Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Long-Chain Branching under Conditions of Nonuniform Branching Probability

R. V. Mullikin[a]; George A. Mortimer[a]
[a] Monsanto Company, Texas City, Texas

To cite this Article Mullikin, R. V. and Mortimer, George A.(1972) 'Long-Chain Branching under Conditions of Nonuniform Branching Probability', Journal of Macromolecular Science, Part A, 6: 7, 1301 — 1310
To link to this Article: DOI: 10.1080/10601327208056897
URL: http://dx.doi.org/10.1080/10601327208056897

J. MACROMOL. SCI.—CHEM., A6(7), pp. 1301-1310 (1972)

Long-Chain Branching under Conditions of Nonuniform Branching Probability

R. V. MULLIKIN and GEORGE A. MORTIMER

Monsanto Company
Texas City, Texas 77590

ABSTRACT

Long-chain branching can occur during free radical polymerization and is especially important for polyethylene. An improved method of calculating the effect of long-chain branching on molecular weight distribution was presented in an earlier paper in which the assumption was made that the probability of branching at each monomer unit was constant throughout the polymerization. A method of including a nonuniform probability of branching in the calculations is presented. Calculation results show that the predictions of the two mathematical models are similar and both models fit published data on polyethylene equally well.

INTRODUCTION

Papers presented in 1953 by Roedel [1], Billmeyer [2], and Beasley [3] suggested the mechanism for long-chain branching in polyethylene, gave evidence of the presence of long-chain branching, and presented a calculation based on long-chain branching to account for the broad molecular weight distribution in polyethylene. Beasley's approach has been extended by Nicolas [4] to include certain kinetic steps which Beasley intentionally did not include in his idealized treatment, but the basic approach and conclusions remained unchanged.

A paper presented by the authors [5] in 1970 employed the same basic assumptions with regard to polymerization conditions (a well stirred, continuous feed and discharge reactor) as employed in the 1953 Beasley paper [3], but gave an alternate mathematical approach to the problem of calculating the effect of long-chain branching on molecular weight distribution and reached calculated results in closer agreement with measured values. The method of calculation employed a probability treatment where the probability of branching at a given monomer unit was assumed constant throughout the polymer (as was also the case in earlier papers).

The assumption can be made, however, that the probability of branching is not constant—specifically that potential branch sites exposed to a branching reaction for a longer length of time would contain more branches per monomer unit than branch sites exposed for a shorter length of time. The mathematical technique presented in our earlier paper [5] is well suited for inclusion of this feature in the calculation.

ASSUMPTIONS AND DEFINITIONS

A number of terms employed in this paper are identical to those used in an earlier paper [5] and are repeated here for convenience.

x = number of monomer units (plus chain transfer agent or initiator fragments) in a straight chain chosen at random—this can be thought of as a primary chain

$M_{i,n}$ = ith moment of polymer having n branch points on the primary chain

M_i = ith moment of the whole polymer

y_u = number of monomer units in the entire branch of the uth branch off the primary chain

p = probability that one monomer unit is attached to another (as a result of straight-chain addition polymerization)

$f(y_u)$ = a frequency function equal to the probability that a given branch from a primary chain is size y

Explanation of new terms relating time or age dependency follow. For a well-stirred reactor, containing a variety of materials, with continuous constant feed and discharge, if one chooses any identifiable group of materials in existence in the reactor at time ϕ = zero, then $f(\phi)$ is the elemental fraction of that group which is leaving the reactor during an element of time, $d\phi$, at a subsequent time, ϕ.

$\int^{\phi_1} f(\phi)$ is the fraction of the originally identified group which has left the reactor during the time interval, zero to ϕ_1. τ is the reciprical of the average dwell time in the reactor. Equation (1) expresses the relationship of these variables.

$$f(\phi) = \tau e^{-\tau\phi} d\phi \tag{1}$$

$$b_\phi = 1 - e^{-A\phi} \tag{2}$$

Equation (2) expresses the variation in branching probability, b, where b_ϕ is the assumed form (for use in this paper) of the time dependency of the probability of branching per monomer unit. In this form it means that the probability of branching is zero at the instant of formation of a chain and increases exponentially toward a value of 1.0 the longer the chain is exposed to branching reaction. It also means that the rate of branching on a given chain at any time subsequent to the formation of the chain is proportional to the number of available unbranched sites at that time. Other forms of time dependency of b_ϕ could be assumed and could be solved mathematically by the method shown below, but this form is felt to represent well the type of time dependency that might be expected if branching probability is dependent on dwell time. A is simply a constant (depending on overall rate of branching, free radical concentration, etc.). $\overline{b}$ is the average probability of branching for the whole polymer. Mathematically, $\overline{b}$ is expressed as

$$\overline{b} = \frac{\int b_\phi f(\phi)}{\int f(\phi)} = \frac{A}{A + \tau} \tag{3}$$

DERIVATIONS

In an earlier paper [5], assuming the probability of branching to be constant, it was shown that the zero, first, and second moments of a fraction of the polymer (having a chosen size of primary chain and a chosen number of branches from the primary chain) could be stated in terms of p, b, y_u, and $f(y_u)$. The moments of the fractions were then summed for all fractions to obtain solutions for the moments of the whole polymer.

A significant feature of this calculation is that b can be considered to be the branching probability for a given primary chain, and that it need not be constant for all primary chains. y_u and $f(y_u)$ refer to the size and frequency of the branches from the primary chain. It happens that the mathematical forms employed here apply equally if one starts computation with the primary chains and computes moments for the whole polymer, or if one starts with the primary chains of all branches and computes moments for all branches off the primary chains [i.e., any chain chosen at random whether primary or otherwise has the same statistical life expectancy, $f(\phi) = \tau e^{-\tau\phi} d\phi$, from the time of its formation until exiting from the reactor as any other chain]. We are therefore justified in making the same statement regarding moments of the branches as made in the earlier paper:

$$\sum_{1}^{\infty} y_u{}^i f(y_u) = M_i, \qquad \text{where } i = 0, 1, 2, \ldots \tag{4}$$

The mathematical technique employed in this paper can then be stated in the following general way: We consider an elemental fraction of polymer exiting from the reactor, having selected values of size of primary chain, number of branches off the primary chain, and age of the primary chain. The moments for this fraction can then be stated in terms of p, b_ϕ, y_u, x, and ϕ. We then sum these moments for all possible ages of the primary chain and all fractions of polymer with regard to variations in size of primary chain and number of branch points on the primary chain to obtain solutions for the moments of the whole polymer.

The zero moment equations for the polymer are

$$M_{0,0} = \int_{\phi=0}^{\infty} \sum^{\infty} (p^{x-1} - p^x)(1 - b_\phi)^x f(\phi) \tag{5}$$

$$M_{0,n} = \int_{\phi=0}^{\infty} \sum^{\infty} \frac{(p^{x-1} - p^x)(1 - b_\phi)^{x-n} b_\phi{}^n (x)(x-1)\ldots(x-n+1)}{n!} f(\phi)$$

$$(\text{for } n \geq 1) \tag{6}$$

The zero moment equations have the solutions

$$M_{0,0} = \int_{\phi=0}^{\infty} \frac{(1 - b_\phi)(1 - p)}{1 - p + pb_\phi} f(\phi) \tag{7}$$

$$M_{0,n} = \int_{\phi=0}^{\infty} \frac{(1 - p)}{p(1 - p + pb_\phi)} \left[\frac{pb_\phi}{1 - p + pb_\phi}\right]^n f(\phi) \tag{8}$$

$$M_0 = M_{0,0} + \sum_{1}^{\infty} M_{0,n} = \int_{\phi=0}^{\infty} (1.0) f(\phi) = 1.0 \tag{9}$$

The first moment equations are

$$M_{1,0} = \int_{\phi=0}^{\infty} \sum_{1}^{\infty} (x)\,(p^{x-1} - p^x)\,(1 - b_\phi)^x f(\phi) \tag{10}$$

$$M_{1,n} = \int_{\phi=0}^{\infty} \sum_{x=n}^{\infty} \sum_{y_1=1}^{\infty} \cdots \sum_{y_n=1}^{\infty} \Big[(x + y_1 + y_2 + \ldots + y_n)\left(\frac{1}{n!}\right)(p^{x-1} - p^x)$$

$$(1 - b_\phi)^{x-n} (b)^n (x)(x-1)\ldots(x-n+1) f(y_1) f(y_2) \cdots f(y_n)\Big] f(\phi) \tag{11}$$

Solutions of the first moment equations are

$$M_1 = M_{1,0} + \sum_{1}^{\infty} M_{1,n} \tag{12}$$

$$M_1 = \int_0^{\infty} \frac{1}{(1 - p)} \left[1 + M_1 b_\phi\right] f(\phi) \tag{13}$$

$$M_1 = \frac{\tau + A}{\tau(1 - p) - pA} = \frac{1}{1 - p - \bar{b}} \tag{14}$$

This form of the solution for polymer first moment seems obvious from the nature of the first moment and the meaning of $\bar{b}$, but the above equations serve to show the path by which the equations for any moment can be solved.

Starting with a modification of Eq. (12) from our earlier paper [5], the second moment equations are

$$M_2 = \int_0^{\infty} \sum_{n=0}^{\infty} \frac{(1 - p)}{(p)(1 - p + pb_\phi)^3} \left[\frac{pb_\phi}{1 - p + pb_\phi}\right]^n \Big[n^2 + (1 + 3n)(p)$$

$$(1 - b_\phi) + (p)^2(1 - b_\phi)^2 + (2n)\left[n + p(1 - b_\phi)\right](1 - p + pb_\phi)(M_1)$$

$$+ (n)(1 - p + pb_\phi)^2 (M_2) + (n)(n - 1)(1 - p + pb_\phi)^2 (M_1)^2\Big] f(\phi) \tag{15}$$

$$M_2 = \int_0^{\infty} \frac{1}{p(1-p)^2} \left[p(1+p) + (M_2 p(1-p) + 2M_1 p(1+p))b_{\phi} + (2M_1^2 p^2) b_{\phi}^2 \right] f(\phi) \tag{16}$$

$$M_2 = \frac{(1+\bar{b})(1+p)((1-p)^2 - (\bar{b})^2 + 4p(\bar{b})^2)}{(1+\bar{b})(1-p)(1-p-\bar{b})^3} \tag{17}$$

and

$$\text{MWD} = \bar{x}_w/\bar{x}_n = M_2 M_0/M_1^2 = \left[1 - p^2 - (\bar{b})^2 + \frac{2p(\bar{b})^2}{(1-p)} \frac{(1-\bar{b})}{(1+\bar{b})}\right] M_1 \tag{18}$$

ANALYSIS OF THE RESULTS

Results for this paper are identical with those of the earlier paper [5], where branching probability was assumed constant, for the zero and first moments (Eqs. 9 and 14). Results are different, however, for the second moment (Eq. 18, as well as for $\bar{x}_w = M_2/M_1$ and MWD = $\bar{x}_w/\bar{x}_n = M_2M_0/M_1^2$. In the earlier paper [5] it was found that

$$\text{MWD} = [1 - p^2 - (\bar{b})^2]M_1 \tag{19}$$

Comparing this result with Eq. (18), it is apparent that broader MWD results from nonconstant probability of branching, but the magnitude of this effect is not fully evident from these equations alone. Figure 1 is a plot of these equations over a range of interest for values of $\bar{x}_n = M_1/M_0$ and $\bar{b}$. At low values of $\bar{b}$ there is a relatively small effect on MWD; at large values of $\bar{b}$ the effect of nonuniform probability of branching is at most a doubling of the MWD.

These calculations can also be considered in another light: comparison with published experimental data. For this purpose we have chosen the data published by Billmeyer in his 1953 paper [2], as shown in Table 1.

Billmeyer measured N on these samples, a property which he called the long-chain branching index. The long-chain branching index was considered to be related in some nonexact way to the

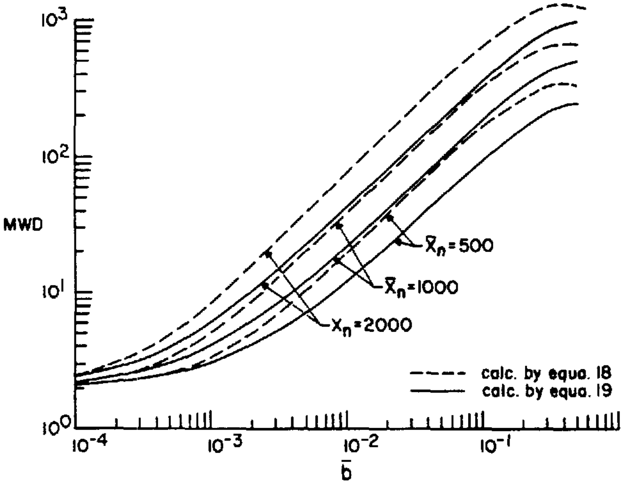

FIG. 1. Calculated effect of molecular weight distribution vs. branching using Eqs. (18) and (19).

number of long-chain branches per molecule. Hence, there is no known exact relation between the long-chain branching index and the term $\bar{b}$, or number of branches per monomer unit. After reviewing the derivation of the term N as developed in earlier papers, we have chosen to write the relationship between $\bar{b}$ and N as

$$\bar{b} = N/2\bar{x}_n = 14N/\bar{M}_n \tag{20}$$

The major difficulty in this assumption concerns the fact that Billmeyer made his viscosity measurements on whole polymer samples instead of fractions of the samples as a basis for calculating branching indices. Mendelson and Drott [6] have shown that branching indices measured by the two methods are related, indices obtained on whole polymer samples tending to be about twice as high as those obtained from fractions. However much this point may be in dispute, molecular weight distributions ($\bar{M}_w/\bar{M}_n$) may be calculated from the measured values of $\bar{M}_n$ and N (using Eqs. 14, 18, 19, and 20) and compared with the measured ratio of $\bar{M}_w/\bar{M}_n$ as shown in Fig. 2. There is a remarkably good general correlation between measured and calculated values over a wide range. The difference between assuming constant branching probability or non constant branching

TABLE 1. Molecular Weight and Branching Index Measurements Reported by Billmeyer [2]

Sample No.	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	N
21	34	190	4.4
26	34	305	7.9
10	34	430	10.6
9	31	560	13.6
19	4.4	72	12.7
20	2.7	43	9.4
1	2.6	38	11.2
23	15	155	8.3
13	34	340	8.4
25	49	370	6.6
28	42	80	0.7
27	36	140	2.3
15	40	305	7.1
17	38	260	5.8
11	34	380	9.1
A38	11.6	580	20.3
14	7.8	340	24.0
29	19	600	20.0
A41	38	1800	21.0
A39	16.7	1000	39.0
A40	26.2	650	12.6
A42	37	480	6.3

probability does not appear to be greater than the scatter in the data. Of course, we do not know how these samples were produced (whether or not they are whole polymers from a well-stirred continuous reactor), and such factors could account for some of the scatter.

More precise data (eliminating the question of branching index

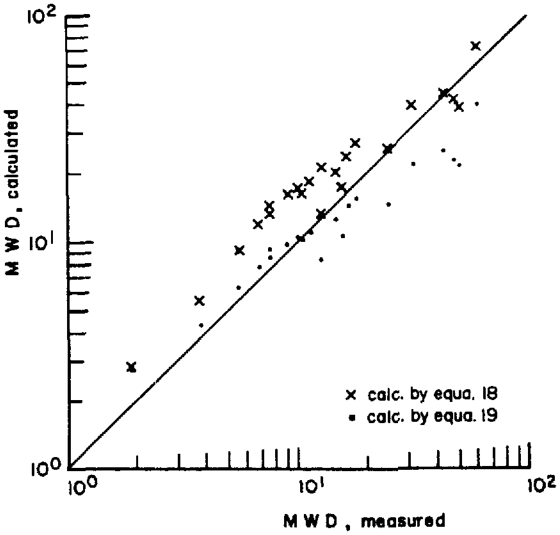

FIG. 2. Comparison of measured molecular weight distribution vs. molecular weight distribution calculated using Eqs. (18) and (19).

measurement on whole polymer rather than on fractions) has been published on one sample by Guillet [7]:

Sample designation:	Polymer A
Polymer density:	0.917
Melt index:	1.62
$\overline{M}_n$:	26,100
$\overline{M}_w/\overline{M}_n$:	6.88

The branching frequency measured on fractions of this polymer varied over the range 0.0008-0.0020 (branches per monomer unit), with lower molecular weight fractions having higher branching frequencies than higher molecular weight fractions. Use of Eq. (18) to calculate branching frequency to be expected from the above values of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ leads to a value of 0.0017 branches per monomer unit. Otocha et al. [8] report that for an autoclave reactor product the branching frequency is constant over the major portion of the polymer when measured on fractions of varying molecular weight. The fact that

Polymer A shows variation in branching frequency in this regard may indicate that it was not polymerized under the ideal conditions assumed for this paper. It is interesting, however, that the branching frequency implied from use of Eq. (18) falls within the range of the measured values.

REFEFENCES

[1] M. J. Roedel, J. Amer. Chem. Soc., 75, 6110 (1953).
[2] F. W. Billmeyer, Jr., J. Amer. Chem. Soc., 75, 6118 (1953).
[3] J. K. Beasley, J. Amer. Chem. Soc., 75, 6123 (1953).
[4] L. Nicolas, J. Chim. Phys., 55, 185 (1958).
[5] R. V. Mullikin and G. A. Mortimer, J. Macromol. Sci.—Chem., A4, 1495 (1970).
[6] E. E. Drott and R. A. Mendelson, Paper presented at the 6th International Seminar on GPC, Miami Beach, 1968.
[7] J. E. Guillet, J. Polym. Sci., Part A, 1, 2869 (1963).
[8] E. P. Otocha, R. J. Roe, M. Y. Hellman, and P. M. Muglio, Macromolecules, 4, 507 (1971).

Received for publication February 7, 1972