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Comprehensive Assignments of ^{1}H- and ^{13}C-NMR Signals of End-Functional Polyisobutylenes Using Spin-Lattice Relaxation Times and 2D ^{1}H- ^{13}C Hetcor Spectroscopy

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COMPREHENSIVE ASSIGNMENTS OF ^{1}H- AND ^{13}C-NMR SIGNALS OF END-FUNCTIONAL POLYISOBUTYLENES USING SPIN-LATTICE RELAXATION TIMES AND 2D ^{1}H-^{13}C HETCOR SPECTROSCOPY

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Key Words: Polyisobutylene; Carbocationic polymerization; Living polymerization; End groups; Functional groups; Chloride; Olefin; Alcohol; Aldehyde; Acetal; Aliphatic initiator; Aromatic initiator; ^{1}H-NMR; ^{13}C-NMR; Spin-lattice relaxation time; T_1; Two-dimensional correlation spectroscopy; HETCOR; DEPT

ABSTRACT

The analysis of ^{13}C spin-lattice relaxation times (T_1's) provides a direct method for the assignment of ^{13}C-NMR signals of the end groups of polymers. The ^{13}C T_1's of polyisobutylenes bearing *tert*-butyl, *tert*-chloride, *exo*-olefin, alcohol, aldehyde, and acetal end groups have been determined, and all the signals in their ^{13}C-NMR spectra were assigned according to the gradient of T_1 along the polymer chain with the minimum in the middle. The assignments are in excellent agreement with those established by other techniques, which indicates the reliability of this novel method for the characterization of various end groups in polyisobutylenes. ^{13}C T_1 analysis has also been used to obtain assign-

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ments for internal polyisobutylene segments adjacent to aromatic initiator residues. The method provides insight into the interaction of hydroxyl end groups of alcohol-capped PIBs, and allows identification of the low molecular weight impurities in the polymers. Assignments of all the ^{1}H-NMR signals of the above polyisobutylenes were obtained by 2D ^{1}H-^{13}C HETCOR spectroscopy. For some polymers, ^{1}H-NMR signals were also assigned based on their ^{1}H T_1 values and the assignments agree with those generated by HETCOR spectroscopy.

INTRODUCTION

This paper concerns a new method for the comprehensive assignment of end-group resonances in ^{13}C- and ^{1}H-NMR spectra of various end-functional polyisobutylenes (PIBs) based on the analysis of spin-lattice relaxation times.

Let the principle of this method be illustrated with *n*-decane [1]: In this molecule the spin-lattice relaxation time T_1 of the carbon nuclei is a function of the position of the carbon along the chain:

^{13}C T_1 (s):	8.74	6.64	5.71	4.95	4.36	4.36	4.95	5.71	6.64	8.74
	CH_3–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_3

Evidently, the ^{13}C T_1's are longest at the chain ends and shortest at the middle of the molecule, and intermediate carbons have intermediate T_1 values. This phenomenon is due to the higher freedom of segmental motions at the chain ends relative to those at internal positions. Slower tumbling in the middle of the chain facilitates relaxation of internal carbons. Reviews concerning detailed discussions of this matter have been published [2–4]. T_1 analysis proved to be a versatile method for the study of segmental motion of various polymers (see, for example, Refs. 5–12).

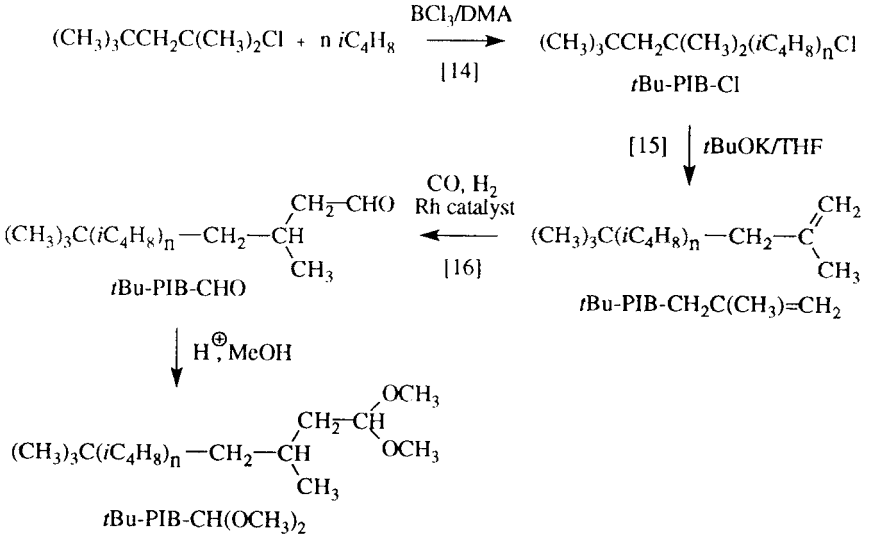
We show how this phenomenon can be exploited for the assignment of end-group signals of various end-functional PIBs which became available as a result of the discovery of living carbocationic polymerization of olefins (for a recent review of this field, see Ref. 13).

EXPERIMENTAL

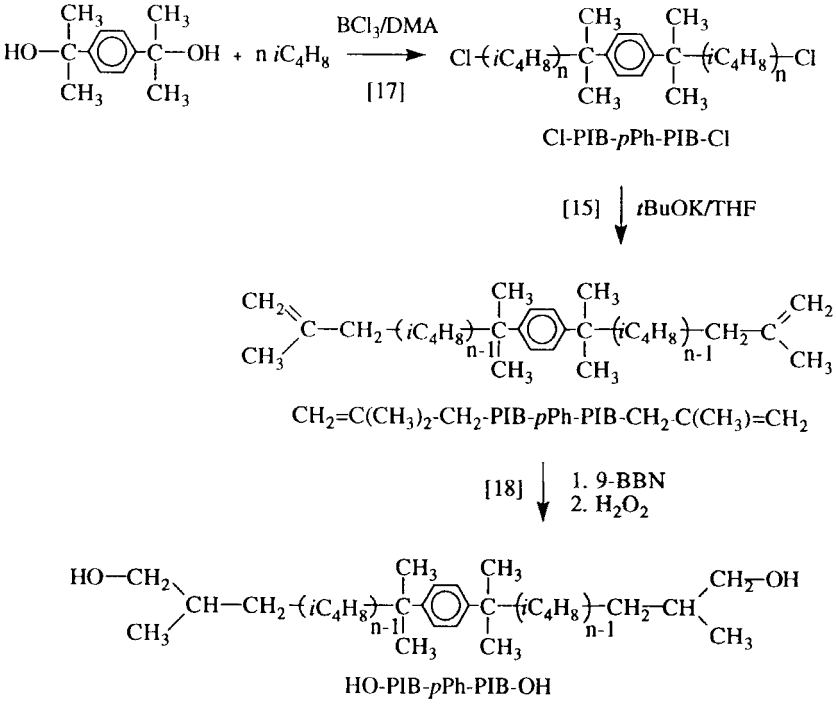
Polymerizations and Functionalizations

Schemes 1 and 2 outline the polymerizations and transformations which produced the desired end-functional PIBs. Except for the methyl acetal-terminated product (*t*Bu-PIB-CH(OCH_3)$_2$, last formula in Scheme 1), all the necessary synthetic, characterization, and structural information has been published (see references in Schemes 1 and 2).

Methyl acetal-terminated PIB was obtained from primary aldehyde-capped PIB. Thus, 1 g *t*Bu-PIB-CHO was dissolved in 10 mL hexanes and the solution was stirred with 100 mL methanol acidified with 5 mL concentrated HCl at room temperature for 1 week. The hexanes were evaporated, and the polymer was separated from methanol and dried in vacuo at 40°C to constant weight. The ^{1}H-NMR spectrum indicated quantitative conversion of the aldehyde termini into the acetal end groups (Scheme 1). The transformation of the acetal back into the aldehyde



SCHEME 1. Syntheses, structures, symbols, and references of the various monofunctional PIBs employed.



SCHEME 2. Syntheses, structures, symbols, and references of the various telechelic PIBs employed.

can be achieved by treating the polymer (1 g) with boiling 1 N aqueous HCl (50 mL) for 5 hours under a blanket of nitrogen.

NMR Spectroscopy

^1H- and ^{13}C-NMR spectra were obtained at ambient temperatures by a Varian Gemini-200 spectrometer operating at 200 and 50 MHz, respectively, using $CDCl_3$ solutions in 5 mm tubes. Sample concentrations were 20 mg/mL for proton and 200 mg/mL for carbon spectroscopy. TMS was used as the internal standard. Typically, 128 transients were accumulated for the proton spectra with 60° pulses (18 μs), 2.7 seconds acquisition time, and 2 seconds delay. ^{13}C-NMR spectra were obtained with the ^{1}H decoupler turned on only during the acquisition time to suppress the NOE. The following parameters were used: 60° pulses (14.7 μs), 1024 transients, 1 second acquisition time, and 2 seconds delay.

DEPT (*D*istortionless *E*nhancement by *P*olarization *T*ransfer) [19] spectra were obtained using a standard Gemini microprogram and the following conditions: 1024 transients, 1 second acquisition time, 2 seconds delay, the widths of the 90° pulses were 27 μs for protons and 22 μs for carbons. ^1J(C,H) was set to 130 Hz.

Spin-lattice relaxation times (T_1's) were determined by the inversion-recovery experiment with a (π-τ-$\pi/2$) pulse sequence [20, 21]. Ten to 13 τ values were chosen ranging from 10 ms to 20 seconds for proton and from 7 ms to 28 seconds for carbon resonances, respectively; 256 acquisitions were accumulated for each τ value. A single exponent was used to fit the relaxation data and regression analysis to calculate T_1's and the errors. The average errors were ~3%, and in no case did they exceed 10%.

Preliminary experiments with degassed and sealed polymer solutions gave somewhat longer T_1's compared to air-saturated solutions. However, the assignments obtained were the same in both cases. Thus, samples for T_1 measurements have not been degassed in order to shorten the duration of experiment.

2D ^1H-^{13}C HETeronuclear chemical shift CORrelated (HETCOR) spectra [22–24] were acquired and processed with a Gemini HETCOR microprogram. Typically, we used a 500-Hz spectral width along the F_1 (proton) axis and 2500 Hz along the F_2 (carbon) axis, 256 increments, 128 acquisitions, 512 data points, 1.5 seconds pulse repetition time.

RESULTS AND DISCUSSION

α-*t*-Butyl-ω-*t*-chloro-polyisobutylene (*t*Bu-PIB-Cl)

The validity of the concept and the methodology was established by analyzing *t*Bu-PIB-Cl, the ^{13}C signal assignments of which were established by other techniques [25, 26]. The following steps were used to obtain comprehensive assignments of end-group signals.

1. Signals were sorted with respect to head or tail groups in the polymer. We compared the ^{13}C-NMR spectrum of *t*Bu-PIB-Cl (Fig. 1b) with those of other polymers, one having the same head group, (*t*Bu-PIB-$CH_2C(CH_3)=CH_2$) (Fig. 1a), and the other with the same tail groups, (Cl-PIB-*p*Ph-PIB-Cl) (Fig. 1c). The

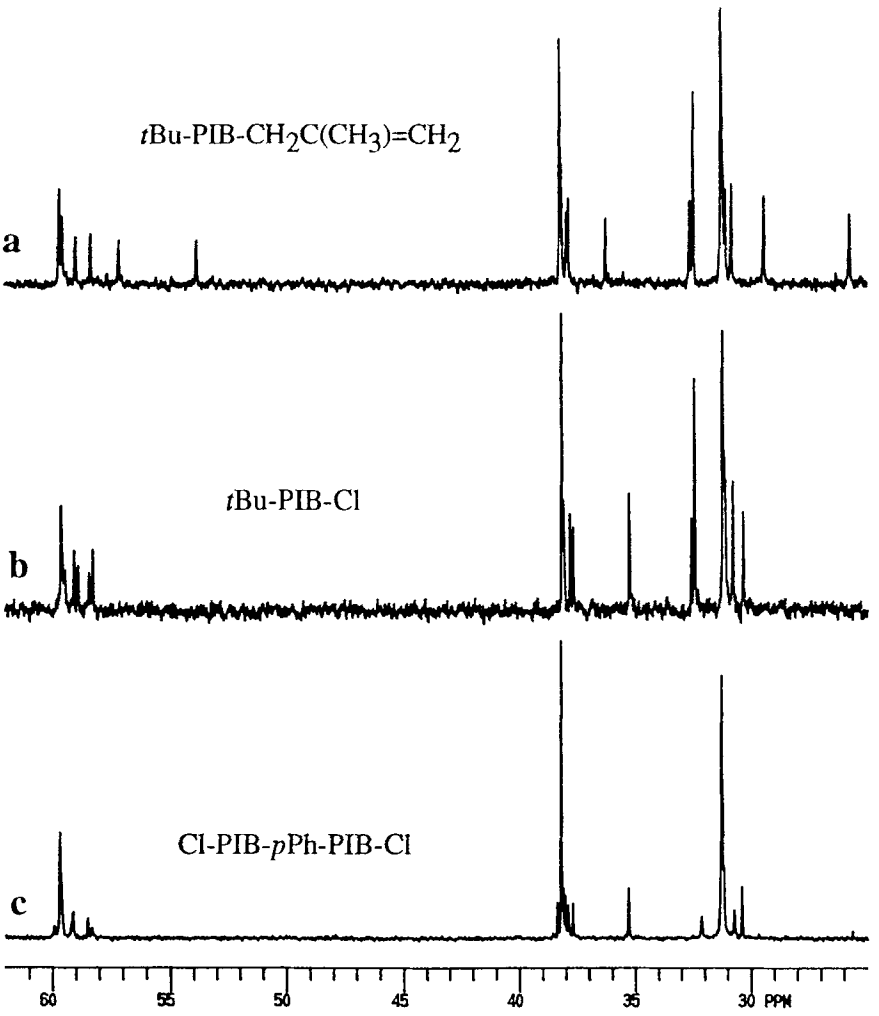


FIG. 1. High field parts of ^{13}C-NMR (50 MHz) spectra of: (a) *t*Bu-PIB-$CH_2C(CH_3)=CH_2$, $\overline{M}_n$ = 670 g/mol; (b) *t*Bu-PIB-Cl, $\overline{M}_n$ = 640g/mol; (c) Cl-PIB-*p*Ph-PIB-Cl, $\overline{M}_n$ = 2000 g/mol.

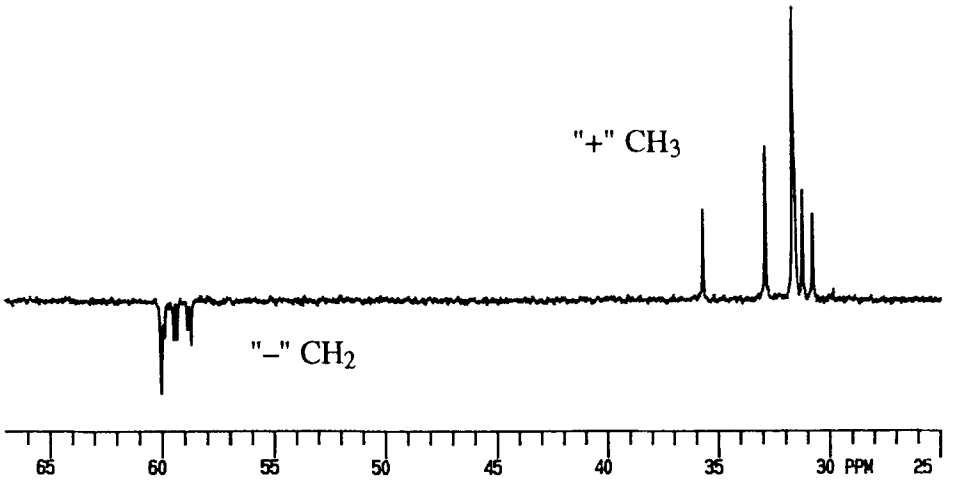


FIG. 2. DEPT-135° spectrum (Θ = 135°) of *t*Bu-PIB-Cl ($\overline{M}_n$ = 640 g/mol). Compare it with Fig. 1(b).

signals common in spectra 1a and 1b are due to the head groups while those in spectra 1b and 1c belong to the tail groups. A comparison with the spectra of other end-functional polymers (Scheme 1) confirmed the assignments.

2. Signals were sorted according to the number of protons attached to carbons using the DEPT mode of spectral data collection [19]. In DEPT-135°spectra (135° is the value for the Θ angle in the original description of DEPT pulse sequence [19]), the carbons bonded to an odd number of hydrogens (i.e., CH and CH_3) produce signals with positive amplitudes while carbons connected to an even number of hydrogens (i.e., CH_2) give signals with negative amplitudes. Consequently, the DEPT-135° spectrum of *t*Bu-PIB-Cl (Fig. 2) shows the positive signals due to the CH_3 groups and the negative signals due to the CH_2 groups. The signals in spectrum 1b (Fig. 1), absent in the DEPT spectrum (Fig. 2), are due to quaternary carbons.

3. Next, the ^{13}C T_1 values were determined by the inversion-recovery method which employs the (π-τ-$\pi/2$) pulse sequence [20, 21] (Fig. 3). The T_1 values were assigned to the carbons by the rule: The longer the relaxation time, the closer the carbon to the chain end (see Scheme 3). This rule was applied to each type of carbons (C, CH_2, CH_3) and with respect to each chain end.

4. Chemical shifts were assigned following the T_1 assignments (Scheme 3). All the assignments obtained for *t*Bu-PIB-Cl by T_1 analysis are in agreement with those obtained by other methods [25, 26] (discrepancies in values of chemical shifts are due to different spectra referencing and sample concentrations).

5. It was of interest to explore whether the ^1H T_1 values could also be helpful in assigning ^1H signals of PIBs. The ^1H-NMR spectra of various PIBs are compared in Fig. 5. As in the case of ^{13}C-NMR spectroscopy, this comparison distinguishes the signals due to the head and tail groups. The ^1H T_1's for *t*Bu-PIB-Cl were determined by the same inversion-recovery method, and the signals were assigned

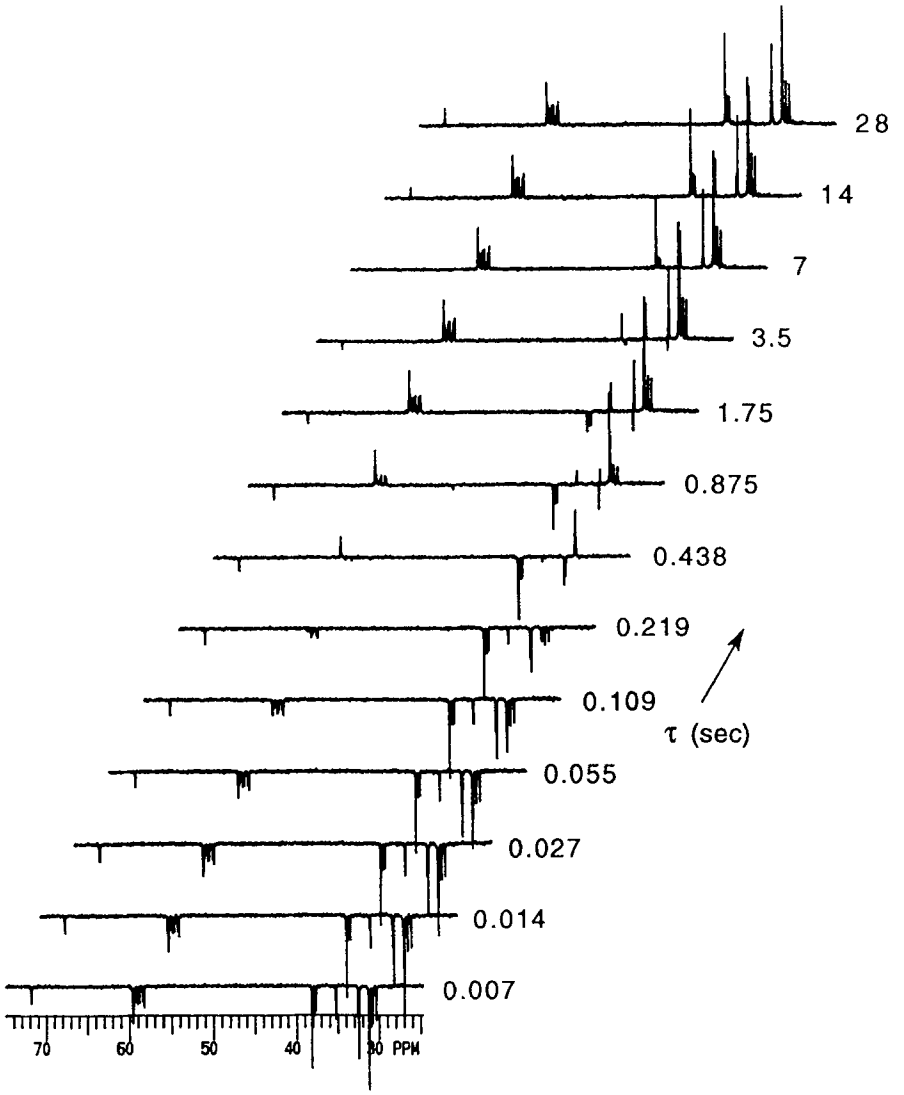
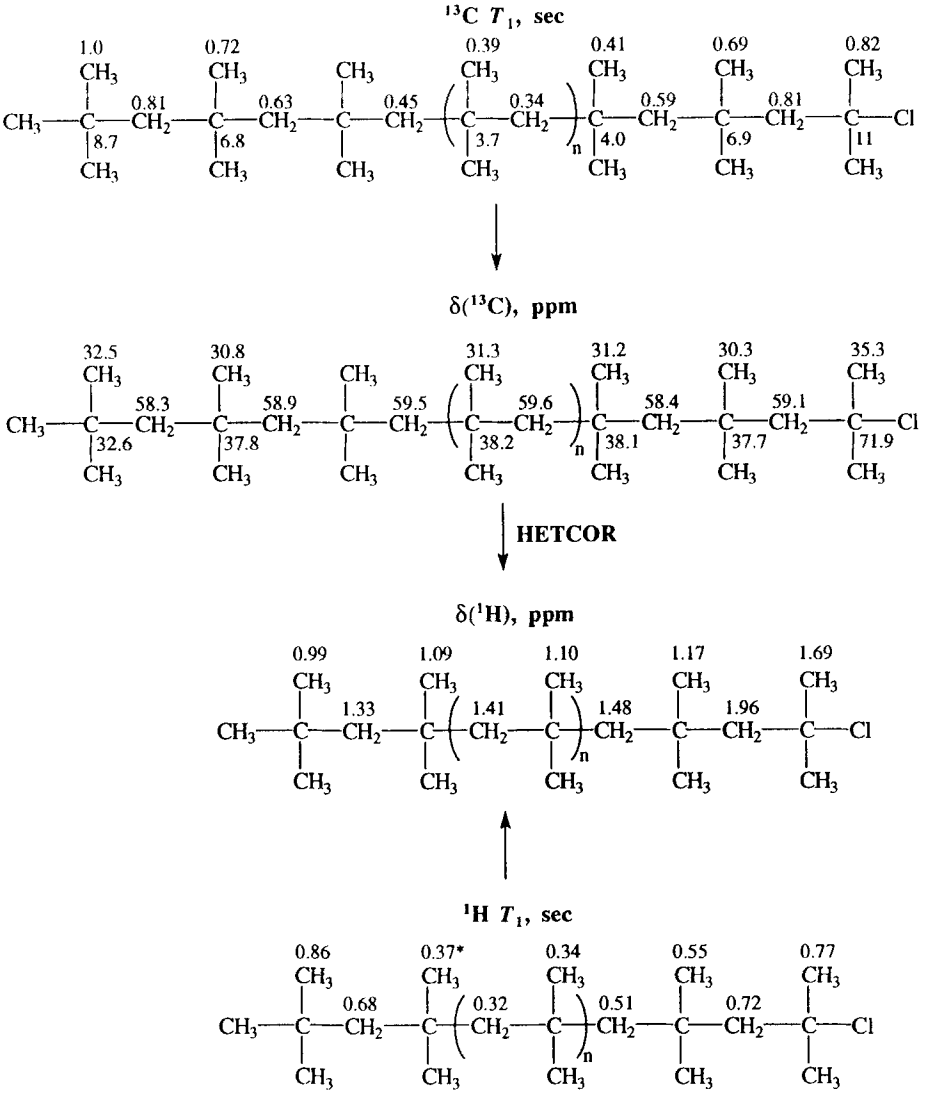


FIG. 3. Set of the inversion-recovery (π-τ-π/2) ^{13}C-NMR spectra for determination of ^{13}C spin-lattice relaxation times (T_1's) for *t*Bu-P1B-Cl, $\overline{M}_n$ = 640 g/mol.



SCHEME 3. ^{1}H T_1 and ^{13}C T_1 values, ^{1}H and ^{13}C chemical shifts, and assignments for *t*Bu-PIB-Cl, $\overline{M}_n$ = 640 g/mol.

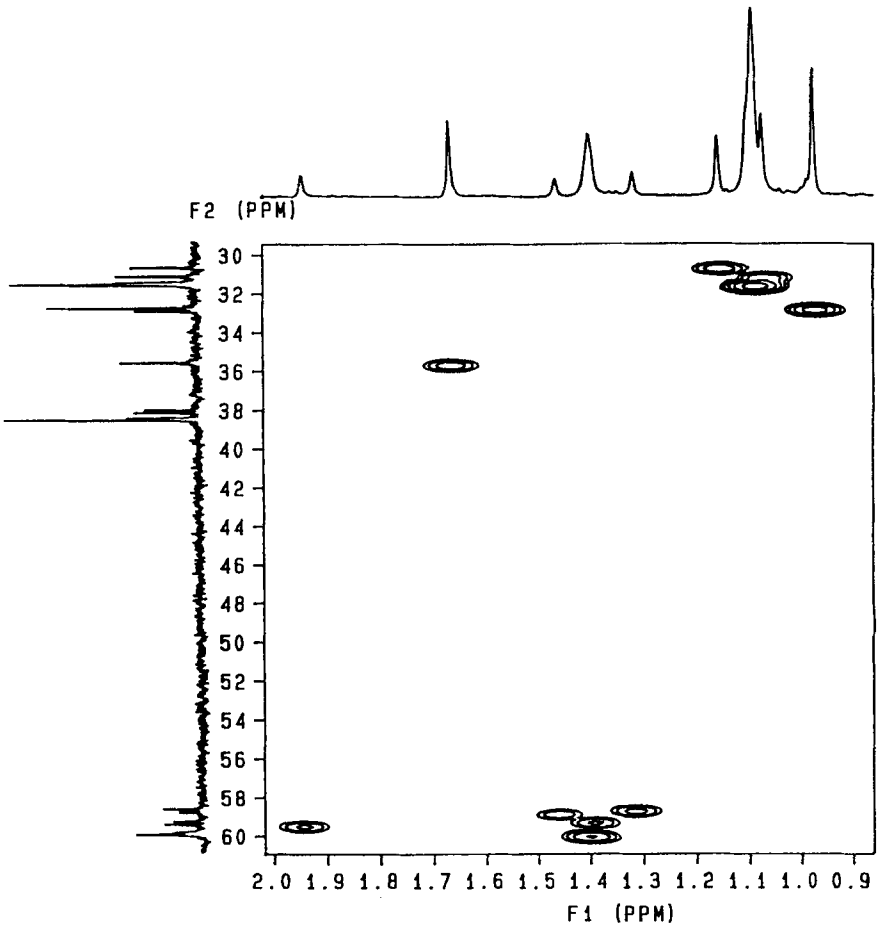
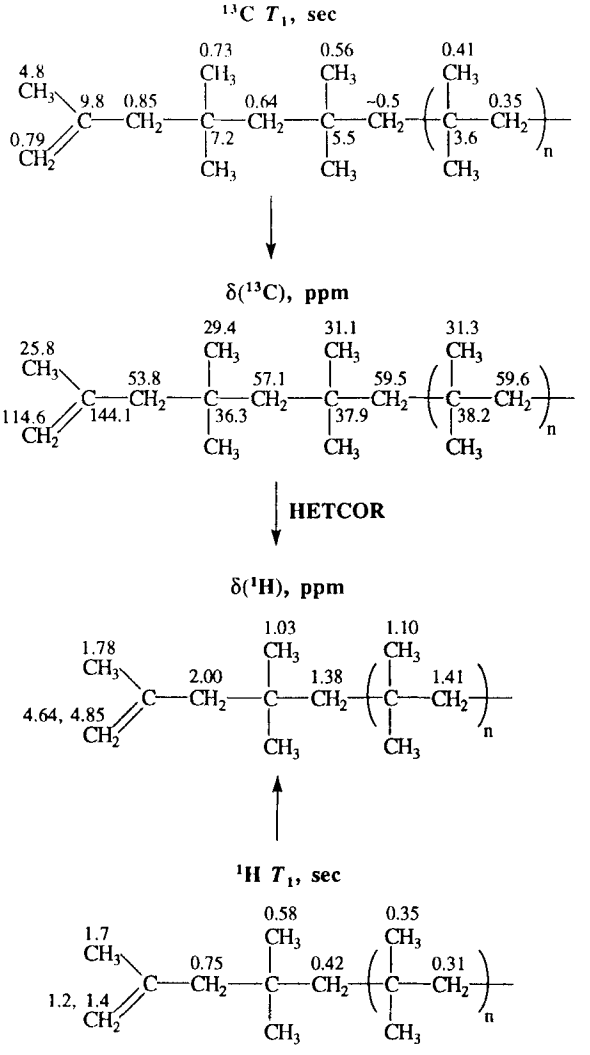


FIG. 4. 2D ^{1}H-^{13}C heteronuclear shift correlated (HETCOR) contour map of *t*Bu-PIB-Cl, $\bar{M}_n$ = 640 g/mol. F_1 = conventional proton spectrum; F_2 = conventional ^{13}C spectrum.

such that the T_1's gradually increased from the middle of the chain toward the ends. (The value marked with an asterisk in the last line of Scheme 3 is most likely underestimated due to overlapping with the intense signal of the faster relaxing inner methyl protons.) The assignments obtained by ^{1}H T_1 analysis completely agree with those provided by the 2D ^{1}H-^{13}C HETCOR spectrum (Fig. 4, Scheme 3). This indicates the applicability of T_1 analysis to proton spectroscopy of PIBs.

Exo-Olefin-Capped Polyisobutylene (*t*Bu-PIB-$CH_2C(CH_3)=CH_2$)

The T_1 analysis has also been tested with *t*Bu-PIB-$CH_2C(CH_3)=CH_2$, the assignments of which have already been established [25]. To our satisfaction, the T_1 method again provided accurate assignments of all ^{13}C and ^{1}H signals (Scheme 4, Figs. 1a, 5a, and 6).



SCHEME 4. ^1H T_1 and ^{13}C T_1 values, ^1H and ^{13}C chemical shifts, and assignments for *exo*-olefin-capped PIB. T_1's for *t*Bu-PIB-$CH_2C(CH_3)=CH_2$, $\bar{M}_n$ = 670 g/mol.

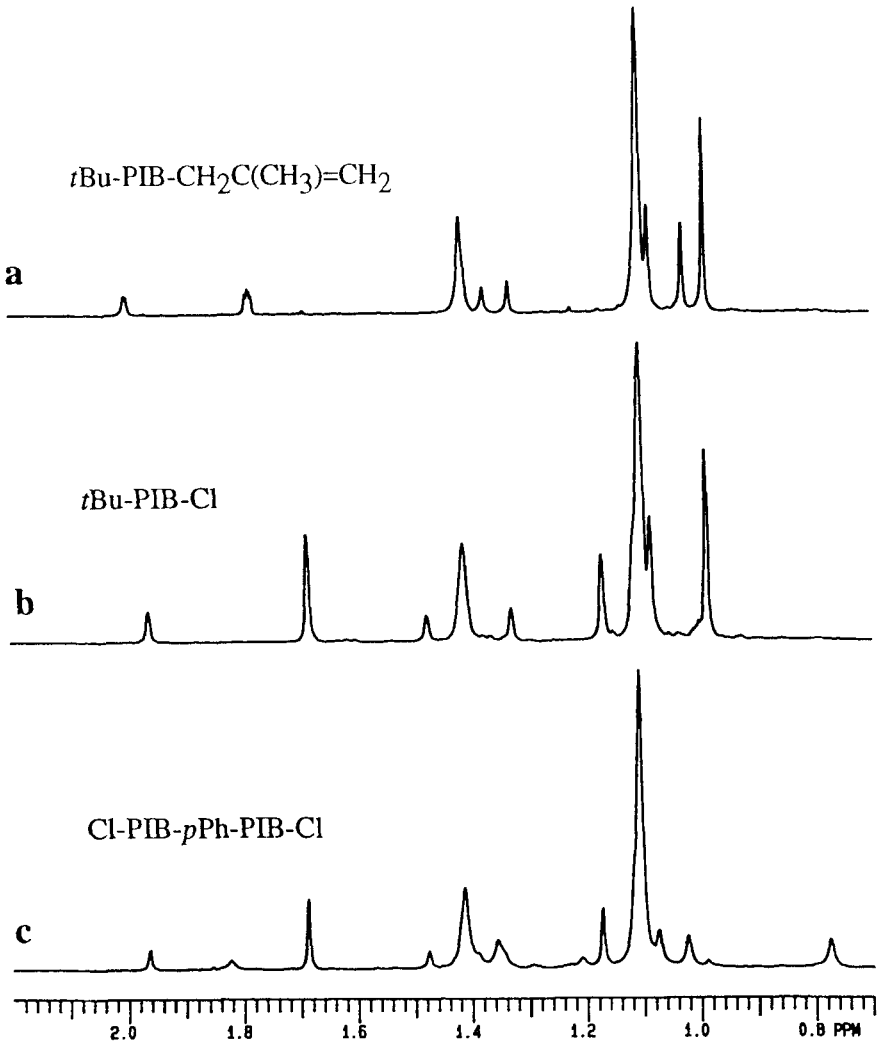


FIG. 5. High field parts of ^{1}H-NMR (200 MHz) spectra of: (a) *t*Bu-PIB-$CH_2C(CH_3)=CH_2$, $\overline{M}_n$ = 670 g/mol; (b) *t*Bu-PIB-Cl, $\overline{M}_n$ = 640 g/mol; (c) Cl-PIB-*p*Ph-PIB-Cl), $\overline{M}_n$ = 2000 g/mol.

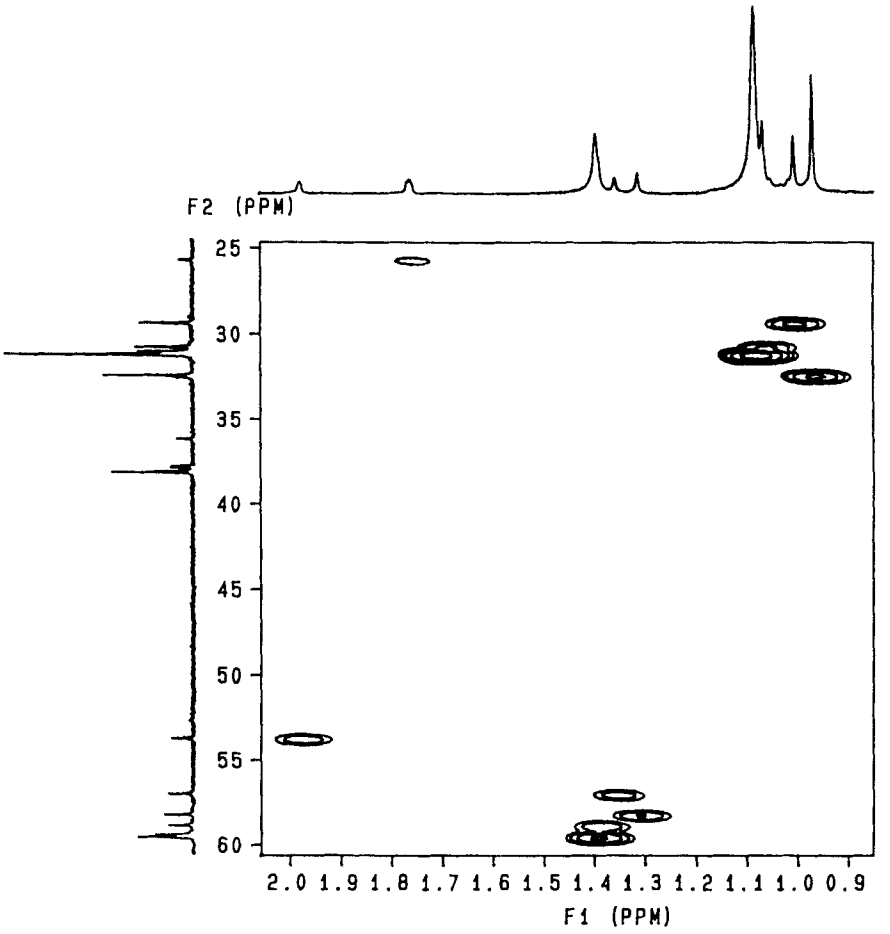
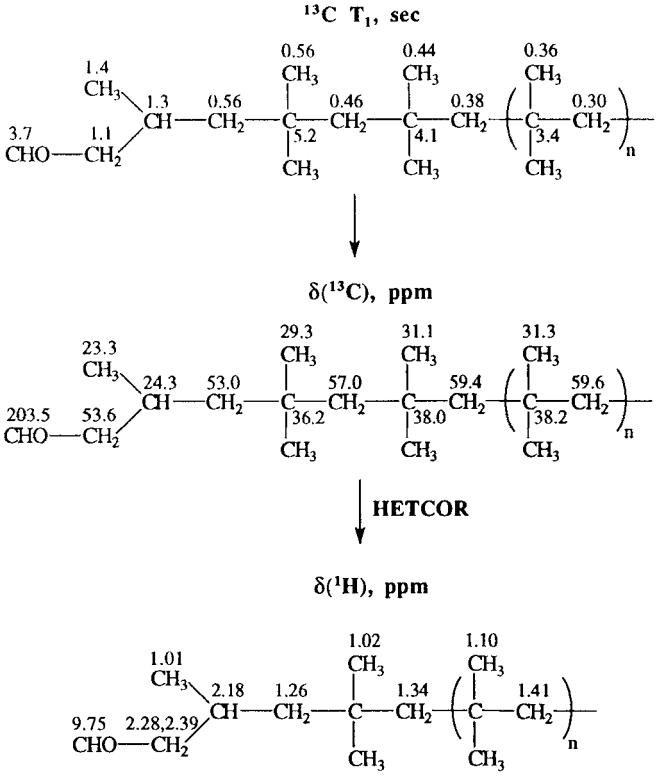


FIG. 6. One-bond heteronuclear shift correlated spectrum with full proton decoupling (HETCOR-FPD) of *t*Bu-PIB-$CH_2C(CH_3)=CH_2$, $\bar{M}_n$ = 670 g/mol.

One comment should be made in respect to the methylene signal at 59.5 ppm. According to the integrated intensity, two signals overlap in this range of the ^{13}C-NMR spectrum: One from the aliphatic side of the chain and the other from the olefinic part. The combined signal exhibits almost the same T_1 (0.48 second) as the single signal in the spectrum of *t*Bu-PIB-Cl (T_1 = 0.45 second) (see Scheme 3). Evidently the signal from the olefinic end has approximately the same T_1 (i.e., ~0.5 second) as the one from the aliphatic end and it can be used for the assignment.

Thus, T_1 analyses of *t*Bu-PIB-Cl and *t*Bu-PIB-$CH_2C(CH_3)=CH_2$ provide comprehensive assignments of the three end groups, *tert*-butyl, *tert*-chloride, and *exo*-olefin, and these assignments are identical with those established by other techniques. Having proven to our satisfaction the reliability of the T_1 method with two end-functional PIBs, we proceeded with the analysis of other end-functional PIBs.



SCHEME 5. ^{13}C T_1 values, ^{13}C and ^{1}H chemical shifts, and assignments for primary aldehyde-capped PIB. ^{13}C T_1's for *t*Bu-PIB-CHO, $\overline{M}_n$ = 740 g/mol.

Aldehyde-Capped Polyisobutylene (*t*Bu-PIB-CHO)

T_1 analysis has been applied to *t*Bu-PIB-CHO [16] (Scheme 1). The results are shown in Scheme 5.

The HETCOR spectrum (Fig. 7) indicates that the carbon with 53.6 ppm (see second formula in Scheme 5) is bonded to two nonequivalent hydrogens (2.28 and 2.39 ppm, see third formula in Scheme 5). This nonequivalency arises from the vicinity of the chiral methine group which renders the two neighboring methylene protons diastereotopic. The other two methylene protons (1.26 ppm) adjacent to the same methine group are less sensitive to the vicinity of the optical center and produce only one crosspeak in the HETCOR spectrum (marked with an asterisk in Fig. 7).

The proton spectrum (top, Fig. 7) is ill-resolved due to signal overlapping and spin coupling. Thus we could not obtain comprehensive assignments by ^{1}H T_1 analysis. However, the assignments of the ^{13}C signals and HETCOR spectroscopy with full proton decoupling provide a complete inventory of ^{1}H chemical shifts and assignments (Scheme 5).

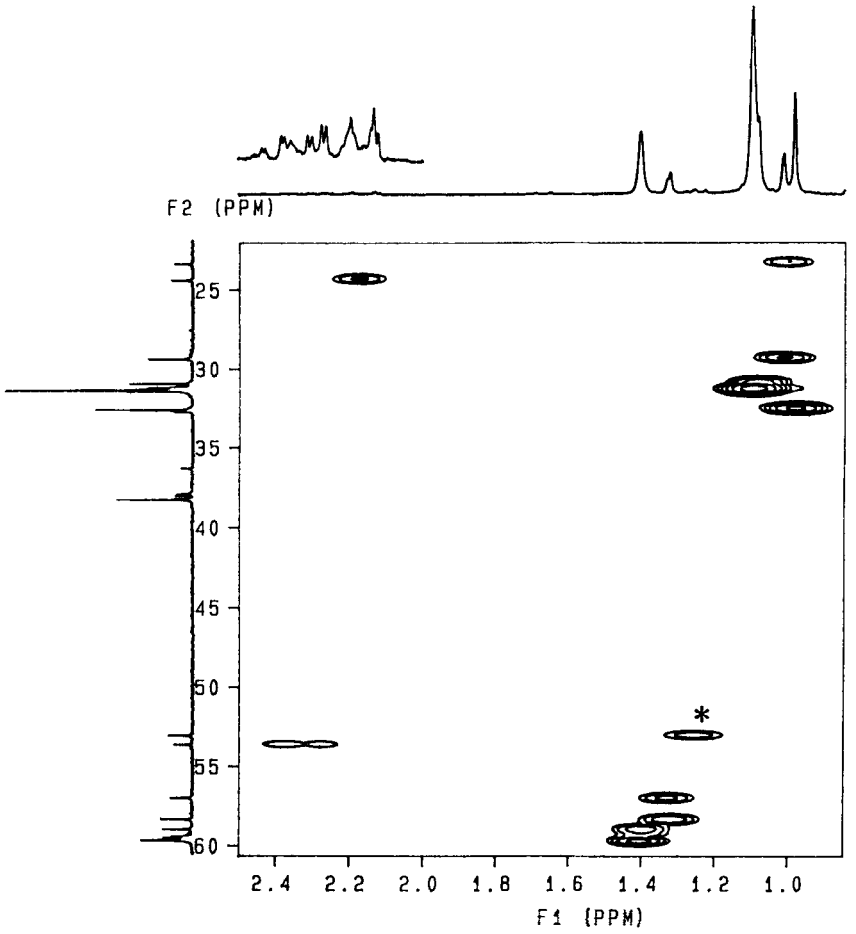
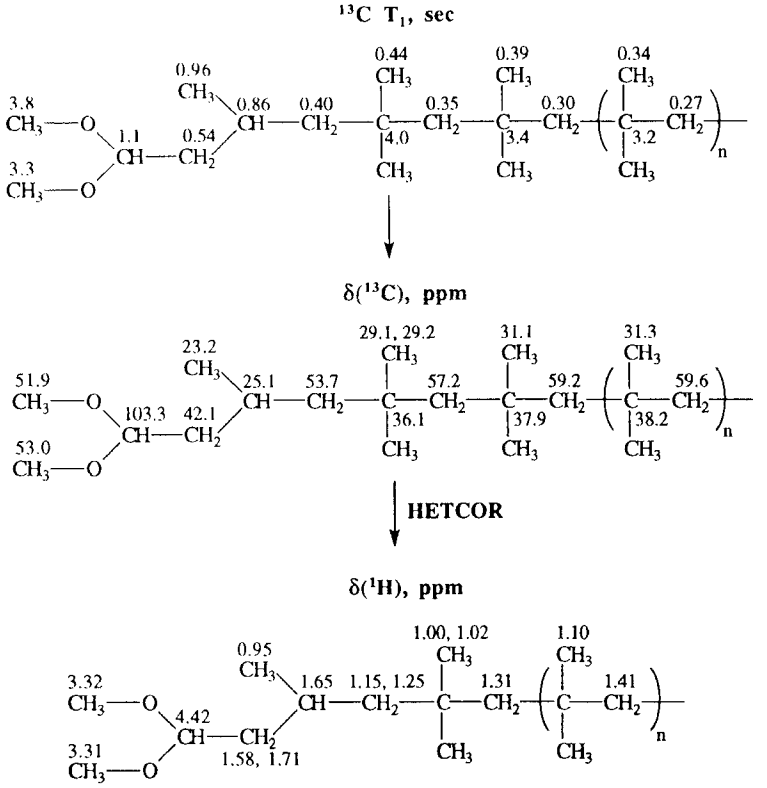


FIG. 7. One-bond heteronuclear shift correlated spectrum with full proton decoupling (HETCOR-FPD) of *t*Bu-PIB-CHO, $\overline{M}_n$ = 740 g/mol.

Acetal-Capped Polyisobutylene (*t*Bu-PIB-CH(OCH_3)$_2$)

If aldehyde-capped PIB is to be stored for an extended time period, the aldehyde groups must be protected, for example, by transforming them into less reactive acetal groups [27]. Acetal-capped PIB can be stored at room temperature, and the aldehyde can be fully recovered by acid hydrolysis (see Experimental Section).

Thus, the *t*Bu-PIB-CHO has been converted to the *t*Bu-PIB-CH(OCH_3)$_2$ (Scheme 1), and the latter was characterized by T_1 analysis (Scheme 6, Fig. 8). Similarly to the aldehyde-capped PIB, the chiral methine group renders the neighboring methylene protons nonequivalent. The crosspeak corresponding to the ^{1}H signal at 1.58 ppm does not appear in Fig. 8; however, it is observable in the enhanced contour map (not shown). The ^{13}C-NMR spectrum shows that the resonances of the two methyls in the γ-position to the chiral methine group and the two methoxy groups are also split into two due to the close vicinity of the optical center.



SCHEME 6. ^{13}C T_1 values, ^{13}C and ^{1}H chemical shifts, and assignments for dimethyl acetal-capped PIB. ^{13}C T_1's for *t*Bu-PIB-CH(OCH_3)$_2$, $\overline{M}_n$ = 780 g/mol.

Alcohol-Capped Polyisobutylene (HO-PIB-*p*Ph-PIB-OH)

The results of ^{13}C T_1 analysis of HO-PIB-*p*Ph-PIB-OH are summarized in Scheme 7, and the HETCOR spectrum is shown in Fig. 9.

The assignments obtained by T_1 analysis completely agree with those obtained earlier by comparison with model compounds [25]. This again corroborates the reliability of the T_1 method. The ^{13}C signal at 31.1 ppm (marked by an asterisk in Scheme 7) overlaps with the signal due to the CH_3's in the PIB segment next to the initiator fragment in the middle of the chain, and its individual T_1 was not available. Therefore the assignment has been taken from Reference 25.

T_1 analysis of HO-PIB-*p*Ph-PIB-OH provides insight into hydroxyl end-groups interaction in this polymer. The formation of hydrogen bridges would place the hydroxyl end groups in the middle of an aggregate and consequently shorten the T_1's of the neighboring groups. This was found, for example, for neat *n*-decanol [28]:

^{13}C T_1 (s):	0.65	0.77	0.77	0.84	0.84	0.84	1.1	1.6	2.2	3.1
	HO—CH_2—	CH_2—	CH_2—	CH_2—	CH_2—	CH_2—	CH_2—	CH_2—	CH_2—	CH_3

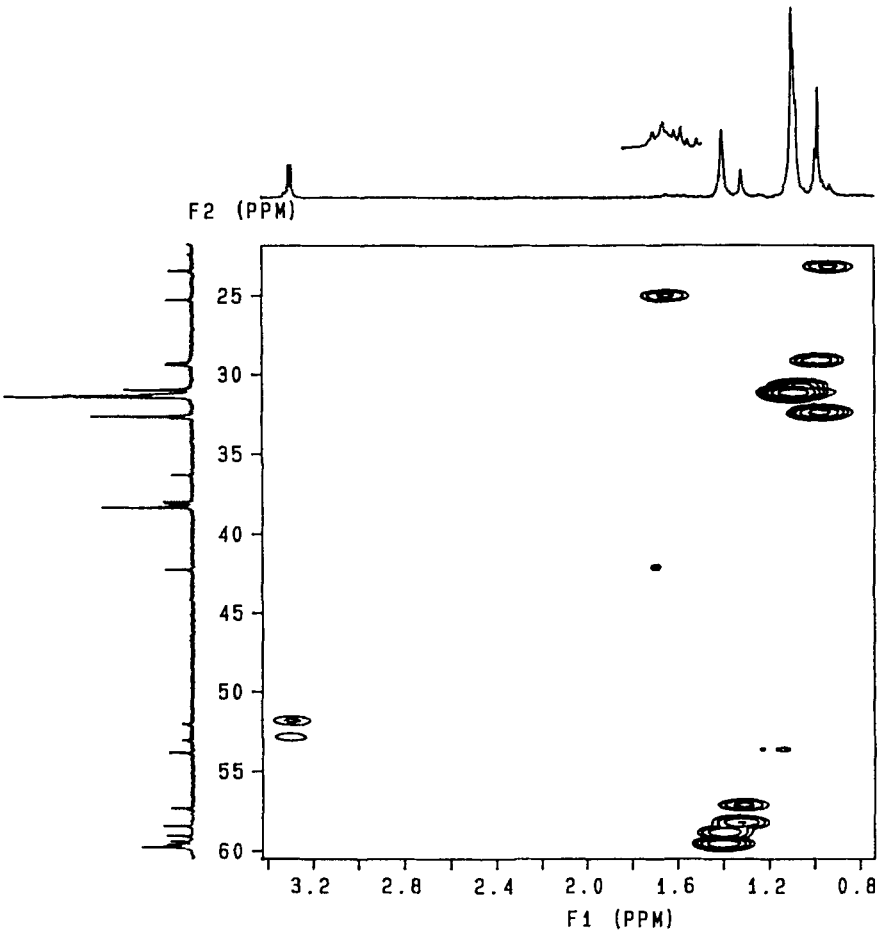


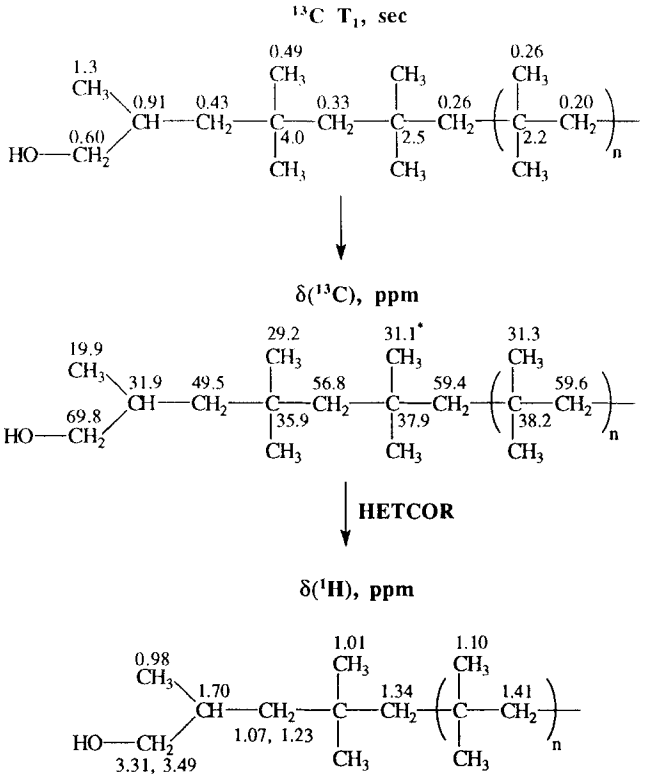
FIG. 8. One-bond heteronuclear shift correlated spectrum with full proton decoupling (HETCOR-FPD) of *t*Bu-PIB-CH(OCH_3)$_2$, $\overline{M}_n$ = 780 g/mol.

In this molecule the minimum T_1 value is associated with the CH_2 group next to the OH terminus.

In contrast to the findings with neat *n*-decanol, the T_1's in the HO-PIB-*p*Ph-PIB-OH solution are longest for the terminal groups (Scheme 7). On the basis of this evidence, we conclude that the alcohol groups are not aggregated in this polymer under the experimental conditions. This is probably due to the low concentration of hydroxyl groups and the polar solvent (chloroform) used to prepare solutions.

Polyisobutylene Obtained with Dicumyl Hydroxide Initiator

T_1 analysis has also been applied to obtain assignments of PIB segments attached to an aromatic initiator residue incorporated into the polymer during initiation (Scheme 2). We hypothesized that the rigid aromatic ring should restrict



SCHEME 7. ^{13}C T_1 values, ^{13}C and ^{1}H chemical shifts, and assignments for primary alcohol-capped PIB. ^{13}C T_1's for HO-PIB-*p*Ph-PIB-OH, $\overline{M}_n$ = 2000 g/mol.

the mobility of neighboring isobutylene units, and consequently facilitate their relaxation. A similar phenomenon has been observed with 1-phenyldecane [29], the ^{13}C T_1's of which are shorter than those in *n*-decane, and the minimum T_1's are displaced from the middle of the aliphatic chain toward the aromatic ring.

As anticipated, the T_1's of the carbons in the repeat units next to the aromatic ring were found to be shorter than those of the other internal carbons (Scheme 8). Thus, we assigned the signals by the following rule: The closer the carbon to the aromatic ring, the shorter its relaxation time. The signals due to quaternary carbons at 37.9, 38.0, and 38.3 ppm were not assigned because the difference in their T_1 values (1.9 ± 0.1 seconds) was within experimental error. The ^{13}C signal at 31.1 ppm (marked with an asterisk in Scheme 8), overlaps with the other signals in all telechelic PIBs studied (see previous section), therefore it is assigned based on the similarity with the other end segments of functional PIBs: In all PIBs studied, the methyl carbons of the third repeat unit with respect to the terminal functional group resonate at ~31.1 ppm (see Schemes 3–7). The results obtained by T_1 analysis are shown in Scheme 8. At least one ^{13}C methyl signal assignment (32.1 ppm) is confirmed independently by isotropic labeling [26].

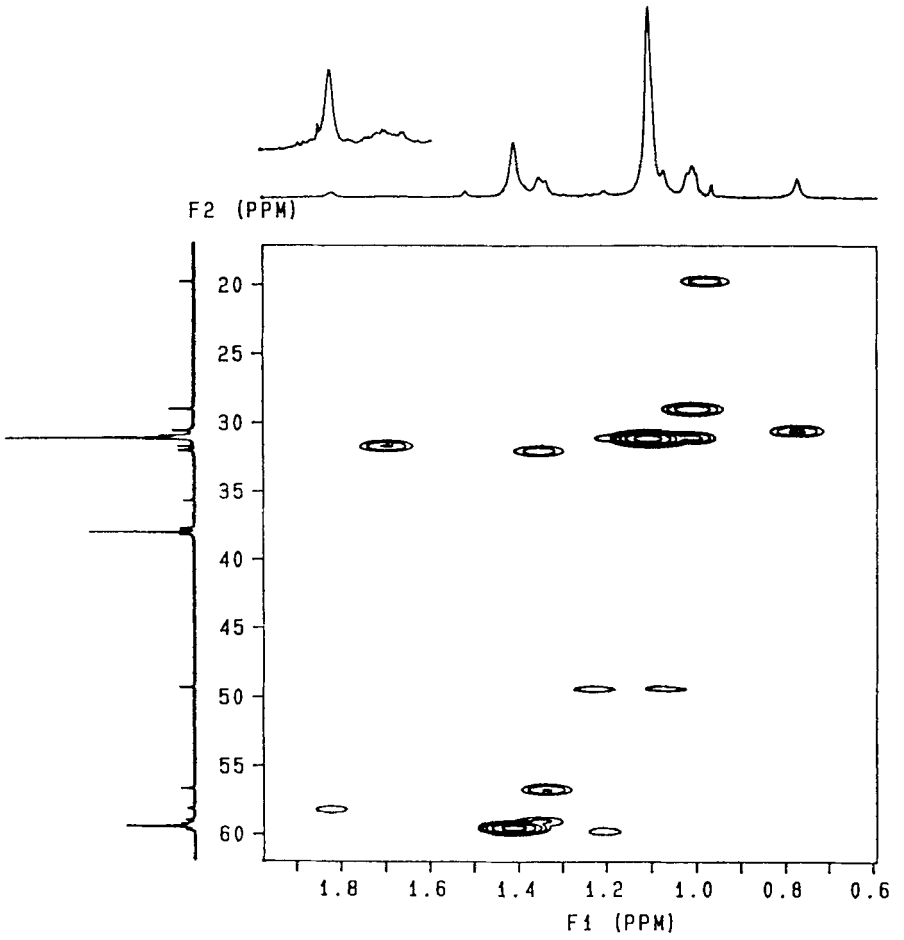


FIG. 9. One-bond heteronuclear shift correlated spectrum with full proton decoupling (HETCOR-FPD) of HO-PIB-*p*Ph-PIB-OH, $\overline{M}_n$ = 2000 g/mol.

Low Molecular Weight Impurities

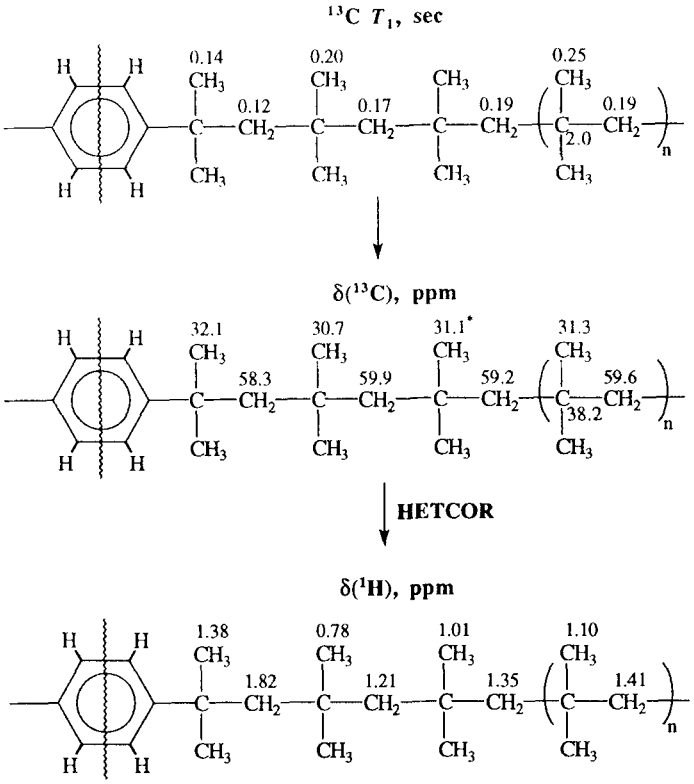
An additional benefit of T_1 analysis is that it can be used for the identification of low molecular weight impurities, such as traces of solvent, unreacted initiator, monomer, etc. Signals due to these impurities may be confused with signals due to end groups of minor structural defects. The following examples illustrate this statement.

The ^{1}H T_1's of the 2-chloro-2,4,4-trimethylpentane initiator were found to be 1 order longer than those of internal PIB segments and at least 3 times longer than the T_1's of corresponding end groups (see Scheme 3):

^{1}H T_1 (s): 2.7 3.2 2.6

$(CH_3)_3CCH_2C(CH_3)_2Cl$

Signals at ~0.9 and 1.3 ppm have been found in the ^{1}H-NMR spectra of certain



SCHEME 8. ^{13}C T_1 values, ^{13}C and ^{1}H chemical shifts, and assignments for the PIB obtained with dicumyl hydroxide initiator. ^{13}C T_1's for $CH_2{=}C(CH_3)_2CH_2$-PIB-*p*Ph-PIB-$CH_2C(CH_3){=}CH_2$, $\overline{M}_n$ = 2900 g/mol.

PIBs. The ^{1}H T_1's were ~3 seconds, indicating that they are due to a small molecule(s). These signals were assigned to traces of hexanes, the solvent used in the polymerization and purification. This assignment was confirmed by recording the spectrum of the same polymer in solution in the presence of a drop of purposely added hexanes.

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