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Fine-Branching Structure in High-Pressure, Low-Density Polyethylenes by 50.10-MHz ^{13}C NMR Analysis

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ABSTRACT: The fine-branching structures in high-pressure, low-density polyethylenes (HP-LDPEs) have been studied by 50.10-MHz ^{13}C NMR analysis. When the ^{13}C NMR spectra of some HP-LDPEs are compared with those of some model polymers, it becomes clear that almost all ethyl branches consist of 1,3-paired ethyl groups and ethyl branches attached to quaternary backbone carbons rather than isolated ethyl branches and that there is no appreciable amount of hexyl branches in HP-LDPEs. The formation mechanism of these branches is consistent with a back-biting mechanism. The relative concentrations for various branch types were as follows: methyl, 2-3%; ethyl, 31-37%; propyl, ~2%; butyl, 34-37%; pentyl, 11-13%; longer branches, 14-16%. The fact that the HP-LDPEs studied here have almost the same relative concentrations for various branch types regardless of their different total methyl contents suggests that HP-LDPEs polymerized under ordinary conditions may be expected to have almost the same branching structure. The demonstration of the nonexistence of hexyl branches has almost dispelled the doubt that the contribution of intermediate-length branches (hexyl, heptyl, octyl, etc.) to the resonance for C-3 (third carbon from the branch end) might cause significant error in the estimation of longer chain branches (LCBs) in HP-LDPE by ^{13}C NMR.

Recently, branching in low-density polyethylenes prepared by free radical polymerization at high pressure (HP-LDPE) has been investigated in detail by ^{13}C NMR.[1-8] Of these branches, short-chain branches (SCBs) are mainly related to morphology and solid-state properties while long-chain branches (LCBs) are related to viscoelastic properties. Consequently, branching fine structure is very important for discussion of HP-LDPE properties. With respect to SCBs, the complexity and variability were pointed out by Axelson et al.[7] and Nishioka et al.,[8] but there are still some ambiguities concerning the type of ethyl branches and the existence of hexyl branches.

One purpose of this work is to elucidate the SCB fine structure in a manner consistent with branch formation mechanisms. Concerning quantitative analysis, the distribution of the various kinds of branches has been demonstrated to change so much depending on polymerization conditions[4] that there may not exist a typical HP-LDPE. However, there have been very few studies to establish this point. The reason seems to be that it is difficult to satisfy the quantitative conditions for ^{13}C NMR measurements and still obtain a high S/N ratio spectrum giving accurate integral intensities of the very small peaks (for example, the peaks from ethyl branches). A second purpose is to make it clear whether or not a typical HP-LDPE exists from the results for some HP-LDPEs prepared under different conditions.

Considering LCBs, it has been pointed out[5] that they could be estimated by ^{13}C NMR using the C-3 (third carbon from the branch end) resonance at ca. 32.2 ppm and some related reports were published.[7,9,10] However, this method has not come into general use despite its directness. On the other hand, two indirect solution methods (GPC-[η] and M_w-[η] methods) are conventionally utilized. There seem to be several reasons for this situation.

Table I
Ethylene/1-Olefin Copolymers Studied in This Work

copolymer	CH$_3$/1000 C main-chain atoms[a]
ethylene/1-propene	10.0, 23.5
ethylene/1-butene	8.0, 14.0, 21.0, 33.5
ethylene/1-hexene	7.5, 14.9
ethylene/1-octene	12.0, 15.5

[a] The concentrations were determined by ^{13}C NMR.

(a) First, there is the possibility of the existence of intermediate-length branches (hexyl, heptyl, octyl, etc.); these branches might cause significant error in the estimation of LCBs by the C-3 resonance because LCBs cannot be distinguished from the intermediate-length branches in the C-3 resonance. Recently, Mattice et al.[11] reported that calculations using a rotational isomeric state model for the chain statistics predict that the concentrations of intermediate-length branches would not be negligibly small.

(b) Second, there are some problems in quantitative analysis by ^{13}C NMR when minute peaks are compared with a large main peak: the dynamic range of both the A/D converter and the computer, differences in the spin-lattice relaxation times (T_1), and the nuclear Overhauser effects (NOEs) for various carbons.

(c) Third, there is interference by low molecular weight impurities: low molecular weight impurities also contribute to the C-3 resonance. Therefore, small amounts of impurities cause intolerable error for the estimation of LCBs. As a result, LCB values obtained by ^{13}C NMR and solution methods are not necessarily in good agreement.

Among these, problems b and c could be settled through refinement in the associated hardware and software, choice of the optimum measurement conditions, and sample purification through fractionation. Therefore, as the third purpose, problem a was studied to establish a reliable

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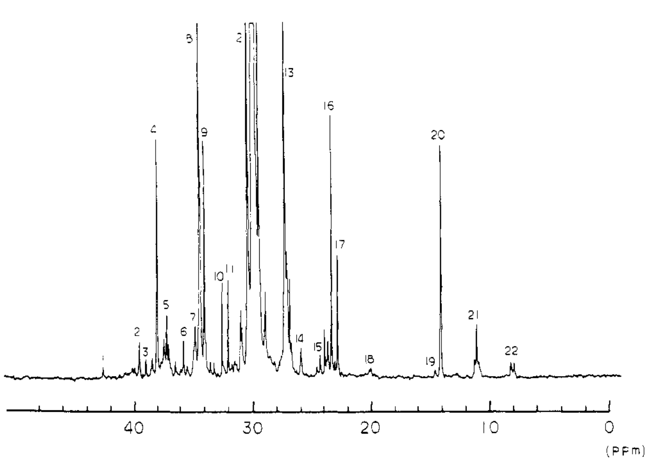

Figure 1. Typical HP-LDPE 50.10-MHz ^{13}C NMR spectrum (sample B) showing peak numbers.

method to estimate the amounts of LCBs in HP-LDPEs.

Experimental Section

The ^{13}C NMR spectra were obtained at 120 °C using a JEOL-FX200 spectrometer equipped with a JEC-980B minicomputer operating with quadrature detection at 50.10 MHz.

The following were studied: some ethylene/1-olefin copolymers prepared by the Ziegler catalyst system shown in Table I, four representative commercial HP-LDPE samples, two HP-LDPE samples with high and low C=O concentrations, and *n*-hexatriacontane (n-$C_{36}H_{74}$) of reagent grade.

About 15% (w/v) of the sample solution in a mixed solvent of 80% (v/v) *o*-dichlorobenzene and 20% (v/v) perdeuteriobenzene was measured using a 10-mm sample tube. The deuterated solvent was used to provide the internal lock signal. A typical measurement was performed for 10–12 h for a copolymer and 40–50 h for a HP-LDPE.

The chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken as 30.00 ppm for Me_4Si. Spectral widths were 8000 Hz with 8192 data points. Chemical shifts were reproducible within 0.01 ppm.

The FIDs were accumulated and Fourier-transformed with a 12-bit A/D converter and a 16-bit minicomputer. The data processing was carried out with double precision (32 bit) to obtain a wider dynamic range.

Pulse widths of 45° (9 μs) and a pulse delay of 2 s were applied. Although complete quantitative requirements were not satisfied,[12] these conditions were adopted to achieve an acceptable S/N ratio.

The infrared spectra were recorded with a Digilab FTS-15C Fourier transform infrared spectrometer.

Results and Discussion

Figure 1 shows a typical 50.10-MHz ^{13}C NMR spectrum of HP-LDPEs. Peak numbers on the spectrum correspond to those in Table II. Figure 2 illustrates the abbreviated expressions for branch types and the numbering system employed here to designate the individual carbons. In the discussion, these carbons are distinguished by the following system.

(a) Isolated branches are described xB_n, where n is the length of the branch and x is the carbon number starting with the methyl group as "1". For example, $1B_4$ designates the methyl in a butyl branch.

(b) For paired branches, lower case subscripts are used for the types and primes for quaternary branch sites. For example, $(1B'_2)_{peq}$ designates the methyl in the ethyl branch attached to the quaternary carbon in the "peq" structure.

(c) Long-chain branches are designated by B_n, where n is greater than 6 carbon atoms.

(d) For the backbone carbons, the greek letters and "br" are used instead of x for methylenes and a branch point, respectively. For the methylene between paired branches, primes to the greek letters are used as shown in Figure 2.

A. Assignments. Ethyl Branches. So far, the no. 2 peak and the no. 21 peak have been assigned to brB_2 and $1B_2$, respectively. However, the splitting observed for the no. 21 peak implies the multiplicity of the ethyl branch structure. In order to investigate the details, the expanded spectra are shown in Figure 3. The expanded spectra for the no. 5 peak are also shown in Figure 4. The comparison of HP-LDPEs with the ethylene/1-butene (E/B) copolymer, which has a high 1-butene concentration, suggests that the large center peak of the no. 21 resonance has the

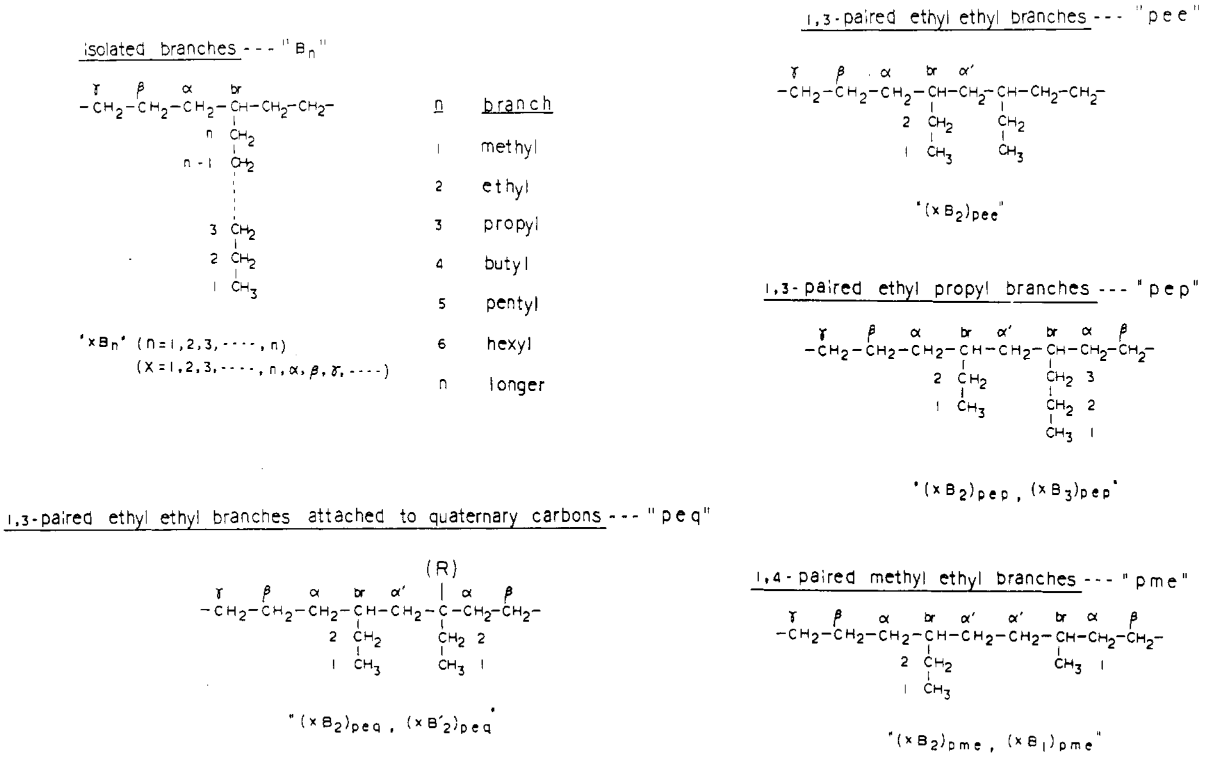

Figure 2. Abbreviated expressions for the branch types and the numbering system for the individual carbons.

Table II
Chemical Shifts and Assignments for the Numbered Peaks in Figure 1

peak no.	chem shift	previous assign-ments	assignments documented in this work	speculative assignments in this work
1	42.86		α-CH_2 to C=O	
2	39.75	brB_2		$(\alpha B'_2)_{peq}$
3	39.19			$(\alpha' B_2)_{pee}$
4	38.23	brB_{4-n}		
5	37.38		$(brB_2)_{pee}$	
6	35.99			$(brB_2)_{peq}$
7	35.00			$(\alpha B_2)_{pee}$
8	34.61	αB_{4-n}		
9	34.22	$4B_4$		
10	32.70	$3B_5$		
11	32.18	$3B_{6-n}$	$3B_n$	
12	30.00	backbone CH_2		
13	27.33	βB_{4-n}		
14	25.99	$\beta B'_2$		$(\beta B'_2)_{peq}$
15	24.36		β-CH_2 to C=O	
16	23.36	$2B_4$		
17[a]	22.88	$2B_5$		
	22.84	$2B_{6-n}$		
18	20.15	$2B_3$		$(2B_3)_{pep}$
	20.04	$1B_1$		$(1B_1)_{pme}$
19	14.59	$1B_3$		$(1B_3)_{pep}$
20[a]	14.08	$1B_4$		
	14.02	$1B_{5-n}$		
21	11.22			$(1B_2)_{peq}$ in (m)
	11.01	$1B_2$	$(1B_2)_{pee}$	$(1B_2)_{pee}$ in (r)
	10.85			$(1B_2)_{peq}$ in (r)
22	8.15			$(1B'_2)_{peq}$ in (m)
	7.87	$1B'_2$		$(1B'_2)_{peq}$ in (r)

[a] The splittings were observed for these peaks in HP-LDPE D.

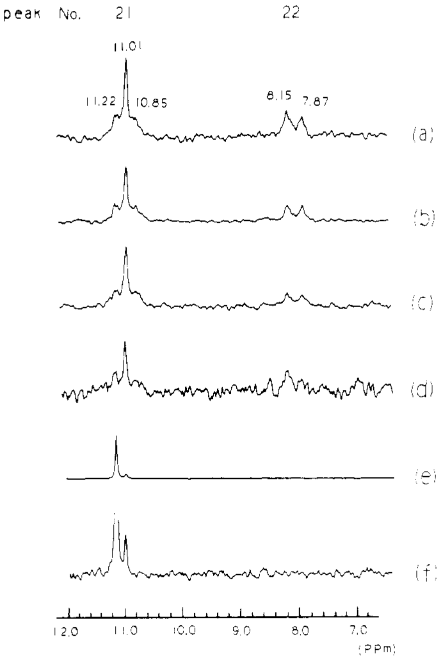

Figure 3. Expanded spectra of the methyl resonance region for the ethyl branches: (a) HP-LDPE A; (b) HP-LDPE B; (c) HP-LDPE C; (d) HP-LDPE D; (e) E/B copolymer (showing the isolated ethyl branch); (f) E/B copolymer (vertically expanded spectrum showing the 1,3-paired ethyl groups)

same chemical shift not as $1B_2$ but as $(1B_2)_{pee}$ and that the no. 5 peak has the same chemical shift as $(brB_2)_{pee}$, as shown in the vertically expanded spectra of the E/B copolymer.

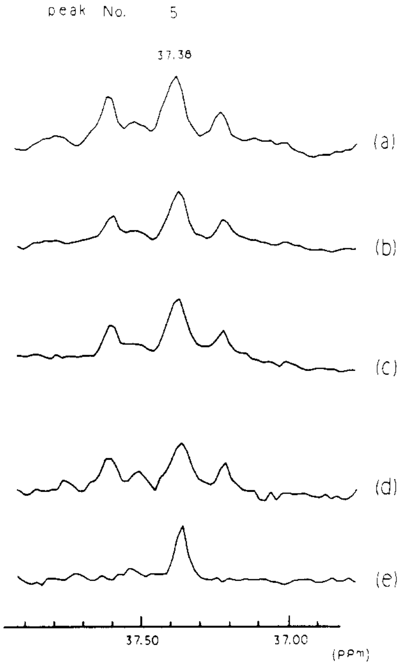

Figure 4. Expanded spectra of the methine resonance region for the 1,3-paired ethyl groups ("pee"): (a) HP-LDPE A; (b) HP-LDPE B; (c) HP-LDPE C; (d) HP-LDPE D; (e) E/B copolymer (showing $(brB_2)_{pee}$).

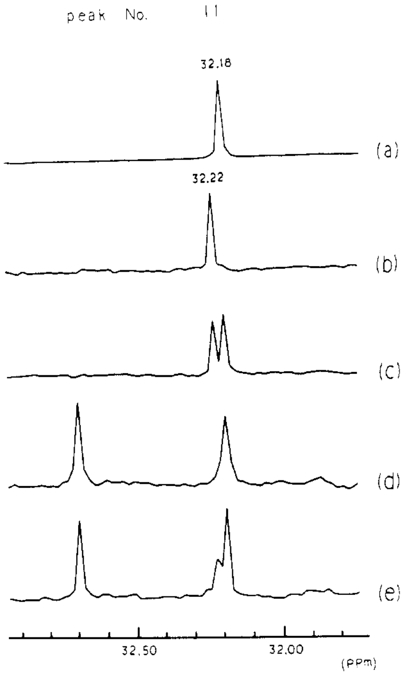

Figure 5. Expanded spectra of the $3B_{5-n}$ resonance region: (a) n-$C_{36}H_{74}$ (longer branch); (b) E/O copolymer (hexyl branch); (c) blend of n-$C_{36}H_{74}$ and E/O copolymer; (d) HP-LDPE B; (e) blend of E/O copolymer and HP-LDPE B.

Hexyl Branches. Recently, Cavagna[13] found that the $5B_6$ and the βB_6 resonances at ca. 27.3 ppm were split at 67.9 MHz in an ethylene/1-octene (E/O) copolymer and pointed out the possibility that B_6 in HP-LDPE could be distinguished from B_n ($n > 6$) by the $5B_6$ resonance. However, in HP-LDPE, the β resonances are extremely large compared with the $5B_6$ resonance. It thus proves to be impossible to analyze B_6 by the $5B_6$ resonance. We then tried to examine the $3B_6$ resonance at ca. 32.2 ppm in detail.

The corresponding resonances from n-hexatriacontane (HTC), E/O copolymer, their blend, HP-LDPE B, and the blend of HP-LDPE B and E/O copolymer are shown in Figure 5. The very clear splitting suggests that B_6 should be readily discriminated from B_n ($n > 6$) in the $3B_6$ reso-

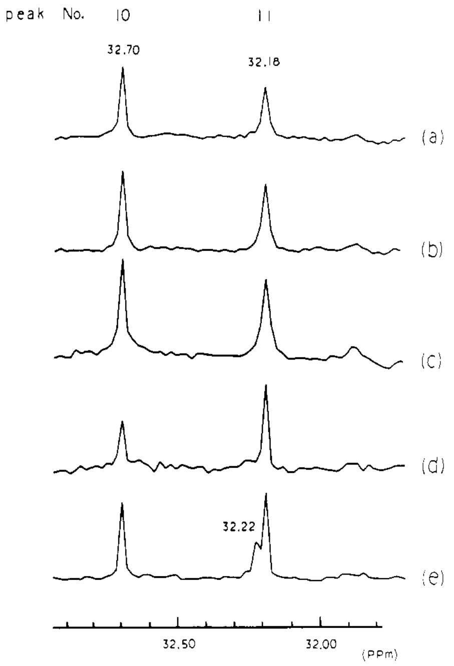

Figure 6. Expanded spectra of the $3B_{5-n}$ resonance region: (a) HP-LDPE A; (b) HP-LDPE B; (c) HP-LDPE C; (d) HP-LDPE D; (e) blend of HP-LDPE B and E/O copolymer.

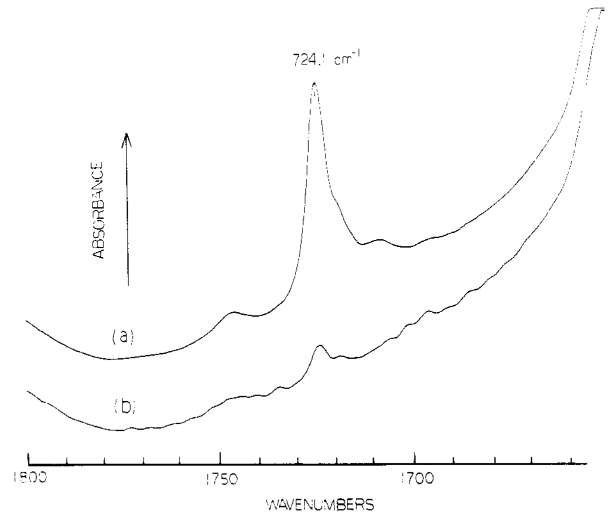

Figure 7. FT-IR spectra of C=O region for two HP-LDPEs: (a) HP-LDPE E; (b) HP-LDPE F.

nance. Figure 6 shows these resonances of HP-LDPEs along with those for the blend of HP-LDPE B and E/O copolymer as reference. From the comparison, we conclude that there is no appreciable amount of hexyl branches in HP-LDPEs.

C=O Groups. From FT-IR results, shown in Figure 7, the main C=O type in HP-LDPEs seems to be ketone at 1724.1 cm^{-1}. According to the report by Cheng et al.,[6] α-CH_2 and β-CH_2 to C=O (ketone) are expected to have peaks at about 43 and 24 ppm, respectively. Now, in order to assign the signals from ketone C=O, two HP-LDPEs (E and F) having very different C=O concentrations, as shown in Figure 7, were investigated by ^{13}C NMR. Figure 8 shows the spectra of the α-CH_2 and β-CH_2 regions. From these results, the peaks at 42.86 ppm (no. 1) and 24.36 ppm (no. 15) can be assigned to α-CH_2 and β-CH_2, respectively.

The assignments documented here are listed in Table II.

B. Speculative Assignments from Branch Formation Mechanisms. Formation of Butyl and Pentyl Branches. The single back-biting mechanism[14] predicts the formation of butyl branches predominantly. However, the formation of pentyl branches by the same mechanism is also expected. Thus, in the back-biting mechanism, both six- and seven-membered-ring intermediates are most likely formed, while the fact that hexyl branches are missing in HP-LDPEs suggests that the eight-membered-ring intermediate is rare.

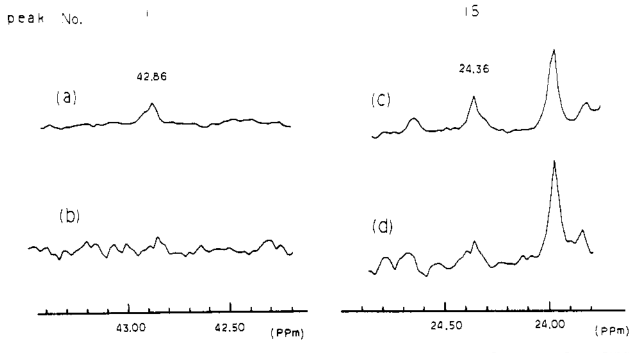

Figure 8. Expanded spectra of the regions of α-CH_2 and β-CH_2 to C=O groups for two HP-LDPEs: (a) and (c), HP-LDPE E; (b) and (d), HP-LDPE F.

Formation of Ethyl, Methyl, and Propyl Branches. By the double-back-biting mechanism[15] through a six-membered-ring intermediate (6MI) and a seven-membered-ring intermediate (7MI), several kinds of paired branches are expected to be formed:

6MI → butyl → 1 monomer → 6MI → "pee"

(2-Ethylhexyl branches are also possible by this scheme, but as mentioned later, those branches are estimated to be minor compared with "pee" from the theoretical molecular orbital calculation[16]

6MI → butyl → 1 monomer → 7MI → "pme"

7MI → pentyl → 1 monomer → 6MI → "pep"

7MI → pentyl → 1 monomer → 7MI →
1,4-paired ethyl ethyl branches

(Formation of 1,4-paired ethyl ethyl branches is expected, but the amounts are expected to be very small).

The triple back-biting mechanism through 6MIs could form "peq"-type branches. On the other hand, the intermolecular proton transfer attached to the tertiary carbons in "pee" could also form "peq".

6MI → butyl → 1 monomer → 6MI → "pee" →
1 monomer (→1 monomer) → 6MI →
"peq" or peq-like structures

and

6MI → butyl → 1 monomer → 6MI → "pee" →
monomers → intermolecular proton transfer → "peq"

Speculative Assignments for Ethyl, Methyl, and Propyl Branches. The assignment of the no. 7 peak to $(\alpha B_2)_{pee}$ and the chemical shift of the no. 3 peak (39.19 ppm) assigned to $(\alpha' B_2)_{pee}$ imply the racemic configuration for two ethyl groups as pointed out by Hsieh et al.[17] As a result, the major fraction of the ethyl branches consists of "pee" in a racemic configuration. The reason the racemic configuration is preferable may be the effect of the steric repulsive interaction between two ethyl groups.

The two shoulder peaks for the no. 21 peak are assigned mainly to $(1B_2)_{peq}$, as discussed in the following. The no. 22 peak at ca. 8 ppm, which is assigned to the methyl carbons in ethyl branches attached to quaternary backbone carbons by Axelson et al.,[7] splits into a doublet-like peak, which implies more complex structures on the ethyl branches attached to quaternary carbons. Since "pee"

Table III
^{13}C NMR Quantitative Results with Different Pulse Delays for an Ethylene/1-Hexene Copolymer

total CH_3/1000 C	pulse delay 2 s	pulse delay 15 s
first run	15.1	14.9
second run	14.9	14.8

Table IV
Calibration Factors for Various Carbons Compared to the β-CH_2 in Ethylene/1-Olefin Copolymers Determined with 2-s Pulse Delays

branch type	integral intensity ratios to β-CH_2: $3B_n$	$2B_n$	$1B_n$
$n = 1$			0.90
$n = 2$		0.95	0.84
$n = 3$			0.83[a]
$n = 4$		0.90	0.81
$n = 5$	0.90[a]	0.81[a]	0.72[a]
$n = n$	0.80	0.72	0.67

[a] Tentatively determined from other results but would be considered as reasonable values and not bring intolerable errors.

branches are the predominant type of ethyl branch and the chemical shift of the no. 22 peak is reasonable for ethyl branches attached to quaternary carbons, the doublet-like peak should be assigned to $(1B'_2)_{peq}$. For poly(1-butene), Mauzac et al.[18] reported that the racemic configuration of two ethyl groups gives higher field shift for the methyl resonance than the meso configuration. From this result, for the doublet-like peak from $(1B'_2)_{peq}$, the methyl in the meso and the racemic configurations for two ethyl groups is expected to give the lower and the higher field peaks, respectively. The reason the amounts of the meso and racemic configurations are comparable in "peq" in spite of the predominance of the racemic structure in "pee" is considered to be that the steric interactions between not only ethyl groups but also ethyl and alkyl should be possible in "peq". Therefore, the population difference between the meso and racemic structures is reasonably expected to be smaller in "peq" than "pee". Figure 3 shows one more important fact, namely, that the intensities of the two peaks from $(1B'_2)_{peq}$ are similar to those of the shoulder peaks of the no. 21 peak, so the lower field shoulder peak could be assigned mainly to $(1B_2)_{peq}$ in the meso configuration and the higher field in the racemic configuration.

Concerning the amount of 2-ethylhexyl branches, Kita et al.[16] obtained the result from molecular orbital calculations that the ethyl branches in "pee" should exist about 2 times more than in 2-ethylhexyl branches in the case of $(B_2/B_4) = 1$. Therefore, the 2-ethylhexyl branch is expected to be minor if it exists at all. However, the possibility of its existence cannot be denied, so there may be a minor contribution of 2-ethylhexyl to ethyl branches.

The existence of propyl and methyl branches was reported by Axelson et al.[7] for the propylene copolymerized HP-LDPEs. The HP-LDPEs studied here are not copolymers, but signals from propyl and methyl branches were observed as the no. 19 and the no. 18 (broad) peaks, respectively. According to the formation mechanism mentioned above, the no. 19 peak might be assigned to $(1B_3)_{pep}$ and the no. 18 peak to $(2B_3)_{pep}$ and $(1B_1)_{pme}$. These speculative assignments are listed in Table II.

C. Quantitative Analysis of Branches. Short-Chain Branches. The quantitative analysis was carried out according to the following procedures.

(a) Determination of the branch concentrations for ethylene/1-olefin copolymers by ^{13}C NMR. The ^{13}C NMR measurement conditions used here do not satisfy the complete quantitative conditions pointed out by Axelson et al.,[12] but the integral intensity ratio of β-CH_2 carbons to the main-CH_2 backbone carbons is expected to give nearly correct branch concentrations because the T_1 values of these two kinds of carbons are not expected to be very different. This is confirmed by our experimental results showing that the quantitative results by the ^{13}C NMR measurements with different pulse delays in Table III are in good agreement.

Full NOEs are also expected for the CH_2 carbons in the polymer main chain as observed in a HP-LDPE[12] because the T_1 values are shorter than 2 s. Therefore, the branch concentrations determined from the integral intensity ratios of β-CH_2 to main-CH_2 for a series of ethylene/1-olefin copolymers should be accurate even if the pulse delay is 2 s.

(b) The calibration factors for various carbons compared to the β-CH_2 in ethylene/1-olefin copolymers were determined by using 2-s pulse delays. In order to get the calibration factors for the branch concentrations, the integral intensity ratios of the carbons in the branches to β-CH_2 were determined from the ^{13}C NMR results for various copolymers, as shown in Table IV (2-s pulse delay measurements).

(c) Determination of the total branch concentrations and the branch type distribution in HP-LDPEs. With the values from (b), the nearly correct total branch concentration and branch distribution results shown in Table V could be obtained from the ^{13}C NMR measurements using a 2-s pulse delay for HP-LDPEs. The influences from T_1 and NOEs can be compensated by this calibration method.

As a result, the great differences in polymerization conditions, which give total branch concentrations between 6.7 and 24.9 (per 1000 carbon atoms), do not have any appreciable effect on the SCB distribution in HP-LDPEs.

Table V
Branch Concentrations and Distributions Determined by ^{13}C NMR Calibration Method

sample	total CH_3/1000 C	B_1	B_2	B'_2	B_3	B_4	B_5	B_n
HP-LDPE A	19.9	0.4	4.4	2.0	0.3	7.4	2.6	2.8
(rel concn, %)		(2)	(22)	(10)	(2)	(37)	(13)	(14)
			(32)					
HP-LDPE B	24.9	0.5	6.2	3.0	0.5	8.5	2.7	3.5
(rel concn, %)		(2)	(25)	(12)	(2)	(34)	(11)	(14)
			(37)					
HP-LDPE C	17.3	0.5	3.8	1.6	0.4	6.4	2.2	2.4
(rel concn, %)		(3)	(22)	(9)	(2)	(37)	(13)	(14)
			(31)					
HP-LDPE D	6.7	0.1	1.6	0.7	0.2	2.4	0.7	1.0
(rel concn, %)		(2)	(23)	(11)	(3)	(35)	(11)	(15)
			(34)					

Long-Chain Branches. Solution methods have been employed to estimate LCBs.[19] However, they are indirect methods and have the following problems:

(a) Solution viscosity is related to molecular structure by $g^{\epsilon} = [\eta]_b/[\eta]_l$,[20] where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosities of branched and linear molecules at the same M_w, respectively, g is the ratio of the mean-square radius of gyration of the branched molecules to that of the linear molecules, and ϵ is a variable parameter ranging from 0.5 to 1.5. For example, ϵ is 0.5 for star-shaped molecules[21] and 1.5 for linear molecules.[22] However, we usually do not have any data on the shape of HP-LDPE, so the estimation of the ϵ value is an important problem.

(b) The amounts of LCBs per M_w unit, λ, were related to the ratio of the mean-square radii of gyration, g, by the following equations:[23]

$$g = \left[\left(1 + \frac{\lambda M}{7}\right)^{1/2} + \frac{4}{9\pi}\lambda M\right]^{-1/2} \tag{1}$$

or

$$g = \frac{6}{\lambda M_w} \times \left[\frac{1}{2}\,\frac{(2 + \lambda M_w)^{1/2}}{(\lambda M_w)^{1/2}} \ln \frac{(2 + \lambda M_w)^{1/2} + (\lambda M_w)^{1/2}}{(2 + \lambda M_w)^{1/2} - (\lambda M_w)^{1/2}} - 1\right] \tag{2}$$

where eq 1 is for monodisperse molecules and eq 2 is for polydisperse molecules. The selection between the equations is another important problem. According to Drott et al.,[19b] the agreement between the calculated and observed log $[\eta]$ vs. log M_w curve for GPC data was good in the case of $\epsilon = 1.5$ with eq 1, or $\epsilon = 0.5$ with eq 2. Even the GPC fraction may be considered as polydispersed molecules.

(c) The dependence of λ on M_w is the third problem. In solution methods, it is assumed that there is no dependence. Recently, Foster[9] obtained good agreement between the ^{13}C NMR and the solution methods using eq 1 for GPC–$[\eta]$ and eq 2 for M_w–$[\eta]$ methods with $\epsilon = 0.75$. However, in this case, this third problem is neglected.

In our work, it was confirmed that no appreciable amount of hexyl branches exists in HP-LDPEs. Therefore, ^{13}C NMR can be employed as a direct method to estimate LCBs. This method should be superior to solution methods. However, as mentioned before, the ^{13}C NMR method has a shortcoming in the presence of low molecular weight impurities. Therefore, careful purification of the sample has to be employed for routine analysis.

Practically, LCBs should be estimated by both ^{13}C NMR and solution methods for the molecular weight fractionated HP-LDPEs. In this case, the ^{13}C NMR data should have higher reliability. Thus, the problems of the solution methods can be solved by the NMR data. The solution methods can then be employed for routine analysis.

Conclusion

The preceding results and discussion lead to the following conclusions:

(1) In HP-LDPEs, the concentration of isolated ethyl branches is very small, and almost all ethyl branches are 1,3-paired ethyl groups and ethyl branches attached to quaternary backbone carbons.

(2) There is no appreciable amount of *n*-hexyl branches in a HP-LDPE.

(3) For HP-LDPEs having 6.7–24.9 methyls per 1000 carbons, the relative concentrations for various branch types are almost constant: methyl, 2–3%; ethyl, 31–37%; propyl, ~2%; butyl, 34–37%; pentyl, 11–13%; longer, 14–16%. Thus, a typical HP-LDPE seems to exist.

(4) A better method for estimating LCBs is the ^{13}C NMR method in the sense that it is more direct than conventional solution methods. However, once the problems of the solution methods are solved with the NMR method, the solution method seems to be more suitable for routine analysis.

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Registry No. (Ethylene)·(1-propene) (copolymer), 9010-79-1; (ethylene)·(1-butene) (copolymer), 25087-34-7; (ethylene)·(1-hexene) (copolymer), 25213-02-9; (ethylene)·(1-octene) (copolymer), 26221-73-8; polyethylene, 9002-88-4; *n*-$C_{36}H_{74}$, 630-06-8.

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