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### The Effect of Backmixing on the Molecular Weight Distribution of Polymers

Thomas E. Corrigan<sup>a</sup>; Michael J. Dean<sup>a</sup>

<sup>a</sup> Mobil Chemical Company, Metuchen, New Jersey

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## The Effect of Backmixing on the Molecular Weight Distribution of Polymers

THOMAS E. CORRIGAN and MICHAEL J. DEAN

*Mobil Chemical Company  
Metuchen, New Jersey*

### SUMMARY

One of the factors that has a great effect on the physical properties of polymers is the molecular weight distribution. There is an increasing trend in the polymer manufacturing industry away from batch processes toward continuous processing. One of the drawbacks of continuous flow reactors is backmixing, which has a deleterious effect on the molecular weight distribution. This paper demonstrates this effect on a specific type of polymer. Equations are presented for batch, semibatch, and single continuous stirred tank reactors.

Kinetics equations based upon the equal reactivity principle are presented and compared with simple series reactions. The case of unequal reactivity of the monomer is also presented.

### INTRODUCTION

One of the major factors that affects the physical properties of a polymer is the molecular weight distribution [5, 19]. In continuous-flow reactors the phenomenon of backmixing may have a large deleterious effect on the molecular weight distribution and thus on the physical properties [5, 15, 19].

In a batch reactor all elements of the reacting mass remain in the reactor the same length of time. If a flow process is used, there is a wide distribution of residence times of the various elements of the fluid in the reactor. The intermixing of particles of fluid which have been in the reactor different lengths of time is termed "backmixing" [7, 10, 11, 14, 24]. It will be demonstrated below how this affects the molecular weight distribution [15, 20].

In chemical processes that do not involve polymerization, back-

mixing usually has a harmful effect on product yield [13, 20, 23]. In these cases its effects can be virtually eliminated by the use of reactors that have very near plug flow characteristics. These are tubular reactors and packed tower reactors, both of which types have dispersion numbers\* less than 0.01 or 0.02 [11, 14, 20]. These reactors do not have the characteristic of low backmixing for the highly viscous polymeric materials that are encountered in bulk polymerizations or in polycondensation reactions [20].

In a long tube reactor the polymer would be in laminar flow, which in itself gives serious backmixing and, in addition, gives no flow at the tube walls. The latter could lead to plugging as the material on the walls would become overpolymerized. The use of a packed tower reactor might be unfeasible for the same reason [5, 10, 14].

Methods that can be used to reduce backmixing in continuous bulk polymerizations involve the use of (1) a series of tanks with powerful agitators, (2) rotary screw polymerizers, or (3) scraped wall heat exchangers. In all of these there is some backmixing.

In this paper we will examine the effect of backmixing on the molecular weight distribution of a linear living polymer by comparing the distributions in a batch, in a semibatch, and in a single continuous stirred tank reactor. The distributions will be derived from kinetics considerations using the principle of equal reactivity. Equations will also be presented for the case of unequal reactivity of the monomer. In all cases instantaneous availability of the initiator is assumed. Since we are considering a living polymer, there will be no termination reactions [5].

### **SIMILARITY TO SERIES AND SERIES PARALLEL REACTIONS** [21, 22, 25]

To relate the molecular weight distribution in polymers to the kinetics of series and series parallel reactions, we will consider first the simple first-order series reaction in batch and continuous stirred tank reactors. This will be extended to the case of an infinitely long series reaction with equal probability of reaction of all end groups. Series parallel reactions will be considered next. This will be developed for batch, semibatch, and continuous stirred tank reactors, for the case of the infinitely long series parallel reaction with equal reactivity. The similarity between the latter case and the case of linear polymerization will be demonstrated. The analogy between the molecular weight distribution equations and the product distribution equations will be discussed.

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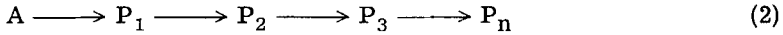
\*The dispersion number is the dimensionless group  $D/uL$ .

**FIRST-ORDER SERIES REACTION [1, 3, 4, 6, 15, 20]**

The first-order series reaction is represented by the equation



Let us consider an infinite series of equal reactivity:



and all of the  $k$ 's are equal. The equation for the conversion of A is

$$-dC_A/dt = kC_A \quad (3)$$

Its integral form is

$$A = C_A/C_{A_0} = e^{-kt} \quad (4)$$

where A is defined as  $C_A/C_{A_0}$ . For the first product,  $P_1$ ,

$$dC_{P_1}/dt = kC_A - kC_{P_1} \quad (5)$$

$$(dC_{P_1}/dt) + kC_{P_1} = kC_A = kC_{A_0} e^{-kt} \quad (6)$$

The integrating factor is  $e^{kt}$  and the solution is

$$C_{P_1} e^{kt} = kC_{A_0} t + I \quad (7)$$

With no higher products in the feed

$$I = 0$$

$$C_{P_1} = kC_{A_0} t e^{-kt} \quad (8)$$

Letting  $P_1 = C_{P_1}/C_{A_0}$ ,

$$P_1 = kte^{-kt} \quad (9)$$

The equation for  $P_2$  is

$$dC_{P_2}/dt = kC_{P_1} - kC_{P_2} \quad (10)$$

This is solved in the same manner to get

$$P_2 = [(kt)^2/2] e^{-kt} \quad (11)$$

The equation for the  $n^{\text{th}}$  product is

$$P_n = [(kt)^n/n!] e^{-kt} \quad (12)$$

From Eq. (12) we can plot  $P_n$  versus time for each product. We can also calculate the moles of each  $P_n$  present at any instant and plot the percent of each against  $n$ . The latter plot would correspond to a number-average molecular weight distribution plot [5, 20].

To get the product distribution in terms of the amount of A reacted we use Eq. (4):

$$A = e^{-kt}$$

$$-\ln A = kt \quad (13)$$

Thus

$$P_n = [A(-\ln A)^n/n!] \quad (14)$$

or

$$P_n = |A(\ln A)^n/n!| \quad (15)$$

Equation (15) is similar to the molecular weight distribution equation in living linear polymers [20].

If the reactions of Eq. (2) are taking place in a continuous stirred tank reactor, the equation for A is obtained by a balance over the reactor. Thus

$$FC_{A_0} - kC_A V = FC_A \quad (16)$$

This reduces to

$$A = C_A/C_{A_0} = 1/(1 + k\theta) \quad (17)$$

A similar balance of  $P_1$  will lead to

$$P_1 = C_{P_1}/C_{A_0} = k\theta/(1 + k\theta)^2 \quad (18)$$

For  $P_n$ ,

$$P_n = (k\theta)^n/(1 + k\theta)^{n+1}$$

Since

$$A \equiv C_A/C_{A_0} = 1/(1 + k\theta) \quad (19)$$

$$k\theta \equiv (1 - A)/A \quad (20)$$

$$P_n = A(1 - A)^n \quad (21)$$

we will show below that Eq. (21) is analogous to the molecular weight distribution in living linear polymers [20].

### LINEAR POLYMERS [1, 2, 5, 20]

The infinitely long series parallel reaction is represented by the equations



The classical equations for polymerization are



and so forth.

If the first step is instantaneous,  $I^*$  becomes B and Eqs. (23) become Eqs. (22).

### PRODUCT DISTRIBUTION EQUATIONS

#### Case I: Batch Reactor

The differential rate equations for the series parallel reactions for equal reactivity are [10, 11, 17, 18]

$$A: -dC_A/dt = kC_A C_B + kC_A C_{P_1} + \cdots + kC_A C_{P_{n-1}} \quad (24)$$

$$B: -dC_B/dt = kC_A C_B \quad (25)$$

$$P_1: dC_{P_1}/dt = kC_A C_B - kC_A C_{P_1} \quad (26)$$

$$P_n: dC_{P_n}/dt = kC_A C_{P_{n-1}} - kC_A C_{P_n} \quad (27)$$

The material balance equations are

$$\begin{aligned} A_0 - A &= P_1 + 2P_2 + 3P_3 + \cdots + nP_n \\ 1 - B &= P_1 + P_2 + P_3 + \cdots + P_n \end{aligned} \quad (28)$$

where

$$A = \frac{C_A}{C_{B_0}} \quad B = \frac{C_B}{C_{B_0}} \quad P_n = \frac{C_{P_n}}{C_{B_0}}$$

The differential equation for A is

$$-dC_A/dt = kC_A (C_B + C_{P_1} + \cdots + C_{P_{n-1}}) \quad (29)$$

Comparing Eqs. (29) and (28) it can be seen that

$$-dC_A/dt = kC_A (C_{B_0} - C_{P_n}) \quad (30)$$

For an infinite series  $C_{P_n} \approx 0$  and Eq. (30) becomes pseudo first order:

$$-dC_A/dt = kC_{B_0}C_A \quad (31)$$

which integrates to

$$C_A = C_{A_0} e^{-kC_{B_0}t} \quad (32)$$

Dividing by  $C_{B_0}$  we get

$$A = A_0 e^{-kC_{B_0}t} \quad (33)$$

Equation (33) gives the amount of unreacted monomer as a function of time for a living polymer with instantaneous initiation (i.e.,  $B = B_0$  at  $t = 0$ ).

The equation for B is

$$-dC_B/dt = kC_A C_B \quad (34)$$

since

$$C_A = C_{A_0} e^{-kC_{B_0}t} \quad (32)$$

$$-dC_B/dt = kC_{A_0} (e^{-kC_{B_0}t}) C_B \quad (35)$$

The solution to Equation (35) is

$$\ln B = -A_0 (1 - e^{-kC_{B_0}t}) \quad (36)$$

Combining Eqs. (32) and (36) leads to

$$-\ln B = A_0 - A \quad (37)$$

Equation (37) will lead to the molecular weight distribution equations.

### PRODUCT DISTRIBUTION EQUATIONS [12, 14, 15, 24]

If the equation for  $P_1$  is

$$dC_{P_1}/dt = kC_A C_B - kC_A C_{P_1} \quad (26)$$

and for B is

$$-dC_B/dt = kC_A C_B \quad (25)$$

dividing Eq. (26) by Eq. (25) leads to

$$dC_{P_1}/dC_B = -1 + (C_{P_1}/C_B) \quad (38)$$

or

$$(dP_1/dB) - (P_1/B) = -1 \quad (39)$$

This is a linear differential equation that can be solved by use of the integrating factor  $1/B$ , giving the solution

$$P_1/B = - \int dB/B \quad (40)$$

or

$$P_1 = -B \ln B \quad (41)$$

The equation for  $P_2$  is

$$dC_{P_2}/dt = kC_A C_{P_1} - kC_A C_{P_2}$$

which, when solved in the same manner, gives

$$P_2 = B(\ln B)^2/2 \quad (42)$$



Likewise,

$$P_n = B(-\ln B)^n/n! \tag{43}$$

Equation (43) gives the number of moles of a polymer of  $n$  units as a function of the moles of remaining initiating molecule (not monomer).

A more convenient equation would be one relating  $P_n$  to  $A$ . Since

$$-\ln B = A_0 - A$$

then

$$B = e^{A_0 - A}$$

and thus

$$P_n = e^{-(A_0 - A)} (A_0 - A)^n/n! \tag{44}$$

If we let  $x_A$  equal the fraction of monomer reacted,

$$x_A = (A_0 - A)/(A_0)$$

and  $A_0 - A = A_0 x_A$ . Thus

$$P_n = (A_0 x_A)^n e^{-A_0 x_A} /n! \tag{45}$$

This gives the moles of polymer of chain length  $n$  in terms of monomer converted per mole of initiator present.

**Case II: Semibatch Reactor [8, 9, 24]**

A common industrial application of reactions such as those illustrated above is in the production of polyethylene or polypropylene glycols or of polyglycol ethers. These products are usually made in a semibatch process wherein the ethylene (or propylene) oxide is added slowly to a reactor containing the initial reactant. The rate of addition is controlled by total pressure in the vessel.

Balances on  $B$  and on  $P_1$  lead to the equations

$$FC_{B_0} - kC_A C_B = \overset{0}{FC_B} + [d(VC_B)/dt] \tag{46}$$

$$\overset{0}{FC_{P_{10}}} + kC_A C_B V - kC_A C_{P_1} V = \overset{0}{FC_{P_1}} + [d(VC_A)/dt] \tag{47}$$

It can be shown that for the case of constant pressure Eqs. (46) and (47) combine to give

$$(dP_1/dB) + (P_1/B) = -1 \tag{48}$$

which is the same equation as for a batch reactor. Thus the molecular weight distribution is the same for semibatch as for batch.

**Case III: Continuous Stirred Tank Reactor [16, 23, 25]**

The molecular weight distribution is very different in a continuous stirred tank reactor than in batch or semibatch. Balances on B and P<sub>1</sub> give

$$FC_{B_0} - kC_A C_B V = FC_B \tag{49}$$

$$FC_{P_1} + kC_A C_B V - kC_A C_{P_1} V = FC_{P_1} \tag{50}$$

Dividing by F and letting V/F = θ, these reduce to

$$C_{B_0} - C_B = kC_A C_B \theta \tag{51}$$

$$C_{P_1} = kC_A C_B \theta - kC_A C_{P_1} \theta \tag{52}$$

Dividing Eq. (52) by Eq. (51) leads to

$$C_{P_1} / C_{B_0} - C_B = (kC_A C_B \theta - kC_A C_{P_1} \theta) / kC_A C_B \theta \tag{53}$$

When we let P<sub>1</sub> = C<sub>P<sub>1</sub></sub>/C<sub>B<sub>0</sub></sub> and B = C<sub>B</sub>/C<sub>B<sub>0</sub></sub>, Eq. (53) becomes

$$P_1 / (1 - B) = 1 - (P_1 / B)$$

or

$$P_1 = B(1 - B) \tag{54}$$

In an analogous manner we get

$$P_2 = B(1 - B)^2 \tag{55}$$

$$P_n = B(1 - B)^n \tag{56}$$

To get  $P_n$  in terms of the monomer reacted we use the balances on A:

$$FC_{A_0} - (kC_A C_B V + kC_A C_{P_1} V + \dots) = FC_A \quad (57)$$

which leads to

$$C_{A_0} - C_A = kC_A (C_B + C_{P_1} + \dots) \theta \quad (58)$$

and since

$$\begin{aligned} C_{P_n} &\approx 0 \\ C_{A_0} - C_A &= kC_A C_{B_0} \theta \end{aligned} \quad (59)$$

Dividing by Eq. (59) we get

$$(C_{B_0} - C_B)/(C_{A_0} - C_A) = C_B/C_{B_0} \quad (60)$$

or

$$(1 - B)/(A_0 - A) = B \quad (61)$$

Thus

$$A_0 - A = (1 - B)/B \quad (62)$$

$$B = 1/[1 + (A_0 - A)] \quad (63)$$

or

$$B = 1/(1 + A_0 x_A) \quad (64)$$

Putting this value of B in Eq. (56) leads to

$$P_n = (A_0 x_A)^n / (1 + A_0 x_A)^{n+1} \quad (65)$$

It can be seen that the equations for calculating  $P_n$  in a polymeric mixture are the same as the equations for a first-order series reaction where the term  $A_0 x_A$  replaces  $kt$  in a batch process and  $k\theta$  in a continuous stirred tank reactor.

The method of application of the above equations to determine both number-average and weight-average molecular weight distribution curves is illustrated in Appendix A. Figure 1 shows an example of a weight-average distribution for both batch and semi-batch and for continuous stirred tank reactors. Figure 2 shows the corresponding number-average plots.

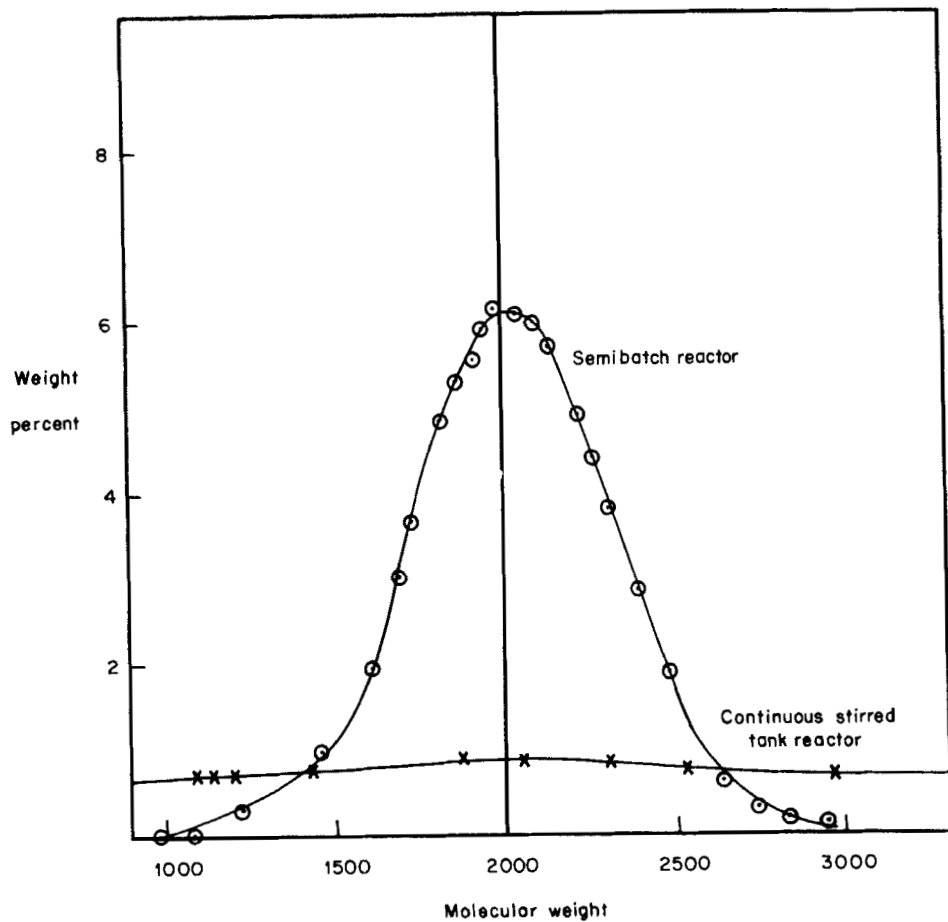


Fig. 1. Molecular weight distribution. Weight % versus molecular weight.

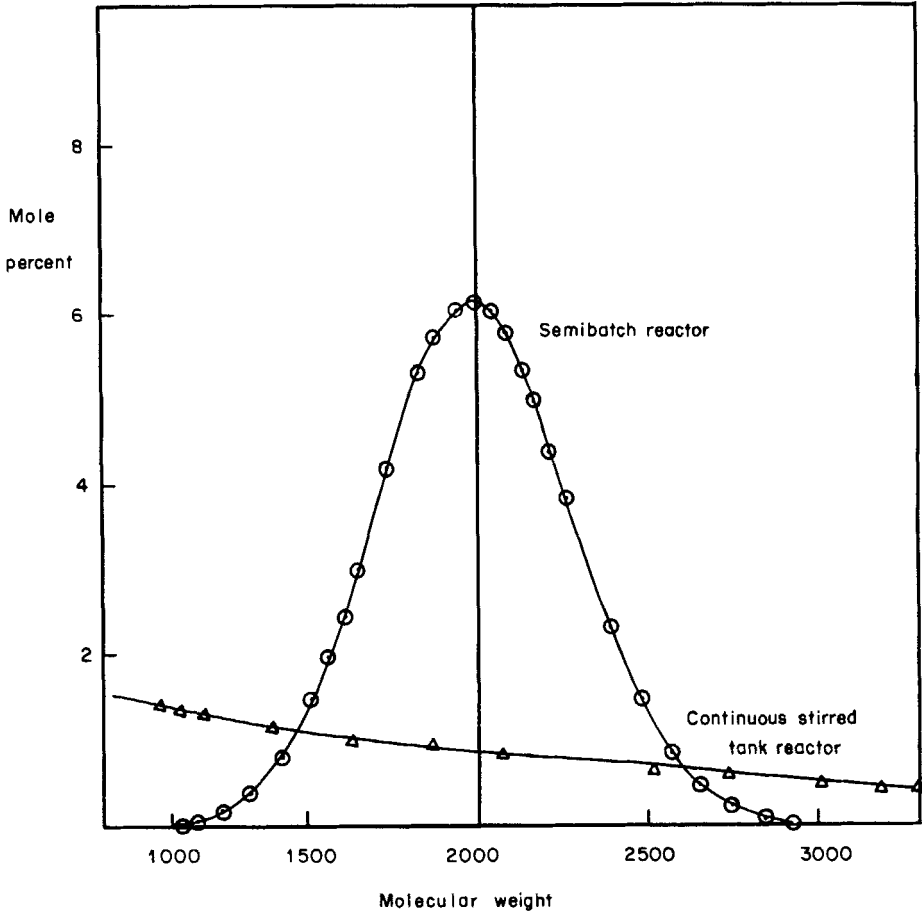


Fig. 2. Molecular weight distribution. Mole % versus molecular weight.

## UNEQUAL REACTIVITY [20]

The assumption of equal activity is usually made in polymerization kinetics. For the case where the rate constant for the monomer reaction is different from the rest of the steps which are alike, the equation for a batch process becomes

$$P_n = \frac{-\kappa}{1-\kappa} \frac{B^\kappa - B}{1-\kappa} + B^\kappa \left[ \sum_1^n \frac{(1-\kappa)^{n-2} (\ln B)^{n-1}}{(n-1)!} \right] \quad (66)$$

where  $\kappa = k/k_1$ .

Equation (66) is not practical except for a computer solution.

## SUMMARY AND CONCLUSIONS

Equations have been derived for molecular weight distribution equations in batch, semibatch, and continuous stirred tank polymerization. The great difference in the molecular weight distribution curves in the two types of reactors emphasizes the large effect of backmixing on this property. From this it can be concluded that even a moderate amount of backmixing will have a considerable effect on molecular weight distribution.

**APPENDIX A:  
PROCEDURE FOR CALCULATING MOLECULAR WEIGHT  
DISTRIBUTION**

**Batch or Semibatch Reactor**

1. Use the equation

$$P_n = \left| \frac{(A_0 x_A)^n e^{-A_0 x_A}}{n!} \right|$$

2. Put this in logarithmic form:

$$\log P_n = n \log A_0 x_A - (A_0 x_A / 2.303) - \log n!$$

3. Calculate  $A_0 x$  from the following equation:

$$A_0 x = (\text{average molecular weight of polymer minus weight of initial unit}) / (\text{molecular weight of repeating unit})$$

4. Tabulate  $P_n$ , molecular weight, total pounds ( $P_n \times MW$ ), and weight per cent.

5. A plot of  $100P_n$  versus molecular weight is the number-average curve.

6. A plot of weight per cent versus molecular weight is the weight-average curve.

### Continuous Stirred Tank Reactor

1. Use the equation

$$P_n = \frac{(A_0x)^n}{(1 + A_0x)^{n+1}}$$

or

$$P_n = \frac{1}{1 + A_0x} \left( \frac{A_0x}{1 + A_0x} \right)^n$$

2. Calculate  $A_0x$  as before.
3. Tabulate  $n$ ,  $P_n$ , molecular weight, total pounds, and weight per cent.
4. Plot  $100P_n$  versus molecular weight.
5. Plot weight per cent versus molecular weight.

### APPENDIX B: ILLUSTRATIVE PROBLEM

Calculate the number-average and weight-average molecular weight distributions of a 2000 average molecular weight polyethylene glycol which is made by adding ethylene oxide to diethylene glycol. Compare the molecular weight distributions obtained in a semibatch process with those obtained in a continuous stirred tank reactor. Plot the weight-per cent and number-per cent molecular weight distributions on regular coordinate paper and on probability paper.

#### Semibatch-Reactor Solution

$$P_n = | A_0x e^{-A_0x} / n! |$$

$$\ln P_n = n \ln(A_0x) - A_0x - \ln n!$$

$$\ln P_n = n \log(A_0x) - (A_0x/2.303) - \log n!$$

Average molecular weight is 2000.

Molecular weight of the repeating unit ( $C_2H_4O$ ) is 44.

Molecular weight of diethylene glycol is 106.

**Table 1.** Molecular Weight Distribution for 2000 Molecular Weight Polymer, Semibatch Reactor

n	Mol. Wt.	Mole%	Wt. %
20	986	0.004	0.002
24	1162	0.054	0.031
28	1338	0.377	0.252
30	1426	0.803	0.572
32	1514	1.700	1.287
34	1602	2.476	1.984
36	1690	3.642	3.077
38	1778	4.979	4.427
40	1866	5.701	5.319
42	1954	5.996	5.858
44	2042	6.013	6.119
46	2130	5.382	5.732
48	2218	4.421	4.903
50	2306	3.346	3.857
52	2394	2.337	2.978
54	2482	1.514	1.879
56	2570	0.870	1.117
58	2658	0.511	0.679
60	2746	0.267	0.367
62	2834	0.131	0.186
64	2922	0.060	0.088

Moles of A reacted ( $A_0x$ ) is  $(2000 - 106)/44$ .

$$A_0x = (1894/44) = 43.0.$$

Therefore,

$$\log P_n = n \log 43.0 - (43.0/2.303) - \log n!$$

$$\log P_n = 1.63347 n - (18.75 + \log n!)$$

The calculations are shown in Table 1. The equations used to calculate the results in this table are



**Table 2.** Molecular Weight Distribution for 2000 Molecular Weight Polymer, Continuous Stirred Tank Reactor

n	Mol. wt.	Mole%	Wt. %
20	986	1.43	0.70
21	1030	1.40	0.72
25	1206	1.28	0.77
30	1426	1.14	0.81
35	1646	1.02	0.83
40	1866	0.91	0.85
45	2086	0.81	0.85
50	2306	0.72	0.83
55	2526	0.64	0.78
60	2746	0.57	0.78
65	2966	0.51	0.76
70	3180	0.45	0.72
73	3306	0.42	0.70

$$P_n = \frac{(A_0x)^n e^{-(A_0x)}}{n!}$$

$$\log P_n = n \log(A_0x) - (A_0x/2.303) - \log n!$$

**Continuous-Stirred-Tank-Reactor Solution**

The equations used for calculating the values in Table 2 are as follows:

$$P_n = \frac{(A_0x)^n}{(1 + A_0x)^{n+1}}$$

$$A_0x = (2000 - 106)/44 = 43.0$$

$$P_n = (43)^n / (44)^{n+1}$$

$$\log P_n = n \log 43 - (n + 1) \log 44$$

$$= 1.6335n - 1.6435(n + 1)$$

$$= 1.6335 - 1.6435n - 1.6435$$

$$= -(1.6435 + 0.01n)$$

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