

Calculation of Molecular Weight for Polymers Produced in Continuous-Flow Stirred Reactors

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Synopsis

For addition polymers produced in continuous flow stirred tank reactors, a method is described for deriving equations for the degree of polymerization directly from the equations for the polymerization kinetics. Through use of this technique, relationships are obtained for calculating the number and weight average degree of polymerization in both homo- and copolymerization.

INTRODUCTION

Several investigators¹⁻³ have solved the kinetic equations for addition polymerization in a continuous-flow stirred tank reactor (CFSTR) to obtain expressions for the polymer size distribution as a function of reactor operating conditions. Such relationships are extremely important if we wish to control the polymer properties; however, in many cases a polymer can be adequately characterized by its number-average and weight-average degree of polymerization, and it is not necessary to know the details of the size distribution. Only the leading moments of the distribution must be determined since DP_n and DP_w are given by

$$DP_n = M_1/M_0 \quad (1)$$

$$DP_w = M_2/M_1 \quad (2)$$

in which M_n is the n th moment of the size distribution as defined by the equation

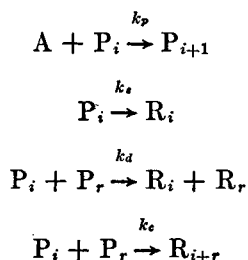
$$M_n = \sum_{i=1}^{\infty} i^n N_i$$

The moments can, of course, be obtained from expressions for the size distribution or by the use of moment-generating functions.^{4,5} However, if they are evaluated directly from the polymerization kinetic equations, DP_n and DP_w for a CFSTR can be determined with relative ease. Although this technique has been previously employed (see, for example, refs. 6 and 7), to our knowledge the moment equations for the general case of addition polymerization in a CFSTR have not appeared in the literature. The purpose of this communication is to present relationships

from which the moments, DP_n , and DP_w may be calculated and to illustrate the derivation of these quantities from the reactor material balances.

CALCULATION OF THE DEGREE OF POLYMERIZATION IN HOMOPOLYMERIZATION

For a polymerization according to the mechanism



in which the growing polymer chains can terminate spontaneously, by disproportionation or by combination, a material balance yields the following equations for the concentration of P_i and R_i in the reactor outlet when there is no polymer in the reactor feed:

$$P_i = [k_p A P_{i-1} - k_p A P_i - P_i(k_s + (k_c + k_d)P_i)] \theta \quad i \geq 2 \quad (3)$$

$$R_i = \left(k_s P_i + k_d P_i P_r + \frac{k_c}{2} \sum_{j=1}^{i-1} P_j P_{i-j} \right) \theta \quad i \geq 2 \quad (4)$$

where $P_i = \sum_{i=1}^{\infty} P_i$. In order to evaluate the moments, the sums $\sum_{i=1}^{\infty} i^n P_i$ and $\sum_{i=2}^{\infty} i^n R_i$ must be determined.

Multiplication of eq. (3) by i^n and summation over the values of i from 2 to ∞ gives

$$(\alpha + \beta) \sum_{i=2}^{\infty} i^n P_i = \beta \sum_{i=2}^{\infty} i^n P_{i-1} \quad (5)$$

where

$$\begin{aligned} \alpha &= 1 + [k_s + (k_c + k_d)P_r] \theta \\ \beta &= k_p A \theta. \end{aligned}$$

If we define

$$\begin{aligned} P_m &= \sum_{i=1}^{\infty} i P_i \\ P_w &= \sum_{i=1}^{\infty} i^2 P_i \end{aligned}$$

and make use of the relationships

$$\sum_{i=2}^{\infty} P_{i-1} = P_t$$

$$\sum_{i=2}^{\infty} iP_{i-1} = P_t + P_m$$

$$\sum_{i=2}^{\infty} i^2P_{i-1} = P_t + 2P_m + P_w,$$

then eq. (5) can be evaluated at n equal to 0, 1, and 2 to give

$$P_t = \frac{(\alpha + \beta)P_1}{\alpha}$$

$$P_m = \frac{\beta P_t + (\alpha + \beta)P_1}{\alpha} \quad (6)$$

$$P_w = \frac{\beta(P_t + 2P_m) + (\alpha + \beta)P_1}{\alpha}.$$

By manipulation of the above three equations, P_m and P_w can be expressed in terms of P_1 by the relationships

$$P_m = \frac{(\alpha + \beta)^2 P_1}{\alpha^2} \quad (7)$$

$$P_w = \frac{(2\beta + \alpha)(\alpha + \beta)^2 P_1}{\alpha^3} \quad (8)$$

Multiplication of eq. (4) by i^n and summation over the values of i from 2 to ∞ yields

$$\sum_{i=2}^{\infty} i^n R_i = \gamma \sum_{i=2}^{\infty} i^n P_i + \delta \sum_{i=2}^{\infty} i^n \sum_{j=1}^{i-1} P_j P_{i-j} \quad (9)$$

where

$$\gamma = (k_s + k_d P_t) \Theta$$

$$\delta = \frac{k_c \Theta}{2}.$$

If we define

$$R_t = \sum_{i=2}^{\infty} R_i$$

$$R_m = \sum_{i=2}^{\infty} i R_i$$

$$R_w = \sum_{i=2}^{\infty} i^2 R_i$$

and make use of the relationships

$$\sum_{i=2}^{\infty} \sum_{j=1}^{i-1} P_j P_{i-j} = \left(\sum_{i=1}^{\infty} P_i \right)^2$$

$$\sum_{i=2}^{\infty} i \sum_{j=1}^{i-1} P_j P_{i-j} = 2 \left(\sum_{i=1}^{\infty} i P_i \right) \left(\sum_{i=1}^{\infty} P_i \right)$$

$$\sum_{i=2}^{\infty} i^2 \sum_{j=1}^{i-1} P_j P_{i-j} = 2 \left(\sum_{i=1}^{\infty} i^2 P_i \right) \left(\sum_{i=1}^{\infty} P_i \right) + 2 \left(\sum_{i=1}^{\infty} i P_i \right)^2,$$

then eq. (9) can be evaluated at n equal to 0, 1, and 2 to yield

$$R_t = \gamma(P_t - P_1) + \delta P_t^2 \quad (10)$$

$$R_m = \gamma(P_m - P_1) + 2\delta P_m P_t \quad (11)$$

$$R_w = \gamma(P_w - P_1) + 2\delta(P_w P_t + P_m^2). \quad (12)$$

Except in the case of low molecular weight polymers, the concentration of P_1 can be neglected in comparison to the sum

$$\sum_{i=1}^{\infty} i^n P_i,$$

and use of eqs. (10) to (12) to obtain expressions for the moments gives

$$M_0 = P_t(1 + \gamma) + \delta(P_t)^2, \quad (13)$$

$$M_1 = P_m(1 + \gamma) + 2\delta P_t P_m \quad (14)$$

$$M_2 = P_w(1 + \gamma) + 2\delta[P_w P_t + (P_m)^2]. \quad (15)$$

Finally, substitution of eqs. (6) to (8) and (13) to (15) into eqs. (1) and (2) gives us the desired results

$$DP_n = \frac{\beta + \alpha [1 + \gamma + 2\delta(\alpha + \beta)P_1/\alpha]}{\alpha [1 + \gamma + \delta(\alpha + \beta)P_1/\alpha]} \quad (16)$$

$$DP_w = \frac{2\beta + \alpha [1 + \gamma + 2\delta(\alpha + \beta)P_1(3\beta + 2\alpha)/\alpha(2\beta + \alpha)]}{\alpha [1 + \gamma + 2\delta(\alpha + \beta)P_1/\alpha]} \quad (17)$$

from which the weight-average and number-average degrees of polymerization of polymers made in a CFSTR can be obtained. In order to use these equations, P_1 , P_t , and A must be known, and these concentrations can easily be calculated by simultaneous solution of the material balances:

$$A^0 - A = k_p A P_t \theta$$

$$P_t = \{I_p - [k_s P_t + (k_c + k_d) P_t^2]\} \theta$$

$$P_1 = \{I_p - P_1 [k_p A + k_s + (k_c + k_d) P_t^2]\} \theta.$$

Depending on the mechanism of the chain initiation process, additional material balances may be required to express the initiation rate, I_p , in terms of known parameters.

If chain termination or transfer occurs with monomer or solvent, eqs. (16) and (17) retain the same form; however, α and γ must be redefined and the material balance equations expanded to account for the additional reactions.

When polymerizing to high molecular weights, the rate of termination is much smaller than the rate of propagation, and eqs. (16) and (17) can be considerably simplified by neglecting α in comparison to β . This procedure gives the results

$$DP_n = \frac{\beta (1 + \gamma + 2\delta\beta P_1/\alpha)}{\alpha (1 + \gamma + \delta\beta P_1/\alpha)}$$

$$DP_w = \frac{2\beta (1 + \gamma + 3\delta\beta P_1/\alpha)}{\alpha (1 + \gamma + 2\delta\beta P_1/\alpha)}$$

The ratio DP_w/DP_n is often used as a measure of the breadth of the molecular weight distribution, and for high molecular weight polymers this ratio is given by

$$\frac{DP_w}{DP_n} = \frac{2(1 + \gamma + 3\delta\beta P_1/\alpha)(1 + \gamma + \delta\beta P_1/\alpha)}{(1 + \gamma + 2\delta\beta P_1/\alpha)^2} \quad (18)$$

As first shown by Denbigh,¹ if no combination termination occurs, δ equals zero and eq. (18) becomes

$$\frac{DP_w}{DP_n} = 2.$$

Thus, in this case the breadth of the molecular weight distribution is independent of the reactor operating conditions.

On the other hand, if only combination termination occurs, γ equals zero and

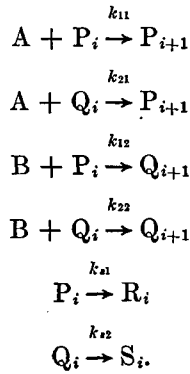
$$\frac{DP_w}{DP_n} = \frac{2(1 + 3\delta\beta P_1/\alpha)(1 + \delta\beta P_1/\alpha)}{(1 + 2\delta\beta P_1/\alpha)^2} \quad (19)$$

For the familiar case of free-radical polymerization in which chain life times are short and $R_i \gg P_i$, $\delta\beta P_1/\alpha \gg 1$ and eq. (19) reduces to

$$\frac{DP_w}{DP_n} = 1.5.$$

CALCULATION OF THE DEGREE OF POLYMERIZATION IN COPOLYMERIZATION

As a final example of this technique we will derive equations for the number-average and weight-average degree of polymerization of copolymers for the copolymerization mechanism:



Material balances yield the following equations for the concentration of living and dead chains in the reactor outlet when there is no polymer in the feed:

$$\begin{aligned}
 P_i &= (k_{11}P_{i-1}A + k_{21}Q_{i-1}A - k_{11}P_iA - k_{12}P_iB - k_{s1}P_i)\theta \\
 Q_i &= (k_{22}Q_{i-1}B + k_{12}P_{i-1}B - k_{22}Q_iB - k_{21}Q_iA - k_{s2}Q_i)\theta \\
 R_i &= k_{s1}P_i\theta \\
 S_i &= k_{s2}Q_i\theta.
 \end{aligned}$$

Multiplication of these equations by i^n followed by summation over the values of i from 2 to ∞ gives

$$(a_3 - a_1) \sum_{i=2}^{\infty} i^n P_i + a_2 \sum_{i=2}^{\infty} i^n Q_i + a_2 b_n + a_3 c_n = 0 \quad (20)$$

$$(a_6 - a_1) \sum_{i=2}^{\infty} i^n Q_i + a_5 \sum_{i=2}^{\infty} i^n P_i + a_5 c_n + a_6 b_n = 0 \quad (21)$$

$$\sum_{i=2}^{\infty} i^n R_i = k_{s1}\theta \sum_{i=2}^{\infty} i^n P_i \quad (22)$$

$$\sum_{i=2}^{\infty} i^n S_i = k_{s2}\theta \sum_{i=2}^{\infty} i^n Q_i \quad (23)$$

where

$$\begin{aligned}
 a_1 &= 1 + (k_{11}A + k_{12}B + k_{s1})\theta \\
 a_2 &= k_{21}A\theta \\
 a_3 &= k_{11}A\theta \\
 a_4 &= 1 + (k_{21}A + k_{22}B + k_{s2})\theta \\
 a_5 &= k_{12}B\theta \\
 a_6 &= k_{22}B\theta
 \end{aligned}$$

and the values of b_n and c_n depend upon the value of n as indicated below:

$n =$	0	1	2
$b_n =$	Q_1	$2Q_1 + \sum_{i=2}^{\infty} Q_i$	$4Q_1 + \sum_{i=2}^{\infty} Q_i + 2 \sum_{i=2}^{\infty} iQ_i$
$c_n =$	P_1	$2P_1 + \sum_{i=2}^{\infty} P_i$	$4P_1 + \sum_{i=2}^{\infty} P_i + 2 \sum_{i=2}^{\infty} iP_i$

Elimination of $\sum_{i=2}^{\infty} i^n Q_i$ between eqs. (20) and (21) gives

$$\sum_{i=2}^{\infty} i^n P_i = \frac{[a_3(a_6 - a_4) - a_2 a_5]c_n - a_4 a_2 b_n}{(a_6 - a_4)(a_1 - a_3) + a_2 a_5} \quad (24)$$

and, by rearrangement of eq. (20), we get

$$\sum_{i=2}^{\infty} i^n Q_i = \frac{1}{a_2} \left[(a_1 - a_3) \sum_{i=2}^{\infty} i^n P_i - a_2 b_n - a_3 c_n \right]. \quad (25)$$

The sums necessary to evaluate the moments from the equation

$$M_n = \sum_{i=1}^{\infty} i^n P_i + \sum_{i=1}^{\infty} i^n Q_i + \sum_{i=2}^{\infty} i^n R_i + \sum_{i=2}^{\infty} i^n S_i$$

can now be obtained by solving eqs. (24), (25), (22), and (23) in succession with values of n equal to 0, 1, and 2.

These calculations can be considerably simplified at high copolymer molecular weights, since for this case

$$\begin{aligned} \sum_{i=1}^{\infty} i^2 P_i &\gg \sum_{i=1}^{\infty} iP_i \gg \sum_{i=1}^{\infty} P_i \gg P_1 \\ \sum_{i=1}^{\infty} i^2 Q_i &\gg \sum_{i=1}^{\infty} iQ_i \gg \sum_{i=1}^{\infty} Q_i \gg Q_1 \end{aligned}$$

and the propagation constants k_{11} , k_{21} , k_{22} , and k_{12} are much greater than the termination constants k_{s1} and k_{s2} . Also, the rate at which P_i is lost by reaction will be much larger than the rate at which it exits from the reactor. By use of these inequalities, eq. (25) reduces to

$$\sum_{i=2}^{\infty} i^n Q_i = \frac{k_{12}B}{k_{21}A} \sum_{i=2}^{\infty} i^n P_i$$

and the equation for the moments becomes

$$M_n = \sum_{i=2}^{\infty} i^n P_i \left[(1 + k_{s1}\theta) + \frac{a_3}{a_2} (1 + k_{s2}\theta) \right].$$

Thus, DP_n and DP_w are given by

$$DP_n = P_m/P_t \quad (26)$$

$$DP_w = P_w/P_m \quad (27)$$

The expressions for b_n and c_n when n is equal to 1 and 2 can also be simplified to the following:

$n =$	1	2
$b_n =$	$a_5 P_t / a_2$	$2a_5 P_m / a_2$
$c_n =$	P_t	$2P_m$

so that eq. (24) yields

$$P_m = rP_t \quad (28)$$

$$P_w = 2rP_m \quad (29)$$

where

$$r = \frac{a_3(a_5 - a_4) - a_2a_5 - a_4a_5}{(a_6 - a_4)(a_1 - a_3) + a_2a_5}$$

Substitution of eqs. (28) and (29) into eqs. (26) and (27) yields the final results

$$DP_n = r$$

$$DP_w = 2r$$

and the ratio DP_w/DP_n again equals 2, as it did for the case of homopolymerization with no termination by combination.

In order to evaluate the parameter r , the monomer concentrations in the reactor outlet must be computed by solution of the material balance equations

$$A^0 - A = (k_{11}P_tA + k_{21}Q_tA)\theta$$

$$B^0 - B = (k_{22}Q_tB + k_{12}P_tB)\theta$$

$$P_t = (I_p + k_{21}Q_tA - k_{12}P_tB - k_{s1}P_t)$$

$$Q_t = (I_q + k_{12}P_tB - k_{21}Q_tA - k_{s2}Q_t).$$

CONCLUSIONS

Determination of the moments of the size distribution of addition polymers made in a CFSTR leads to relatively simple equations for the polymer's number-average and weight-average molecular weight as a function of the reactor operating conditions. These results are exact, and no simplifying assumptions need to be made in their derivation. Also, even for very complex polymerization systems, the determination of DP_n and DP_w from the moments involves only the successive solution of algebraic equations, and the cumbersome calculations often necessary to evaluate the degree of polymerization from expressions for the size distribution are avoided.

Nomenclature

A	monomer A and its concentration
B	monomer B and its concentration
DP_n	number-average degree of polymerization
DP_w	weight-average degree of polymerization
I_p	rate of initiation of polymer chains P_i
I_q	rate of initiation of polymer chains Q_i
i	number of monomer units in a polymer chain
k_c	rate constant for combination termination
k_d	rate constant for disproportionation termination
$k_p, k_{11},$ $k_{21}, k_{12},$ k_{22}	rate constants for propagation
k_s	rate constant for spontaneous termination
M_n	n th moment of the polymer size distribution
N_i	concentration of all polymer chains i monomer units long
P_i, Q_i	living polymer chains i monomer units long ending in monomers A and B, respectively, and their concentrations
R_i, S_i	dead polymer chains i monomer units long ending in monomers A and B respectively, and their concentrations
θ	residence time in a stirred reactor

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