

## Analysis of Condensation Polymerization Reactors. III. Continuous Reactors

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### Synopsis

The kinetic model for polycondensation reactions has been derived and techniques for validating the model have been described in Parts I and II of this work. This paper is concerned with using the results of Part I and II for the analysis and design of continuous polycondensation reactors.

### INTRODUCTION

When a kinetic model has been proven valid by experiments, and sufficient rate data have been obtained, then tools must be developed to use the model in the design of commercial reactors. This many times means developing design criteria for continuous reactors. It is the purpose of this paper to develop a method for the analysis and design of continuous polycondensation reactors.

Parts I and II of this work<sup>1,2</sup> should be referred to for definitions of the various symbols employed.

### CONTINUOUS FLOW STIRRED TANK REACTOR

#### Perfect Mixing

From the equal reactivity model and a steady-state material balance on a perfectly stirred reactor, the required hold-up time is given by

$$\bar{\tau} = \frac{p - {}^0p}{k(1 - p)(\alpha - p) - p\gamma} \quad (1)$$

where  $\bar{\tau} = \tau k_r {}^0A$ ,  $\tau = V/F = (\text{volume of the reactor})/(\text{flow rate})$ ,  ${}^0p$  is the degree of polymerization in the feed, and  $\gamma$  is the dimensionless by-product concentration  $\phi/{}^0A$ . This definition is made to include the case of open reaction systems.

From eq. (1) one can determine the required hold-up time if the feed concentration, the rate constants, and the degree of polymerizations are known.

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Assuming that the operating variables are known, it would be interesting to derive expressions for the molecular weight distributions in perfectly stirred reactors. An unsteady-state material balance may be made for each endgroup,  $A_i$  and  $B_i$ , and the sum of them,  $A$  and  $B$ .

$$\frac{dA}{dt} = \frac{A_0 - A}{\tau} - k_f AB + k_r M \phi \quad (2)$$

$$\frac{dA_i}{dt} = \frac{A_{i0} - A_i}{\tau} + R_i^A \quad (3)$$

$$\frac{dB}{dt} = \frac{B_0 - B}{\tau} - k_f AB + k_r M \phi \quad (4)$$

$$\frac{dB_i}{dt} = \frac{B_{i0} - B_i}{\tau} + R_i^B \quad (5)$$

where  $R_i^A$  and  $R_i^B$  are specific reaction rates for the  $i$ -th species.

New variables of the following form will now be defined.

$F_i^A = A_i/A$  is the fraction of  $A$  endgroups with monomers in the chain;  $F_i^B = B_i/B$  is the fraction of  $B$  endgroups with  $B$  monomers in the chain. Taking the total

$$\frac{dF_i^A}{dt} = \frac{1}{A} \frac{dA_i}{dt} - \frac{A_i}{A^2} \frac{dA}{dt} \quad (6)$$

$$\frac{dF_i^B}{dt} = \frac{1}{B} \frac{dB_i}{dt} - \frac{B_i}{B^2} \frac{dB}{dt} \quad (7)$$

Equations (2)–(5) may be substituted into eqs. (6) and (7). At steady state, the total derivatives will be zero.

$$\frac{dF_i^A}{dt} = \frac{dF_i^B}{dt} = 0 \quad (8)$$

The resulting equations may be solved for the  $F_i$ 's. The details of the derivations may be found in the Appendix.

### General Form for the Molecular Weight Distribution

The form to be used for the distributions of endgroups will be the following:

$$F_n^A = \frac{\sum_{j=0}^5 N_{nj}^A}{\sum_{j=0}^5 D_{nj}^A} \quad (9)$$

$$F_n^B = \frac{\sum_{j=0}^7 N_{nj}^B}{\sum_{j=0}^7 D_{nj}^B} \quad (10)$$

where  $N_{nj}$  and  $D_{nj}$  represent the contribution of each reaction to the numerator and denominator respectively. The index,  $j$ , will be designated according to Table I.

TABLE I

$j$	Reaction
0	Feed conditions
1	Forward reaction
2	Reverse reaction
3	A + M ester exchange
4	B + M ester exchange
5	M + M ester exchange

The index,  $n$ , denotes the number of structural units in the polymer chain. In any reactor where the polymer chains are being built up, terms of  $j = 0$  and 1 are required. Among the four other reactions the appropriate combination must be determined from experimental data and order of magnitude estimates of the reaction rate constants.

### Effect of Feed Conditions

The contributions of the feed to the molecular weight distributions are derived easily. The form of  $N_{n0}$  and  $D_{n0}$  becomes

$$\begin{aligned} N_{n0}^A &= (1 - p^{i-1})^{i-1} F_n^A \\ N_{n0}^B &= (\alpha - p^{i-1})^{i-1} F_n^B \\ D_{n0}^A &= (1 - p^{i-1}) \\ D_{n0}^B &= (\alpha - p^{i-1}) \end{aligned}$$

where  $p = \text{degree of polymerization} = 1 - (A/{}^0A)$ ,  $i$  is the reactor number counting from the first,  $\alpha = \text{ratio monomers in the feed} = {}^0B/{}^0A$ .

**Forward Reaction.** For  $n$  odd,

$$\begin{aligned} N_{n1}^A &= 2K\bar{\tau}(1 - p)(\alpha - p) \sum_{s=1}^{n-1/2} F_{2s-1}^A G_{n-2s+1}^B \\ N_{n1}^B &= 2K\bar{\tau}(1 - p)(\alpha - p) \sum_{s=1}^{n-1/2} F_{2s-1}^B F_{n-2s+1}^A \\ D_{n1}^A &= D_{n1}^B = K\bar{\tau}(1 - p)(\alpha - p) \end{aligned}$$

$\gamma$  is fixed by the pressure in the case of an open reactor system.

For  $n$  even,

$$\begin{aligned} N_{n1}^A &= N_{n1}^B = K\bar{\tau}(1 - p)(\alpha - p) \sum_{s=1}^{n-1} F_s^A F_{n-s}^B \\ D_{n1}^A &= K\bar{\tau}(1 - p)^2 \\ D_{n-1}^B &= K\bar{\tau}(\alpha - p)^2 \end{aligned}$$

**Reverse Reaction.** For  $n$  odd,

$$N_{n2}^A = 2\bar{\tau}\gamma(1-p)\left(1 - \sum_{s=1}^{n-1} F_s^A\right)$$

$$N_{n2}^B = 2\bar{\tau}\gamma(\alpha-p)\left(1 - \sum_{s=1}^{n-1} F_s^B\right)$$

$$D_{n2}^A = (n+1)\bar{\tau}\gamma(1-p) + \bar{\tau}\gamma p$$

$$D_{n2}^B = (n+1)\bar{\tau}\gamma(\alpha-p) + \bar{\tau}\gamma p$$

For  $n$  even,

$$N_{n2}^A = \bar{\tau}\gamma(1-p)\left[1 - \sum_{s=1}^{n-1} F_s^A + \frac{(\alpha-p)}{(1-p)}\left(1 - \sum_{s=1}^{n-1} F_s^B\right)\right]$$

$$N_{n2}^B = \bar{\tau}\gamma(\alpha-p)\left[1 - \sum_{s=1}^{n-1} F_s^B + \frac{(1-p)}{(\alpha-p)}\left(1 - \sum_{s=1}^{n-1} F_s^A\right)\right]$$

$$D_{n2}^A = (n+1)\bar{\tau}\gamma(1-p) + \bar{\tau}\gamma p$$

$$D_{n2}^B = (n+1)\bar{\tau}\gamma(\alpha-p) + \bar{\tau}\gamma p$$

**A + M Ester Exchange.** For  $n = 1$ ,

$$N_{13}^A = 2(1-p)2K_3$$

$$N_{13}^B = 0$$

$$D_{13}^A = 2K_3\bar{\tau}(1-p)$$

$$D_{13}^B = 0$$

For  $n$  odd  $\neq 1$ ,

$$N_{n3}^A = 2K_3\bar{\tau}(1-p)^2\left[\left(1 - \sum_{s=1}^{n-1} F_s^A\right) + \sum_{K=1}^{n-1/2} F_{2K-1}^A\left(1 - \sum_{s=1}^{n-2K+1} F_s^A\right)\right]$$

$$N_{n3}^B = 2K_3\bar{\tau}(1-p)(\alpha-p)\sum_{K=1}^{(n-1)/2} F_{2K}^B\left(1 - \sum_{s=1}^{n-2K} F_s^B\right)$$

$$D_{n3}^A = 2K_3\bar{\tau}(1-p)p + (n+1)K_3\bar{\tau}(1-p)^2$$

$$D_{n3}^B = (n-1)K_3\bar{\tau}(1-p)(\alpha-p)$$

For  $n$  even,

$$N_{n3}^A = K_3\bar{\tau}(1-p)(\alpha-p)\left[\left(1 - \sum_{s=1}^{n-1} F_s^B\right) + \sum_{k=1}^{n/2} F_{2k-1}^A\left(1 - \sum_{s=1}^{n-2k+1} F_s^B\right)\right] \\ + K_3\bar{\tau}(1-p)^2\sum_{K=1}^{n-2/2} F_{2K}^A\left(1 - \sum_{s=1}^{n-2K} F_s^A\right)$$

$$N_{n3}^B = K_3\bar{\tau}(1-p)(\alpha-p)\left[\left(1 - \sum_{s=1}^{n-1} F_s^B\right) + \sum_{k=1}^{n/2} F_{2k-1}^A\left(1 - \sum_{s=1}^{n-2k+1} F_s^B\right)\right] \\ + \sum_{k=1}^{n-2/2} F_{2k}^B\left(1 - \sum_{s=1}^{n-2k} F_s^A\right)$$

$$D_{n3}^B = K_3 \bar{\tau} (1 - p) p + nK_3 \bar{\tau} (1 - p)^2$$

$$D_{n3}^A = K_3 \bar{\tau} (\alpha - p) p + nK_3 \bar{\tau} (1 - p) (\alpha - p)$$

where  $K_3 = k_3/k_r$  and  $k_3$  is the specific rate constant for A + M ester exchange.

**B + M Ester Exchange.** The previous expressions for A + M ester exchange may be converted to B + M ester exchange by interchanging the symbol pairs A and B and  $(1 - p)$  and  $(\alpha - p)$  and substituting  $K_4$  for  $K_3$  where  $K_4 = k_4/k_r$  and  $k_4$  is the specific rate constant for B + M ester exchange.

**M + M Ester Exchange (Ester-Ester Interchange).** For  $n = 1$ ,

$$N_{15}^A = N_{15}^B = D_{15}^A = D_{15}^B = 0$$

For  $n$  odd  $\neq 1$ ,

$$N_{n5}^A = 2K_5 \bar{\tau} (1 - p)^2 \left[ \sum_{k=1}^{n-1} \left( 1 - \sum_{s=1}^k F_s^A \right) \left( 1 - \sum_{s=1}^{n-k} F_s^A \right) \right]$$

$$N_{n5}^B = 2K_5 \bar{\tau} (\alpha - p)^2 \left[ \sum_{k=1}^{n-1} \left( 1 - \sum_{s=1}^k F_s^B \right) \left( 1 - \sum_{s=1}^{n-k} F_s^B \right) \right]$$

$$D_{n5}^A = (n - 1)K_5 \bar{\tau} (1 - p)p$$

$$D_{n5}^B = (n - 1)K_5 \bar{\tau} (\alpha - p)p$$

For  $n$  even,

$$N_{n5}^A = K_5 \bar{\tau} (1 - p) (\alpha - p) \left[ \sum_{k=1}^{n-1} \left( 1 - \sum_{s=1}^k F_s^A \right) \left( 1 - \sum_{s=1}^{n-k} F_s^B \right) \right]$$

$$N_{n5}^B = N_{n5}^A$$

$$D_{n5}^A = (n - 1) K_5 \bar{\tau} (1 - p) p$$

$$D_{n5}^B = (n - 1) K_5 \bar{\tau} (\alpha - p) p$$

where  $K_5 = k_5/k_r$  and  $k_5$  is the specific rate constant for M + M ester exchange.

The number distribution function is now given by

$$F_n = \frac{AF_n^A + BF_n^B}{A + B} \quad (11)$$

Each of the  $F_i$ 's may be calculated by starting with  $i = 1$  and calculating each succeeding one in order. This very convenient initial value nature of the calculation is a direct result of the very simple form of eq. (1) of Part I.<sup>1</sup>

For a number of reactors in series, the molecular weight distribution may be calculated from the molecular weight distribution of the feed from the last previous stage.

### Well Stirred Reactor

Now consider a continuous flow stirred tank reactor in which the distribution of residence times is the same as the perfectly stirred tank. In this

case, however, there is no mixing at the molecular scale. The yields and molecular weight distributions will now be found by superimposing the distribution of residence times upon the batch predictions. The degree of polymerization is given by

$$p(\tau) = \int_0^{\infty} p(t) e^{-t/\tau} / \tau dt \quad (12)$$

where  $p(t)$  is the batch degree of polymerization.

This is simply a Laplace transform

$$p\left(\frac{1}{s}\right) = sL [p(t)] \quad (13)$$

where the Laplace variable,  $s$ , equals  $1/\tau$ .

$$p(\bar{\tau}) = \frac{r_2}{1 + (r_2 - r_1) \bar{\tau}} + \sum_{n=1}^{\infty} \left(\frac{r_2}{r_1}\right)^n \left[ \frac{r_1}{1 + (n+1)(r_2 - r_1) \bar{\tau}} - \frac{r_1}{1 + (n-1)(r_2 - r_1) \bar{\tau}} \right] \quad (14)$$

which converges for  $r_1/r_2 > 1.0$ .

The molecular weight distribution in this case becomes

$$\bar{F}(n) = \frac{\int_0^{\infty} F(n,t) [(\alpha + 1) - 2p(t)] \frac{e^{-t/\tau}}{\tau} dt}{\alpha + 1 - 2p(\tau)} \quad (15)$$

where  $F(n, t)$  is the batch molecular weight distribution which is available from Flory<sup>3</sup> or Case.<sup>4</sup>

The well-stirred reactor model will give yields between the yields of batch and perfectly stirred reactors with the same hold-up times. It represents an idealization of the agitation system, but less agitation is required to meet the requirements of this model. For this reason the model might be quite useful in highly viscous systems such as encountered in the last stages of polymerization.

## CONCLUSIONS

In this paper the kinetic model and results of batch experiments were employed to develop design criteria for continuous reactors. In the case of perfectly mixed reactors, reactor size and molecular weight distribution may be computed directly from algebraic equations. The molecular weight distributions are computed by computing the fraction of each component in the mixture beginning with the lowest molecular weight. The kinetic model permits this initial value type calculation.

## APPENDIX

Derivation of Molecular Weight Distributions  
in a Perfectly Stirred Tank

The molecular weight distributions may be derived from a transient material balance on a perfectly stirred continuous reactor. The fractions of each end group are determined by solving

$$\frac{1}{A} \frac{dA_i}{dt} - \frac{F_i^A}{A} \frac{dA}{dt} = 0 \quad (\text{A-1})$$

for  $F_i^A$ . The second term of the above equation is not affected by ester exchange. This leaves the first term which is multiplied by  $A/{}^0A$  to give

$$\frac{\tau}{{}^0A} \frac{dA_i}{dt} = 0 \quad (\text{A-2})$$

which must be solved for  $F_i^A$  to determine the contribution of ester exchange to the molecular weight distribution. Take, for instance,  $A + M$  ester exchange

$$\frac{\tau}{{}^0A} \frac{dA_i}{dt} = -2\tau k_3 A_1 \frac{M}{{}^0A} + 2\tau k_3 \left[ \sum_{n=1}^{\infty} M_{1n}^A + \sum_{n=1}^{\infty} M_{2n,2n+1}^A \right] = 0 \quad (\text{A-3})$$

note furthermore than

$$\sum_{n=1}^{\infty} M_{1,n}^A + \sum_{n=1}^{\infty} M_{2n,2n+1}^A = A - A_1 \quad (\text{A-4})$$

therefore

$$-2\tau k_3 \frac{A_1}{{}^0A} M + \tau k_3 \frac{A}{{}^0A} (A - A_1) = 0$$

The  $A_1$  may be transformed into  $F_1^A$

$$-2k_3 \tau F_1^A \frac{A}{{}^0A} (A + M) + 2\tau k_3 \frac{A^2}{{}^0A} = 0$$

The second term above contributes to the numerator

$$N_{13}^A = 2\tau k_3 {}^0A (1-p)^2 = 2K_3 \bar{\tau} (1-p)^2 \quad (\text{A-5})$$

where it is recalled that

$$\bar{\tau} = k_r {}^0A \tau$$

$$K_3 = k_3/k_r$$

The first term coefficient contributes to the denominator.

$$D_{13}^A = 2K_3 \bar{\tau} (1-p) \quad (\text{A-6})$$

For  $dA_2/dt$

$$\begin{aligned}
 dA_2/dt = & -k_3A_2M - k_3AM_{12}^A + k_3A \\
 & \times \left[ \sum_{n=2}^{\infty} M_{2n-2,2n} + \sum_{n=1}^{\infty} M_{2,2n+1}^{BB} + \sum_{n=1}^{\infty} M_{2n-1,2n+1}^{BB} \right] \\
 & + k_3A_1 \left[ \sum_{n=1}^{\infty} M_{2n-1,2n}^A + \sum_{n=1}^{\infty} M_{1,2n+1}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n+1}^{BB} \right]
 \end{aligned}$$

Here the middle group terms reduce to

$$\sum_{n=2}^{\infty} M_{2n-2,2n}^A + \sum_{n=1}^{\infty} M_{2,2n+1}^{BB} + \sum_{n=1}^{\infty} M_{2n-1,2n+1}^{BB} = B - B_1 - A_2 \quad (\text{A-7})$$

$$\sum_{n=1}^{\infty} M_{2n-1,2n}^A + \sum_{n=1}^{\infty} M_{1,2n+1}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n+1}^{BB} = B - B_1 \quad (\text{A-8})$$

Also

$$M_{12}^A = A_2 \quad (\text{A-9})$$

then

$$\begin{aligned}
 \frac{\tau}{{}^0A} \frac{dA_2}{dt} = & -k_3\tau \frac{A_2}{{}^0A} M - k_3\tau \frac{A}{{}^0A} A_2 + k_3\tau \frac{A}{{}^0A} (B - B - A_2) + k_3\tau \frac{A_1}{{}^0A} \\
 & \times (B - B_1) = 0
 \end{aligned}$$

which becomes

$$\begin{aligned}
 -K_3\bar{\tau} p(10p)F_2^A - 2K_3\bar{\tau} (1-p)^2 F_2^A + K_3\bar{\tau} (1-p) (\alpha - p) (1 - F_1^B) \\
 + K_3\bar{\tau} F_1^A (1-p) (\alpha - p) (1 - F_1^B) = 0
 \end{aligned}$$

The last two terms contribute to the numerator

$$N_{23}^A = K_3\bar{\tau} (1-p) (\alpha - p) [(1 - F_1^B) + F_1^A (1 - F_1^B)] \quad (\text{A-10})$$

The coefficients of the first two terms contribute to the denominator

$$D_{23}^A = K_3\bar{\tau} (1-p) p + 2K_3\bar{\tau} (1-p)^2 \quad (\text{A-11})$$

In the case of M + M ester exchange, the following substitutions are necessary.

$$\sum_{n=1}^{\infty} M_{1n}^A + \sum_{n=1}^{\infty} M_{2n,2n+1}^A = A - A_1 \quad (\text{A-12})$$

$$\sum_{n=1}^{\infty} M_{2n-1,2n}^A + \sum_{n=1}^{\infty} M_{1,2n+1}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n+1}^{BB} = B - B_1 \quad (\text{A-13})$$

Equation (A-2) becomes

$$\frac{\tau}{{}^0A} \frac{dA_2}{dt} = k_5MA_2 \frac{\tau}{{}^0A} + k_5 \frac{\tau}{{}^0A} (A - A_1) (B - B_1) = 0$$



The  $A_2$  may be transformed to  $F_2^A$  by dividing  $A_1$  by  $A$

$$-K_5 \bar{\tau} F_2^A (1-p)p + K_5 \bar{\tau} (1-p)(\alpha-p)(1-F_1^A)(1-F_1^B) = 0$$

The second terms contributes to the numerator

$$N_{25}^A = K_5 \bar{\tau} (1-p)(\alpha-p)(1-F_1^A)(1-F_1^B) \quad (\text{A-14})$$

The coefficient of  $F_2^A$  contributes to the denominator

$$D_{25}^A = K_5 \bar{\tau} (1-p)p \quad (\text{A-15})$$

If eq. (A-1) is multiplied by  $\tau A / {}^0A$  the following form results

$$\frac{\tau}{{}^0A} \frac{dA_i}{dt} = -\frac{\tau}{{}^0A_0} F_i^A \frac{dA}{dt} = 0 \quad (\text{A-16})$$

The contributions of the flow rates to the material balances is

$$\frac{dA_n}{dt} = \frac{{}^{i-1}A_n - {}^iA_n}{\tau}$$

$$\frac{dA}{dt} = \frac{{}^{i-1}A - {}^iA}{\tau}$$

Substituting these into eq. (A-16) gives

$$\frac{\tau}{{}^0A} \frac{{}^{i-1}A_n - {}^iA_n}{\tau} - \frac{\tau}{{}^0A} F_n^A \frac{{}^{i-1}A - {}^iA}{\tau} = 0$$

noting that  $F_n^A {}^iA = {}^iA_n$ , this reduces to

$$\left(1 - p\right) \left({}^{i-1}F_n^A\right) - F_n^A \left(1 - p\right) = 0$$

The first term contributes to the numerator

$$N_{n0}^A = \left(1 - p\right)^{i-1} F_n^A \quad (\text{A-17})$$

The coefficient of the second term contributes to the denominator

$$D_{n0}^A = \left(1 - p\right)^{i-1} \quad (\text{A-18})$$

The derivations presented here may all be performed for B type end-groups also. Equation (A-1) then becomes

$$\frac{1}{B} \frac{dB_i}{dt} - \frac{F_i^B}{B} \frac{dB}{dt} = 0 \quad (\text{A-19})$$

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Received April 25, 1968