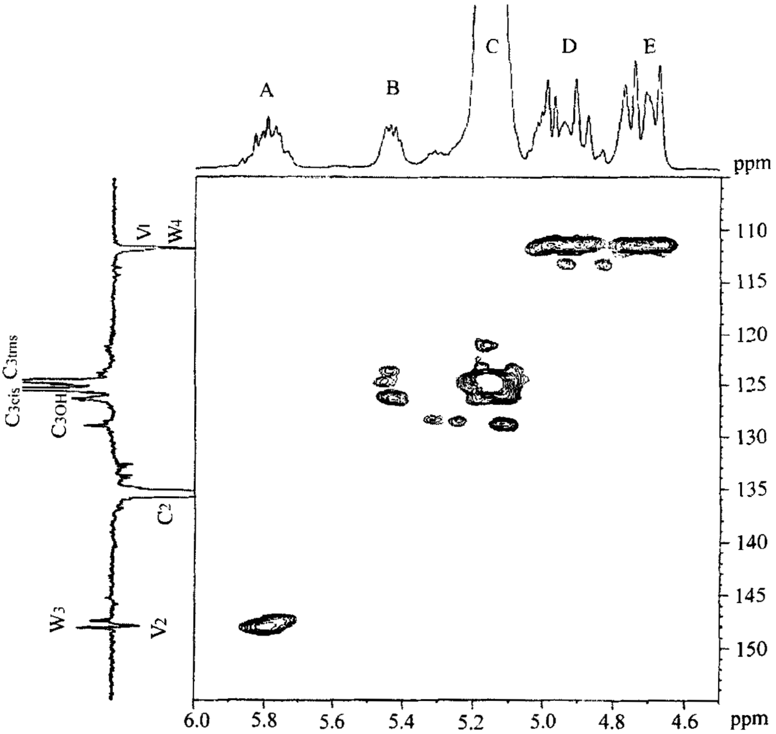


FIGURE 9 ^1H- ^{13}C 2D NMR spectrum of the olefinic region.

integrations, the 1,4-unit content was found to be 89% which is similar to the ^1H value.

Finally, we can notice that the *B* region is correlated with three different carbons. According to the attribution made by ^1H-NMR, two of them correspond to *cis*- and *trans*-$CH_2(CH_3)C{=}\underline{C}H{-}CH_2{-}OH$ carbons of the 1,4-end units. The third signal is due to the *trans*-$CH_2{-}\underline{C}H{=}C(CH_3)CH_2OH$ carbon (Fig. 7b: correlation with C_{3OH}).

CONCLUSION

The microstructure of a hydroxytelechelic polyisoprene was characterized by NMR techniques. The fractions of 1,4, 1,2 and 3,4-units were determined as well as the distribution of head-to-head (4, 1-1, 4), tail-to-tail (1, 4-4, 1) and head-to-tail (1, 4-1, 4) linkages. The hydroxyl functionality was found to be close to 2.0, which is lower than the manufacturer's value. Only primary alcohol functions were found, with a majority on 1,4-end units (68%) but a preferential initiation by 1,2- or 3,4-vinyl units was observed. By using the correction parameters, the predictive model provided very close agreement of the experimental and calculated values.

References

[1] W. S. Richardson and A. Sacher (1953). *J. Polym. Sci.*, **10**, 353.
[2] J. L. Binder and H. C. Ransaw (1957). *Anal. Chem.*, **29**, 503.
[3] F. Ciampelli, D. Moreno and M. Cambini (1963). *Makromol. Chem.*, **61**, 250.
[4] A. V. Tobolsky and C. E. Rogers (1959). *J. Polym. Sci.*, **40**, 73.
[5] J. L. Binder (1962). *Rubber Chem. Techn.*, **1**, 57.
[6] M. A. Golub (1959). *J. Polym. Sci.*, **36**, 257.
[7] M. A. Golub (1959). *J. Polym. Sci.*, **36**, 522.
[8] D. O. Hummel (1971). *Infrared Analysis of Polymers, Resins and Additives, an Atlas*, **1**(1), 139 (Wiley Intersience, New York).
[9] Y. Tanaka, Y. Takeuchi, M. Kobayashi and H. Tadokoro (1971). *J. Polym. Sci. A-2*, **9**, 43.
[10] M. J. Hackathorn and M. J. Brock (1970). *J. Polym. Sci., Polym. Lett. Ed.*, **8**, 617.
[11] M. Galin (1973). *J. Macromol. Sci. (A)*, **7**, 873.
[12] M. J. Hackathorn and M. J. Brock (1972). *Rubber Chem. Techn.*, **45**, 1295.
[13] M. J. Hackathorn and M. J. Brock (1975). *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 945.
[14] H. Y. Chen (1962). *Anal. Chem.*, **34**, 1134.
[15] F. Schué and J.-P. Dole-Robbe (1963). *Bull. Soc. Chim. Fr.*, p. 975.
[16] J.-P. Kistler, G. Friedmann and B. Kaemp (1967). *Bull. Soc. Chim. Fr.*, p. 4759.
[17] K.-F. Elgert, B. Stützel, P. Frenzel, H.-J. Cantow and R. Streck (1973). *Makromol. Chem.*, **170**, 257.
[18] K.-F. Elgert, G. Quack and B. Stützel (1975). *Polymer*, **16**, 154.
[19] F. Conti, A. Segre, P. Pini and L. Porri (1974). *Polymer*, **15**, 5.
[20] A. D. Clague, J. A. M. Van Broekhoven and L. P. Blaauw (1974). *Macromolecules*, **7**, 348.
[21] M. W. Duch and D. M. Grant (1970). *Macromolecules*, **3**, 165.
[22] Y. Tanaka, H. Sato and T. Seimiya (1975). *Polym. J.*, **7**, 264.
[23] W. Gronsky, N. Maruyama, H.-J. Cantow and T. Miyamoto (1976). *Polymer*, **17**, 358.
[24] Y. Tanaka and H. Sato (1976). *Polymer*, **17**, 113.
[25] Y. Tanaka and H. Sato (1976). *Polymer*, **17**, 413.
[26] H. Sato, A. Ono and Y. Tanaka (1977). *Polymer*, **18**, 580.
[27] Y. Camberlain, J.-P. Pascault, J. G. De la Campa and Q. T. Pham (1980). *Eur. Polym. J.*, **16**, 1031.
[28] M. Laleg, Y. Camberlain, D. Gulino and J.-P. Pascault (1982). *Eur. Polym. J.*, **18**, 821.
[29] B. Boutevin, E. Fleury and J.-P. Parisi (1986). *FR 86 03617, French patent.*

[30] B. Boutevin, E. Fleury, J.-P. Parisi and Y. Pietrasanta (1989). *Makromol. Chem.*, **190**, 2363.
[31] B. Ameduiri, B. Boutevin and M. Nouiri (1993). *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 2069.
[32] A. Priola, F. Ferrero, G. Gozzolino and M. Parretti (1984). *Chim. Ind.*, **66**(7/8), 471.
[33] A. Priola, F. Ferrero and M. Parretti (1983). *Pitture Vernici*, **10**, 85.
[34] C. Pinazzi, J. C. Soutif and J. C. Brosse (1975). *Eur. Polym. J.*, **11**, 523.
[35] G. G. Cameron and M. Y. Ourish (1981). *Makromol. Chem., Rapid Comm.*, **2**, 287.
[36] X. Guo, F. Rajeev and G. L. Rempel (1990). *Macromolecules*, **23**(24), 5047.
[37] D. N. Schulz, S. R. Turnen and M. A. Golub (1982). *Rubber Chem. Techn.*, **55**(3), 809.
[38] C. Pinazzi, J. C. Soutif and J. C. Brosse (1973). *Bull. Soc. Chim. Fr.*, **5**, 1652.
[39] D. Zuchowska (1980). *Polymer*, **21**, 513.
[40] M. Aguiar, S. Cabralde Menezes and L. Akcelrud (1994). *Makromol. Chem., Phys.*, **195**, 3937.
[41] W. K. Huang, G. H. Hsive and W. H. Hou (1988). *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 1867.
[42] F. Schapman, J.-P. Couvercelle and C. Bunel (1998). *Polymer*, **39**(20), 4955.
[43] G. Fages and Q. T. Pham (1978). *Makromol. Chem.*, **179**, 1011.
[44] Q. T. Pham (1981). *Makromol. Chem.*, **182**, 1167.
[45] R. M. Silverstein and F. X. Webster (1998). *Spectrometric Identification of Organic Compounds*, 6th edn. (Wiley & Sons, New York), pp. 315-324.
[46] A. J. Durbetaki and C. M. Miles (1965). *Anal. Chem.*, **37**, 1231.
[47] R. V. Gemmer and M. A. Golub (1978). *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2985.
[48] S. Poletto and Q. T. Pham (1994). *Makromol. Chem., Phys.*, **195**, 3901.
[49] R. S. Silas and V. Thernton (1959). *Anal. Chem.*, **31**, 529; A. J. Durbetaki and C. Miles (1965). *Anal. Chem.*, **37**, 1231.
[50] W. L. Senn (1963). *J. Anal. Chem. Acta*, **29**, 505.
[51] G. Odian (1994). *La Polymérisation. Principes et applications* (Polytechnica, Paris), p. 722.
[52] R. M. Silverstein and F. X. Webster (1998). *Spectrometric Identification of Organic Compounds*, 6th edn. (Wiley & Sons, New York), pp. 223-225.
[53] D. E. Dorman, M. Jautelat and J. D. Roberts (1971). *J. Org. Chem.*, **36**, 2757.
[54] D. R. Paulson, F. Y. N. Tang, G. F. Moran, A. S. Murray, B. P. Pelka and E. M. Vasquez (1965). *J. Org. Chem.*, **40**, 184.
[55] D. K. Tang and S. Y. Ho (1984). *J. Polym. Sci. Polym., Chem. Ed.*, **22**, 1357.