Polymer Bulletin 16, 445–452 (1986)

Polymer Bulletin

# Determination of polyethylene branching through computerized $^{13}C$ NMR analysis

**H.N. Cheng**

Hercules Incorporated Research Center, Wilmington, DE 19894, USA

Summary. Computerized analysis has been devised to maximize the information content available from the $^{13}C$ NMR spectrum of low-density polyethylene. Both long and short chain branches can be readily quantified. Two types of long chain branching have been identified, from which the number-average molecular weight and the average size of the long chain segments can be determined. The mathematical expressions relating these parameters have also been derived.

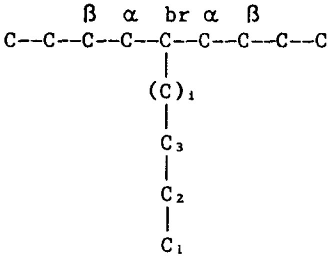
## Introduction

In low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), the type and the degree of branching strongly affect the end-use properties. Studies of branching have been extensively carried out by $^{13}C$ NMR (1-13,24). A major point of repeated investigations is the accuracy of the NMR determination (6,9). Recent studies indicate that extra care is needed in setting the NMR experimental parameters in order to obtain precise data (9).

In earlier work (14-20), a computerized NMR analysis with built-in optimization procedures has been shown to be useful for a number of copolymer systems. This is called the FITCO method and is particularly useful for spectra with overlapping resonances (18-20). This method can also be used to measure polyethylene branching. In this way, all the observable NMR resonances are included in the computation, thereby providing more accurate branching information. In addition, the computerized analysis simplifies the calculations and speeds up the analysis.

## Methodology

A $^{13}C$ NMR spectrum of LDPE is shown in Figure 1. Apart from the major $(CH_2)_n$ line in the middle of the spectrum (at 29.9 ppm), there are many smaller lines on both sides, corresponding to various forms of branch structures. The terminology for branching follows that of earlier workers (1-5):



$$\begin{array}{c} \beta\quad \alpha\quad br\quad \alpha\quad \beta \\ C-C-C-C-C-C-C-C-C \\ | \\ (C)_i \\ | \\ C_3 \\ | \\ C_2 \\ | \\ C_1 \end{array}$$

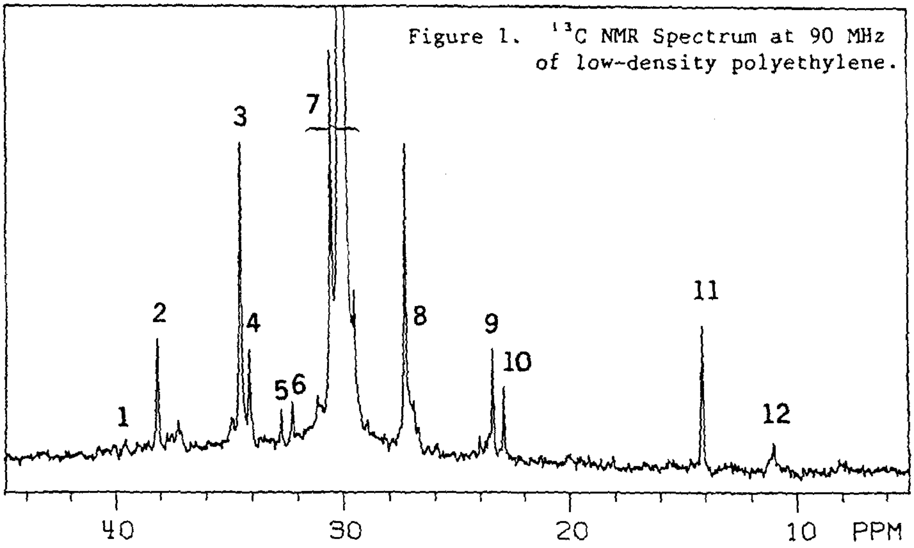


Figure 1. $^{13}C$ NMR Spectrum at 90 MHz of low-density polyethylene.

Table 1. $^{13}C$ NMR Peaks and Assignments for LDPE

| Peak # | Shift (ppm) | Assignments | Terms |
|---|---|---|---|
| 1 | 39.9 | Et-br | E |
| 2 | 38.2 | Bu-br,Am-br,L-br | B+A+$L_1$ |
| 3 | 34.7 | Bu-α,Am-α,L-α;<br>Am-$C_5$ | 2B+3A+3$L_1$ |
| 4 | 34.1 | Et-α;<br>Bu-$C_4$ | 2E+B |
| (4a* | 33.9 | V-α | V) |
| 5 | 32.8 | Am-$C_3$ | A |
| 6 | 32.2 | L-$C_3$ | $L_2$ |
| 7 | 29.9 | $(CH_2)_n$; Bu-$C_3$ | 1000-10A-8B-7E-7$L_1$-3$L_2$-V |
| 8a | 27.3 | Am-$C_4$ | |
| 8b | 27.3 | Et-β,Bu-β,Am-β,L-β | 3E+2B+3A+3$L_1$ |
| 8c | 26.9 | Et-$C_2$ | |
| 9 | 23.3 | Bu-$C_3$ | B |
| 10 | 22.8 | Am-$C_2$,L-$C_2$ | A+$L_2$ |
| 11 | 14.0 | Bu-$CH_3$,Am-$CH_3$,L-$CH_3$ | B+A+$L_2$ |
| 12 | 11.7 | Et-$CH_3$ | E |

* Peak 4a is only present for polymers made from chromium catalysts.

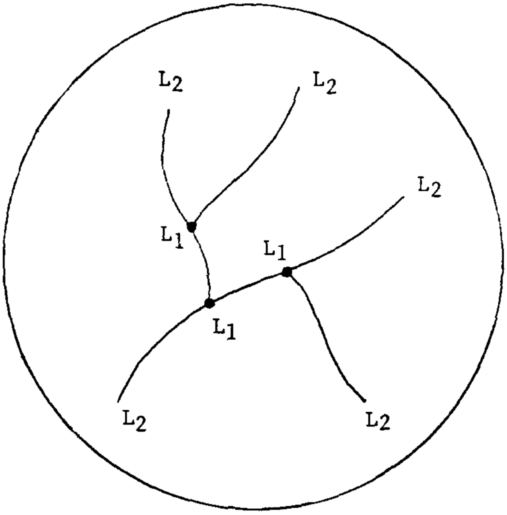


Figure 2. Example of branched polymer:
$L_1$ = Long chain branch points = 3
$L_2$ = Long chain ends = 5
S = Number of segments = 7

In general,
$S = L_2+2 = L_1+4$
$L_2 = L_1+2$

The $^{13}C$ NMR spectral assignments for LDPE have been made previously (1-8). These are summarized in Table 1. In the table, E(Et), B(Bu), A(Am) refer respectively to ethyl, butyl, amyl branches; these collectively make up the short chain branching (SCB). Other smaller resonances have been reported for 1,3-paired ethyl-ethyl branches, 1,3-paired ethyl-ethyl branches attached to quaternary carbons, and ethylhexyl branches (12). Owing to their low abundances, these branches will be ignored in this work.

On the basis of the assignments, the relative amounts of the various branches can be estimated. In all previous work (1-13), only one kind of long chain branching (LCB) has been defined. The terminology of long chain branching is, however, ambiguous, since there are in fact two measures of LCB: the chain ends and the branch points. In this work, these two kinds of chain ends are designated $L_1$ and $L_2$, where $L_1$ corresponds to the number of long chain branch points, and $L_2$ refers to the number of long chain ends. It is clear that there will always be more chain ends than branch points (Figure 2). In fact, the two quantities can be shown to be related by the number-average molecular weight, $M_n$.

Assume that for 1000 methylene units, there are $L_2$ chain ends and $L_1$ branch points.

$$\text{Total number of long chain ends} = \frac{M_n}{14} \bullet \frac{L_2}{1000} \qquad (1)$$

$$\text{Total number of long chain branch points} = \frac{M_n}{14} \bullet \frac{L_1}{1000} \qquad (2)$$

There should be exactly two more chain ends than branch points (Figure 2). Therefore,

$$\frac{M_n L_2}{14000} - \frac{M_n L_1}{14000} = 2 \tag{3}$$

$$\text{i.e.,} \quad L_1 = L_2 - \frac{28000}{M_n} \tag{4}$$

The value $L_1$ can be evaluated from peaks 2,3, and 8b, and $L_2$ from peaks 6,10, and 11. Thus, a knowledge of $M_n$ permits interconversion of $L_1$ and $L_2$. Conversely, if the precisions in $L_1$ and $L_2$ are good, this equation can be used to determine $M_n$.

In the above discussion, no account has been taken of vinyl chain ends. It is well known that in titanium catalyzed polyethylenes, only saturated chain ends are present; however, in chromium-catalyzed polyethylenes, vinyl end group is also present (10):

$$\begin{array}{lllll} -CH_2 - & CH_2 - & CH_2 - & CH = & CH_2 \\ & 29.0 & 33.9 & 139.0 & 114.1 \end{array}$$

If the vinyl chain ends are present (e.g., peak 4a at 33.9 ppm), then equations 1-4 should be slightly modified by replacing $L_2$ with $L_2$+V, where V = number of vinyl end groups per 1000 methylene units.

## Computerized Analysis

The analysis of LDPE usually entails picking out selected NMR peaks in Table 1 and carrying out the necessary computations. This method, however, makes little use of the peaks with overlapping signals, e.g. peaks 2,3,4,7,8,10,11. A better method (in the view of this author) is to utilize all the observed spectral peaks. This is most conveniently done with the computerized FITCO approach devised earlier (14-20) for a number of copolymer systems.

A logic diagram of the computerized approach is shown in Figure 3. After the spectral intensities are entered, the computer program will provide the estimated value of LCB and SCB from selected peaks in the usual fashion. The user then has the option of terminating or continuing with the optimization. In the optimization procedure, the first step is to generate theoretical intensities for all the spectral peaks on the basis of the estimated SCB and LCB. The observed and the theoretical intensities are then compared, and the mean deviation calculated. The values of SCB and LCB are then changed systematically to minimize the deviation and to obtain the optimized values of A, B, E, $L_1$, and $L_2$. The entire process is done automatically without user intervention.

The above procedures have been written into a BASIC computer program, called FITCO.LDPE on the Apple IIe. An equivalent program is also available for the Nicolet 1280 computer. Interested readers may write to the author for a program listing.

Table 2. Observed Peak Intensities[a]

| Peak | J[b] | A-1[c] | A-2[c] | A-9B[c] | A-10B[c] | A-12[c] | A-13[c] |
|---|---|---|---|---|---|---|---|
| 1 | 3.60 | 0 | 0 | 1.7 | 0 | 0 | 0 |
| 2 | 1.19 | 8.6 | 6.3 | 8.5 | 6.4 | 8.2 | 9.6 |
| 3 | 2.71 | 26.8[d] | 26.4[d] | 22.8[d] | 31.3[d] | 28.6[d] | 23.2[d] |
| 4 | 8.11 | 19.3[d] | 22.8[d] | 13.5[d] | 22.7[d] | 11.7[d] | 13.8[d] |
| 4a | 0.72 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 0.22[f] | 1.5 | 1.8 | 2.0 | 2.2 | 1.5 | 0 |
| 6 | 0.81 | 2.2 | 1.8 | 2.8 | 2.2 | 1.5 | 12.5 |
| 7 | 966.05 | 855.6 | 883.1 | 886.4 | 887.8 | 897.9 | 854.0 |
| 8 | 11.73 | 49.4 | 29.8 | 32.3 | 27.9 | 17.6 | 33.5 |
| 9 | 0.67 | 6.9 | 4.7 | 6.6 | 4.1 | 11.1 | 6.3 |
| 10 | 0.93 | 5.8 | 3.5 | 4.6 | 2.7 | 6.5 | 16.6 |
| 11 | 1.18 | 19.4 | 14.1 | 14.3 | 9.3 | 15.4 | 26.6 |
| 12 | 2.09 | 4.5 | 5.7 | 4.5 | 3.4 | 0 | 3.9 |
| $M_n$[e] | - | 1.11 | 2.42 | 1.23 | 1.87 | 9.0 | 0.186 |

---

[a] The precision in each value is probably no better than ± 1.0

[b] Results reported by L. F. Johnson (21)

[c] From ref. 9, Table I

[d] Estimated; the intensities of peaks 3 and 4 were combined in ref. 9

[e] All numbers in $10^4$ a.m.u.

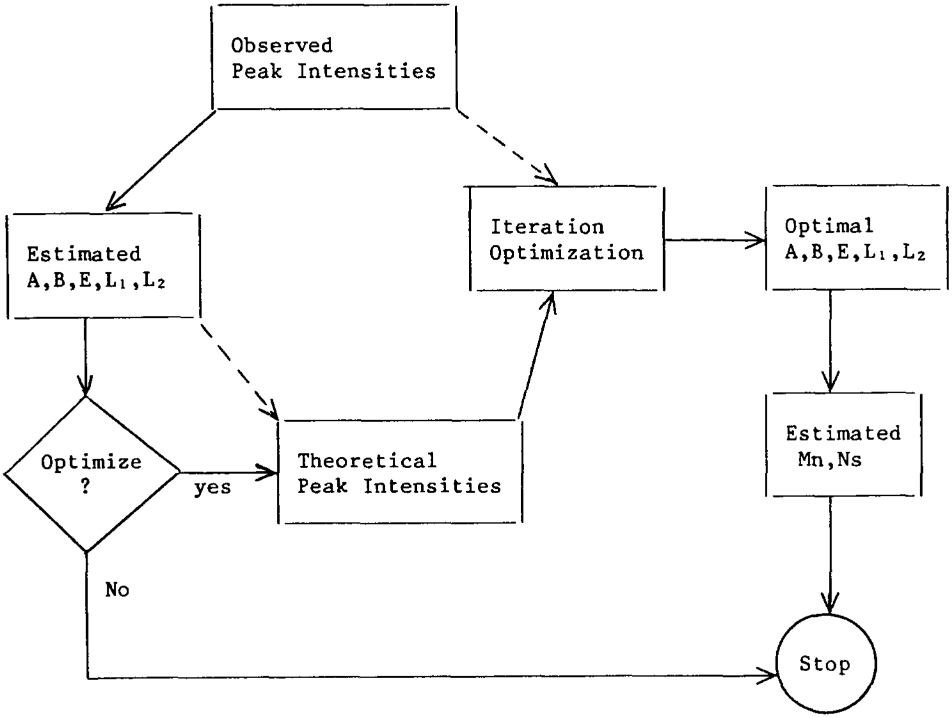
[f] Estimated from spectral height

Table 3. FITCO.LDPE Results for the Polyethylene Samples

| | J | A-1 | A-2 | A-9B | A-10B | A-12 | A-13 |
|---|---|---|---|---|---|---|---|
| SCB | | | | | | | |
| Am | 0.2 | 2.2 | 1.3 | 1.9 | 1.3 | 1.0 | 0 |
| Bu | 0.5 | 9.9 | 8.6 | 6.7 | 8.7 | 9.6 | 14.0 |
| Et | 3.1 | 4.9 | 3.8 | 3.3 | 3.5 | 0 | 1.7 |
| LCB | | | | | | | |
| $L_1$ | 0.43 | 0.17 | 0.42 | 1.15 | 0.17 | 0.07 | 0.04 |
| $L_2$ | 0.80 | 2.53 | 1.95 | 3.12 | 1.48 | 4.74 | 12.56 |
| $M_n$[a] | 2.57 | 1.19 | 1.84 | 1.42 | 2.14 | 0.60 | 0.22 |
| $N_s$ | 384 | 205 | 288 | 196 | 358 | 106 | 40 |

[a] Values in $10^4$ a.m.u.

Figure 3: Schematic of Program FITCO.LDPE



## Results and Discussion

The peak intensities for several LDPE samples reported by Johnson (21) and Axelson, et al. (9) are given in Table 2. The use of program FITCO.LDPE is straightforward. The results are shown in Table 3. In general, the goodness of fit depends very strongly on the quality of the data at hand. Axelson, et al. (9) had earlier outlined the experimental conditions needed for precise NMR data for these systems. It is clear that using the present approach, their data are readily amenable to analysis. It may be emphasized that for each spectrum all of their integrated intensities have been used.

The branching content varies widely among the samples. The results are consistent with earlier findings. Apparently the backbiting reactions that produce the branches (12, 22-23) are dependent upon the reaction conditions. The. $M_n$ values computed from the $^{13}C$ NMR method agree reasonably well with the $M_n$ measured by size exclusion chromatography. The only exception is sample A-12. In this case, there is inherent inconsistency in the spectral data (cf. the intensities of peak # 10 vs. peaks # 5,6).

Additional information is available from the $^{13}C$ NMR data. In Figure 2, it was shown that the number of long chain segments is related to $L_1$ and $L_2$ in a simple relationship. The average sizes of the segments can then be readily estimated. Let $N_s$ = number of carbons per segment, thus

$$N_s = \frac{\text{total no. of carbons}}{\text{number of segments}}$$

The total number of carbons is simply $M_n/14$, and the number of segments can be derived from Equation 1.

$$N_s = \frac{M_n/14}{(L_2/1000)(M_n/14)+2}$$

$$= \frac{1000\ M_n}{L_2 \bullet M_n + 28000} \qquad (5)$$

Thus, the average size of the long chain segment is dependent on $M_n$. In Table 3, the $N_s$ values have also been included.

## Experimental Section

The sample shown in Figure 1 was dissolved as a 20% solution in 1,2,4-trichlorobenzene with 3 drops of $d_6$-benzene added as a lock solvent. The free induction decay was collected in 8K memory locations with 60° pulses and 11-second delay times. A sweep width of 6000 Hz was used at 90 MHz (on the Nicolet NT360) with proton decoupling. The probe temperature was kept at circa 115°C.

## References and Notes

1. D. E. Dorman, E. P. Otocka, and F. A. Bovey, Macromolecules, 5, 574 (1972).
2. J. C. Randall, J. Polym. Sci., Polym. Phys. Ed., 11, 275 (1973).
3. M. E. A. Cudby and A. Bunn, Polymer, 17, 345 (1976).
4. F. A. Bovey, F. C. Schilling, F. L. McCracken, and H. L. Wagner, Macromolecules, 9, 76 (1976).
5. H. N. Cheng, F. C. Schilling, and F. A. Bovey, Macromolecules, 9, 363 (1976).
6. D. E. Axelson, L. Mandelkern, and G. C. Levy, Macromolecules, 10, 557 (1977).
7. J. Spavacek, Polymer, 19, 1149 (1978).
8. J. C. Randall, J. Appl. Polym. Sci,. 22, 585 (1978).
9. D. E. Axelson, G. C. Levy, and L. Mandelkern, Macromolecules, 12, 41 (1979).
10. J. C. Randall, ACS Symp. Ser., 142, 93 (1980).
11. J. Vile, et al., Polymer, 25, 1173 (1984).
12. T. Usami and S. Takayama, Macromolecules, 17, 1756 (1984), and references therein.
13. U. W. Gedde, Polymer, 27, 269 (1986).
14. H. N. Cheng In "Transition Metal Catalyzed Polymerizations. Alkenes and Dienes", R. P. Quirk, Ed., Harwood Academic Publishers, New York, 1983, pp 617-638.
15. H. N. Cheng, Anal. Chem., 54, 1828 (1982).
16. H. N. Cheng, J. Polymer Sci., Polym. Phys. Ed., 21, 573 (1983).
17. H. N. Cheng, Polymer Comm. 25, 99 (1984).
18. H. N. Cheng and G. H. Lee, Polymer Bull., 12, 463 (1984).
19. H. N. Cheng, Polymer Bull., 14, 347 (1985).
20. H. N. Cheng, J. Chem. Info. Computer Sci., to be published.
21. L. F. Johnson, private communication.
22. M. J. Roedel, J. Amer. Chem. Soc., 75, 6110 (1953).
23. A. H. Willbourn, J. Polymer Sci., 34, 569 (1959).
24. While this paper was in preparation, a paper appeared on quantitation in LDPE: J. N. Hay, P. J. Mills, and R. Ognjanovic, Polymer, 27, 677 (1986).

*Accepted September 29, 1986 K*