Carbon-13 Observations of the Nature of the Short-Chain Branches in Low-Density Polyethylene

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ABSTRACT: The ^{13}C nmr spectra of low-density polyethylenes are compared to those of model copolymers and to calculated spectra based on model hydrocarbons. It is unequivocally demonstrated that the short branches are *n*-butyl, thus confirming the Roedel "backbiting" hypothesis.

It is well known that the morphology and solid-state properties of polyethylene are critically dependent on the frequency of short-chain branches. It seems highly probable that they are also influenced to some degree by the length of these branches, as well as the tri- or tetrafunctional character of the branch points. There appears to have grown up during the past decade a presumption that the short-chain branch length is known and is no longer subject to question. This is borne out by the virtual absence of any current or recent studies of this problem. Nevertheless, a critical examination of the literature shows that the accepted conclusions, largely drawn from infrared and irradiation measurements, are ambiguous. Even where clear answers seem to have been provided, it is highly probable, as we shall show in this paper, that they are at least qualitatively in error.

Carbon-13 Nmr Spectra of Saturated Hydrocarbons

Carbon-13 magnetic resonance spectroscopy (cmr) promises to be extremely useful in the elucidation of alkane and large alkyl structures. This is due not only to the large range of chemical shifts (*ca.* 40 ppm) in which saturated carbons are found to occur, but also to the simple empirically derived relationships which allow the prediction of the chemical shift of any carbon for which the local structure is known.[1-3] In general, it is found that carbons at or near a branch point are the least shielded in such structures, while methyl resonances are most frequently found at highest field. These conclusions suggest that ^{13}C chemical shifts of polyethylenes should provide new information regarding the structure and extent of substitution at the branch point.

As shown in Figure 1, the cmr spectra of polyethylene samples can also be used to identify the short branches themselves. The partial structures in Figure 1 show branches representative of those which have been considered for polyethylene. The chemical shifts of the carbons of these substructures were calculated by an adaptation[4] of a standard procedure,[3] and may be considered to have a probable accuracy of ±0.5 ppm. Carbons which are more than three carbons removed from a branch point, end of chain, or other functionality will resonate at approximately 163.5 ppm.[5] Because the branch frequencies of polyethylenes are considered to be rather low, the spectra of these compounds should consist of one very large peak at 163.5 ppm and several smaller peaks at chemical shifts such as those shown in Figures 1 and 2. The identity of the branch can be established from the chemical shifts of these smaller peaks, while in principle the branch frequency can be derived from the relative heights of the large and small peaks. While the present results amply demonstrate the value of the qualitative aspects of such measurements, the quantitative results are at present not in satisfactory agreement with those of other methods.

Experimental Section

Materials. Two polymers were chosen as standards for ethyl and *n*-butyl branches. Hydrogenated polybutadiene, designated 108 MH, from the Phillips Petroleum Co. contains *ca.* 20 ethyl branches per 1000 carbons and less than 1 double bond per 1000 carbons according to the supplier. An ethylene–1-hexene copolymer also from the Phillips Petroleum Co. provides a purely *n*-butyl branched polymer.

A variety of high-pressure polyethylenes were examined. These materials had been preparatively fractionated by GPC and subjected to conventional characterization for long-chain and short-chain branching as a function of molecular weight.[6] PBE-I is a short-tube reactor product of the Union Carbide Co., designated DYNK. BPE-II is a stirred autoclave product of Du Pont from the Alathon series. BPE-III was obtained from Monsanto Co. and represents a long-tube reactor product. The fractions employed are indicated in the first column of Table I.

Methods. Carbon-13 nuclear magnetic resonance spectra were measured on a Varian XL-100 spectrometer which has been modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet (formerly Fabritek) Model 1080 computer.[7] The free-induction decay was stored in 8K computer locations, using a dwell time of 500 μsec. The pulse was located at the high-field end of the alkyl region of the cmr spectrum (25.16055 MHz). Repetition times were varied between 3 and 8 sec.

The spectra were measured using 10% (w/v) solutions of the polymer samples in 1,2,4-trichlorobenzene at 134–135°. Most samples appeared to be homogeneous at this temperature, with the exception of the high molecular weight Alathon sample (BPE-II), which was incompletely dissolved.

Experimental Results

The polyethylenes employed are shown in Table I, together with pertinent molecular weight information, and estimates of short and long branching by infrared and hydrodynamic measurements, respectively.[6] The type and frequency of short branches, estimated from the present study, are indicated in the last columns. The type of branch is deduced from comparison of the observed line pattern to the calculated patterns shown in Figure 2. Representative spectra are shown in Figure 3. The first two spectra are accompanied by calculated spectra corresponding to the type of branch which they are known to contain. The experimental

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Table I
Polyethylenes Studied by ^{13}C Spectroscopy

Polymer designation[a]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	Long-branch frequency, per 1000 main-chain CH$_2$	Short-branch frequency, per 1000 CH$_2$		Short-branch type, from cmr
				From ir	From cmr[b]	
(a) Hydrogenated polybutadiene	80	108		25	21	Ethyl
(b) Ethylene-1-hexene copolymer	18	92		16	12	Butyl
(c) BPE-I	38.3	150	1.0	23	12	Butyl
(d) BPE-I, low mol wt fraction	6.5	19	8.4	33	15	Butyl/ethyl, ~3:1
(e) BPE-II, middle mol wt fraction	~100	~300	1.0	23	12	Butyl
(f) BPE-II, high mol wt fraction	~900	~2500	8.0	17	12	Butyl
(g) BPE-III middle mol wt fraction	~100	~300	1.5	18	8.5	Butyl

[a] See Experimental Section and references. [b] These figures are probably somewhat lower than the true branch content; see text.

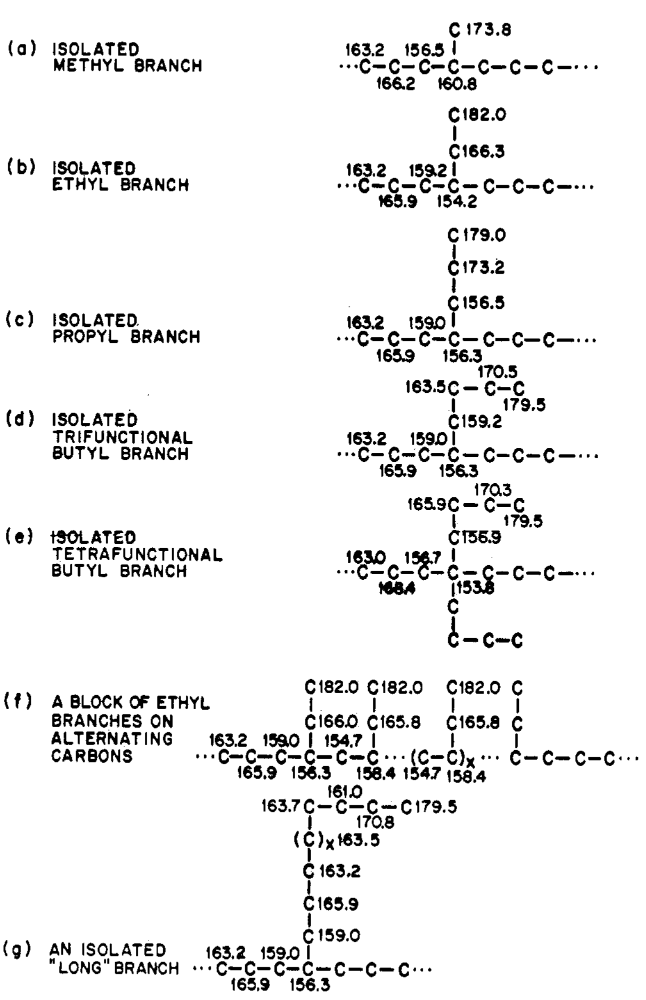


Figure 1. Calculated ^{13}C chemical shifts of model hydrocarbon structures corresponding to possible polyethylene branches.

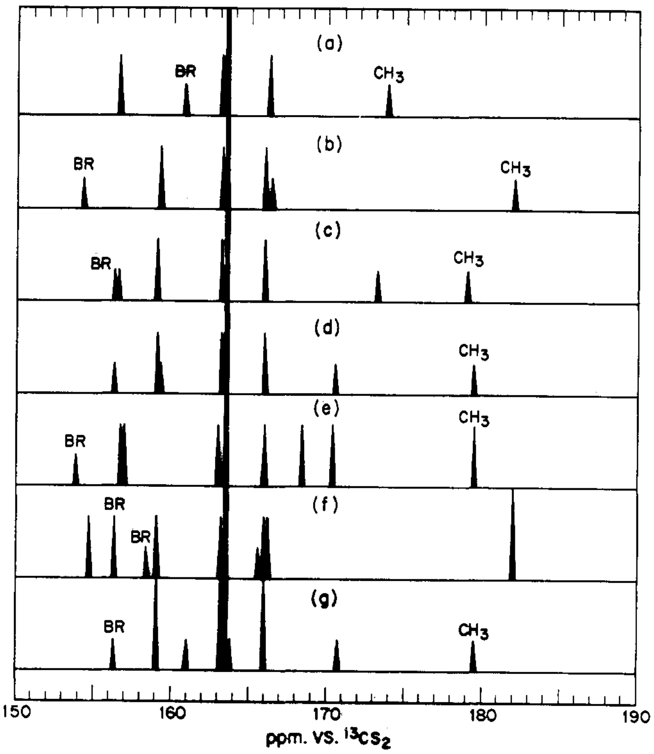


Figure 2. Calculated ^{13}C spectra (^{13}CS$_2$ as zero) for possible branch structures in polyethylene. The heavy line at 163.5 ppm represents the spectrum of all methylene groups more than three carbons removed from a branch point or chain end, and is the strongly dominant peak in all experimental spectra: (a) isolated methyl branch, (b) isolated ethyl branch, (c) isolated *n*-propyl branch, (d) isolated trifunctional butyl branch, (e) isolated tetrafunctional butyl branch, (f) a block of three ethyl branches ($x = 0$ in Figure 1f), (g) an isolated "long" branch.

patterns of both (a) and (b) correspond closely to those calculated. For both copolymers it further appears that comonomer units occur at random, there being no indication of any deviations or additional resonances such as would be expected if monomer blocks were present (compare to Figure 2, spectrum f).

The whole polymer BPE-I (Figure 3c) is clearly demonstrated to have predominantly *n*-butyl branches, with no clear indication of any other type. The spectrum of the low molecular weight fraction (Figure 3d) is consistent with the presence of ethyl branches to the extent of *ca.* one-third the frequency of the butyl branches, but this fraction represents only about 10 wt % of the whole polymer. This suggests that in at least some polyethylene specimens the occasional

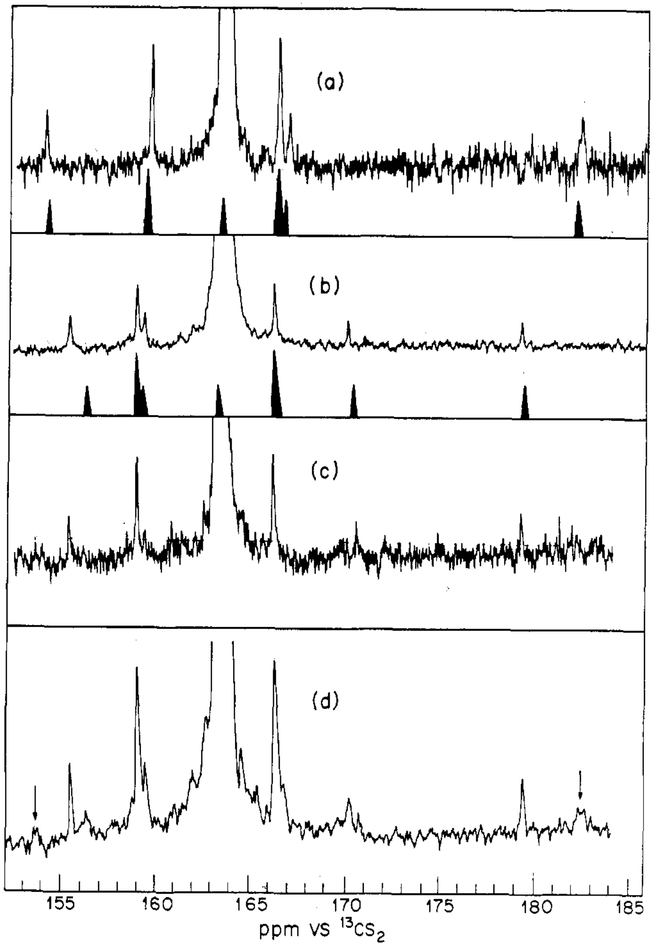


Figure 3. Experimental ^{13}C spectra ($^{13}CS_2$ as zero) of (a) hydrogenated polybutadiene, (b) ethylene-1-hexene copolymer, (c) polyethylene BPE-I; (d) a low molecular weight fraction of BPE-I; peaks marked with arrows may be due to ethyl branches. See Experimental Section and Table I for further description of the polymers.

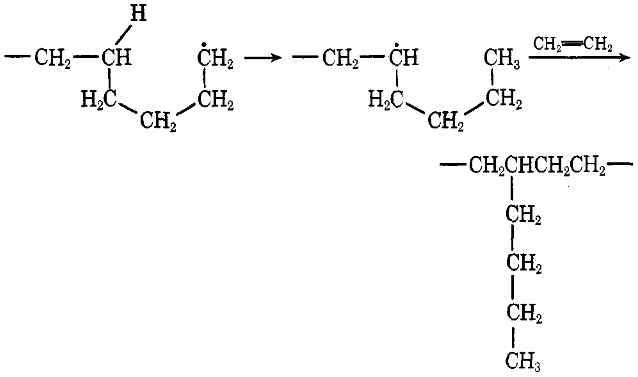
ethyl branches tend to concentrate in the shorter chains. The other polyethylene samples (spectra c–g) showed no measurable content of ethyl branches.

Among the small peaks of the spectra, the relative peak heights are generally in accord with prediction. Thus, in (a) the peaks at 166.1 and 159.4 ppm are roughly twice as intense as those at 182.4, 166.8, and 153.8 ppm. Similarly, in (b) the peak intensities are in approximately the correct ratios for *n*-butyl branches. As is seen from Figures 1 and 2, these resonances should occur in the ratio of 1:2. Figures 3c and 3d show, however, that the peak at 158.9 ppm is considerably more than twice as intense as the higher field peak. Comparison to Figure 2 suggests that this could result from the presence of long branches in the polymer. Such a formulation, however, requires that the long branches terminate in some group other than methyl, for only under this condition can the absence of the peak at 161.0 ppm (see Figures 1 and 2) be rationalized. In the absence of detailed information regarding the spin–lattice relaxation of the ^{13}C nuclei in these compounds, we feel that the relative intensities or integrations of these peaks should not be considered accurate measures of the relative frequencies of occurrence of the short branches.

The same *caveat* applies to the use of the relative heights of the large and small peaks to determine the over-all branch frequencies. As seen from Table I, the branch frequencies derived from the present results are not in good agreement with those from infrared spectroscopy. A similar problem was noted in the relative peak heights in the cmr spectrum of hexatriacontane ($C_{36}H_{74}$), which was studied as a model compound. In this latter compound the relative peak heights can be calculated from the known structure, and in all experimental conditions used to date, the relative intensity of the large peak at 163.5 ppm has been found to be at least 50% greater than predicted. Additional experiments to investigate this matter are planned.

Discussion

In 1953, Roedel[8] proposed the well-known "backbiting" mechanism for the formation of short branches in high-pressure polyethylene.



Subsequent experimental work has been interpreted in a way that has cast some doubt on this mechanism. Infrared measurements are rather ambiguous with regard to the determination of branch length, but Willbourn,[9] in a much quoted paper,[10] concluded from observations of a band at 770 cm^{-1} (considered by him to be specific for ethyl) and also the traditional band at 1378 cm^{-1} (methyl group umbrella distortion) that the branches were all either ethyl or *n*-butyl, and that ethyl branches predominated by a factor of at least 2:1. In this paper, Willbourn also presented results of high-energy electron irradiation of polyethylene, but these were limited to copolymers known to have *n*-butyl branches. This paper supported earlier conclusions of a similar study by Harlen, *et al.*,[11] and is further supported by a subsequent γ-irradiation study of Kamath and Barlow.[12] Despite the agreement of these workers, however, we feel that their conclusions are incorrect in this regard, and that for all practical purposes only *n*-butyl branches are present in commercial high-pressure polyethylene. In justice to the careful analytical work of Willbourn, however, it is only fair to point out that his values for methyl group content are probably accurate.

The Roedel mechanism thus appears to be entirely vindicated. It is perhaps somewhat surprising that the 1,5 transfer of hydrogen, even though favored by the formation of a quasi-six-membered ring as a transition state, appears to be exclusively preferred over a possible 1,4 transfer (producing a propyl branch), which evidently can occur in the reaction of

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methyl radicals with ethylene.[13] The very small fraction of ethyl branches for which there is ^{13}C evidence may be introduced *via* the extension of the Roedel mechanism described by Willbourn;[1] this must now be regarded as a reaction of very low probability. The possibility of occurrence of significant proportions of tetrafunctional branches, proposed by some authors, can be excluded.

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Tacticity of Poly(vinyl alcohol) Studied by Nuclear Magnetic Resonance of Hydroxyl Protons

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ABSTRACT: The high-resolution nmr spectrum of the hydroxyl protons in poly(vinyl alcohol) dissolved in dimethyl sulfoxide shows three well-separated triad peaks with spin–spin splitting. These hydroxyl peaks can be assigned to isotactic, heterotactic, and syndiotactic triads with increasing field strength. This assignment is ascertained by dimer and trimer model compounds as well as polymers with known stereoregularities. An interesting variation of coupling constants *J*(H–O–C–H) with configurational structures is observed.

The accurate determination of tacticity in poly(vinyl alcohol) (PVA) has been difficult and troublesome. Formerly it was investigated by X-ray diffraction[1] and infrared spectroscopy.[1–3] Dyad and triad tacticities were studied[4–7] by methylene and methine nmr spectra, respectively, but the overlapping of peaks is so severe, especially for the methine portion, that a quantitative determination has been difficult. On the other hand, it was disclosed that acetoxyl protons in poly(viny lacetate)[5,8–11] derived from PVA are rather useful to the triad tacticity study although overlap still remains.

Little attention has been paid to the nmr spectra of the hydroxyl protons in PVA. This neglect seems natural because heavy water was usually selected as the solvent and the hydroxyl protons and deuterons necessarily exchange between PVA hydroxyl groups and water so rapidly that hydroxyl protons under different environments cannot be discriminated by their nmr spectra.

There is another good solvent for PVA, dimethyl sulfoxide (DMSO), which turned out to give the key to a useful investigation of the hydroxyl protons in this polymer. In DMSO solution, the hydroxyl proton resonance of PVA shows three well-resolved triad peaks with spin–spin splitting. It has been well known that spin–spin splitting of hydroxyl peaks in some alcohols can be observed in DMSO solution.[12] The solvation of DMSO molecules to hydroxyl protons reduces the rate of proton exchange sufficiently to permit such an observation.

In order to assign and interpret the triad peaks of PVA, the model compounds meso and racemic pentane-2,4-diol, and isotactic, heterotactic, and syndiotactic heptane-2,4,6-triol were also investigated. (The former is abbreviated diol and the latter triol in the following discussions.) The nmr spectra of the diol[13–16] and triol[15] were published previously, but the splitting of the hydroxyl lines was not reported, even though various solvents including DMSO were used. This is probably because impurities such as water and traces of acid in the solution gave rise to rapid proton exchange.

Experimental Section

Materials. Four samples of PVA which were different in stereoregularity were used. Sample I is commercially produced PVA (Kuraray Co.), which was prepared by hydrolysis of radical polymerized poly(vinyl acetate). Samples II and III were derived from poly(vinyl *tert*-butyl ether) prepared by cationic polymerization. Polymerization of vinyl *tert*-butyl ether was carried out at −78° with BF$_3$O(C$_2$H$_5$)$_2$ as catalyst in toluene (sample II) and in methylene chloride (sample III). From poly(vinyl *tert*-butyl ether), PVA was derived by way of poly(vinyl acetate). Vinyl *tert*-butyl ether was synthesized from vinyl benzyl ether by an ether exchange reaction. Sample IV was derived from poly(vinyl trimethylsilyl ether), polymerized with FeCl$_3$ as catalyst in nitro-

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