(the number of radioactive labels gives a measure of the amount of associated active sites).

Comparison between the results of the present study and those obtained in investigating the polymerization of butadiene[1] indicates that the introduction of alkyl substituent into butadiene decreases the tendency of "living" macromolecules to dimerization; the same effect is observed with increasing homologue difference (Figure 4). With the number-average molecular weight of about 2000 the polybutadiene "living" chains are essentially dimeric (the amount of labels upon deactivation is 1.7), poly(isoprenylnickel iodide) is predominantly monomeric (the amount of labels is 1.2) (Table I), and the "living" chains of 2-ethyl- and 2-isopropylbutadienes are exclusively monomeric (Tables II and III). That the dissociation of poly(2-isopropylbutadienylnickel iodide), in particular, occurs at lower molecular weights is seen from the data in Table IV. The difference in the association degree between poly(butadienyllithium) and poly(isoprenyllithium) has already been reported.[4] From the foregoing it is evident that the binodal MWD will result if sufficient quantities of both the dimeric and monomeric active sites are present in the system. This is readily seen from the data on polymerization of butadiene[1] and isoprene. In the polymerization of 2-ethyl- and 2-isopropylbutadienes the active sites are dimeric only at the earliest stages of transformations, which accounts for the unimodal MWD of these polymers.

For poly(dienylnickel iodides), an increase in the dissociation degree with molecular weight can be well rationalized on the basis of generally accepted ideas of thermodynamics of polymeric systems; i.e., in good solvents, the molecular forces increasing the effective repulsion of macromolecules can weaken the nickel–iodine bridge bonds in the dimer.

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A Quantitative Analysis of Low-Density (Branched) Polyethylenes by Carbon-13 Fourier Transform Nuclear Magnetic Resonance at 67.9 MHz

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ABSTRACT: By utilizing predetermined equilibrium magnetization conditions and the measured nuclear Overhauser enhancement factors for the appropriate carbon atoms, we have obtained the high-field carbon-13 NMR spectra of a large number of different low-density (branched) polyethylene samples. It becomes clear from this study that there is a great diversity in structure among the different samples; thus with respect to branch type and concentration there is no unique low-density polyethylene molecule since the concentration, type, and distribution of subgroups vary widely. Previously assigned resonances are used to determine the standard side-group concentrations and the long-chain branching. However, when all the observed resonances are analyzed there is an internal inconsistency among all possible combinations that should yield identical results. Thus, other branch types, such as tetrafunctional and nonlinear ones, must also be present so that all the quantitative structural information available from the spectra has not as yet been extracted. The mechanisms that have been postulated for the generation of short-chain branches will have to be modified to account for these results.

Low-density, or branched, polyethylenes prepared conventionally under high pressure are polymers of great structural complexity and versatility with respect to properties. These unusual features result from the type and concentration of the branch groups associated with a given polymer. Thus, a quantitative analysis of the branching characteristics can be useful for several important reasons. The thermodynamic, morphological, and physical properties of the polymers should depend on the kind, distribution, and concentration of the branches. Identification of the specific branches should also help in the further elucidation of the details of the polymerization mechanisms.

Carbon-13 NMR studies have the great potential, if properly employed, of being able to specifically identify a particular branch group and determine its concentration and location relative to other branches. The indirect solution methods, with their attendant assumptions in determining the long-chain branching, are avoided. Short-chain branches can be specifically identified, rather than grouped together. A series of carbon-13 NMR studies of branching in low-density polyethylene have already been reported,[1-6] and the results have been ambiguous in many respects. The problems that have been encountered, which have not always been obvious, fall into several categories. These include the independent specification of the proper pulse NMR experimental conditions, instrumental sensitivity, peak assignments, requirements for quantitative analysis, and confirmation of internal consistency among the assignments. In addition, the extraordinarily large number of different types of low-density polyethylenes, with quite different branching characteristics, that are available for study has apparently not been fully recog-

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nized. Hence unnecessary generalizations have been made which have led to some difficulty in interpretation.

The need to use the proper experimental parameters for the acquisition of quantitative Fourier transform spectra is obvious and very important. Many problems arise when nonequilibrium magnetization data are acquired. For instance, short-pulse repetition rates selectively saturate carbons having the longest relaxation times and lead to the conclusion that branch types associated with such carbons are quantitatively reduced or are not present. Even if all the resonances can be identified they will contain very little useful quantitative information. In an ideal experiment, each pulse should sample the equilibrium magnetization of all carbons. This would require a wait between pulses of at least five times the longest carbon spin–lattice relaxation time, T_1. In order to keep the total accumulation time resonable, a compromise is usually made between the minimum number of pulses necessary for adequate signal to noise and the delay time between pulses necessary to avoid severe differential saturation of the carbon resonances of interest. This requirement can, however, cause an acute problem for the quantitative analysis of branching in that the final signal-to-noise ratio must be sufficient to allow identification and integration of branching at very low concentrations at a level of 1 branch carbon per 1000 main-chain carbons (hereafter also denoted by branch carbons per 1000 CH_2). Low branch concentrations, in concert with long pulse delays, could result in very long data collection times, approaching 15 h or more.

Until recently, no measurements had been made of T_1 for the major carbons of interest in a branched polyethylene sample. Thus the optimum delay times were essentially unknown. While T_1 data for a molten linear polyethylene had been reported,[7,8] previous work with branched polyethylene was carried out under this handicap. It has been shown that there is a large gradation in relaxation times in the branch carbons themselves.[9] These values range from approximately 1.1 to 7 s at 118 °C in solution.[9] With this wide variation in T_1 it became apparent that quantitative, equilibrium conditions had not been attained in previous studies for most branched carbons, let alone the entire structures. While certain combinations of pulse delays and pulse widths yield optimum signal-to-noise values for a small range of T_1 values, the majority of resonances cannot be quantitatively compared or evaluated under these conditions. In general, for short delay times the integrated intensities of the end methyls of most branches will be severely distorted so that their use in quantitative analysis is impossible. In very long chain branches even the methylene carbon intensities near the terminus of the chain will be adversely affected. The fact that there were differences in results between investigations is not surprising for this reason alone. Experiments must be designed which take into account the wide range in spin–lattice relaxation times characteristic of the carbons of branched polyethylene. Although these relaxation times are generally frequency dependent, they are not in this case because of the short correlation times involved.

For quantitative analyses of the branch groups, the nuclear Overhauser enhancement factors (NOEF's) must also be evaluated for the pertinent carbons. Completely molten linear polyethylene exhibits a maximum NOEF of 2.0.[9] It has then been tacitly assumed in all previous work[3-5] that the carbons in branched polyethylene also exhibit the maximum NOEF. Fortunately, this surmise has now been directly confirmed for branched polyethylene samples and a related copolymer.[9] The experiments that will be reported here are the first that have been designed for low-density polyethylenes with a full knowledge of the spin–lattice relaxation times and the NOEF's. The data were thus obtained under true equilibrium magnetization conditions. The high-field instrumentation used here enabled equilibrium conditions to be established with the alleviation of both the time and sensitivity problems.

The problems of experimental design, particularly the selection of the appropriate delay time, and the apparent lack of recognition of the many different types of branched polyethylenes have lead to discord in the reported results. In one of the first reports Dorman et al. studied a whole polymer and three fractions.[3] They found long chain branching frequencies which ranged from 1.0 to 8.4 per 1000 main chain carbons and short chain branching frequencies from 8.5 to 21 carbons per 1000 backbone carbons. Disagreements were found with conventional type infrared analysis. They concluded from this particular work that for all practical purposes only *n*-butyl branches, presumably referring to short-chain branching, are present in commercial high-pressure polyethylene. The possibility of the occurrence of a significant proportion of tetrafunctional branches could be excluded. Shortly thereafter Randall[2] studied another low-density polyethylene whole polymer and was able to identify ethyl, butyl, amyl, hexyl, and longer branches. The relative concentration of these branches was obtained from a least-squares analysis of the peak intensities of the assigned major resonances. The relative concentrations of ethyl branches were quite low and no evidence was found for propyl branches. Hama et al.[1] studied three fractions of low-density polyethylene that had been prepared respectively from three different whole polymers.[1] Two of the samples showed only butyl short-chain branches. The third sample contained both butyl and methyl branches. The presence of the latter group was attributed to the possibility of the addition of a small amount of propylene during the polymerization.

In further studies, Bovey et al.[5] examined two fractions obtained from yet another whole polymer. With respect to short-chain branching they found that trifunctional *n*-butyl groups predominated with smaller amounts of amyl and ethyl branches also being detected. They also hypothesized that the resonance at 32.23 ppm (from Me_4Si) provided a measure of the long-chain branching content, i.e., hexyl and greater, which could not be separated. Considering the assumptions involved, good agreement was found between the long-chain branching values obtained from the carbon-13 measurements and from the accompanying solution studies. Cudby and Bunn[4] studied a series of four representative commercial low-density polyethylene samples. They found that the ratio of ethyl to butyl branches was highly variable depending on the reactor conditions. For example, the ethyl group concentrations reported ranged from less than 1 to 11 per 1000 C atoms while the butyl content remained essentially constant. They questioned the assignment of the 32.6 ppm to the amyl branch and obtained almost a threefold variation in the long-chain branch resonance at 32.23 ppm. These quantities are subject to some error due to the pulsing times chosen. Additionally, therefore, a reason for one of the major differences that had been reported is beginning to emerge.

In view of the divergent results that have been reported it seemed advisable to quantitatively examine the branching characteristics, by carbon-13 NMR, of a large number of low-density polyethylene samples, utilizing the proper experimental conditions that had been established.[9]

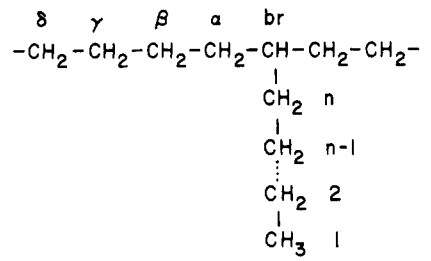


Figure 1. Carbon numbering scheme for branched polyethylene.

Our immediate objective is to quantitatively identify as many of the branched groups that can be resolved as possible. It is quite obvious from the reports to date that there is no typical low-density polyethylene. From the present structural analysis it is hoped that guidelines will be developed for studies leading to a more detailed understanding of the polymerization mechanisms and the specific relation between structure and properties for this class of polymers.

Experimental Section

The carbon-13 spectra were obtained at 118 °C, using a Bruker-HX-270 spectrometer with quadrature detection operating at 67.905 MHz. Sample concentrations were approximately 40% (w/v) in 1,2,4-trichlorobenzene; 13-mm sample tubes were used. The chemical shifts were referenced internally to the major recurring backbone methylene carbon resonance which was taken as 29.99 ppm from Me_4Si. Spectral widths were ±6000 Hz, with 8192 data points acquired on a Nicolet 1089 series computer. Ninety degree pulse widths of approximately 54 μs and delay times between pulses of 30–40 s were used. Since the dynamic ranges of these spectra are very large, they were obtained with full 12 bit digitization of the FID's. Lock was provided by an internal capillary containing pure tetrachlorethane-d_2. These conditions assured that the equilibrium magnetization was sampled and that saturation of any resonance would not occur. A typical experiment was performed in 3–5 h.

Thirteen representative commercial samples, prepared under high pressure, were studied. In addition two fractions, which had been previously characterized by light scattering, osmometry, viscosity, and infrared spectroscopy,[10] were also studied. These samples are designated as numbers 14 and 15 in Table I. Sample 13 was kindly provided to us by Dr. M. E. A. Cudby and corresponds to sample C of ref 4.[24] We will thus be able to make a direct comparison with this sample. The designation B or P after some of the sample numbers indicates that either butene-1 or propylene was deliberately added to the polymerization reaction mixture.

Results and Discussion

Assignments. Before discussing and analyzing the results for samples that have been studied here, and quantitatively assigning branch types, it is not only helpful but is in fact necessary to consider first the general characteristics of the spectra and the basis for the carbon-13 chemical shift assignments. Figure 1 illustrates the numbering system employed to designate the individual carbons involved. The numerals indicate the side-group carbons and the greek letters the distinguishable backbone carbons. Figure 2 is a very general overall view of a branched polyethylene spectrum. It was selected to demonstrate the wealth of information that is potentially available by this technique.

The spectra of all low-density polyethylenes are dominated by a very intense central peak at 29.99 ppm. This peak represents the major recurring CH_2 resonance of carbons which are more than four bonds removed from a site of substitution. In addition, at least 16 other resonances can be identified in this case. Although all but one of the resonances are of low intensity, they all can still be quantitatively analyzed. Most of the resonances have been

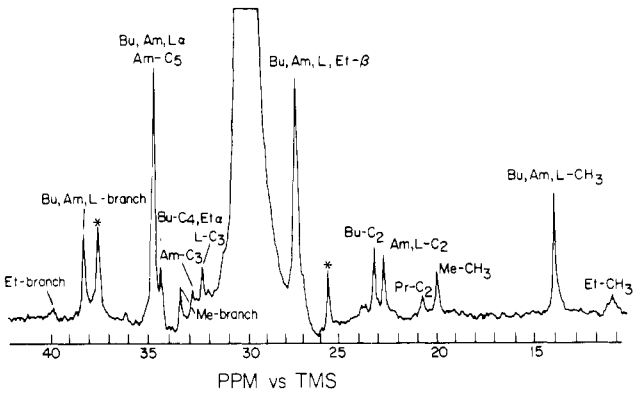


Figure 2. Branched polyethylene (sample 6) ^{13}C spectrum (67.9 MHz) showing detailed branch assignments. Spectral details: sweep width ±6 KHz, pulse width 42 μs (90°), 428 scans accumulated, pulse delay 35 s, 8192 data points. Resonances marked with an asterisk are discussed in the text.

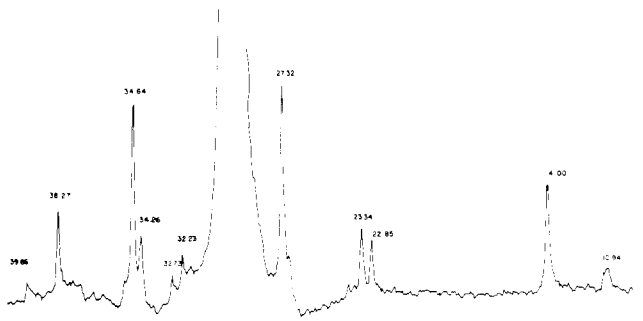


Figure 3. Branched polyethylene (sample 9) ^{13}C spectrum representing less detailed branch information characteristic of a majority of the samples studied. Conditions as noted in Figure 2 with 250 scans accumulated.

assigned, as is indicated, in a manner which will be described below. The unassigned resonances, marked by asterisks, will be discussed later. The spectrum in Figure 3 is another type that is commonly observed and is of the kind previously reported by others.[1-6] In the present work it is found with samples 1–4 and 9–15. In this spectrum not nearly as many resonances are observed. Figures 2 and 3 serve to introduce the concept, from purely an observational point of view, of the lack of uniqueness of the branched polyethylene molecule. In discussing the details of the chemical shift assignments we shall first consider the short-chain branches and then those lines resulting from long-chain branching.

The chemical shifts for the different unique carbons at or near the site of an isolated ethyl branch have been calculated using the Grant and Paul[11] and Lindeman and Adams[12] substituent chemical shift parameters. These calculations as well as the experimental results for copolymers and the low-density polyethylenes are given in Table IIa. In general the calculations agree with each other and with the experimental results. We use the word unique in the sense that these resonances do not theoretically overlap with those belonging to any other branch types. Hence, they can be unambiguously used to determine the presence of ethyl branches. Examination of Figures 2, 3, and 4, as well as other spectra, shows that the predicted resonance at 10.94 ppm is the only one that is always observed when ethyl branches are present. However, its concentration varies among the different samples. This resonance represents the methyl carbon of the ethyl branch. For some samples a low-intensity peak at 39.86 ppm, representing the methine carbon, is also observed, as is shown in Figure 5a. However, the spectra

Table I
Properties of Polymers Studied and Integrated Resonance Intensities (Branches per 1000 Carbons)

	39.86 (±0.09)	38.27 (±0.07)	34.64 34.27 (±0.07)	33.33 (±0.04)	32.73 (±0.05)	32.23 (±0.05)	27.32 (±0.04)	23.34 (±0.04)	22.85 (±0.04)	20.85	19.95 (±0.07)	14.00 (±0.07)	10.94 (±0.14)	total branch[a]	$M_n \times 10^{-4}$	$M_w \times 10^{-3}$
1		8.6	46.1		1.5	2.2	49.4	6.9	5.8			19.4	4.5	15.1	1.11	2.19
2		6.3	49.2		1.8	1.8	29.8	4.7	3.5			14.1	5.7	14.0	2.42	2.28
3		9.5	39.5		1.3	1.2	51.3	8.5	9.5			19.9	6.0	17.0		
4		4.7	18.9		(2)	(2)	15.1	4.6	3.1			7.2	1.2	9.8		
5-P		7.4	59.9		1.1	1.6	39.7	5.3	5.5		2.2	13.2	6.2	16.5		
6-P		10.1	40.5	3.2	1.7	1.7	42.9	8.2	6.8	2.4	5.6	18.0	4.8	24.4	1.13	1.01
7-P		6.6	53.4	0.6	0.6	1.2	34.1	3.9	3.8		2.5	15.3	11.3	19.5	1.66	9.50
8-P		10.1	38.8		2.2	2.2	36.4	4.0	3.9		2.6	15.9	4.4	15.4	1.87	3.46
9-B	1.7	8.5	36.3		2.0	2.8	32.3	6.6	4.6			14.3	4.5	15.9	1.23	1.56
10-B		6.4	54.0		2.2	2.2	27.9	4.1	2.7			9.3	3.4	11.9	1.87	2.06
11-B		4.6	19.6		0.8	0.5	28.4	5.0	5.0			10.9	2.3	8.6		
12		8.2	40.3		~1.5	~1.5	17.6	11.1	6.5			15.4	none	9.0	1.96	0.937
13		9.6	37.0		*b*	12.5	33.5	6.3	16.6			26.6	3.9	22.7	0.186	0.187
14		10.7	42.2		⩽1.3	⩽1.3	28.4	7.3	9.2			16.5	none	16.5		40
15		9.9	49.3		1.0	2.5	34.7	11.9	8.2			20.5	8.7	24.1		33

[a] Calculated from unique assignments. [b] Not measured.

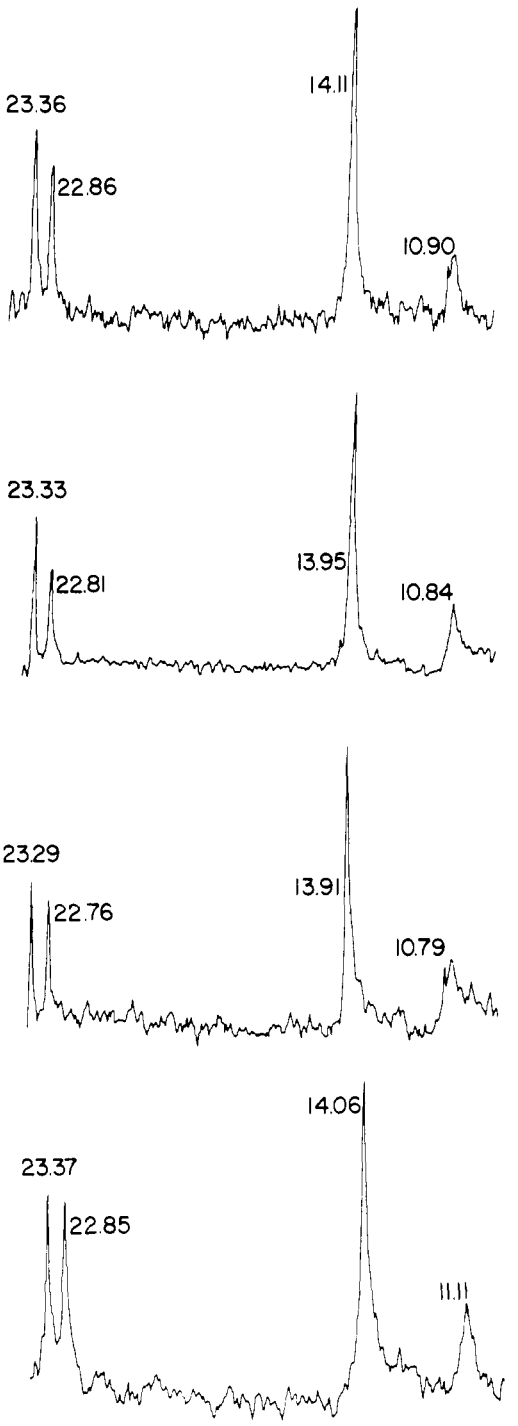


Figure 4. High-field regions of samples 9, 2, 10, and 3 (from top to bottom). Chemical shifts in ppm from Me_4Si as marked.

for a majority of the samples exhibit either no well-defined resonance or a very weak one in this region, as is typically seen in samples 6 and 8 of Figure 5a.

A detailed inspection of the observed chemical shift data reveals an unduly large deviation from that which would be expected for a single ethyl CH_3 line. This type of evidence can be taken to indicate that isolated ethyl branch resonances are not being observed. The fact that the intensities of the methyl (10.94 ppm) and methine (39.86 ppm) are not equal (see below), as would be expected under equilibrium conditions, further supports this contention. By contrast the carbon-13 spectrum for the ethylene–butene-1 copolymer reported by Randall[2] shows equal intensities for these peaks since the ethyl branches are isolated from one another; however, equilibrium

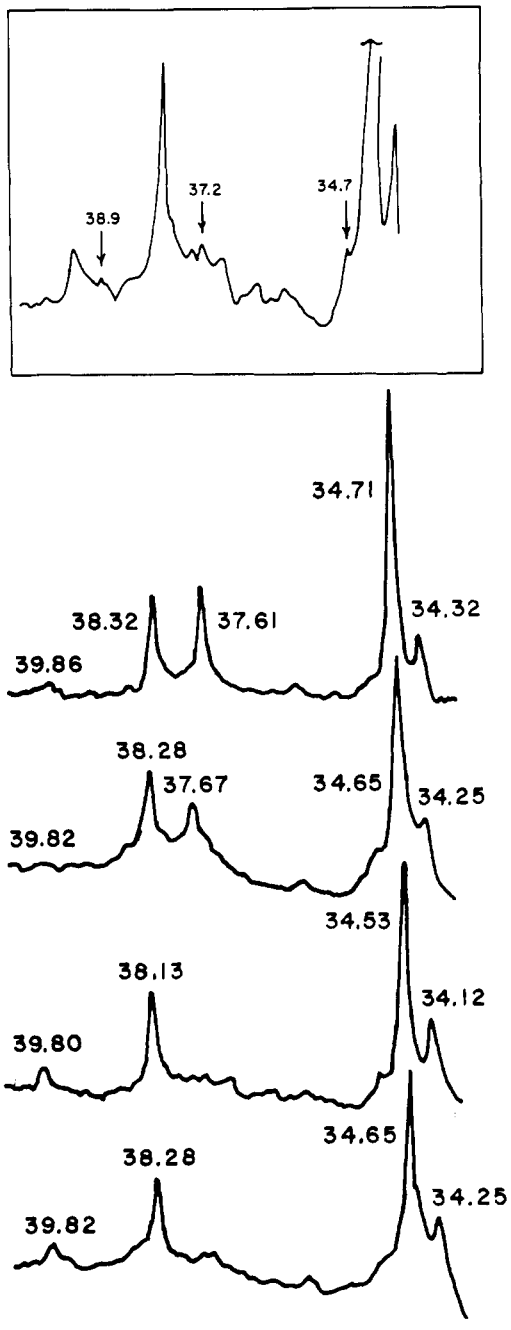
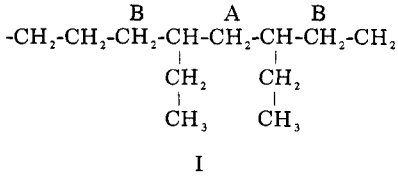


Figure 5. (a, bottom) Low-field regions of samples 6, 8, 9, and 10 (from top to bottom). Chemical shifts in ppm from Me_4Si as marked. (b, top) Less expanded spectra for sample 9. Resonances at 38.9, 37.2, and 34.7 ppm indicated by vertical arrows.

conditions were not used in that study. For some of the samples studied here, as well as in some previously published spectra, the 39.86-ppm resonance cannot be observed while there is a significant 10.94-ppm peak present. A logical explanation is the presence of nonisolated ethyl branches in structures such as:



I

Calculations using the Lindeman–Adams[12] parameters indicate that the methine CH's in I should be at 37.8 ppm, i.e., 2.07 ppm upfield from a methine located in an isolated

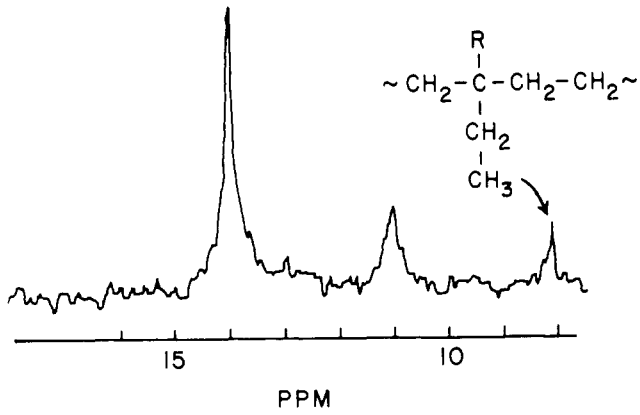


Figure 6. High-field region of sample 3. Resonance marked with arrow is the CH_3 carbon of an ethyl branch attached to a quaternary carbon.

ethyl branch. As is seen in Figure 5a there is a resonance close to this position at 37.5–37.7 ppm, for all the spectra which either do not exhibit the 39.86-ppm resonance or for which it is very weak. Other assignments could possibly be made for this region (e.g., a resonance associated with methyl branching as discussed shortly). The A methylene carbons in I should resonate at 38.5 ppm by Lindeman–Adams calculations and the B methylene carbons should appear at about 34.5 ppm. There is evidence for these minor resonances in published spectra[2,13] as well as a number of samples studied here. While no single resonance can be taken as proof of the presence of structure I, the overall data presented strongly suggest that such sequences could be present. The 34.5 ppm region is, however, usually obscured by the large α backbone carbon resonance. A recent study[13] involving the ^{13}C NMR and the analysis of the radiolysis decomposition products of two low-density polyethylene samples has shown similar spectral characteristics which have been interpreted in the same way.

The monomer sequence distribution in a number of butene/propylene copolymers has been analyzed by C-13 NMR and the data provide an opportunity to elucidate the possibility of nonrandom sequences in the low-density branched polyethylenes. For instance, the chemical shifts exhibited by various arrangements of sequences (BBB, BBP, PBP) result in an ethyl branch methyl resonance at 9.92 ppm.[14] We have carefully sought and have not observed any resonance at this position and so can rule out these sequences. In addition, the methylene carbon resonances of the ethyl branch in these sequences absorb at 27.00, 27.19, and 27.34 ppm, respectively. They would, therefore, be obscured by the backbone β-methylene resonance and would not be detected.

There is, therefore, strong evidence that not only are ethyl side groups present, albeit of varying concentrations, but they can occur in one of two major types: either as isolated groups or as in structure I. The presence of butene-1 in the polymerizing mixture has the effect of significantly increasing the integrated intensity of the resonance at 39.86 ppm, which represents the methine carbon of an ethyl branch. As we have noted in Table IIa, this peak is associated with isolated ethyl branches. Despite the ethyl distribution differences that result, the presence of butene-1 in the polymerization mixture did not enhance the total ethyl branch content.

Sample 3 exhibits a rather high-field resonance at about 8 ppm as is illustrated in Figure 6. This resonance is compatible with the predicted shift of the CH_3 carbon of ethyl groups attached to quaternary backbone carbons.[11,12]

Table II
Calculated and Observed Chemical Shifts for Short-Chain Branches in Polyethylene

A: For Unique Carbons of Isolated Ethyl Branches

calcd		obsd		
G-P[a]	L-A[b]	copolymer[c]	branched PE[d]	assignment
37.41	39.12	39.68	39.86 ± 0.09	methine
34.28	34.22	34.09	34.26 ± 0.07	α
27.37	27.16	26.79	27.15 ± 0.04	2
11.36	11.36	11.19	10.94 ± 0.14	methyl

B: For Methyl and Propyl Branches

branch length		methine	α	β	γ	3	2	1
1	a	31.66	36.77	27.38	30.18			19.66
	b	32.52	36.91	27.27	30.21			19.63
	c	33.21	37.54	27.50	30.40			20.04
3	a	37.41	34.28	27.69	30.29	36.77	20.47	13.87
	b	37.05	34.47	27.52	30.21	36.91	20.20	14.35
	c	37.78	34.37	27.22	30.44	36.79	20.28	14.60

C: For Butyl Branches

carbon	4	3	2	1	br	α	β	γ
G-P[a]	34.28	29.87	22.96	13.56	35.23	34.70	27.80	30.29
L-A[b]	34.22	29.96	22.90	13.66	37.05	34.47	27.52	30.21
copolymer[c]	34.09	*e*	23.37	14.13	38.10	34.48	27.26	30.44
branched PE[d]	34.26 ± 0.07	*e*	23.34 ± 0.07	14.00 ± 0.07	38.27 ± 0.07	34.64 ± 0.06	27.32 ± 0.04	30.47 ± 0.02

D: For Amyl Branches

carbon	5	4	3	2	1	br	α	β	γ
G-P	34.59	27.38	32.36	22.65	13.45	35.34	34.70	27.80	30.29
L-A	34.47	27.27	32.65	22.65	13.86	37.05	34.47	27.52	20.21
copolymer	34.01	22.63	32.46	22.70	14.72	37.86	34.25	27.06	30.28
branched PE	34.26 ± 0.07	26.83	32.73 ± 0.05	22.85 ± 0.04	14.00 ± 0.07	38.27 ± 0.07	34.64 ± 0.06	27.32 ± 0.04	30.47 ± 0.02

[a] Reference 11. [b] Reference 12. [c] Reference 2. [d] Present results. [e] Not observed as separate resonance.

Although this resonance is most intense for sample 3, it can also be discerned in samples 1, 2, 4, and 10, at somewhat reduced concentrations. Other carbons in this branching group do not exhibit any other unique shifts.

Methyl and propyl branches have been found in samples 5–8 to which propylene has been added to the polymerization mixture. Although methyl groups are always found in these samples, indicating that copolymerization is taking place, propyl branches are only found in one sample. From the calculated chemical shifts associated with methyl and propyl branches, Table IIb, and from the observed copolymer resonances, the presence of either of these branch types should result in a unique resonance in the region of 20 ppm. This is a region which is free of extraneous resonances from branches of any other length, excluding the possibility of complicated tetrafunctional branching or nonrandom branch distributions.

As is demonstrated in Figure 7, samples of 5–8 exhibit a unique peak at 19.95 ± 0.07 ppm. Significant resonances are also present in these samples at 33.33 ± 0.04 ppm as is shown in Figure 8. The Lindeman–Adams[12] and Grant–Paul[11] chemical shift assignments indicate that the high-field peak is due to methyl branches while the low-field peak represents the backbone methine carbon to which the methyl group is attached. The α backbone CH_2 resonance associated with a methyl branch at ~37.7 ppm is partially obscured by the nature of the ethyl branching distribution that has been discussed above. The integrated intensity of this resonance is, however, enhanced for propylene modified polymers. Hama et al.[1] have observed a similar set of resonances in a low-density polyethylene sample which did not have this ethyl branching problem. Their observed chemical shifts at 19.84, 33.13, and 37.40 ppm assigned to the methyl branch compare quite favorably with those made here.[25] No other published spectra have shown any evidence for methyl branching. Hama et al.[1] assumed that their sample was polymerized with the addition of propylene. Samples 5–8 were known to have been prepared in this way and were deliberately chosen for the present work. Copolymerization is thus clearly demonstrated. Other samples, not polymerized with propylene, do not exhibit the 19.95 resonance. Thus methyl branches are only observed when propylene is present in the polymerization mixture. Certain sequences of branching, as evidenced from the study of a number of butene/propylene copolymers, can result in methyl branch resonances in the region just discussed.[14] These shifts can vary from 20.60 ppm for the BPB sequence to 20.97 ppm for a PPP sequence. An intermediate value of 20.74 is characteristic of the sequence BPP. However, as has been previously noted, there is no evidence for the presence of such sequences in the present set of polymer samples.

Sample 6 exhibits a unique resonance at 20.85 ppm, as is shown in Figure 7, which corresponds to the requisite resonance for a propyl branch group. The C-3 carbon of the propyl branch as well as the methine backbone carbon should contribute in the region of 37 ppm. There is an asymmetric peak of relatively large intensity at this position but the various contributing carbons cannot be individually recognized. The Grant and Paul[11] substituent parameters predict a difference of 0.81 ppm between the methyl resonance of a methyl branch and the C-2 carbon of a propyl branch. Similarly, the Lindeman–Adams[12] parameters predict a difference of 0.57 ppm. In each case the propyl resonance is shifted to lower field. The observed difference of 0.82 ppm in sample 6 is close to these predictions. In this series of samples, the unique observation of a propyl side group is found in the polymer containing the largest concentration of methyl branches. The evidence enumerated above makes clear that in the presence

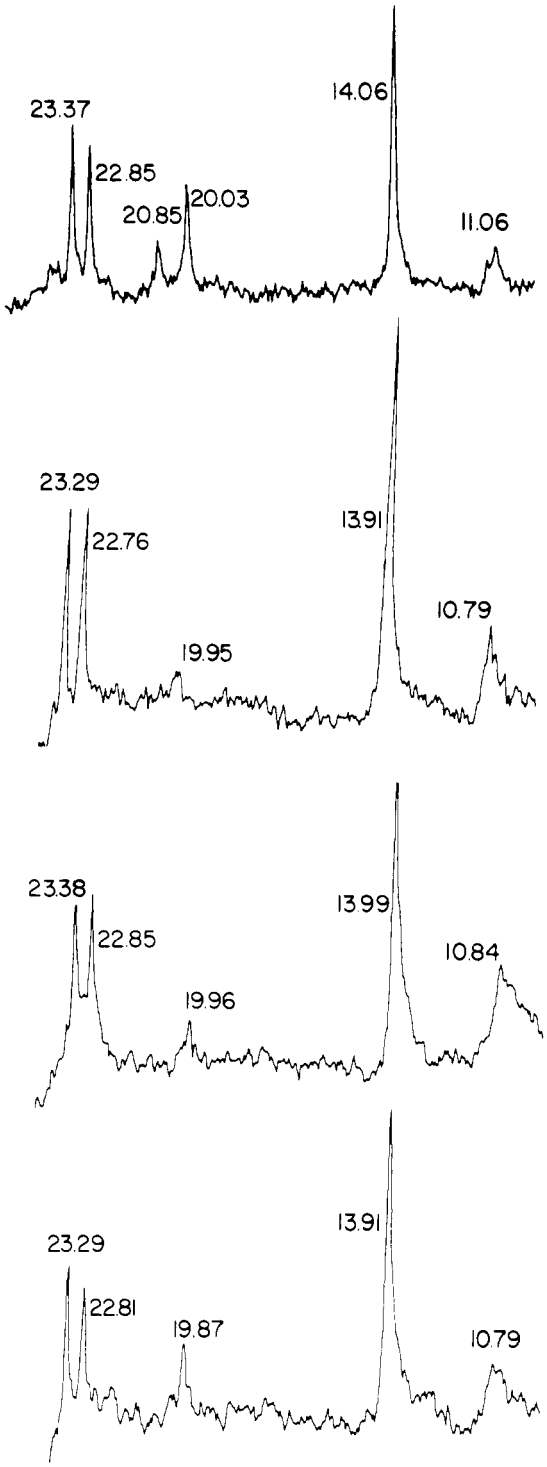


Figure 7. High-field region of samples 6, 5, 7, and 8 (from top to bottom). Chemical shifts in ppm from Me_4Si as marked.

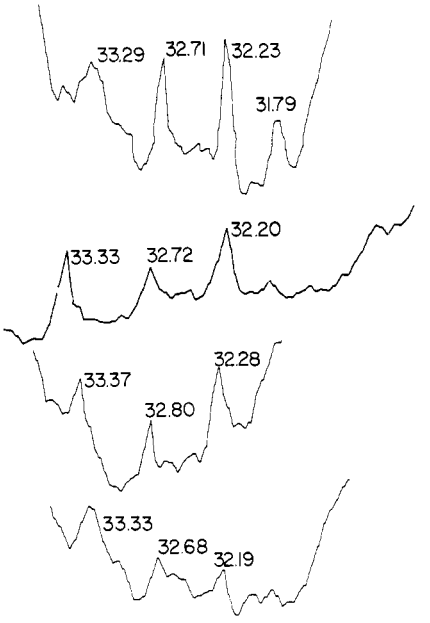


Figure 8. Expanded region of samples 5, 6, 7, and 8 (from top to bottom). Chemical shifts in ppm from Me_4Si as marked.

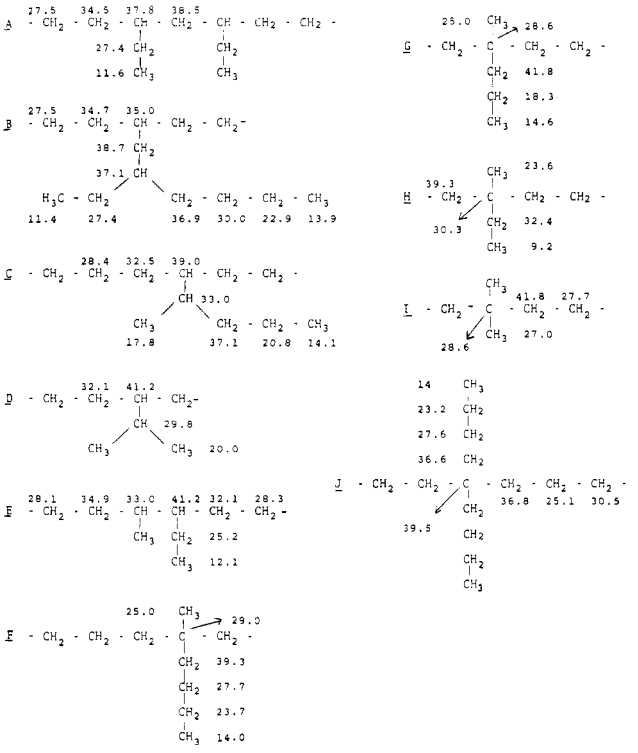


Figure 9. Possible branch types and predicted chemical shifts.

of propylene it is possible to introduce propyl side groups into the chain polymerized under conditions which also lead to the incorporation of other type branches and to a low density.

The dominant branching type that has been universally observed in the past,[1-6] as well as in all the present samples, is the butyl group. As is indicated by the assignments in Table IIc, butyl is defined by its resonances at 38.27, 23.34, and 14.00 ppm. However, only the resonance at 23.34 ppm due to the 2-methylene carbon is uniquely indicative of the butyl branch. The resonance at 23.34 is then usually taken to indicate the concentration of butyl branches present. We should also note that sample 6 exhibits the largest unassigned resonance observed among all the samples studied. It occurs at 25.7 ppm as can be seen in Figure 2. Isolated tetrafunctional *n*-butyl branches[11,12] could contribute to this peak as is indicated by some of the structures illustrated in Figure 9 but this structure alone could not account for the entire intensity observed.

The calculated chemical shifts for the amyl branches,[11,12] Table IId, indicate a unique resonance at approximately 32.7 (Lindeman-Adams) or 32.4 ppm (Grant-Paul). This shift is attributed to the C-3 carbon. The remaining shifts are, however, obscured due to overlap with other types of branching. While a resonance at 32.7 ppm is observed in the overwhelming majority of spectra, Cudby and Bunn[4] have argued that the absence of a unique amyl methyl resonance in the region of 14.7 ppm in branched poly-

ethylene, since it is apparently observed in an ethylene/heptene copolymer, is also evidence that the amyl C-3 carbon cannot be unambiguously assigned. A recent paper by Randall[2b] has corrected some apparent discrepancies in previously reported chemical shift data and further supports the amyl C-3 carbon assignment. The recent data[2b] alleviate the problems which resulted in the questioning of the amyl assignment. The quantitative data to be presented below will further obviate this situation and confirm the Randall assignment. In addition to the C-3 region (32.7 ppm), the 22.85-ppm resonance represents a composite contribution from the C-2 methylenes of amyl and longer chains. Thus, a quantitative internal comparison of the integrated intensities of resonances involving amyl branching could allow a firmer conclusion to be made regarding the validity of the C-3 assignment.

Side chains longer than amyl are characterized by a resonance at 32.23 ppm representing the C-3 methylene carbons of such long chains. This peak has received special consideration since it has been hypothesized that it represents the very long branches. Short branches longer than amyl were assumed absent or of minor importance. Moreover, long branches cannot be distinguished from hexyl at the present time.[5] As noted previously the 22.85-ppm resonance theoretically contains contributions from all branches longer than butyl. Thus, if this latter peak is to be used, quantitative information must be obtained from other unique resonances to delete the contribution of amyl branches. The C-3 resonances are predicted to have the same chemical shifts for hexyl and longer chains and to be located at 32.23 ppm.[11,12] Support for this assignment was based on the agreement between the carbon-13 results and solution determination for two samples.[5]

While high magnetic field strengths usually lead to a greater dispersion of chemical shifts, we have found that a comparison of spectra obtained at 67.9 with those at 22.6 MHz does not reveal significant differences in the information content, specifically in the long-chain branching region as had been anticipated.[5] It is very important, however, that the high magnetic field produces a significant sensitivity advantage over lower fields, and thus allows for equilibrium magnetization experiments as has been discussed previously.[9]

Quantitative Results. A proper quantitative analysis should utilize all the experimentally available data. Randall,[2] utilizing the standard assignments, noted that a fairly high standard deviation resulted from the fit of the peak intensities of the particular low-density polyethylene sample that he studied. Substantial improvement in the calculation could be obtained by excluding the 2-CH_2 and the CH_3 resonances from consideration.[2] Since equilibrium conditions were not employed in the data acquisition and the NOEF's were not known at the time, no definite conclusions could be drawn from this analysis.

With the proper experimental conditions having now been established, we have performed a multiple regression analysis on all of the resonances for the samples studied here, assuming the standard assignments listed in Table II. Although acceptable results can be obtained for a few samples, for most of them the standard deviations in side-group concentrations were on the order of 30%. It is clear then that this approach is not adequate for most of the samples using the present assignments. Thus, even when equilibrium conditions are employed the resulting standard deviations are rather high. In addition, physically unrealistic parameters are generated, as for example, negative branching values. A quantitative analysis on the simple basis outlined will therefore not be as straightforward as had been anticipated by studying only a limited number of samples. The reasons for this problem clearly must involve a lack of recognition of all the branching types that are present.

Although the quantitative analysis on the basis outlined suffers from obvious shortcomings it is informative at this point to examine the branching frequencies utilizing just the unique assignments. Reliable information with respect to the known side groups can be obtained in this manner. These results are recorded in Table I. Two of the samples, 12 and 14, show no detectable ethyl branching, while for the others the ethyl content ranged from 1.2 to 11.3 carbons per $1000CH_2$.

Cudby and Bunn[4] found values of <1 to 11 per $1000CH_2$ in the four samples they studied although two had about 4 per $1000CH_2$. Our subsequent reinvestigation of their sample which contained the lowest reported ethyl content revealed approximately 4 ethyl branches per $1000CH_2$. Their original study did not detect an ethyl resonance at $\sim$10.9 ppm due to a combination of saturation effects and insufficient signal-to-noise. They estimated an upper limit of about 1 branch per $1000CH_2$. We have determined that there are 3.9 ethyl branches per $1000CH_2$ in this sample using a more appropriate pulse delay and obtaining a high signal-to-noise ratio spectrum. Cheng et al.[6] found 2.6 and 1.9 per $1000CH_2$ while Bovey et al.[5] reported 1.3 and 1.4 for their fractions. There is thus a very large variation in the total ethyl content and, as has been previously discussed, in their types. Limiting considerations to the very small concentrations would obviously be incorrect. The ethyl to butyl ratio can be obtained from the resonance at 23.34 ppm, indicative of the butyl branching, and the resonance at 10.94 ppm which represents the ethyl content. The data in Table I reveal that the ethyl/butyl ratio is also highly variable. Some of the samples exhibit ratios less than 1.0 while others are approximately 1.1–1.2; sample 7 has a much greater value than the others. Literature values have tended to be less than 1 (i.e., an excess of butyl over ethyl branching).[1,6]

Willbourn[15] concluded from an infrared study that the ethyl branches predominated over the butyl ones. This condition is obviously not always satisfied. He suggested an extended back-biting mechanism which could lead to 5-ethylhexyl branches and 1,3-paired ethyl branches. While Bovey et al.[5] were unable to detect such branching it is apparent from our previous discussion of ethyl branching that the 1,3-paired ethyl branching is highly likely in many samples studied here. The chemical shifts predicted for the 5-ethylhexyl branch are given in Figure 9. Their multiplicity as well as the minor contribution of this branch type make identification difficult. Evidence is available, however, from samples 9 and 10 (Figure 5) as well as in a recent report[13] which indicates the presence of these branches, based particularly on the resonances observed at approximately 38.9, 37.2, and 34.7 ppm. Since the spectra in Figure 5a were expanded horizontally to illustrate other points, these weaker resonances have become artifically obscured. Therefore, we have plotted in Figure 5b a less expanded spectrum of sample 9, which clearly demonstrates the resonances in the region of 38.9, 37.2, and 34.7 ppm, respectively, typical of other samples.

The four samples which were polymerized with propylene contain methyl branches. Samples 5, 7, and 8 yield comparable branching frequencies of about 2.2–2.6-$CH_3/1000CH_2$ while more than twice this amount, 5.6-$CH_3/1000CH_2$, is found in sample 6. The latter sample, with the largest concentration of methyl branches, also

Table III
Quantitative Comparison of Resonances Representing the Sum ($n_4 + n_5 + n_{6^+}$)

		sample no.														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
38.27	(1)	8.6	6.3	9.5	4.7	7.4	10.1	10.1	6.6	6.4	4.6	8.5	8.2	9.6	10.7	9.9
23.34, 22.85	(2)	12.7	8.2	18.0	7.7	10.8	15.0	7.9	7.7	6.8	10.0	11.2	17.6	22.9	16.5	10.1
14.00	(3)	19.4	14.1	19.9	7.2	13.2	18.0	15.9	15.3	9.3	10.9	14.3	15.4	26.6	16.5	20.5
Δ1 − 2		4.1	1.9	8.5	3.0	3.4	4.9	2.2	1.1	0.4	6.4	2.7	9.4	13.3	5.8	10.2
Δ2 − 3		6.7	5.9	1.9	0.5	2.4	3.0	8.0	7.6	2.5	0.9	3.1	2.2	3.7	0	0.4
Δ1 − 3		10.8	7.8	10.4	2.5	5.8	7.9	5.8	8.7	2.9	6.3	5.8	7.2	17	5.8	10.6

Table IV
Quantitative Internal Comparison of Resonances Related to the β-Methylene Backbone Carbons

	sample no.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1[a]	49.4	29.8	51.3	15.1	39.7	42.9	34.1	36.4	32.3	27.9	28.4	17.6	33.5	28.4	34.7
2[b]	50.0	41.4	53.0	17.8	42.0	52.9	56.9	45.4	40.4	27.6	26.9	31.0	73.5	33.0	58.4
5[c]	0.6	11.6	1.7	2.7	2.3	10.0	22.8	9.0	8.1	0.3	1.5	13.4	40.0	4.6	23.7

[a] Integrated intensity number of branches/1000C using 27.32 peak. [b] Composite from 2 × (19.95) + 2 × (10.94) + 32.2. [c] Δ1 − 2.

contains the only observable propyl side group. The presence of this group represents another finding for low-density polyethylene polymers. The percentage of the methyl branching is at the level of 13–23% of the total branching for these four samples. Ethyl branching is present in almost all of the samples. When this type is observed it represents a significant portion of the total branch content, ranging from 12–57%. *n*-Butyl branches, which range from 3.9 to 8.5 per 1000CH_2, represent from 20–58% of the branching content. The amyl side group content ranges from 0.6 to 2.2 per 1000CH_2 and represents the lowest concentration of short-chain branching. Hexyl and longer branches, i.e., the long-chain branching, range from 0.5 to 2.8 per 1000CH_2 except for sample 13. Here the value for the long-chain branching is much greater but is enhanced by the contribution from the end groups. Thus, long-chain branching represents about 15% of the total branching. Based only on the unique assignments the total branching varies from 8 to 25 branches per 1000C. One of the major conclusions of these results, which are summarized in Table I, is the very versatility in composition and concentration that is found among the low-density polyethylenes. It becomes quite obvious that when the branching is examined in terms of specific types, each polymer is essentially different. Thus generalizations with respect to structure and properties can be expected to be quite difficult. The data in Table I and the discussion thereof are based on the unique resonances that are assigned to each branch type.

As we have noted previously there is a major inconsistency in the quantitative analysis of the spectra when all the resonances characteristic of the given branch types are considered simultaneously for a particular sample. This factor cannot be ignored and to explore the reasons we examine the internal consistency of the various resonances, or combinations thereof, that should yield identical integated intensities since they represent the same branching contributions.

From Table II we note that the resonances at 38.27 ppm and 14.00 ppm each represent contributions from butyl and longer branching and can be defined as $n_4 + n_5 + n_{6^+}$. In addition, the sum of the intensities of the resonances at 23.34 and 22.85 ppm represents the same total branching. This sum is given in Table III and provides a quantitative internal comparison of these resonances and illustrates the differences in branching frequencies that can be obtained, using standard chemical shift assignments when they are not unique. It is evident from examining the data in Table III that the low-field resonance consistently underestimates the branching frequency for this grouping. The largest differences between the data sets occur on comparing lines 1 and 3. Smaller, but consistent, differences also are observed between lines 2 and 3. The fact that the comparison is better for lines 1 and 2 suggests that it is the 14.00-ppm resonances which have been enhanced. In support of this idea line 2 is consistently smaller than line 3. More complicated, i.e., nonlinear, branching can readily contribute differentially to these regions, particularly enhancing the 14.00-ppm resonance when the branches contain two or more terminal methyls. The necessary differences are relatively small being only 2 branches/1000CH_2. The methine branch point should be relatively insensitive to substitution more than four carbons removed from it. Conversely, branching (i.e., branched branches) closer to this position should result in a spread of the methine chemical shifts. The quantitative relationship between these tertiary carbon resonances and any other resonance becomes quite ambiguous.

We next consider the internal consistency that is obtained in the branching frequencies as determined in conjunction with the β-carbon resonance located at 27.32 ppm, which is common to all the side groups. The integrated intensity of this peak should be equal to the appropriate linear combination of the methyl and longer branching resonances represented by the peaks at 10.94, 14.00, 19.95, and 32.2 ppm. This sum is designated as ($2n_1 + 2n_2 + 2n_4 + 2n_5 + 3n_{6^+}$) and is given in Table IV. A superficial examination of the data in this table appears to reveal that the internal consistency for this combination is not very good.[26] The calculated chemical shifts for more elaborate branches such as tetrafunctional ones as well as nonlinear structures such as 5-ethylhexyl reveal that the 27.3-ppm resonance would contain contributions from non-main-chain carbons. Thus the branching which differentially enhances the 14.00-ppm peak could have a similar effect on the 27.3-ppm region. Similar type structures have previously been postulated from infrared analysis by Casey et al.[16] The differences observed in Table IV only represent the order of 1–4 branches per 1000 main chain carbons. Within these limits, the data could possibly be considered to represent good internal consistency in these spectral regions.

Table V
Quantitative Internal Comparison of Resonances Related to α-Methylene Backbone Carbon

	sample no.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1[a]	46.1	49.2	39.5	18.9	59.9	40.5	53.4	38.8	36.3	54.0	18.6	40.3	37.0	42.2	49.3
2[b]	35.2	30.3	40.5	16.5	64.6	39.9	42.4	39.1	34.5	26.0	18.4	24.6	36.6	48.6	58.9
3[c]	68.2	53.7	71.7	24.0	52.0	63.6	68.3	56.5	51.9	34.7	37.3	46.2	87.6	49.5	78.9
4[d]	10.9	18.9	1.0	2.4	4.7	0.6	11.0	0.3	1.8	28.0	0.2	15.7	0.4	6.4	9.6
5[e]	22.1	4.5	32.2	5.1	7.9	23.1	14.9	17.7	15.6	19.3	18.7	5.9	50.6	7.3	29.6

[a] 34.64 + 34.27. [b] 3 × (38.27) + 2 × (10.94). [c] 3 × (14.00) + 2 × (10.94). [d] Δ1 − 2. [e] Δ1 − 3.

Table VI
Quantitative Internal Comparison of Resonances Related to Amyl and Hexyl + Branches

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1[a]	3.7	3.6	2.5	4.0	2.7	3.4	1.8	4.4	4.8	4.4	1.3		12.5	⩽2.6	3.5
2[b]	5.8	3.5	9.5	3.1	5.5	6.8	3.8	3.9	4.6	2.7	5.0		26	16.5	8.2
3[c]	2.1	0.1	7.0	0.9	2.8	3.4	2.0	0.5	0.2	1.7	3.7		~14	~14	4.7

[a] 32.73 + 32.23. [b] 22.85. [c] Δ1 − 2.

The next set of resonances that we examine for internal consistency involve the α-methylene carbons located in the region of 34.66 ppm. As the shoulder at 34.26 ppm could not be resolved the entire region was integrated for the quantitative comparisons. This sum is therefore designated ($2n_2 + 3n_5 + 3n_{6+}$) using the assignments of Randall.[2] Since the 14.00- and 38.27-ppm resonances both represent the sum ($n_4 + n_5 + n_{6+}$) to a first approximation, either resonance can be used in obtaining the proper linear combination to be compared with that obtained for the α-methylene region. The results are summarized in Table V. The consistency in Table V using the 38.27-ppm resonance is better than that obtained with the 14.00-ppm resonance. The major discrepancies occur in about 5 of the 15 samples. Although these inconsistencies are qualitatively similar to those obtained for the β carbon, the quantitative deviations are more severe in this case.

The discussion of the lack of internal consistencies given above formally explains the failure of the multiple regression analysis cited earlier. These results have pointed out quite forcibly that there must be other, more complex, types of short-chain branching present whose identification should be actively sought. Their identification and concentration will presumably play an important role in establishing the mechanisms for the polymerization of low-density polyethylene. Despite these complexities, however, the set of unique resonances that have been established allows for the identification and quantification of the simple type short-chain branches.

The composite resonance at 22.85 ppm represents the contributions from amyl, n_5, and the longer, n_{6+}, branching. Each of these can be separately identified from the resonances at 32.73 ppm (n_5) and 32.23 ppm (n_{6+}). Thus an internal comparison of these branch frequencies can be obtained. The results are given in Table VI. The majority of the samples exhibit good quantitative internal consistency. However, four or five samples show large deviations. Of the samples showing these large deviations it is evident that the 22.85-ppm resonance is causing the excess difference, which is of the order of 3–5 unidentified branches per $1000CH_2$. As the consistency is generally acceptable using these resonances one can conclude that the resonance at 32.73 ppm represents amyl branching. The quantitative differences noted in Table VI are attributed to additional branching contributions to the resonance at 22.85 ppm.

As has been previously indicated,[5] besides the standard shift assignments[11,12] the only confirmation of the quantitative validity of the assignment of the 32.23-ppm resonance to the long-chain branching, i.e., C_6 and greater, is the agreement found for two molecular weight fractions from intrinsic viscosity and molecular weight measurements, and utilizing the Zimm–Kilb[17] and Zimm–Stockmayer[18] theories for fractions. The accord between the two methods was very good in this particular instance, giving credence to the procedure. However, the branching frequencies were virtually identical for the two samples and were less than 1 per $1000CH_2$. More general applicability of the method clearly needs further study so that it was deemed advisable to expand this type of comparison to the samples studied here. The results from solution studies for samples 14 and 15 are in the literature.[10] The long-chain branching frequencies for most of the other samples were obtained from the combination of GPC and intrinsic viscosity.[27] The principles involved in this latter procedure have been described in great detail by Westerman and Clark[19] and Mendelson and Drott.[20] The solution and NMR results are summarized in Table VII. In making comparisons we should note that there are two different solution methods, and that NMR yields number average values while the solution methods yield weight averages. It is important to recognize that there is also considerable variation in the character of the resonances in the long-chain branching region among the different

Table VII
Comparison of Long-Chain Branching from NMR and Solution Measurements

polymer	from ^{13}C NMR	from soln measurements
11	0.5	
3	1.2	
7	1.2	3.1[a]
14	1.3	0.41[b]
5	1.5	
12	1.5	1.3[a]
6	1.7	2.0[a]
2	1.8	1.2[a]
4	2.0	
1	2.2	1.8[a]
8	2.2	2.5[a]
10	2.2	2.1[a]
15	2.5	0.42[b]
9	2.8	2.0[a]
13	12.5	26 ± 8[a,c]

[a] From GPC and intrinsic viscosity; data provided by Dr. L. Westerman. [b] From ref 10 by light scattering and intrinsic viscosity. [c] Large uncertainty due to uncertainty in intrinsic viscosity because of the very low molecular weight of this sample.

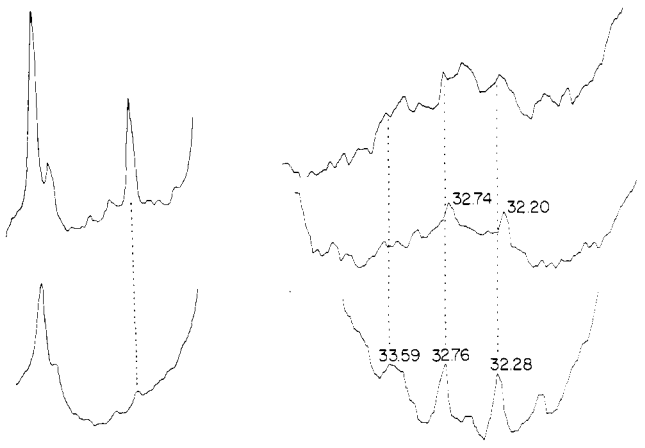


Figure 10. (a, left) Long-chain branching region (~30–35 ppm shown) of samples 13 (top) and 15 (bottom). Resonances connected by dotted line represent long-chain branching frequencies of 12.5 branches per 1000 carbons and 2.5 branches per 1000 carbons, respectively. (b, right) Expanded long-chain branching region of samples 4, 11, and 2 (from top to bottom). Chemical shifts in ppm from Me_4Si as marked. All spectral widths are identical.

samples as can be clearly discerned in Figure 10a,b, In particular, the presence of resonances which overlap with the 32.23 ppm (n_6) peak, as well as the 32.73-ppm peak (n_5), can make quantitative analysis difficult in many cases. This region provides further qualitative evidence that unidentified branch groups are present. Studies with model compounds would be extremely helpful in understanding this spectral region in more detail. The NMR values that are obtained vary from 0.5 to 2.8C/1000C. However, sample 13, which exhibits an intense sharp peak in the region of 32 ppm, yields a long-chain branching frequency of 12.5 per $1000CH_2$. Although this is a substantial value for long-chain branching frequency, it is appreciably less than the value previously reported[4] of 21 per $1000CH_2$. This discrepancy can again be attributed to the differences in the pulse delay times and the enhanced signal-to-noise ratio obtained in the present study. The previously determined equilibrium magnetization conditions[9] are being utilized in the present work.

A comparison of the NMR and solution results appears to depend on the samples and method of analysis by the latter method. When the combination of GPC and intrinsic viscosity is used, the branching frequencies are mainly of the order of 1–3 per $1000CH_2$ by NMR; the agreement can be considered to be relatively good, although not quantitatively exact. For the highest value of the long-chain branching, sample 13, the differences between the two methods may be more apparent than real. The large uncertainty listed for the solution method is merely a reflection of the effect of small changes in the intrinsic viscosity (normal experimental error) because of the low value associated with this very low molecular weight sample. A major disagreement is found with the very high molecular weight fractions, samples 14 and 15, where the solution method yields much lower values. Since the resonances are relatively sharp in this case, there is no ambiguity in their integration. Thus the difficulty would not appear to be in the NMR method if the basic assignment is correct. For these samples the combination of light scattering and intrinsic viscosity was used to determine the long-chain branching.[10] An exponent of $^1/_2$ was used in this analysis.[18] However, the results are very sensitive to the value of this parameter and the long-chain branching frequency will increase from 0.4 to 7.0 as this parameter increases from $^1/_2$ to 1. A more quantitative and objective comparison of the methods will require a detailed study of fractions covering a wide range in molecular weights and branching frequencies. However, when the 32.23-ppm resonance can be unambiguously observed, it should be the preferred method until all the assumptions involved in the different methods of solution analysis are independently assessed.[19,20]

Summary and Conclusion

By deliberately selecting a large number of different samples for study, the wealth of structural information that is available from a high-field carbon-13 NMR spectrum of low-density polyethylene becomes readily apparent. It also becomes quite clear, almost by inspection, that there is a great diversity in structure among the different samples. Thus, with respect to branch type and concentration, there is no unique low-density polyethylene molecule. This fact is undoubtedly a major factor for past disagreements[1,3–5] from spectroscopic studies where only a very limited number of different samples were studied by each investigator. It also explains the wide range in properties that can be observed with this class of polymers and the difficulties that have existed in developing a comprehensive and coherent understanding of structure–property relations.

More specifically, utilizing predetermined equilibrium experimental conditions for such studies we have found that *n*-butyl branches are present in all the samples and generally represent the highest concentration of branch groups. This finding, for most of the samples, gives strong support to the original "back-biting" mechanism proposed by Roedel[21] as does the very much lower, but perceptible, amyl content. However, in contradiction to this simple mechanism, both isolated and 1,3-paired ethyl branches are also observed to a significant extent. In a few samples the presence of ethylhexyl groups is also suggested. Both the total concentration and relative amounts of the two types of ethyl groups vary among the samples and depend on the polymerization conditions. Obviously the simple mechanism[21] for generating short-chain branching has to be modified. Willbourn's proposal,[15] which leads to the formation of 5-ethyl hexyyl branches and 1,3-paired ethyl branches, requires that the concentration of ethyl groups be much greater than butyl. Although the species required by this mechanism are detected, the general condition is not fulfilled except in a few cases. It becomes clear from this study that a much more detailed and systematic investigation of the polymerization mechanism needs to be undertaken in view of the ethyl group findings as well as the clear evidence that there are as yet significant concentrations of unassigned branch groups that must be present. We have also found that under special conditions copolymerization with propylene can occur with the introduction of methyl groups along the chain as well as propyl side groups.

Uniquely assigned resonances can be used to determine the standard side-group concentrations and the long-chain branching. However, when all the observed resonances are analyzed there is an internal inconsistency for all possible combinations that should yield identical results. Other branch types, such as tetrafunctional and nonlinear ones, must also be present for internal quantitative consistency. These species remain to be identified and their presence explained in a rational way from the polymerization mechanism. Thus, all the quantitative structural information available from the spectra has not as yet been extracted.

With the specific detailed information that is now available for each branch type it should be possible to

assess the influence of the different types, amounts, and distribution of the short- and long-chain branching on the polymer properties. A study of the specific influence of these factors on the morphology and related properties,[22] similar to that recently reported for linear polyethylene,[23] will be presented shortly.

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(24) We wish to thank Dr. M. E. A. Cudby and Dr. T. Hama for providing us with these samples.
(25) The data of Hama et al.[1] have been corrected such that the major recurring CH_2 resonance has the same value as found in the present study.
(26) The data for the very low molecular weight sample, 13, have been ignored for obvious reasons.
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Dynamic Mechanical Behavior of Polystyrene–(Ethene-*co*-butene)–Polystyrene, Triblock Copolymer Films Cast from Various Solvents

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ABSTRACT: Films of Kraton G-1650, a styrene–(ethene-*co*-butene)–styrene triblock copolymer, have been cast from a variety of solvents with solubility parameters in the range 15.1 to 20.5 $(J\ m^{-3})^{1/2}$. The complex modulus E^*, measured at 298 K, was found to vary from 4.4×10^6 N m^{-2} for films cast from low δ solvents to 2.05×10^8 N m^{-2} for films cast from high δ solvents. The areas under the damping peaks in the dynamic mechanical spectra were also altered by the casting solvent, which influences the manner in which the two component blocks are distributed in the solid state. Evidence of limited crystallinity in Kraton-G was found using differential scanning calorimetry and this was also used to estimate the heat capacity changes ΔC_p for the glass transitions associated with each block. These were always found to be less than that expected for the pure component.

It is now well documented that cast films of many block copolymers will exhibit a two-phase morphology which arises from the microphase separation of incompatible blocks into clearly defined regions or domains in the solid state.[1] The extent and nature of this separation will depend on a number of factors. Molau[2] showed that in an (AB) type diblock copolymer, five morphological states can be distinguished which depend on the molecular weight ratio of block B to block A. The shape of these various domain structures can be predicted using a statistical thermodynamic theory of microphase separation developed by Meier[3-5] who has shown that the final structure of a copolymer film will depend not only on the block composition but also on the casting solvent. The importance of the casting solvent in exercising substantial control on the morphology of the cast film was first recognized by Aggarwal et al.[6] and elaborated on by Kawai and co-workers.[7] The latter showed that a systematic change in structure could be detected in diblock copolymer films by changing the nature of the casting medium.

If the casting solvent can affect the sample morphology then it is likely that it will also change the dynamic mechanical response of the film. Miyamoto et al.[8] examined the physical properties of styrene–butadiene–styrene (SBS) films cast from four solvents and observed significant differences in behavior. During the course of this work Hourston et al.[9,10] extended the solvent range and found differences in the longitudinal sonic velocities, densities, and equilibrium swelling behavior of several SBS copolymer films cast from different solvents.

A systematic study of the dynamic mechanical behavior of films of Kraton G-1650, cast from solvents covering a wide range of polarity, is reported here. Kraton G-1650 is a triblock copolymer of styrene–(ethene-*co*-butene)–

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