mental motions dominate the relaxation of the backbone carbons of PMA in its extended conformation, while slower overall molecular tumbling may play a role in the relaxation of these carbons in the random coil conformation. These findings are the converse of those for poly(γ-benzyl L-glutamate)[1] and the collagen peptide α1-CB2.[14] For these polypeptides it was found that the relaxation of the α carbons in the extended helical conformation was dominated by overall molecular tumbling, while rapid segmental motions dominated the relaxation in the random coil conformation. No doubt this difference between the polypeptides and PMA is structure related and reflects the significance of the peptide bond in determining the molecular motions which characterize a given polypeptide configuration. The present work thus indicates that comparisons of correlation times for polypeptides and nonpeptide containing models such as PMA may provide a useful experimental approach with which to elucidate the details of molecular motions observed in polypeptides.

Acknowledgment. This work was performed at the New England Area NMR Research Resource Facility and was supported by NIH Grant RR 639 awarded to Jay A. Glasel. The authors gratefully acknowledge the help of Ms. Christine Reid who assisted with and performed some of the sedimentation experiments, and Dr. Hermann E. Bleich who designed and constructed the circuitry used in some of the NOE experiments. One of us (John D. Cutnell) also acknowledges Dr. J. Schaefer for informative discussions on the ^{13}C relaxation of polymers.

References and Notes

(1) A. Allerhand and E. Oldfield, *Biochemistry*, **12**, 3428 (1973).
(2) A. Oth and P. A. Doty, *J. Phys. Chem.*, **56**, 43 (1952).
(3) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", Wiley, New York, N.Y., 1967, Chapter IV.
(4) J. Schaefer, *Macromolecules*, **4**, 98 (1971).
(5) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).
(6) Y. Inoue, A. Nishioka, and R. Chûjô, *Polym. J.*, **4**, 535 (1971).
(7) T. K. Wu and D. W. Ovenall, *Macromolecules*, **7**, 776 (1974).
(8) J. G. Powles, B. I. Hunt, and D. J. H. Sandiford, *Polymer*, **5**, 505 (1964).
(9) T. Kawai, *J. Phys. Soc. Jpn.*, **16**, 1220 (1961).
(10) V. J. McBrierty, *Polymer*, **15**, 503 (1974), and references cited therein.
(11) J. E. Anderson, K. Liu, and R. Ullman, *Discuss. Faraday Soc.*, **49**, 257 (1970).
(12) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).
(13) G. Hermann and G. Weill, *Macromolecules*, **8**, 171 (1975).
(14) D. A. Torchia, J. R. Lyerla, Jr., and A. J. Quattrone, *Biochemistry*, **14**, 887 (1975).
(15) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 788 (1960).
(16) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).
(17) S. J. Opella, D. J. Nelson, and O. Jardetzky, *J. Chem. Phys.*, submitted for publication.
(18) A. H. Blatt, Ed., "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 7.
(19) E. C. Horning, Ed., "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 560.
(20) J. A. Glasel, V. J. Hruby, J. F. McKelvy, and A. F. Spatola, *J. Mol. Biol.*, **79**, 555 (1973).
(21) D. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).
(22) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
(23) D. E. Woessner, *J. Chem. Phys.*, **36**, 1 (1962).
(24) D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).
(25) J. Schaefer, *Macromolecules*, **5**, 590 (1972).
(26) J. Schaefer, *Macromolecules*, **6**, 882 (1973).
(27) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961, Chapter 8.
(28) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1967, Chapter 10.
(29) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **8**, 291 (1975).
(30) J. Schaefer, *Macromolecules*, **5**, 427 (1972).
(31) J. A. Glasel, *J. Am. Chem. Soc.*, **92**, 375 (1970).
(32) Such a difference raises complications when integrated ^{13}C spectra are being used to provide a carbon count. In other systems this problem is not present (see ref 12).
(33) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).
(34) J. D. Cutnell, J. A. Glasel, and V. J. Hruby, *Org. Magn. Reson.*, **7**, 256 (1975).
(35) P. Keim, R. A. Vigna, R. C. Marshall, and F. R. N. Gurd, *J. Biol. Chem.*, **248**, 6104 (1973).

Short-Chain and Long-Chain Branching in Low-Density Polyethylene

F. A. Bovey,* [1] F. C. Schilling,[1] F. L. McCrackin,[2] and H. L. Wagner[2]

Bell Laboratories, Murray Hill, New Jersey 07974, and the National Bureau of Standards, Washington, D.C. 20234. *Received September 17, 1975*

ABSTRACT: The branch content of two fractions of low-density polyethylene has been examined by ^{13}C NMR (at 25 MHz) and by limiting viscosity number (intrinsic viscosity) measurements. The ^{13}C spectra, interpreted with the aid of modified Grant–Paul chemical shift rules and the spectra of model copolymers, confirm that the principal type of short branch is trifunctional *n*-butyl (5–6 per 1000 CH_2) with smaller contents of *n*-amyl (ca. 2 per 1000 CH_2) and ethyl (ca. 1 per 1000 CH_2). A resonance at (32.1$_6$) ppm (from TMS), corresponding to the third carbon (C-3) from the branch end, provides a measure of branches longer than *n*-amyl, but does not at present distinguish such branches, presumably formed by intramolecular "backbiting", from the truly "long" branches, containing possibly many tens or hundreds of carbons and formed by intermolecular chain transfer to other polymer chains. If it is assumed that this resonance provides in fact a direct measure of the "long" branch content, "short" branches longer than *n*-amyl being of negligible probability, the results agree well with the long branch content estimated from the intrinsic viscosities of branched and linear polyethylene via the Zimm–Kilb *g* value. The long branch content thus deduced is ca. 0.8 per 1000 CH_2. For these samples, no marked dependence on molecular weight is observed for either the long- or short-branch frequencies.

Next to molecular weight and its distribution, branching is the most important structural variable influencing the properties of polymers and polymer solutions. Short-chain branching is well known to be particularly critical in its effects on the morphology and solid state properties of semicrystalline polymers such as polyethylene, while long-chain branching has a comparably profound effect on solution viscosity and melt rheology. It is therefore important to

have as much information as possible concerning the nature and number of these branches.

It has previously been demonstrated by carbon-13 NMR[3,4] that the principal type of short branch in low-density polyethylene is trifunctional *n*-butyl, together with ethyl[3,4] and possibly *n*-amyl[4] and *n*-hexyl[4] in smaller proportions. It is commonly assumed that such relatively short branches are formed by intramolecular "backbiting" reactions[5] of the growing polymer chain radical, and are to be distinguished from truly "long" branches, containing many tens or hundreds of carbon atoms and produced by intermolecular chain transfer to polymer chains already formed.

In this paper, we report the ^{13}C spectra of two well-characterized fractions of polyethylene, prepared by column chromatography. We give qualitative and quantitative results for all detectable branch structures: ethyl, *n*-butyl, *n*-amyl, and *n*-hexyl and longer. Although no distinction can be made under our observing conditions between *n*-hexyl and longer branches, we propose that the unique resonance at 32.1_6 ppm (from TMS) corresponding to these structures (that of the third carbon from the end of the branch) in fact provides a measure of the content of truly "long" branches. The long branch frequency calculated on this assumption agrees with that estimated from the limiting viscosity number (intrinsic viscosity) measurements, employing the theoretical treatment of Zimm and Kilb[6] and Zimm and Stockmayer.[7]

Experimental Section

Materials. The low-density branched polyethylene fractions were obtained from SRM 1476, a Standard Reference Material issued by the National Bureau of Standards. A column elution technique, previously described,[8] was used for the fractionation. Ten batches of 20 g each were fractionated separately and corresponding fractions were grouped together to give 12 main fractions which were then refractionated into 122 subfractions. Two of these subfractions, 5AS5 and 11AS2, were used in this study.

Ethylene–hexene, ethylene–heptene, and ethylene–octene copolymers were obtained from the Phillips Petroleum Co.,[25] the latter through the courtesy of Dr. J. C. Randall.[4]

Methods. NMR spectra were observed using a Varian XL-100 spectrometer modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet Model 1080 computer.[9] The protons were decoupled from the carbon nuclei using a random noise decoupling field. The free induction decays were stored in 8K computer locations using a dwell time of 100 μsec, i.e., a spectral window of 5000 Hz. The pulse was located at the high-field end of the spectrum at 25.160320 MHz. The pulse width was 63 μsec (for a ca. 60° pulse) and the pulse interval 3.0 sec. Hexamethyldisiloxane (HMDS) was employed as internal reference (2.0 ppm vs. TMS). DMSO-d_6 in a capillary provided the deuterium lock signal.

The polymers were observed as 20% (w/v) solutions in 1,2,4-trichlorobenzene at 110°. At this temperature, T_1 for the backbone carbons is ca. 1.5 sec;[10] for side-chain carbons, particularly that of the terminal methyl group, T_1 values are somewhat longer. (Quantitative measurements are currently being carried out in our laboratory and will be reported later.) The pulse interval chosen permits quantitative intercomparison of all carbon resonances except those of methyl groups, which were not employed for analytical purposes.

Light-scattering measurements were made in 1-chloronaphthalene at 135°C using a Sofica light-scattering photometer previously calibrated with benzene. Unpolarized light at 546 nm was employed with solutions which had been clarified with a Millipore filter of 0.22 μm nominal pore size. Weight average molecular weights were determined from extrapolation of the scattering data at five concentrations and 11 angles by the Zimm method. The other details of the measurement are similar to those reported for the work on SRM 1475.[11] The value of the differential refractive index, dn/dc, employed for each fraction was the one reported previously for linear polyethylenes of approximately the same molecular weight.[12]

Osmotic pressure determinations of number average molecular weight were made in a Hewlett-Packard Membrane Osmometer in 1-chloronaphthalene at 130°C using a 450D Arro Laboratory gel cellophane membrane. Data from five concentrations were extrapolated to zero concentration. The details of technique and data analysis are essentially similar to what has been described previously.[13]

Gel permeation chromatography (GPC) data were obtained on a Waters Model 200 in 1,2,4-trichlorobenzene at 135°C. A five-column set was employed which consisted of one of each of the following Waters styragel columns: 10^3, 10^4, 10^5, 10^6, and 10^7 Å, where the designation, according to the manufacturer, refers to the column exclusion limits. The calibration of the columns and the data analysis will be discussed below.

The limiting viscosity number, $[\eta]$, was measured in 1,2,4-trichlorobenzene at 130°C. The method has been described elsewhere.[14]

Results

In Figure 1 is shown the ^{13}C spectrum of the low molecular weight polyethylene fraction, designated 5AS5. (That of the high molecular weight fraction 11AS2 is essentially identical.) Figure 1 also shows the numbering and lettering of the carbon positions, which is that of Randall.[4] The peak assignments are based in part on the empirical rules which are now recognized as reliably predicting the ^{13}C chemical shifts of paraffinic hydrocarbon structures.[15–19] As a test of these rules, a comparison of observed and predicted spectra of ethylene copolymers of known structure is presented in Figure 2. (The first two experimental spectra are the same as those shown in ref 3.)

The predicted chemical shifts of all carbons except the branch carbons are based on the constants of Carhart et al.;[18] those of the branch carbons are based on the constants of Carman et al.[19] The latter represent an improvement over earlier results for these carbons, which are always the most difficult to predict, but they nevertheless overpredict the shielding by some 0.6 ± 0.1 ppm. Finer distinctions in assignment, as for example the small but important difference between the C-3 carbons of *n*-amyl and *n*-hexyl and longer sidechains, are based on the experimental spectra from normal alkanes.

The long-chain branching of the samples was estimated from viscosity and GPC measurements by a previously described method.[20] In this method, the GPC column was first calibrated with the subfractions for which absolute molecular weights were determined by light scattering and osmometry. This calibration applies only to polyethylene with the degree and distribution of branching of SRM 1476.

The limiting viscosity numbers, $[\eta]_m$, and the GPC chromatograms of the subfractions were measured. The values of the limiting viscosity number of the subfractions may also be computed by integration of the chromatograms by

$$[\eta]_{ch} = \int H(v)[\eta]dv \qquad (1)$$

where H is the height of the chromatogram, normalized to unit area, and $[\eta]$ is the limiting viscosity number of the branched polymer as a function of the retention volume v. We assume that the value of $[\eta]$ of the branched polymer is related to its molecular weight, M, by:

$$\log [\eta] = P + Q \log M + R(\log M)^2 \qquad (2)$$

Because every subfraction contains a distribution of molecular weights, its limiting viscosity number cannot be obtained directly by eq 2 but instead must be obtained by eq 1, which requires an integration over the molecular weight distribution. This is obtained from the chromatogram and its calibration with the subfractions mentioned above. A set of values of P, Q, and R for eq 2 was first assumed. Then for each value of the retention volume, v, of the chromatogram a corresponding value of M was obtained from the calibration and a value of $[\eta]$ was obtained from eq 2.

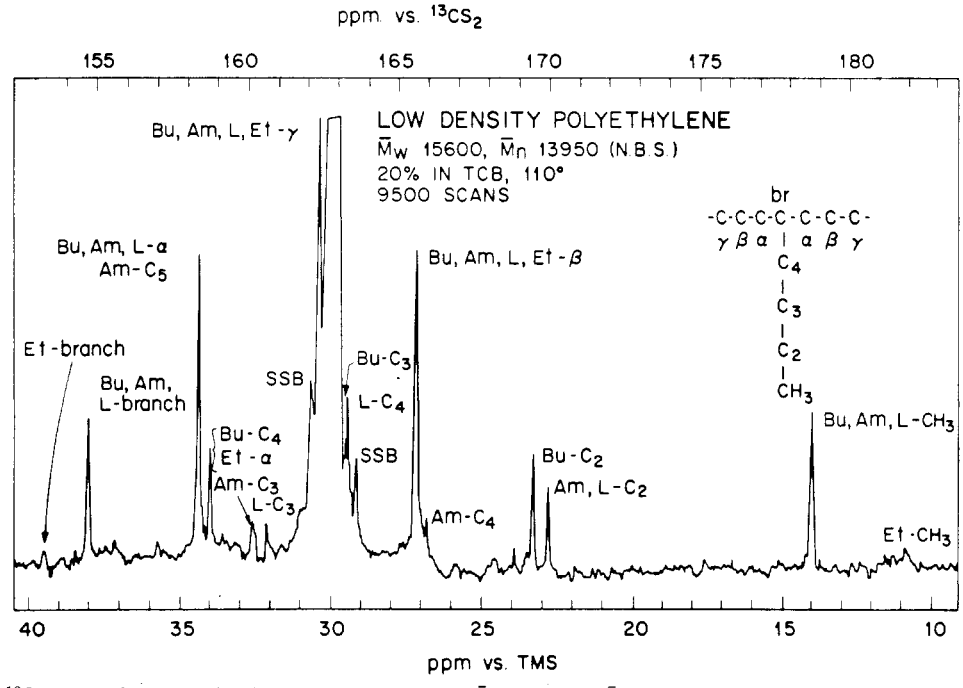

Figure 1. 25 MHz ^{13}C of low-density polyethylene (sample 5AS5); $\bar{M}_w$ = 15600, $\bar{M}_n$ = 13950; 20% in 1,2,4-trichlorobenzene at 110°; 9500 scans. The diagram at the upper right shows the nomenclature employed for the carbons associated with a branch. The end carbon (i.e., C_1) is designated as CH_3; Et = ethyl, Bu = *n*-butyl, Am = *n*-amyl, and L = "long" in the sense described in the text. "SSB" designates spinning side bands to the principal methylene resonance.

The integral in eq 1 was then numerically evaluated to give the limiting viscosity number, $[\eta]_{ch}$, of the entire subfraction.

The values of $[\eta]_{ch}$ of the subfractions were compared with their directly measured values, $[\eta]_m$. New values for the limiting viscosity numbers of the subfractions were then computed from the chromatograms using different values of P, Q, and R until the differences between the measured and calculated limiting viscosity numbers were minimized, thus determining P, Q, and R. Equation 2 then gives the limiting viscosity number of the polymer vs. molecular weight.

Once the values of P, Q, and R were determined, we defined the viscosity average molecular weight, M_v, as the solution of the equation:

$$\log [\eta]_{ch} = P + Q \log M_v + R(\log M_v)^2 \qquad (3)$$

The limiting viscosity numbers calculated by the relationship of eq 2 with the final values of P, Q, and R are shown by the solid curve in Figure 3. The values of $[\eta]_m$ for subfractions 5AS5 and 11AS2 vs. M_v calculated by eq 3 are shown by the square and triangle in Figure 3, and values of $[\eta]_m$ vs. M_v for the other subfractions are shown as circles.

The limiting viscosity number of the branched polymer is less than that of the linear polymer of the same molecular weight. Their ratio

$$G = [\eta]_b/[\eta]_l \qquad (4)$$

was calculated, where the limiting viscosity number of the linear polymer in ml/g is given by[21]

$$[\eta]_l = 0.0392\, M^{0.725} \qquad (5)$$

and is shown in Figure 3 by the dashed line. The number of long branches per molecule was computed from the G values following the procedure of Drott and Mendelson[22] by computing the ratio of the mean-square radii of gyration given by

$$g = \langle s^2 \rangle_b / \langle s^2 \rangle_l = G^2 \qquad (6)$$

Table I
Branch Frequencies in
Two Fractions of Low-Density Polyethylene

Sample	5AS5		11AS2	
$\bar{M}_w$	15600		186000	
$\bar{M}_n$	13950		81790	
$[\eta]^a$	40		134	
Branch points	Per wt av molecule	Per 1000 CH_2	Per wt av molecule	Per 1000 CH_2
Ethyl	1.3	1.2	19	1.4
n-Butyl	5.8	5.2	75	5.6
n-Amyl	1.7	1.5	25	1.9
"Long"				
By ^{13}C	1.0	0.9	8.3	0.6
By viscosity	0.9	0.8	12	0.8
Total branch points (assuming ^{13}C "long" branch value)	9.8	8.8	127	9.5

[a] Limiting viscosity number (ml g^{-1}) in 1,2,4-trichlorobenzene at 130°.

according to Zimm and Kilb[6] and then computing the number of long branches per molecule by the equations of Zimm and Stockmayer.[7] The number of long branches per molecule is plotted vs. the molecular weight in Figure 4. From Figure 4 the number of branch points are seen to be 0.9 and 12 for subfractions 5AS5 and 11AS2 with molecular weight values of 15600 and 186000. These values are given in Table I.

The preceding calculation neglects the effects of the short-chain branches on the limiting viscosity number and the G value. The G value, G_{scb}, that would be obtained only if the short chain branches were present may be estimated from the equation given by Kraus and Stacy[23]

$$G_{scb} = 1 - 1.56 w_s \qquad (7)$$

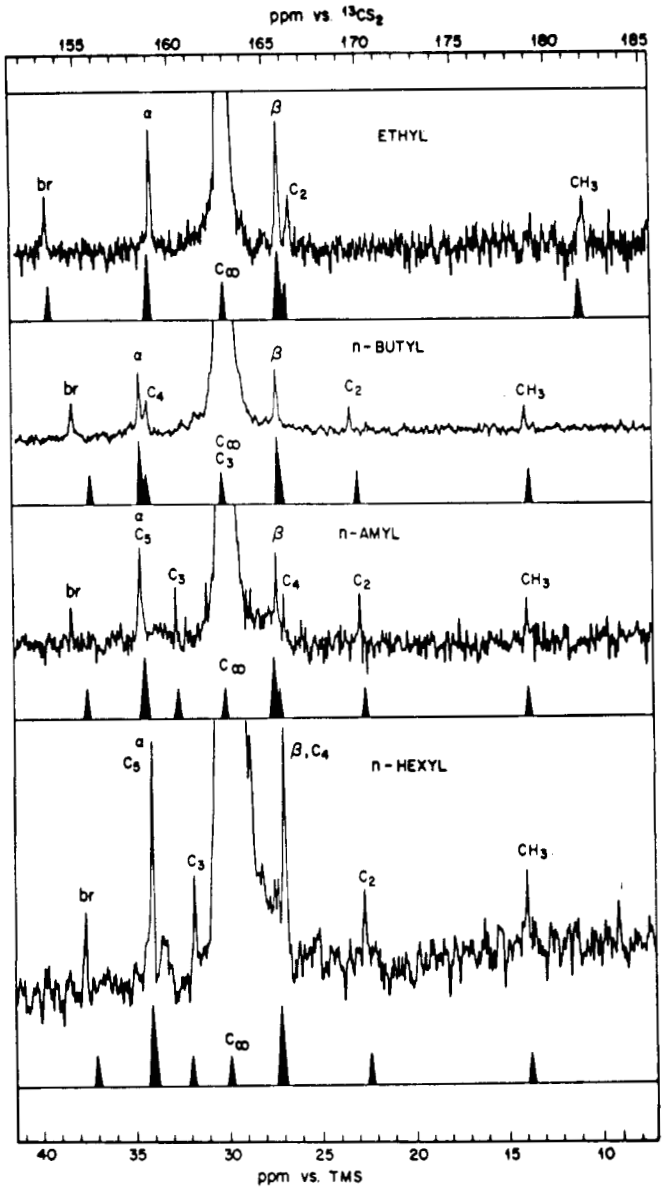

Figure 2. Observed ^{13}C spectra of model copolymers having (top to bottom) ethyl, *n*-butyl, *n*-amyl, and *n*-hexyl branches. The predicted spectra for each of the model copolymers are shown below their observed spectra.

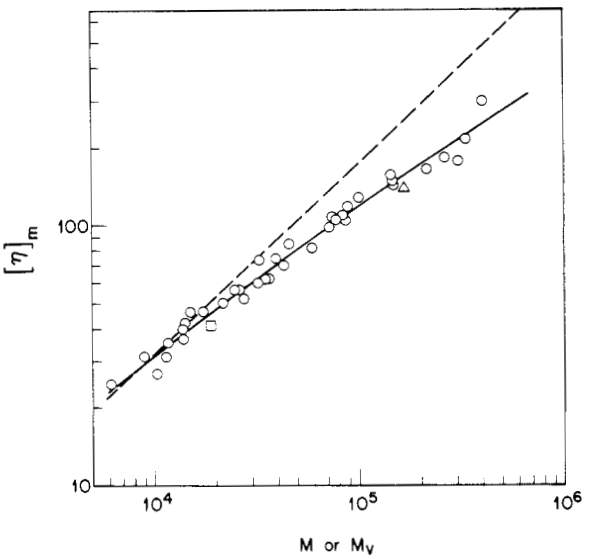

Figure 3. The measured limiting viscosity numbers, $[\eta]_m$, of branched subfractions. Subfractions 5AS5 and 11AS2 are shown by a square and triangle, respectively, other subfractions are shown by circles, and the calculated relationship is shown by the curve. The limiting viscosity number of linear polyethylene is shown by the dashed line.

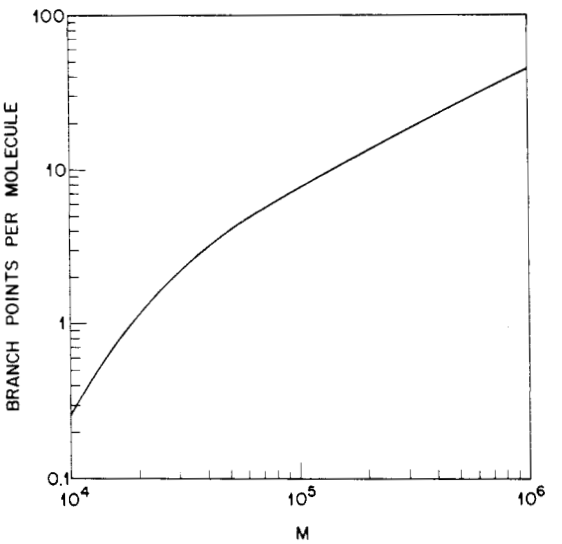

Figure 4. The number of long branches per molecule vs. molecular weight for SRM 1476 calculated from the curve of limiting viscosity numbers shown in Figure 3.

where w_s is the weight fraction of short-chain branches. For the frequencies of ethyl, *n*-butyl, and *n*-amyl branches given in Table I, w_s is found to be 0.031 and 0.035 for samples 5AS5 and 11AS2, respectively. Thus by eq 7, G_{scb} = 0.95 for both samples. The neglect of the short branches can thus cause an error of about 5% in the G values.

In Table I the branch content of the samples is presented, expressed as branch points per weight average molecule and per 1000 CH_2 groups. The ^{13}C measurement of the long-branch point frequency is based on the assumption, alluded to earlier, that the intensity of the "hexyl and longer" C-3 resonance is actually a measure of the truly "long" branches, short branches longer than *n*-amyl (if any) being neglected. It is also assumed that the low-density polyethylene molecule cannot be entirely paraffinic, there being one end, presumably representing the point of chain growth initiation, which is not a methyl group. (There are a number of small peaks, as yet unassigned, which may correspond to this end structure. At all other terminals, methyl groups may be assumed to be generated by inter- or intramolecular chain transfer.) This second assumption clearly becomes less important with increasing molecular weight, but is necessary for a reasonable interpretation of the spectrum of sample 5AS5. Here, only two long-chain C-3 carbons are observed per molecule; if all chain ends were assumed to be methyl groups, the molecule would appear to have no long branches, which is contrary to the conclusions from viscosity measurements.

Discussion

The ^{13}C observations reported here confirm earlier findings[3] that the predominant type of short branch is trifunctional *n*-butyl, with a smaller content of ethyl. We further observe, in agreement with Randall,[4] that there is a substantial probability of trifunctional *n*-amyl branch formation. Both butyl and amyl branches may be formed by the "backbiting" reaction originally proposed by Roedel.[5] The formation of still longer branches by this process evidently occurs with very low probability.

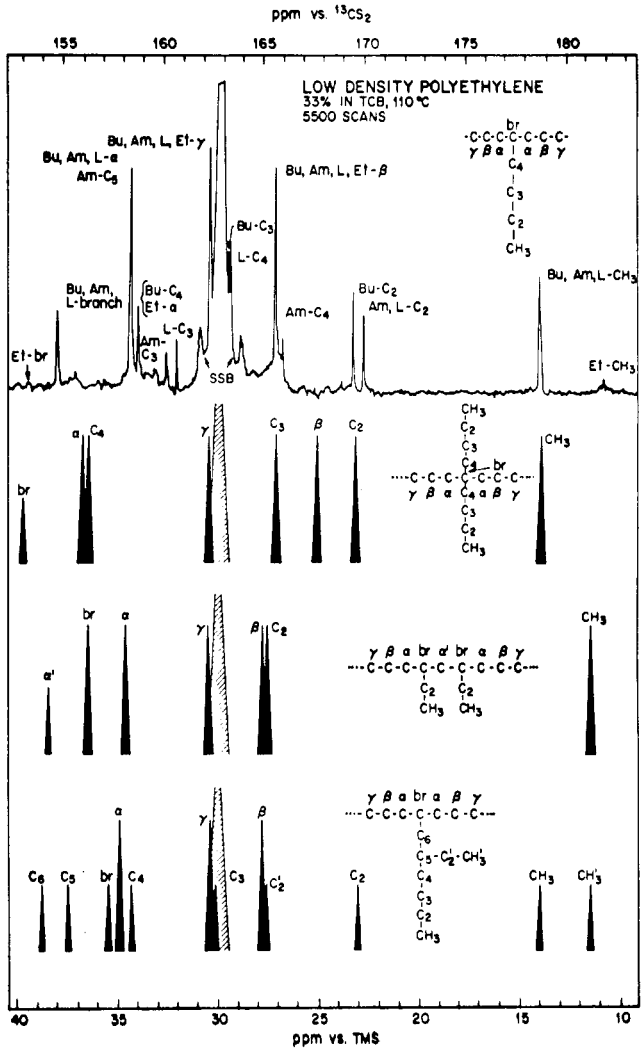

Figure 5. Experimental ^{13}C spectrum for an unfractionated low-density polyethylene (33% in 1,2,4-trichlorobenzene, 110°, 5500 scans) compared to predicted spectra for (top to bottom) a tetrafunctional *n*-butyl branch; 1,3-paired ethyl branches; a 5-ethylhexyl branch.

The mode of formation of ethyl branches is not clear. Willbourn,[24] whose infrared study led to the conclusion that ethyl branches predominated over *n*-butyl, suggested an extended backbiting mechanism which would lead to the formation of 5-ethylhexyl branches and 1,3-paired ethyl branches. In Figure 5, the predicted ^{13}C spectra of these structures are shown. Also shown is the predicted spectrum of a tetrafunctional *n*-butyl branch, a plausible structure because of the presumed enhanced reactivity of a branch point carbon toward a second hydrogen abstraction. A spectrum of an unfractionated commercial branched polyethylene is included in Figure 5 for comparison. It is evident that these structures are generated only in negligible proportions, if at all.

The agreement between the viscosity and ^{13}C measurements of "long" branch frequency is within the probable experimental error of the methods employed. The assumptions underlying the ^{13}C measurements can at present only be justified on the grounds that they lead to this satisfactory agreement. Using a higher frequency (90 MHz) ^{13}C spectrometer now at our disposal, we are currently undertaking a more searching study of the branch structures in a variety of low-density polyethylenes.

It is noteworthy that both the short- and long-branch frequencies show at most only a small dependence on molecular weight. It is not expected that this behavior will prove to be general.

Acknowledgment. We wish to thank R. G. Christensen, J. R. Maurey, and J. E. Brown for their assistance in the fractionation and characterization of the branched polyethylene fractions.

References and Notes

(1) Bell Laboratories.
(2) National Bureau of Standards.
(3) D. E. Dorman, E. P. Otocka, and F. A. Bovey, *Macromolecules*, **5**, 574 (1972).
(4) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 275 (1973).
(5) M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).
(6) B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).
(7) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 301 (1949).
(8) R. G. Christensen, *J. Res. Natl. Bur. Stand., Sect. A*, **76**, 149 (1972).
(9) H. Sternlicht and D. M. Zuckerman, *Rev. Sci. Instrum.*, **43**, 525 (1972).
(10) Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol. Chem.*, **168**, 163 (1973).
(11) L. J. Frolen, G. S. Ross, A. Wims, and P. H. Verdier, *J. Res. Natl. Bur. Stand., Sect. A*, **76**, 155 (1972).
(12) H. L. Wagner, *J. Res. Natl. Bur. Stand., Sect. A*, **76**, 151 (1972).
(13) J. E. Brown and P. H. Verdier, *J. Res. Natl. Bur. Stand., Sect. A*, **76**, 161 (1972).
(14) R. G. Christensen, *J. Res. Natl. Bur. Stand., Sect. A*, **76**, 147 (1972).
(15) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
(16) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(17) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
(18) R. E. Carhart, D. E. Dorman, and J. D. Roberts, unpublished results.
(19) C. J. Carman, A. R. Tarpley, Jr., and J. H. Goldstein, *Macromolecules*, **6**, 719 (1973).
(20) H. L. Wagner and F. L. McCrackin, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **16**, 35 (1975).
(21) H. L. Wagner and C. A. J. Hoeve, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1189 (1973).
(22) E. E. Drott and R. A. Mendelson, *J. Polym. Sci., Part A-2*, **8**, 1361 (1970).
(23) G. Kraus and C. J. Stacy, *J. Polym. Sci., Polym. Symp.* **43**, 329 (1973).
(24) A. H. Willbourn, *J. Polym. Sci.*, **34**, 569 (1959).
(25) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.