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^{13}C NMR chemical shifts of polyisobutylene end groups and related model compounds

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SUMMARY

The detailed end-structures of CH_3-, -Cl, exo-olefin, endo-olefin, and -OH ended polyisobutylenes (PIB) have been characterized by high resolution ^{13}C NMR spectroscopy. Specifically, the ^{13}C chemical shifts characteristic of the various carbons in the following structures have been determined: $\sim CH_2C(CH_3)_2$-$CH_2C(CH_3)_3$, $\sim CH_2C(CH_3)_2CH_2C(CH_3)_2Cl$, $\sim CH_2C(CH_3)_2CH_2C(CH_3){=}CH_2$, $\sim CH_2C(CH_3)_2CH{=}C(CH_3)_2$, and $\sim CH_2C(CH_3)_2CH_2CH(CH_3)CH_2OH$. The structure analysis of model compounds was of utmost help in these investigations. The above information is of great value for the identification of terminally functional PIBs and analysis of reaction mixtures.

INTRODUCTION

In the course of ongoing investigations in these laboratories directed toward the synthesis of end-functionalized PIBs, need arose to generate detailed spectroscopic information for end-group identification purposes. Thus intensive studies were carried out to assemble comprehensive ^{13}C chemical shifts data in regard to five important end-groups:

$(CH_3)_3C\sim\sim\sim PIB\sim\sim\sim CH_2C(CH_3)_2Cl$ abbreviated by PIB-Cl
$(CH_3)_3C\sim\sim\sim PIB\sim\sim\sim CH_2C(CH_3){=}CH_2$ abbreviated by PIB=CH_2
$(CH_3)_3C\sim\sim\sim PIB\sim\sim\sim C(CH_3)_2CH{=}C(CH_3)_2$ abbreviated by PIB-$CH{=}C(CH_3)_2$
$(CH_3)_3C\sim\sim\sim PIB\sim\sim\sim CH_2CH(CH_3)CH_2OH$ abbreviated by PIB-OH

This paper concerns a summary of these studies, specifically, an analysis and tabulation of all the ^{13}C NMR chemical shifts associated with the above structures.

EXPERIMENTAL

^{13}C NMR spectra were obtained by a Varian Gemini-200 spectrometer operating in the Fourier transform mode under conditions of broad-band proton decoupling, using $CDCl_3$ solutions (∿30% w/v) at 50.3 MHz. The main parameters were: acquisition time = 1s, pulse width = 10 μs, pulse delay = 0, number of transients for model compounds and polymers = 256 and 1280 respectively, number of data points = 30,016; temperature = ambient.

The chemical shift assignments were made by comparing the spectra of model compounds and correlating the systematic shifts with structural differences (1-5). Where necessary the assignments were checked by APT ("attached proton test") experiment (11-14).

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2,2,4,4-Tetramethylpentane was obtained from Chemical Samples Co., and 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-1-pentanol from Aldrich Chemical Co. 2-Chloro-2,4,4-trimethylpentane was prepared from 2,4,4-trimethyl-1-pentene by hydrochlorination (15).

The synthesis of the starting PIB-Cl: $(CH_3)_3C(CH_2C(CH_3)_2)_n$-$CH_2C(CH_3)_2Cl$ where n $\approx$18($\overline{M}_n$ = 1130 and $\overline{M}_w/\overline{M}_n$ = 1.11) and its functionalizations to PIB=CH_2 and PIB-OH have been described (16-18). The PIB-CH=$C(CH_3)_2$ was obtained by quantitative thermal dehydrochlorination (19) from PIB-Cl, which gave a mixture of PIB=CH_2 (67%) and PIB-CH=$C(CH_3)_2$ (33%).

RESULTS AND DISCUSSION

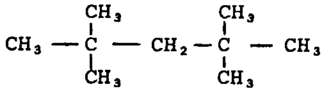
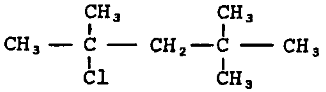
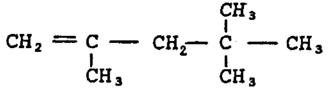
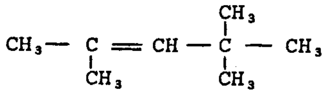
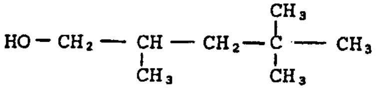
The ^{13}C NMR spectra of PIB-Cl, PIB=CH_2, PIB-CH=$C(CH_3)_2$ and PIB-OH have been investigated in detail. The analysis of the spectra of model compounds has proven invaluable in anticipating and interpreting the spectra of the polymer samples. Figures 1-4 and Tables I and II summarize the data obtained. Previous ^{13}C chemical shift information in regard to PIB repeat units and some model compounds is available in references 6-10.

In agreement with earlier studies (9,10) the ^{13}C NMR chemical shifts of the methyl, methylene and quaternary carbons of the PIB repeat unit appear, respectively, at 31.54, 59.86, and 38.43 ppm. The chemical shifts of the end-structures were assigned by first determining the chemical shifts of simple model compounds with unambiguous assignments and subsequently constructing the more complex polymeric structures by the use of known additivity parameters and substituent effects (1-5). Our assignments and those reported in the literature agree although concentration and solvent effects are noticeable.

The comprehensive identification of the various carbons was accomplished by the use of a variety of methodologies and techniques: 1) By the quantitative conversion sequence of PIB-Cl $\rightarrow$ PIB=CH_2 $\rightarrow$ PIB-OH (17-18) and following the disappearance/appearance of characteristic chemical shifts. Quantitative dehydrochlorination of PIB-Cl by t-BuOK (17) was confirmed by the complete disappearance of resonances at δ = 71.86 and 35.55 ppm characteristic of $\sim C(CH_3)_2Cl$ with the simultaneous appearance of resonances at δ = 144.27, 114.97, and 26.01 ppm characteristic of $\sim C(CH_3)(=CH_2)$. Similarly, the quantitative hydroboration/peroxidation of PIB=CH_2 (18) was substantiated by the disappearance of resonances characteristic of $\sim C(CH_3)=CH_2$ with the simultaneous appearance of resonances at δ = 69.99, 32.06, and 20.16 ppm characteristic of $\sim CH(CH_3)CH_2OH$ 2) By making use of the APT experiment. Thus the terminal methyl groups $(\underline{C}H_3)_3C$- were differentiated from the terminal quaternary carbon $(CH_3)_3\underline{C}$- by observing the inversion of the resonance at δ = 32.83 ppm 3) In spite of the nuclear Overhauser effect, an examination of the relative intensities gave important clues as to the number of carbons associated with the individual resonances: For example, the resonances at δ = 32.83, 37.90, and 38.05 ppm indicate one carbon atom, those at δ = 35.55, 30.63, and 31.07 ppm indicate two carbons, those at δ = 32.74 ppm three carbons, and, finally, the very large signals at δ = 31.54, 38.43 and 59.86 ppm are characteristic of the large number of carbons in the

TABLE I

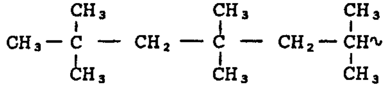
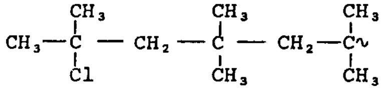
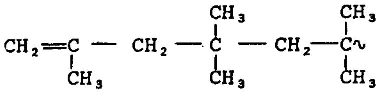
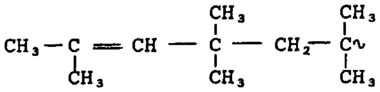
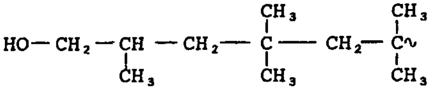
^{13}C NMR Chemical Shifts and Assignments for Model Compounds

	Chemical Shift, ppm						
Compound / Identification 1 2 3 4 5	C_1	C_2	C_3	C_4	C_5	Pendent carbons	Reference
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	31.8	32.4	56.5	32.4	31.8	$2\text{-}CH_3$, $4\text{-}CH_3$ 31.8	2
	32.14	32.56	56.82	32.56	32.14	$2\text{-}CH_3$, $4\text{-}CH_3$ 32.14	This work
 $CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	34.8	71.05	57.9	32.4	31.4	$2\text{-}CH_3$ 34.8; $4\text{-}CH_3$ 31.4	9
	34.97	71.71	58.07	32.51	31.60	$2\text{-}CH_3$ 34.97; $4\text{-}CH_3$ 31.60	This work
 $CH_2=\underset{CH_3}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	113.83	143.88	51.86	31.37	30.13	$2\text{-}CH_3$ 25.23; $4\text{-}CH_3$ 30.13	20
	113.5	142.8	51.3	30.7	29.5	$2\text{-}CH_3$ 24.5; $4\text{-}CH_3$ 29.5	21*
	114.17	144.31	51.88	31.47	30.18	$2\text{-}CH_3$ 25.36; $4\text{-}CH_3$ 30.18	This work
 $CH_3-\underset{CH_3}{C}=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	27.98	130.04	135.20	32.17	31.24	$2\text{-}CH_3$ 18.76; $4\text{-}CH_3$ 32.17	20
 $HO-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	69.37	32.31	47.34	30.98	30.07	$2\text{-}CH_3$ 19.70; $4\text{-}CH_3$ 30.07	This work

*δ_C ppm from TMS. Original data converted using $\delta^{CS_2} = 192.8$

TABLE II

^{13}C NMR Chemical Shifts and Assignments for Polyisobutylene End Groups

PIB / Identification	Chemical Shift, ppm C_1	C_2	C_3	C_4	C_5	C_6	Pendent carbons	Reference
1 2 3 4 5 6  $CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-CH_2-CH(CH_3)\sim$	32.74	32.83	59.15	38.05	58.54	-	$2-CH_3$ 32.74	This work
							$4-CH_3$ 31.07	This work
 $CH_3-C(CH_3)(Cl)-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2\sim$	35.55	71.86	59.31	37.90	58.69	-	$2-CH_3$ 35.55	This work
							$4-CH_3$ 30.63	This work
	-	71.55	-	-	-	-	-	9
	-	71.6	-	-	-	-	-	6
 $CH_2{=}C(CH_3)-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2\sim$	114.97	144.27	54.03	36.47	57.32	38.13	$2-CH_3$ 26.01	This work
							$4-CH_3$ 29.67	This work
	114.30	143.75	53.65	-	-	-	2-CH 25.65	8
	114	144	-	-	-	-	-	10
 $CH_3-C(CH_3){=}CH-C(CH_3)_2-CH_2-C(CH_3)_2\sim$	28.68	128.51	136.03	37.36	58.22	37.88	$2-CH_3$ 19.21 $4-CH_3$ 32.60 $6-CH_3$ 31.33	This work
 $HO-CH_2-CH(CH_3)-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2\sim$	69.99	32.06	49.74	36.08	57.05	38.11	$2-CH_3$ 20.16 $4-CH_3$ 29.41 $6-CH_3$ 31.30	This work

repeat unit in the chain 4) By making use of known additivity parameters (1-5) and substituent effects on chemical shifts (5), additional clues were obtained as to the nature of the various resonances.

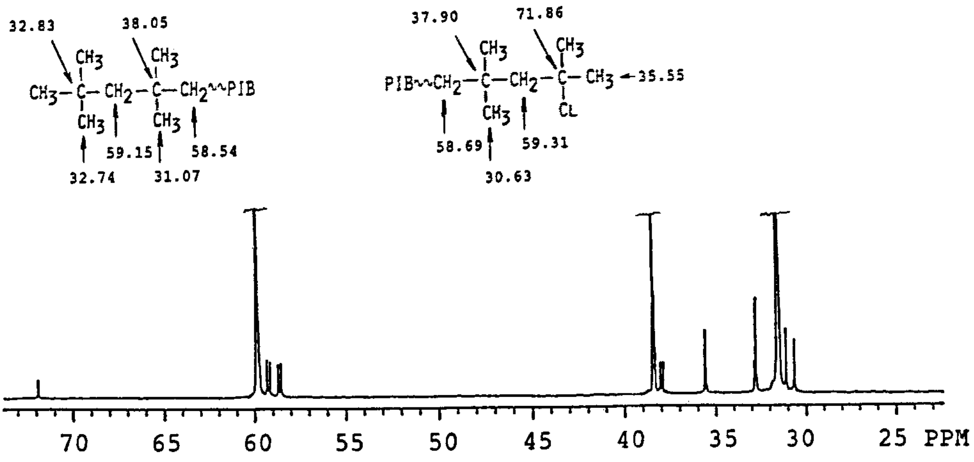


Figure 1. ^{13}C NMR spectrum of a $(CH_3)_3C\sim PIB\sim C(CH_2)_2Cl$ ($\overline{M}_n$ = 1130 and $\overline{M}_w\overline{M}_n$ = 1.11)

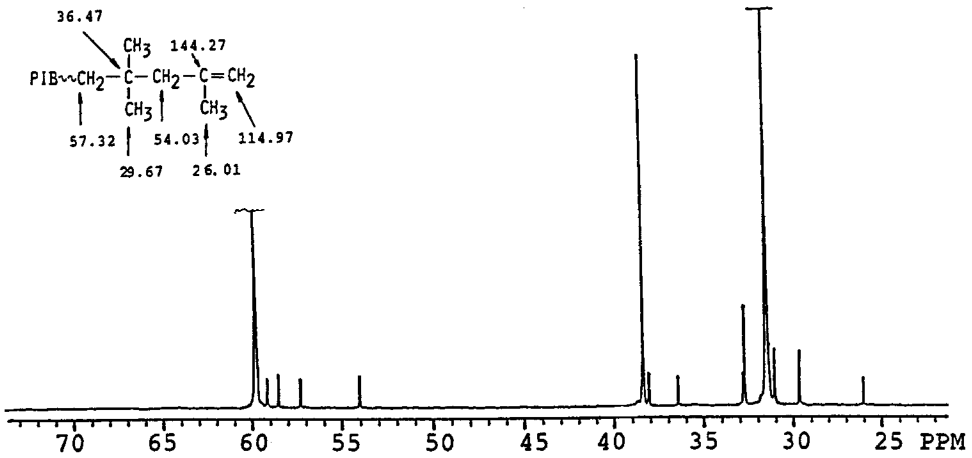


Figure 2. Aliphatic region of the ^{13}C NMR spectrum of a $(CH_3)_3C\sim PIB\sim C(CH_3)(=CH_2)$ ($\overline{M}_n$ = 1130 and $\overline{M}_w/\overline{M}_n$ = 1.11)

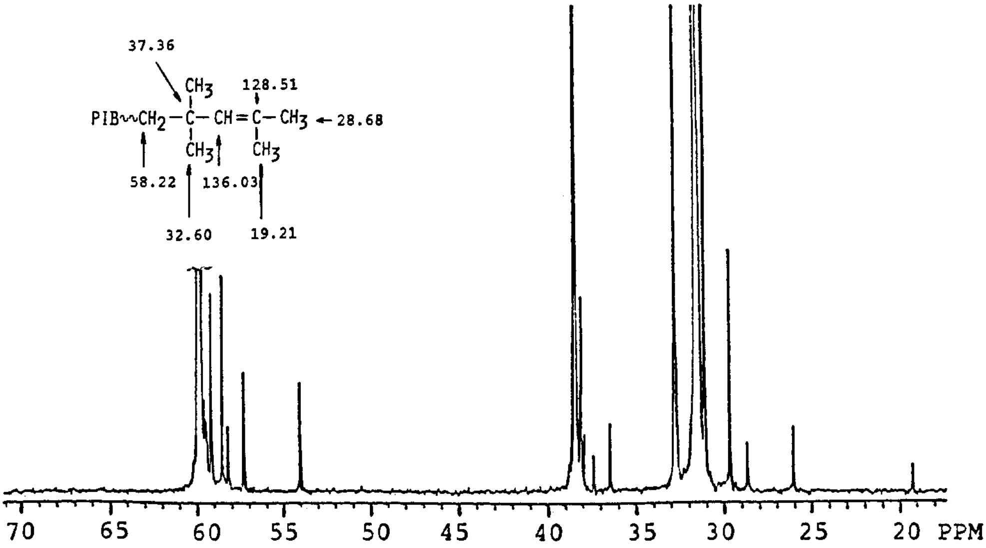


Figure 3. Aliphatic region of the ^{13}C NMR spectrum of a $(CH_3)_3C\sim PIB\sim C(CH_3)(=CH_2)$ (67%) and $(\underline{C}H_3)_3\sim PIB\sim C(CH_3)_2CH=C(CH_3)_2$ (33%) mixture ($\overline{M}_n$ = 1130 and $\overline{M}_w/\overline{M}_n$ = 1.11) obtained by thermal dehydrochlorination

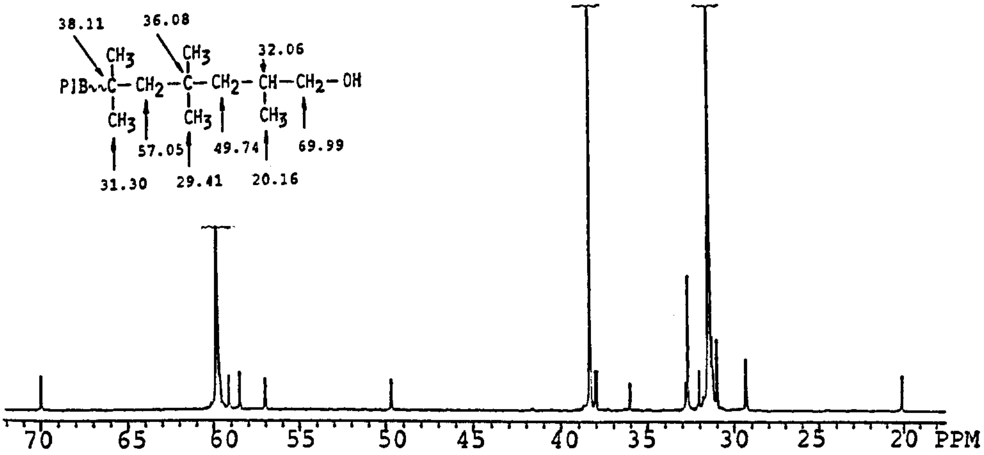


Figure 4. ^{13}C NMR spectrum of a $(CH)_3C\sim PIB\sim CH(CH_3)CH_2OH$ ($\overline{M}_n$ = 1130 and $\overline{M}_w/\overline{M}_n$ = 1.11)

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