Sizes of Long Branches in Low Density Polyethylenes

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Synopsis

^{13}C-NMR spectroscopy and size exclusion chromatography have been used to determine the mean length of long branches in a number of high pressure process low density polyethylenes (LDPEs). ^{13}C-NMR analyses count all branches longer than C5 as "long." The polyethylenes studied all had 2–3 long branches per 1000 carbons. The mean branch length was of the order of 200–300 carbons in length. The size of long branches increases with increasing $\bar{M}_n$ of the parent polyethylene, but the size of long branches relative to the overall macromolecular size decreases with increasing $\bar{M}_n$. The mean molecular weight of the long branches is some 5–20% of $\bar{M}_n$ of the particular polymer and decreases as $\bar{M}_n$ increases. Both autoclave and tubular reactor products were studied.

INTRODUCTION

Considerable efforts have been directed towards the determination of long chain branch (LCB) concentrations in low density polyethylenes (LDPEs) by both size exclusion chromatography (SEC)[1-3] and by ^{13}C nuclear magnetic resonance (NMR) spectroscopy.[4-7] Long chain branches are believed to be important structural features in LDPE since they influence rheological and visoelastic properties.[8,9] Intuitively, it might be expected that the length and architecture of the LCBs would be important, along with their concentration. Little progress has been made in the determination of LCB lengths in LDPEs, or other synthetic polymers, because of analytical difficulties.

In general, LCBs have been accepted to be comparable in length to the main chain of the polyethylene molecule.[8] It is evident, however, that the LCB length (and thus LCB concentration) will differ somewhat according to the method by which it is being measured. For instance, the minimum length of a straight chain alkane branch detected as a long chain branch by SEC measurements is greater than six and less than 12 carbons,[1,10] while branches six carbons and longer are considered to be long when measured by ^{13}C-NMR spectroscopy.[11] The minimum length required for branches to be considered "long" by rheological measurements has not been established. It may in fact depend on the particular rheological property that is being considered.

In this report, we determine a number-average length for the long chain branches in high pressure, low density polyethylenes. This is possible by a combined knowledge of the number-average molecular weight of the polymer,

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$\overline{M}_n$, from SEC, and the LCB concentration as determined by ^{13}C-NMR spectroscopy.

EXPERIMENTAL

The low density polyethylene samples used for this study are all commercial polyethylene homopolymers, except for one sample which is National Bureau of Standards, Standard Reference Material 1476 (NBS 1476). Samples A, B, D, E, and G are autoclave reactor products while the remaining samples are tubular reactor products.

The ^{13}C-NMR spectra were obtained with a Bruker AM-250 spectrometer at 62.5 MHz with 10 mm o.d. tubes and approximately 50–60% (w/w) sample concentrations in 1,2,4-trichlorobenzene (TCB). The spectra were acquired with no nuclear Overhauser effect, 35-s pulse delay and typically between 2000 and 2500 scans. The samples were heated at about 155°C for 0.5 h prior to their analyses in the NMR spectrometer at 100°C. This procedure has been shown to increase both spectral resolution and signal sensitivity while simultaneously minimizing sample degradation during data acquisition. Full details of this method and other NMR experimental details have been described elsewhere.[4]

Following NMR analyses, the samples were dried under high vacuum for 24 h to remove the solvent. Molecular weights were then determined by SEC in TCB solutions using a low-angle laser light scattering detector. Details of the molecular weight determinations have been described elsewhere.[12]

RESULTS

A ^{13}C-NMR spectrum acquired under proper experimental conditions can provide detailed quantitative information on the molecular architecture of LDPE, including the concentrations of both long and short chain branches. The branch concentrations can be determined by accurate area measurements of unique resonance lines in the ^{13}C-NMR spectrum that correspond to a specific branch type.[4–7]

Five different branch types can be identified and accurately measured from the ^{13}C-NMR spectrum of LDPE. These include long (> C6), amyl, butyl, and two types of ethyl branches: one originating from a trifunctional and the other from a tetrafunctional branch site. Methyl branches can also be detected, if they occur. The two ethyl branch types will be designated here as ethyl (3°) and ethyl (4°), respectively. The various branch concentrations can be measured to within ±7%, in replicate determinations.

Table I lists the molecular weight characteristics of the polyethylenes studied here. Number-average molecular weights range from 14,000 to 60,000. Table II gives branch concentrations per 1000 carbons, which is the way ^{13}C-NMR analyses are usually presented. Sample H is the only polyethylene that contained methyl branches. This may reflect copolymerization with propylene. Table III lists branch concentrations per number average molecule, calculated in an obvious fashion from the data in Tables I and II. The relative fractions of each branch type are reported in Table IV. These results are similar to others that have been reported.

TABLE I
Molecular Weights of Low Density Polyethylenes Measured by SEC–LALLS

Sample	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_z \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$SD(N)^a \times 10^{-3}$	$SD(W)^a \times 10^{-4}$	SKEW(N)	SKEW(W)
A	14.1	16.1	7.3	11.4	45.6	30.4	16.7	3.8
B	18.7	16.8	7.3	9.0	36.3	21.5	12.8	8.2
C	20.1	13.0	4.9	6.5	45.5	21.4	11.2	4.5
NBS 1476	26.2	10.3	33.4	3.9	44.9	57.8	97.6	8.1
D	28.4	17.6	11.3	6.2	64.7	41.0	19.5	4.1
E	31.4	24.6	6.5	7.8	82.2	31.5	7.8	2.2
F	33.4	17.7	7.0	5.3	64.2	33.5	10.8	12.9
G	42.9	17.5	7.1	4.1	75.4	30.7	10.6	3.4
H	60.4	14.5	3.7	2.4	132.1	29.5	5.8	8.8

[a]Standard deviation of number (N) and weight (W) distributions.[16]
[b]Skewness of number (N) and weight (W) distributions.[16]

TABLE II
Branch Concentrations, per 1000 carbons,
in Low Density Polyethylenes

Sample	LCB	Amyl	Butyl	Ethyl (3°)[a]	Ethyl (4°)[b]	Total
A	2.9	2.0	9.3	4.8	2.3	21.3
B	2.8	2.0	9.6	5.8	1.7	21.9
C	2.6	2.2	8.7	4.6	2.1	20.2
NBS 1476	2.4	2.2	6.1	3.9	c	14.6
D	3.0	1.8	6.9	2.6	1.9	16.2
E	2.4	1.7	9.0	5.2	2.6	20.9
F	2.7	1.6	9.7	4.4	2.7	21.1
G	2.4	1.8	7.8	4.6	1.6	18.2
H	2.6	1.6	8.5	3.7	1.8	20.2[d]

[a](3°C) = at trifunctional branch site.
[b](4°C) = at tetrafunctional branch site.
[c]Not measured.
[d]Sample contains 1.9 methyls per 1000 carbons.

TABLE III
Branch Concentrations per Number Average Molecule in Low Density Polyethylenes

Sample	LCB	Amyl	Butyl	Ethyl (3°)	Ethyl (4°)	Total
A	2.9	2.0	9.3	4.8	2.3	21.3
B	3.8	2.6	12.8	7.8	2.3	29.3
C	3.7	3.2	12.5	6.7	3.0	29.1
NBS 1476	4.5	4.1	11.3	7.3	a	27.2
D	6.1	3.7	14.1	5.3	3.9	33.1
E	5.3	3.8	20.1	11.7	5.7	46.6
F	6.4	3.8	23.1	10.5	6.3	50.1
G	7.3	5.5	23.9	14.1	4.8	55.6
H[b]	11.2	7.0	36.5	16.1	7.6	87.1

[a]Not measured.
[b]Sample contains 8.7 methyls per number average molecule.

TABLE IV
Branch Concentrations Expressed as Relative Percent of Total Branches

Sample	LCB	Amyl	Butyl	Ethyl (3°)	Ethyl (4°)
A	13.6	9.4	43.7	22.5	10.8
B	13.0	8.9	43.7	26.6	7.9
C	12.8	11.0	43.0	23.0	10.3
NBS 1476	16.5	15.1	41.5	26.8	a
D	18.4	11.2	42.6	16.0	11.8
E	11.4	8.2	43.1	25.1	12.2
F	12.8	7.6	46.1	21.0	12.6
G	13.1	9.9	43.0	25.4	8.6
H[b]	12.9	8.0	41.9	18.5	8.7

[a]Not detected.
[b]Remaining 10% of branches are methyls.

Results from Tables II–IV are consistent with the proposed backbiting,[13] double backbiting,[14] and triple backbiting[5] mechanisms which are presumed to be responsible for short chain branch formation. These branching mechanisms lead to a high butyl branch content and the formation of two types of ethyl branches. The long chain branches, which are formed by intermolecular H-atom abstractions,[15] vary from 2 to 3 per 1000 carbons in these polymers. This corresponds to 11–18% of the total branch concentration.

Determination of the mean LCB length requires information on the concentrations of the various branch types (Table II) and M_n of the polymer (Table I). The procedure is as follows: Let C_T = the total number of carbons in one mole of the sample. This is easily obtained from $\overline{M}_n$, since

$$C_T = \overline{M}_n/14 \tag{1}$$

to a good enough approximation (assuming that the polymer consists effectively of methylene units). One must then determine the total number of carbons that belong to short chain branches, C_{SCB}. This is given by the following equation:

$$C_{SCB} = C_{BS} + 5[\text{amyl}] + 4[\text{butyl}] + 2[\text{ethyl }(3°)] + 2[\text{ethyl }(4°)] \tag{2}$$

where the square brackets represent the concentration of the appropriate branch type per molecule, given in Table III, and C_{BS} is the total number of branch sites in the molecule. The difference between C_T and C_{SCB} is the number of carbons that pertain to the long chain branches and the two chain ends (which are assumed to be "long"); thus

$$C_{LCB} = C_T - C_{SCB} \tag{3}$$

where C_{LCB} represents the total number of long chain branch carbons. Finally, $\overline{L}_n$, average number of carbons in a LCB, is given by

$$\overline{L}_n = \frac{C_{LCB}}{[\text{LCB}] + 2} \tag{4}$$

Here the denominator is the sum of the long chain branch content per molecule plus the two chain ends. The number average molecular weight of long branches, designated as M_L, can easily be determined from

$$\overline{M}_L = 14\overline{L}_n \tag{5}$$

Table V lists the $\overline{L}_n$ and $\overline{M}_L$ values for the LDPEs. It shows that although the LCB content, expressed as LCB per 1000 carbons, is relatively constant over a wide molecular weight range (Table II), $\overline{L}_n$ (and therefore $\overline{M}_L$) increases with $\overline{M}_n$ of the polyethylene. Figure 1 is a plot of $\overline{L}_n$ vs. C_T. Even though there is some data scattering (coefficient of correlation = 0.86), the increase in $\overline{L}_n$ with increasing size of the polymer is clear.

It is also interesting that the ratio of the mean long branch size to the number-average molecular weight of the polymer decreases with increasing $\overline{M}_n$. This is shown in Figure 2.

In the samples examined, the branching frequency is relatively uniform regardless of the molecular weight or the breadth of the molecular weight distribution. The polymers do, however, differ in the mean length of long branches. The higher molecular weight polyethylenes have higher long chain

TABLE V
Calculated Number-Average Long Chain Lengths, $\bar{L}_n$ (in Terms of Number of Carbons)
and the Corresponding Number Average Molecular Weights, $\bar{M}_L$, of Long Branches[a]

Sample	LCB[b]	LCB[c]	$\bar{M}_n \times 10^{-3}$	$C_T \times 10^{-2}$	$\bar{L}_n$	$\bar{M}_L \times 10^{-2}$
A	2.9	2.9	14.1	10.1	189	26
B	2.8	3.8	18.7	13.4	213	30
C	2.6	3.7	20.1	14.4	232	32
NBS 1476	2.4	4.5	26.2	18.7	273	38
D	3.0	6.1	28.4	20.3	235	33
E	2.4	5.3	31.4	22.4	283	40
F	2.7	6.4	33.4	23.9	262	37
G	2.4	7.3	42.9	30.6	306	43
H	2.6	11.2	60.4	43.1	304	43

[a] C_T is the total number of carbons in the LDPE molecule.
[b] Long chain branches per 1000 carbons.
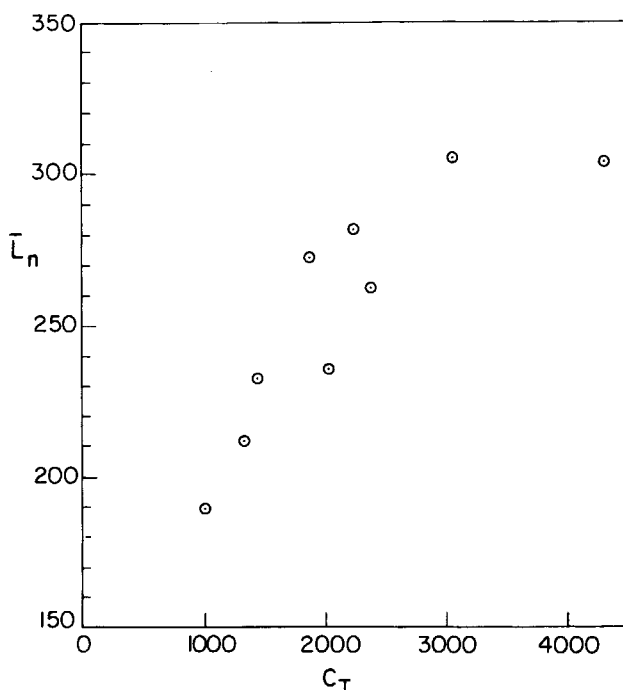[c] Long chain branches per number average molecule.

Fig. 1. Number-average long chain branch length $\bar{L}_n$ as a function of the total number of carbons in the LDPE molecule, C_T.

branch lengths, on the average. This is to be expected, since the polymerization conditions (e.g., higher ethylene pressures) that promote the growth of larger molecules will also favor the formation of longer "long" branches.

It seems that long branches in LDPE are not the same size as the parent molecule. In the polymers studied here, the highest molecular weight sample has 4 times as great an $\bar{M}_n$ as the lowest molecular weight material. The mean branch length in the former polyethylene is, however, less than double that of the latter LDPE.
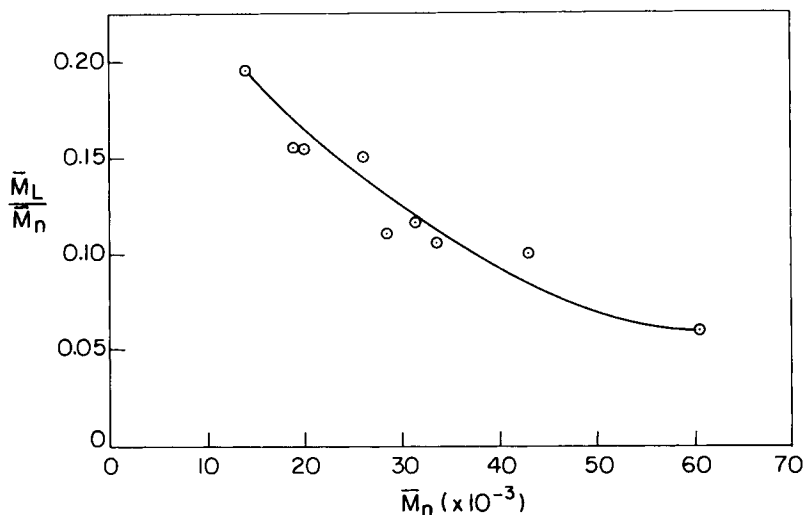
Fig. 2.   Ratio of mean size of long branches $(\overline{M}_L)$ to $\overline{M}_n$ vs. $\overline{M}_n$.

As mentioned, ^{13}C-NMR analyses count all branches longer than C5 as "long," while the minimum branch length to be measured as "long" in SEC determinations lies between C6 and C12. The mean long branch lengths that actually exist in LDPEs appear to be of the order of 200–300 carbons in length. These analytical techniques certainly do not underestimate the frequency of long branching in polyethylenes. It remains to be determined whether they measure long branches that are too short to have much effect on properties like melt rheology.

References

1. A. Rudin, V. Grinshpun, and K. F. O'Driscoll, *J. Liq. Chromatogr.*, **7**, 1809 (1984).
2. V. Grinshpun, A. Rudin, and D. Potter, *Polym. Bull.*, **13**, 71 (1985).
3. D. E. Axelson and W. C. Knapp, *J. Appl. Polym. Sci.*, **25**, 119 (1980).
4. D. C. Bugada and A. Rudin, *J. Polym. Sci., Polym. Phys. Ed.*, (1986) paper submitted.
5. T. Usami and S. Takayama, *Macromolecules*, **17**, 1756 (1984).
6. J. C. Randall, *Am. Chem. Soc. Symp. Ser.*, **142**, 93 (1980).
7. D. E. Axelson, G. C. Levy, and L. Mandelkern, *Macromolecules*, **12**, 41 (1979).
8. P. A. Small, *Adv. Polym. Sci.*, **18**, 1 (1975).
9. L. Wild, R. Ranganath, and D. C. Knobeloch, *Polym. Eng. Sci.*, **16**, 811 (1976).
10. V. Grinshpun, A. Rudin, K. E. Russell, and M. V. Scammell, *J. Polym. Sci., Polym. Phys. Ed.*, (1986), **24**, 1171 (1986).
11. F. A. Bovey, F. C. Schilling, F. L. McCrackin, and H. L. Wagner, *Macromolecules*, **9**, 76 (1976).
12. V. Grinshpun, K. F. O'Driscoll, and A. Rudin, *Am. Chem. Soc. Symp. Ser.*, **245**, 273 (1984).
13. M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).
14. A. H. Willbourn, *J. Polym. Sci.*, **34**, 569 (1959).
15. P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937); **69**, 2893 (1947).
16. A. Rudin, J. Chem. Ed., **46**, 595 (1969).