

Segregated and Two-Environment Reactor Models— Calculation of Molecular Weight Distributions

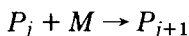
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Synopsis

An efficient procedure is presented for calculating molecular weight distributions for segregated reactors and two-environment reactor models.

Calculation of molecular weight distributions for segregated flow or two-environment mixing models by conventional methods are long and require a considerable amount of computer time. Therefore, few, if any, calculated molecular weight distributions have been presented in the literature for these mixing models.

If the method of characteristics and the continuous variable assumption as presented by Zeman and Amundson¹ and used by Timm et al.⁶ are used, the time required to calculate a distribution is greatly reduced. This calculation procedure is illustrated as follows for a stepwise polymerization with no termination. The method can, however, be readily extended to other types of polymerization mechanisms. The reaction mechanism is



For the batch reactor, the production of polymer chains is given by

$$\frac{dP_j}{dt} = \alpha M (P_{j-1} - P_j) \quad (2)$$

or in terms of the continuous variable assumption,

$$\frac{\partial P}{\partial t} = -\alpha M \frac{\partial P}{\partial \eta} \quad (3)$$

where η is the continuous variable for the chain length and j is the discrete variable. By use of the method of characteristics, the solution for eq. (3) is

$$P(\eta(t), t) = P_1(t_0) \quad (4)$$

and

$$\eta(t) = 1 + \alpha \int_{t_0}^t C_m dt \quad (5)$$

$P_1(t_0)$ is obtained by integration of the following equation

$$\frac{dP_1}{dt} = \beta_i IM - \alpha MP_1 \quad (6)$$

The initiator concentration I is given by

$$I = I_0 e^{-\beta_i \tau} \quad (7)$$

where

$$\tau = \int_0^t M dt \quad (8)$$

Hence, eq. (6) can now be solved in terms of τ to yield

$$P_1 - P_1^0 = \frac{\beta_i I_0}{\alpha - \beta_i} [e^{-\beta_i \tau} - e^{-\alpha \tau}] \quad (9)$$

The monomer concentration for the batch reactor is given by

$$-\frac{dM}{dt} = \beta_i IM - \alpha P_T M \quad (10)$$

$$t = 0, \quad M = M^0, \quad P_T = P_T^0$$

Equations (2) through (10) constitute the set of equations which must be solved for a batch reactor. Equation (5), however, allows for a finite time for a polymer of length η to grow. This time will be referred to as T_η . For all times less than T_η , $P(\eta(t), t) = 0$.

For the segregated reactor with a well-stirred residence time distribution,

$$P(\eta)_{\text{seg}} = \frac{1}{\theta} \int_0^\infty \{P(\eta)\}_{\text{batch}} e^{-t/\theta} dt \quad (11)$$

$$P(\eta) = 0 \text{ for } t < T_\eta.$$

Therefore,

$$P(\eta)_{\text{seg}} = \frac{1}{\theta} \int_{T_\eta}^\infty \{P(\eta)\}_{\text{batch}} e^{-t/\theta} dt \quad (12)$$

From the batch solution, $P(\eta(t), t) = P_1(t_0)$, and a change of variable for the integration yields

$$P(\eta)_{\text{seg}} = \int_{y_n}^1 P_1(y_0) dy \quad (13)$$

where

$$y = 1 - \exp(-t/\theta)$$

Equation (5), in terms of y , becomes

$$\eta(y) = 1 + \int_{y_0}^y \alpha c_m \left(\frac{\theta}{1-y} \right) dy \quad (14)$$

The maximum chain length is obtained by setting $y_0 = 0$ and $y = 1$ in the above equation.

Figure 1 shows the characteristic curves for polymer chains in a batch reactor. From this figure, it is clear that for $y < y_{\eta'}$, there would be no polymer of chain length η' . For a chain length η' , the upper limit of integration of eq. (14) would vary from $y_{\eta'}$ to 1.0. For every value of y , there is a corresponding value of y_0 , and the value of y_0 would vary between 0 and $y_{0,m}$. The solution procedure that was followed is described below.

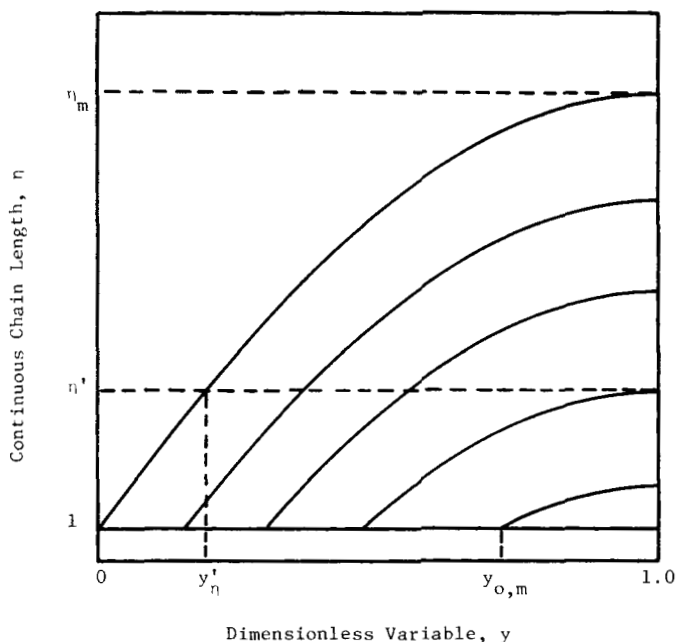


Fig. 1. Characteristic curves for growth of polymer chain lengths in a segregated CSTR.

For any chain length η , the value of the limit y_η in eq. (13) may be obtained by setting $y_0 = 0$ eq. (14). Next, for every value of y ($y_\eta < y \leq 1$), the corresponding value of y_0 is obtained from eq. (14). The value of P_1 at every value of y_0 is obtained from eq. (9). Finally, $\{P(\eta)\}_{\text{seg}}$ is calculated by integrating eq. (13).

MWD FOR CHEN AND FAN MODEL

The method of calculating MWD for the segregated model may be extended further to calculate the MWD for the two-environment reactor model proposed by Chen and Fan.² Molecular weight distributions may be calculated separately for the two environments and then combined in an appropriate manner² to get the overall distribution. The theory for calculating the MWD for this model is described below.

For the entering environment (micromixed), the distribution is readily calculated² from the material balance equations. For chain length 1,

$$P_{1E} \left(\frac{\theta R + 1}{\theta} \right) - \beta_{iE} C_{iE} C_{mE} + \alpha_E P_{1E} C_{mE} = 0 \tag{15}$$

Rearranging eq. (15),

$$P_{1E} = \frac{\beta_{iE} C_{mE} C_{iE} \theta}{1 + \theta R + \alpha_E \theta C_{mE}} \tag{15a}$$

For any chain length η ,

$$P_{\eta E} \left(\frac{\theta R + 1}{\theta} \right) - \alpha_E C_{mE} P_{\eta-1,E} + \alpha_E C_{mE} P_{\eta E} = 0 \tag{16}$$

By making the continuous variable assumption

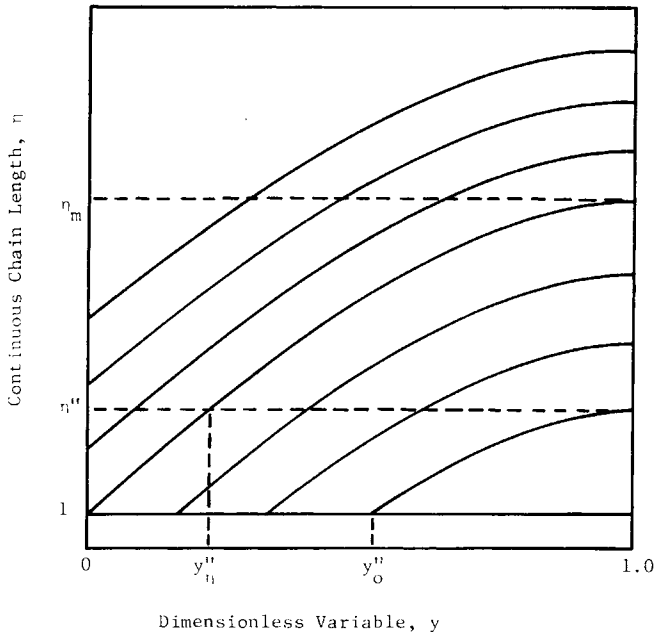


Fig. 2. Characteristic curves for growth of polymer chain lengths for Chen and Fan model.²

$$P_{\eta E} = P_{1E} e^{-(\eta-1)/\alpha E C_m E \theta'} \quad (17)$$

where

$$\theta' = \frac{\theta}{1 + R\theta} \quad (17a)$$

For the leaving environment,

$$\eta = \eta(0) + \int_0^t \alpha C_m dt \quad t \leq t_\eta \quad (18)$$

and

$$\eta = 1 + \int_{t_0}^t \alpha C_m dt \quad t \geq t_\eta \quad (19)$$

Making the change of variable from t to y ,

$$\eta = \eta(0) + \int_0^y \alpha C_m \left(\frac{\theta}{1-y} \right) dy \quad y \leq y_\eta \quad (20)$$

and

$$\eta = 1 + \int_{y_0}^y \alpha C_m \left(\frac{\theta}{1-y} \right) dy \quad y \geq y_\eta \quad (21)$$

Figure 2 shows the characteristic curves for polymer chain lengths in the leaving environment. From this figure, it is clear that for any chain length η'' , the value of $\eta(0)$ will vary between 1 and η'' . The upper limit of integration of eqs. (20) and (21) varies between $y_{\eta''}$ and 1.0, and the corresponding value of y_0 varies between 0 and y_0'' .

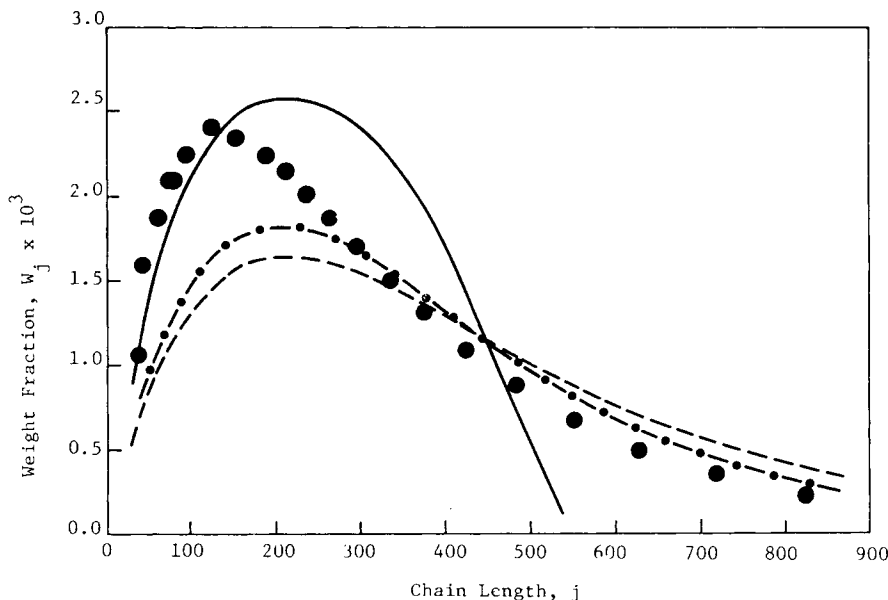


Fig. 3. Comparison between experimental and calculated differential molecular weight distribution for a typical run in reactor A: (●) experimental, A02; (—) segregated model; (- - -) micromixed model; (- · -) Chen and Fan model ($R = 0.025$).

The distribution from the leaving environment is given by

$$P_{\eta L} = \frac{R}{1 + R\theta} \int_0^\infty \{P(\eta(t), t)\}_{\text{batch}} e^{-t/\theta} dt \tag{22}$$

The two boundary conditions for this equation are

$$P(\eta(t), t) = P(\eta(0), 0) \quad t \leq t_\eta \tag{22a}$$

$$P(\eta(t), t) = P_1(t_0) \quad t \geq t_\eta \tag{22b}$$

Therefore, the equation for the leaving environment becomes

$$P_{\eta L} = \frac{R}{1 + R\theta} \int_0^{t_\eta} P(\eta(0), 0) e^{-t/\theta} dt + \frac{R}{1 + R\theta} \int_{t_\eta}^\infty P_1(t_0) e^{-t/\theta} dt \tag{23}$$

The value of $P(\eta(0), 0)$ is obtained from the entering environment. Thus,

$$P(\eta(0), 0) = P_{1E} e^{-1/\alpha_E C_{mE} \theta'(\eta(0)-1)} \tag{24}$$

where

$$\eta(0) - 1 = \eta - 1 - \int_0^y \alpha_E C_{mE} \left(\frac{\theta}{1 - y} \right) dy \tag{25}$$

After these substitutions, the final equation for the leaving environment in terms of the transformed variable y is

$$P_{\eta L} = \frac{R\theta}{1 + R\theta} \int_0^{y_\eta} P_{1E} e^{-1/\alpha_E C_{mE} \theta'(\eta(0)-1)} dy + \frac{R\theta}{1 + R\theta} \int_{y_\eta}^1 P_1(y_0) dy \tag{26}$$

The above equation for the leaving environment is valid up to a chain length of $\eta = \eta_m$. However, it is clear from Figure 2 that chain lengths higher than η_m

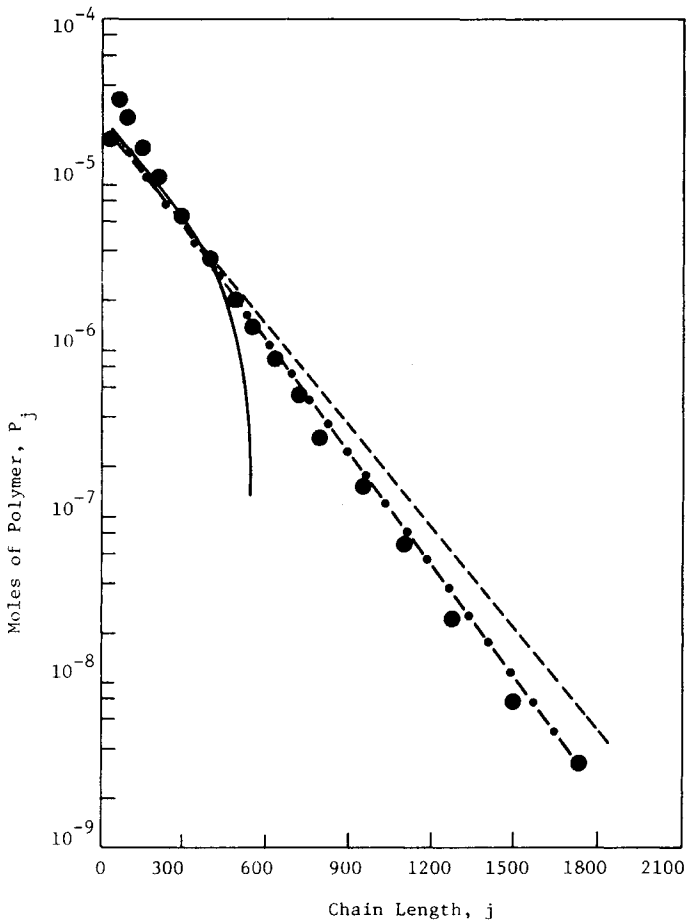


Fig. 4. Comparison between experimental and calculated molar molecular weight distribution for a typical run in reactor A: (●) experimental A02; (—) segregated model; (---) micromixed model; (- · -) Chen and Fan model ($R = 0.025$).

may grow for this model. Above this chain length, the contribution of the second term of eq. (26) becomes zero and the upper limit of integration of the first term of the equation becomes 1.0. Therefore,

$$P_{\eta L,1} = \frac{R\theta}{1 + R\theta} \int_0^{\eta} P_1 E^{-1/\alpha E C_m E \theta'(\eta(0)-1)} dy + \frac{R\theta}{1 + R\theta} \int_{\eta}^1 P_1(y_0) dy \quad \eta \leq \eta_m \quad (27)$$

and

$$P_{\eta L,2} = \frac{R\theta}{1 + R\theta} \int_0^1 P_1 E^{-1/\alpha E C_m E \theta'(\eta(0)-1)} dy \quad \eta > \eta_m \quad (28)$$

Combining the equations for the two environments,² the final equations for the overall molecular weight distribution for this model are

$$P_{\eta F,1} = \frac{1}{1 + R\theta} P_{\eta E} + P_{\eta L,1} \quad \eta \leq \eta_m \quad (29)$$

and

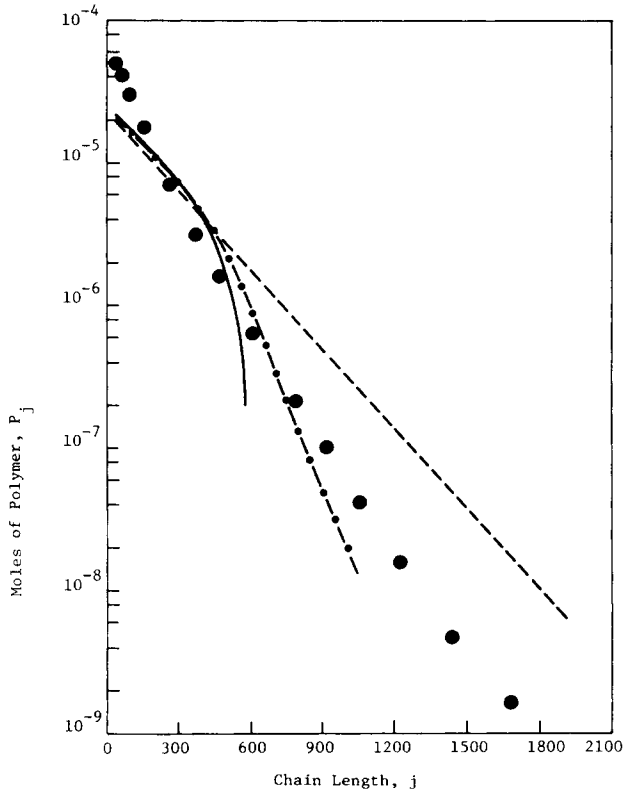


Fig. 5. Comparison between experimental and calculated molar molecular weight distribution for a typical run with mixed feed: (●) experimental A08; (—) segregated model; (---) micromixed model; (- · -) Chen and Fan model ($R = 2.26$).

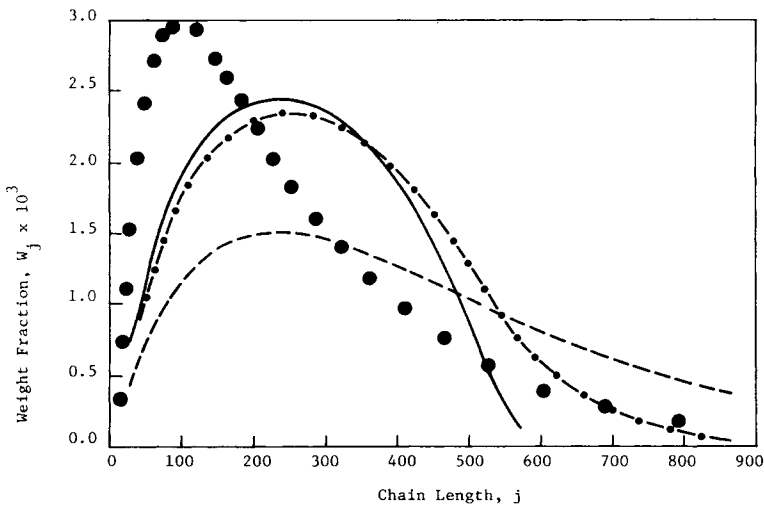


Fig. 6. Comparison between experimental and calculated differential molecular weight distribution for a typical run with mixed feed: (●) experimental A08; (—) segregated model; (---) micromixed model; (- · -) Chen and Fan model ($R = 2.26$).

$$P_{\eta F,2} = \frac{1}{1 + R\theta} P_{\eta E} + P_{\eta L,2} \quad \eta > \eta_m \quad (30)$$

The method of molecular weight distribution calculation for the Chen and Fan model² should, in general, be applicable to other two-environment reactor models, with some modifications. For the model proposed by Ng and Ripplin,³ the calculation should follow directly from Chen and Fan model² and should be simpler, since the entering environment, for that model, is segregated.

Calculated distributions for micromixed, segregated, and Chen and Fan's model are illustrated in Figures 3, 4, 5, and 6. The kinetic model used for these calculations was proposed by Porter et al.⁴ for the polymerization of isoprene in hexane with butyllithium. The experimental data were reported by Ahmad.⁵ We have also used this procedure to calculate distributions when α is a function of chain length.

An efficient procedure has been presented for calculation of molecular weight distributions. Even though a nonterminating polymerization mechanism was used, the method may be extended to more complex mechanisms.

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