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Another Look at Long-Chain Branching

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SUMMARY

Long-chain branching can occur during radical polymerization and is especially important for polyethylene. An improved method of calculating the effect of long-chain branching on molecular weight distribution is presented. This method uses a probability treatment. The results are more consistent with both kinetic theory and experimental data than the results of previous long-chain branching calculations. In contrast to previous calculations, the present work shows that gelation cannot occur from long-chain branching alone.

INTRODUCTION

Simultaneously, in 1953, Roedel [1] suggested a mechanism for long-chain branching in polyethylene, Billmeyer [2] demonstrated its presence, and Beasley [3] presented a calculation based on long-chain branching to account for the broad molecular weight distribution of polyethylene. Beasley's approach was general for any polymer that can branch due to intermolecular chain transfer, and was applied to polyethylene where long-chain branching plays an important role. Beasley's approach has been extended by Nicolas [4] to include certain kinetic steps which Beasley intentionally ignored in his idealized treatment, but the basic approach and conclusions remained unchanged.

There are, however, certain weaknesses in these approaches which lead to disagreement between calculation and experiment (which were accounted for by postulating a shielding effect) and, in the limit, lead to a kinetically incorrect situation.

This paper will present an improved calculation believed to avoid some of the pitfalls of the earlier approaches. The results are only slightly different at low levels of branching from the results of Beasley, but differ substantially at high levels of branching. Calculated molecular weight distributions are much closer to the measure values and, in the limit, the calculation agrees with kinetic expectations.

Assumptions and Definitions

The same basic process assumptions made by Beasley are retained: the process is considered to take place in a well-stirred reactor with continuous feed and discharge and all process conditions constant [3].

The algebraic symbols are defined as follows:

k_b = rate constant for long-chain branching

k_p = rate constant for propagation

k_t = rate constant for bimolecular disproportionation termination (termination by combination is assumed non-existent in this calculation)

k_s = rate constant for chain transfer to a transfer agent

$2fk_dI$ = rate of initiation of new polymer chains by initiator radicals

k_c = over-all rate constant for radical scission reactions producing unsaturation

$[m]$ = monomer concentration

$[S]$ = chain transfer agent concentration

$[R]$ = free radical concentration

$[P]$ = polymer concentration

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

$\bar{x}_n$ = number average degree of polymerization

$\bar{x}_w$ = weight average degree of polymerization

MWD = molecular weight distribution, $\bar{x}_w/\bar{x}_n$

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

b = probability that there is a long-chain branch point on a given monomer unit in a polymer chain

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

Expressed in kinetic terms,

$$p = \frac{k_p[m][R] - k_c[R] - k_b[P][R]}{D}$$

and

$$b = \frac{k_b[P][R]}{D}$$

where

$$D = k_p[m][R] + k_s[S][R] + 2fk_dI$$

The quantity $2k_t[R]^2$ may be used instead of $2fk_dI$ at steady state if the number of radicals exiting from the reactor is negligible. Note that an initiator fragment or a transfer agent fragment, when in the polymer chain, is taken as equivalent to a monomer unit.

Comparing this terminology with that of Beasley, it can be seen that, very nearly, b = βa of Beasley, and p = 1 - a of Beasley.

Before commencing the calculations, some implicit assumptions should be identified. It will be assumed that a maximum of one branch point can occur on a single monomer unit. This restriction considerably simplifies the mathematical treatment. A mathematical conjecture will be made later showing how the solution can be generalized to accommodate more than one branch point per monomer unit and also more than one rate constant for branching, as would be needed to treat long-chain branching in polymers where all polymer hydrogens are not equivalent in their tendency to be abstracted. As is the case for extensions of Beasley's calculations, these refinements and extensions to more general cases will not alter the major conclusions.

At this juncture it may be appropriate to point out the differences between the present approach and calculations published in earlier papers. The present derivation utilizes a single mathematical technique, arithmetic summation of discontinuous functions. The earlier approaches mixed the use of arithmetic summations and calculus integration of continuous functions. Further, in the present derivation, the summations embody a restriction on the number of branches possible on a single monomer unit in the polymer. This restriction might have been 2, 3, 4, etc., but 1 was chosen for simplicity and later generalized. It is not clear that the mathematical technique employed earlier [3, 4] restricted the number of branches that can occur at a given site to the number that is chemically possible.

Before commencing the calculations, it should be pointed out that the function $f(y_u)$ itself is not known, but it is known that

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

since branches chosen at random have the same probabilities p and b governing their structure as is the case for the whole polymer.

Derivations

For a polymer whose structure is defined completely by the above probability terms for monomer addition in a straight chain and branching from a monomer unit, one can set up and solve the probability expressions for the zero, first, and second moments of molecular size.

The zero moment equations for the polymer are:

$$M_{0,0} = \sum^{\infty} (p^{x-1} - p^x)(1 - b)^x \tag{1}$$

$$M_{0,n} = \sum^{\infty} \frac{(p^{x-1} - p^x)(1 - b)^{x-n} b^n (x)(x - 1) \cdots (x - n + 1)}{n!} \quad (\text{for } n \geq 1) \tag{2}$$

The zero moment equations have the solutions:

$$M_{0,0} = \frac{(1 - b)(1 - p)}{(1 - p + pb)} \tag{3}$$

$$M_{0,n} = \frac{(1 - p)}{(p)\,(1 - p + pb)} \left[\frac{pb}{(1 - p + pb)}\right]^{n} \tag{4}$$

$$M_0 = M_{0,0} + \sum_{1}^{\infty} M_{0,n} = 1.0 \tag{5}$$

The first moment equations are:

$$M_{1,0} = \sum_{1}^{\infty} (x)\,(p^{x-1} - p^{x})\,(1 - b)^{x} \tag{6}$$

$$M_{1,n} = \sum_{x=n}^{\infty} \sum_{y_1=1}^{\infty} \cdots \sum_{y_n=1}^{\infty} \Big[(x + y_1 + y_2 + \cdots y_n)\,(\tfrac{1}{n!})$$

$$\cdot\,(p^{x-1} - p^{x})\,(1 - b)^{x-n}(b)^{n}(x)\,(x - 1) \cdots (x - n + 1)$$

$$\cdot\,f(y_1)f(y_2) \cdots f(y_n)\Big] \quad (\text{for } n \geq 1) \tag{7}$$

The first moment equations have the solutions:

$$M_{1,n} = \frac{(1 - p)}{(p)(1 - p + pb)^{2}} \left[\frac{pb}{(1 - p + pb)}\right]^{n}$$

$$\cdot\,[p(1 - b) + n + (n)(1 - p + pb)(M_1)] \tag{8}$$

$$M_1 = \sum_{n=0}^{\infty} M_{1,n} = \frac{1}{1 - p - b} \tag{9}$$

The second moment equations are:

$$M_{2,0} = \sum_{1}^{\infty} (x)^{2}(p^{x-1} - p^{x})(1 - b)^{x} \tag{10}$$

$$M_{2,n} = \sum_{x=n}^{\infty} \sum_{y_1=1}^{\infty} \cdots \sum_{y_n=1}^{\infty} \Big[(x + y_1 + y_2 + \cdots y_n)^{2}(\tfrac{1}{n!})$$

$$\cdot\,(p^{x-1} - p^{x})(1 - b)^{x-1}(b)^{n}(x)(x - 1) \cdots (x - n + 1)$$

$$\cdot\,f(y_1)f(y_2) \cdots f(y_n)\Big] \quad (\text{for } n \geq 1) \tag{11}$$

Solutions for the second moment equations are:

$$
\begin{aligned}
M_{2,n} = {} & \frac{(1-p)}{(p)(1-p+pb)^3}\left[\frac{pb}{(1-p+pb)}\right]^n \\
& \cdot\ [n^2 + (1+3n)(p)(1-b) + (p)^2(1-b)^2 \\
& + (2n)(n + p(1-b))(1-p+pb)(M_1) \\
& + (n)(1-p+pb)^2(M_2) \\
& + (n)(n-1)(1-p+pb)^2(M_1)^2]
\end{aligned}
\tag{12}
$$

$$
M_2 = \sum_{n=0}^{\infty} M_{2,n} = \frac{1-p^2-b^2}{(1-p-b)^3} \tag{13}
$$

The degrees of polymerization and molecular weight distribution therefore are:

$$
\bar{x}_n = \frac{M_1}{M_0} = \frac{1}{1-p-b} \tag{14}
$$

$$
\bar{x}_w = \frac{M_2}{M_1} = \frac{1-p^2-b^2}{(1-p-b)^2} \tag{15}
$$

$$
\mathrm{MWD} = \frac{M_0 M_2}{M_1^2} = \frac{1-p^2-b^2}{1-p-b} = (1-p^2-b^2)\bar{x}_n \tag{16}
$$

Figure 1 is constructed from these equations to show the effect of long-chain branching on molecular weight distribution graphically.

Analysis of the Results

Comparing these results (below on the left) converted into the a and β of Beasley, with Beasley's original results (below on the right) which are the same as Nicolas' results [4] when his $\rho = 0$, we see that there is agreement on $\bar{x}_n$ but not on $\bar{x}_w$ and MWD.

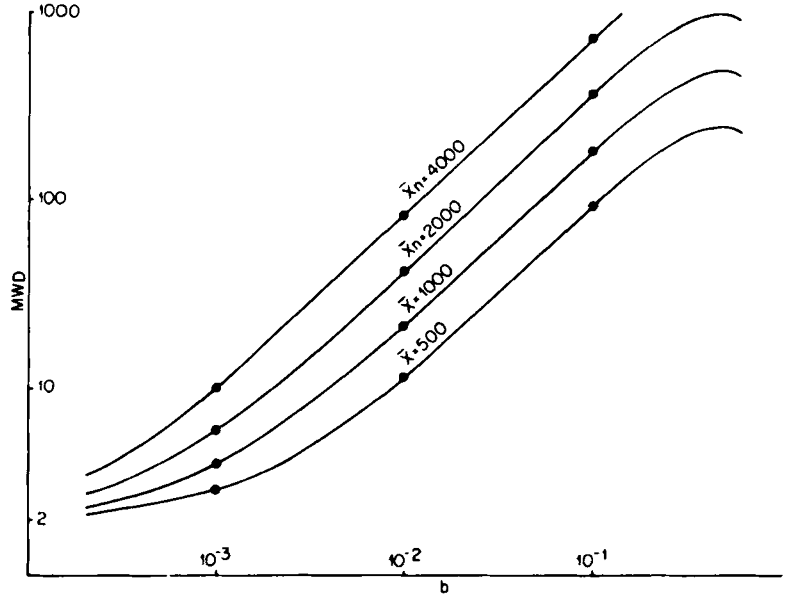

Fig. 1. Calculated effect of molecular weight distribution vs. branching using Eqs. (14) and (16).

$$\bar{x}_n = \frac{1}{a(1-\beta)} = \frac{1}{a(1-\beta)} \tag{17}$$

$$\bar{x}_w = \frac{2 - a(1+\beta^2)}{a(1-\beta)^2} \neq \frac{2}{a(1-2\beta)} \tag{18}$$

$$\mathrm{MWD} = \frac{2 - a(1+\beta^2)}{1-\beta} \neq \frac{2-2\beta}{1-2\beta} \tag{19}$$

There is a useful test of the consistency of these expressions with existing theory on molecular weight distribution. If b is set to zero while p remains finite (or vice versa), Eqs. (14), (15), and (16) simplify to the most probable distributions for linear polymers as described by Flory [5], which indeed they should if they are correct. Although p and b are not exactly equatable to a and β, it is still true that β is zero and a is finite if there is propagation and no branching. It can be seen that setting β to zero in

Table 1. Generalization of Branching Expressions

Branching assumption	$\bar{x}_n$	$\bar{x}_w$	MWD	
Two branching possibilities per monomer unit, probability $b_1 \neq b_2$	$\frac{1}{1 - p - b_1 - b_2}$	$\frac{1 - p^2 - b_1^2 - b_2^2}{(1 - p - b_1 - b_2)^2}$	$\frac{1 - p^2 - b_1^2 - b_2^2}{1 - p - b_1 - b_2}$	(20)
Same as above, but $b_1 = b_2$	$\frac{1}{1 - p - 2b}$	$\frac{1 - p^2 - 2b^2}{(1 - p - 2b)^2}$	$\frac{1 - p^2 - 2b^2}{1 - p - 2b}$	(21)
Four possible branches per monomer unit, $b_1 = b_2 = b_3 = b_4$	$\frac{1}{1 - p - 4b}$	$\frac{1 - p^2 - 4b^2}{(1 - p - 4b)^2}$	$\frac{1 - p^2 - 4b^2}{1 - p - 4b}$	(22)
n Branching probabilities of $i, j, \cdots, k$ possibilities per monomer unit	$\frac{1}{1 - p - ib_1 - jb_2 \cdots - kb_n}$	$\frac{1 - p^2 - ib_1^2 - jb_2^2 \cdots - kb_n^2}{(1 - p - ib_1 - jb_2 \cdots - kb_n)^2}$	$\frac{1 - p^2 - ib_1^2 - jb_2^2 \cdots - kb_n^2}{1 - p - ib_1 - jb_2 \cdots - kb_n}$	(23)

Beasley's and Nicolas' equations (18 and 19 of this paper) does not give Flory's expressions for the most probable values of $\bar{x}_w$ and MWD in a linear polymer. Numerically, they are close if a is very small, but the fact that they are not exact in the absence of branching is, we feel, a weakness in the previous calculations and raises the question of how much additional error is introduced when β is not zero.

A different limit on MWD is predicted in the two different sets of equations. In this connection, it is significant to note that the number of molecular chain terminations must be greater than the number of branch points, following the chemistry given under the assumptions for the calculations. This is true because the mechanism for creating a branch site involves a molecular chain termination of the attacking radical. If molecular terminations also occur by other mechanisms (chain transfer to monomer or transfer agent, kinetic chain termination by disproportionation, etc.) then the probability of molecular chain termination must be greater than the probability of branching, or $(1 - p) > b$. Mathematically, $\bar{x}_n = (1 - p - b)^{-1}$ cannot be truly infinite under the chemical mechanisms assumed. It can similarly be seen that $\bar{x}_w$ and MWD cannot become infinite. Indeed, the new expressions derived in this paper predict MWD will reach a finite maximum value at $b = p$ for any value of $\bar{x}_n$, whereas the previously published MWD expressions become discontinuous at $\beta = 0.5$, at which point they predict MWD to be infinite.

It is recognized that other polymerization mechanisms can exist which may correctly predict a truly infinite molecular weight [5], but these were not included as permissible reactions in the derivations under discussion here.

Generalization of the Results

Equations (14) through (16) have been rigorously developed by exact solution. It has thus been shown that there are no interaction terms in which p and b are multiplied. This seems reasonable. Although the probabilities p and b are related such that $p + b < 1$ by virtue of their definitions, the actual branching and propagation reactions do not depend upon each other in any manner (assuming all radicals have equal reactivity).

Although we have not rigorously solved the case of two branching reactions of probabilities b_1 and b_2, we believe from the form and nature of the previous solution that it can be conjectured as given by expressions (20) in Table 1. We have not demonstrated methematically that third-order terms (pb_1b_2 terms) are absent, but we believe that, in a real situation controlled by chemical kinetics in which the various reactions take place

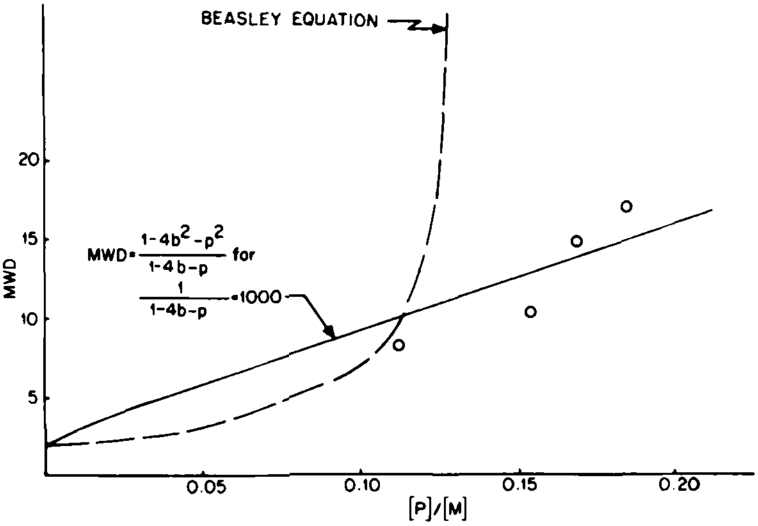

Fig. 2. Comparison of calculated and experimental molecular weight distributions. The data points are from Beasley's Fig. 4.

independently of one another and in which there are known to be no second-order terms in which different probabilities are multiplied, third-order terms will also be absent.

The solution may then be further generalized as shown in Table 1. Expressions (21) follow directly from (20). Expressions (22) would apply to polyethylene where there are four transferable hydrogen atoms per monomer unit, all of which should be equally reactive. The most general case is given by expressions (23) and should apply to any polymer formed by radical addition processes.

Predictions for polyethylene using expressions (22) are plotted in Fig. 2 versus Beasley's equation and the experimental data reported by Beasley. It is seen that agreement is acceptable without postulating any shielding effects.

The inclusion of other kinetic steps, especially combination termination, is also possible. Such possibilities will be dealt with at another time.

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