

Comments on the Length of Long Chain Branches in LDPE Calculated by Bugada and Rudin

The influence of long chain branching (LCB) on the processing characteristics of low density polyethylene (LDPE) and some types of high density polyethylene (HDPE) is well recognized.^{1,2} Unfortunately, characterization of the long chain branches with regard to number and size is very difficult, even in samples of LDPE where considerable numbers of branches are expected, and involves careful chromatographic work.³ Bugada and Rudin have attempted to estimate the size of long chain branches in various samples of LDPE by carefully counting all types of branches and subtracting the carbons present in short chain branches.⁴ The remaining carbon atoms belong either to the backbone or to long chain branches; thus

$$C_{LCB} = C_T - C_{SCB}$$

where C_T is the total number of carbons in a chain. For a molecule with three arms, the average length of the arms, or the long chain branch, is given by eq. (4) from Bugada and Rudin:

$$\bar{L}_n = C_{LCB}/([LCB] + 2)$$

where $[LCB] = 1$. Unfortunately, Bugada and Rudin applied their eq. (4) to samples containing more than one long chain branch in each molecule and thereby did not account for the internal chain segments between the long chain branches. For example, a molecule with two long chain branching points, as determined by nuclear magnetic resonance spectroscopy, actually has four terminal branches joined by one internal segment rather than four segments, as implied by their eq. (4).

By making an additional assumption, the approach of Bugada and Rudin can be modified to provide an upper limit to the length of the long chain branches in these LDPEs. Because the long chain branches should not contain further long chain branches themselves, it seems reasonable to assume that the average length of a long chain branch will be less than the average length of a segment separating two long chain branches. Or in the limit the length of a long chain branch will

TABLE I
Calculated Number-Average Segment Length \bar{S}_n and Segment Mass \bar{M}_L for LDPE Samples
Analyzed by Bugada and Rudin

Sample	LCB ^a	$M_n \times 10^{-3}$	$C_T \times 10^{-2}$	\bar{S}_n	$\bar{M}_L \times 10^{-2}$
A	2.9	14.1	10.1	136	19
B	3.8	18.7	13.4	143	20
C	3.7	20.1	14.4	158	22
NBS 1476	4.5	26.2	18.7	177	25
D	6.1	28.4	20.3	145	20
E	5.3	31.4	22.4	178	25
F	6.4	33.4	23.9	159	22
G	7.3	42.9	30.6	183	26
H	11.2	60.4	43.1	171	24

^a Long chain branches per average molecule.

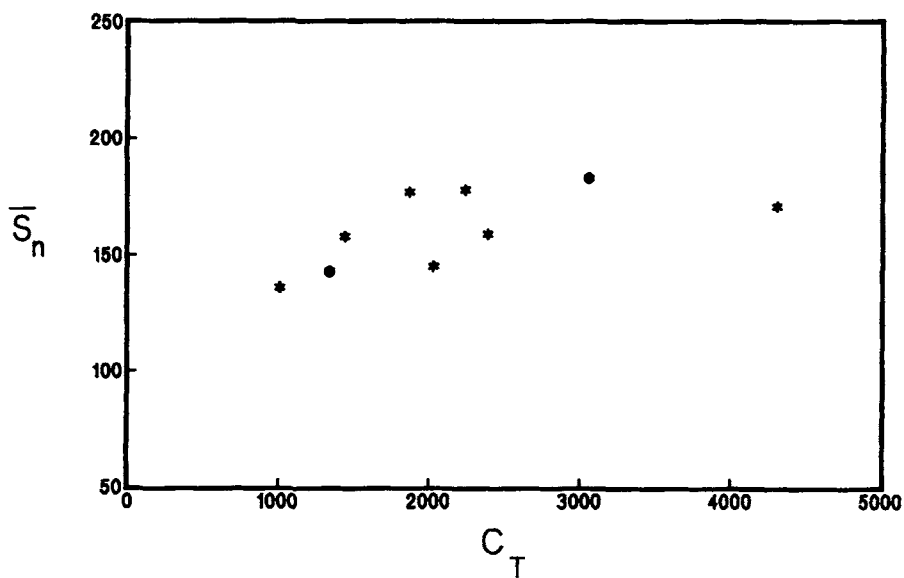


Fig. 1. Number average segment length \bar{S}_n as a function of the total number of carbons in the LDPE molecule, C_T .

equal the length of the separating segment. By making all segments equal, long chain branches included, Bugada and Rubin's eq. (4) can be modified as follows:

$$\bar{S}_n = C_{LCB} / (2[LCB] + 1)$$

where \bar{S}_n is the average length of a segment and therefore the upper limit on the length of the long chain branches. The denominator of the above eq. comes from the sum of two end groups, [LCB]

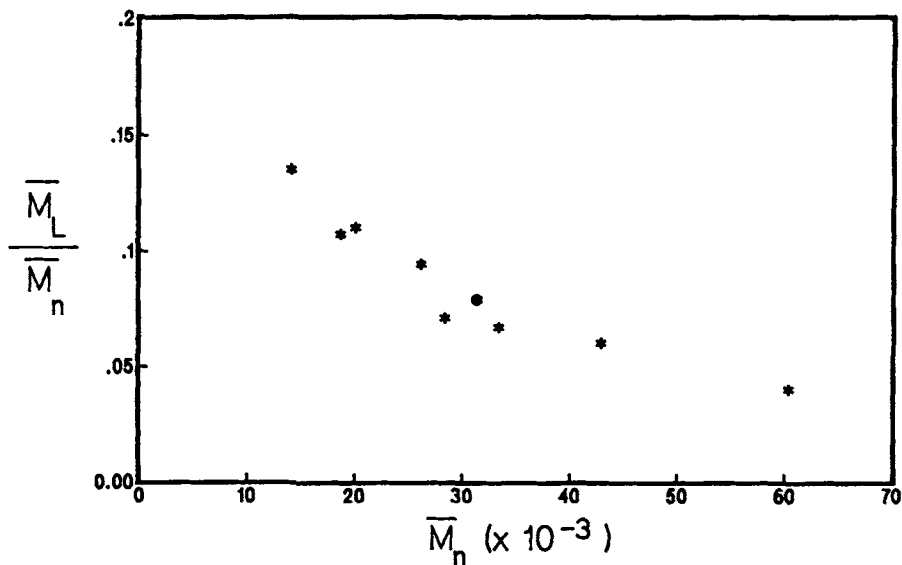


Fig. 2. Ratio of mean segment size (\bar{M}_L) to \bar{M}_n vs. \bar{M}_n .

long chain branches and [LCB] - 1 segments separating the long chain branches. Table V of Bugada and Rudin is therefore modified here (Table I).

The average is quite similar for the various samples and suggests that the maximum length of a long chain branch is about 160 carbon atoms. Figure 1 shows a plot of the average segment length against the number of carbon atoms in a chain. There is a very small increase with the lengthening of the chain. This increase gives rise to a slight curvature when the ratio of segment mass to molecular mass is plotted against the molecular mass, as shown in Figure 2. Brauer, Wiegleb, and Gebrauer have estimated the length of long chain branches in ethylene-vinyl acetate copolymers at about 28 carbon atoms and suggest that similar values should be observed in LDPE because the two polymers are prepared in similar fashion.⁵ These authors suggested that their method may slightly underestimate the length of the long chain branches. Together the two methods place some limits on the size of the branches, but the estimate of Brauer, Wiegleb, and Gebrauer must be given more weight.

References

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Received March 3, 1989
Accepted August 23, 1989