

Analysis of Condensation Polymerization Reactors. II. Batch Reactors

T. T. SZABO and J. F. LEATHRUM,* *Plastics Division, Union Carbide Corporation, Bound Brook, New Jersey*

Synopsis

The kinetic model for polycondensation reactions was developed in Part I of this work. This kinetic model is now to be utilized as a framework for the analysis of batch experiments.

INTRODUCTION

Before using a kinetic model in the design of a commercial reactor, one must devise experiments which will validate the model and give measures of the reaction rate parameters. Batch experiments are quite useful for these purposes, and it is the analysis of batch polycondensation reactors which will be discussed in this paper.

Part I of this work¹ should be referred to for definitions of the various symbols employed.

ANALYSIS OF BATCH POLYCONDENSATION

By beginning an experiment with a mixture of monomers, it is possible to ignore completely the ester exchange reactions. In fact any batch reaction which begins at a "most probable molecular weight distribution" as defined by Flory² and Case³ will remain at a most probable distribution. In such cases ester exchange reactions will not affect the distribution.

Beginning with the above postulate the kinetic model will be used as a framework in analyzing batch experiments.

Test of the Model and Calculation of Forward and Reverse Reaction Rates

At this point it is convenient to introduce a normalized reaction parameter p , which will be called the degree of polymerization. This parameter will be defined only in the case in which the reaction is begun with pure monomers and a closed one-phase system. The degree of polymerization is then defined by the following four equalities.

$$p = 1 - (A/^0A) = \alpha [1 - (B/^0B)] = (\phi/^0A) = M/^0A \quad (1)$$

* Present address: Department of Statistics and Computer Science, University of Delaware, Newark, Delaware.

where

$$\alpha = {}^0B/{}^0A$$

Here 0A = initial concentration of A type monomers, 0B = initial concentration of B type monomers.

Equation (4) of Part I¹ in terms of p then becomes

$$dp/dt = k_f{}^0A(1 - p)(\alpha - p) - k_r{}^0Ap^2 \quad (2)$$

By letting $\theta = p_r{}^0At$, eq. (2) becomes

$$dp/d\theta = k(1 - p)(\alpha - p) - p^2 \quad (3)$$

By carrying out the reaction isothermally, k and k_r remain constant and eq. (3) may be integrated directly to give

$$\ln [(p - r_1)(p_0 - r_2)/(p - r_2)(p_0 - r_1)] = d_1(r_1 - r_2)k_r{}^0At \quad (4)$$

where p_0 = first isothermal measurement of the degree of polymerization.

$$r_1 = (-d_2 + \sqrt{d_2^2 - 4d_1d_3})/2d_1$$

$$r_2 = (-d_2 - \sqrt{d_2^2 - 4d_1d_3})/2d_1$$

$$d_1 = k - 1$$

$$d_2 = -k(\alpha + 1)$$

$$d_3 = k\alpha$$

It is often most convenient to measure the degree of polymerization p , by measuring the by-product concentration, ϕ . The final value of p will be used to calculate the equilibrium constant.

$$K = \frac{p^2}{(1 - p)(\alpha - p)} \quad (5)$$

The test of the kinetic model is achieved by plotting the left side of eq. (4) versus time. If a straight line results, then the kinetic model is appropriate. The slope of the straight line may then be used directly to calculate k_r .

Ester Exchange in Batch Reactions

The problem of changing molecular weight distribution without change in the degree of polymerization will now be considered. In each rate expression for A_n or B_n the total concentrations, A , B , M , and ϕ will remain constant. The resulting rate expressions may be divided by A and B , respectively, to give a set of ordinary first order differential equations.

$$\begin{aligned}
 dF_1^A/dt &= -2k_tBF_1^A + 2k_r\phi(1 - F_1^A) - 2k_3MF_1^A + 2k_3A(1 - F_1^A) \\
 dF_1^B/dt &= -2k_tAF_1^B + 2k_r\phi(1 - F_1^B) - 2k_4MF_1^B + 2k_4B(1 - F_1^B) \\
 dF_2^A/dt &= k_tBF_1^AF_1^B - k_tF_2^A(A + B) + k_r\phi[1 - F_1^A + (B/A)(1 - F_1^B) \\
 &\quad - 3F_2^A] - k_3F_2^A(M + A + B) + k_3B(1 - F_1^B) + k_3F_1^A(1 - F_1^B)B \\
 &\quad - k_4F_2^B(M + A + B) + k_4A(1 - F_1^A) + k_4AF_1^B(1 - F_1^A) \\
 &\quad - k_5MF_2^A + k_5B(1 - F_1^A)(1 - F_1^B) \\
 dF_2^B/dt &= (A/B)(dF_2^A/dt) \\
 &\quad \cdot \\
 &\quad \cdot \\
 &\quad \cdot
 \end{aligned}$$

where

$$F_i^A = A_i/A$$

and

$$F_i^B = B_i/B$$

In every case these equations have the form

$$dF_n^A/dt = -CF_n^A + H'(F_1^A, F_2^A, \dots, F_{n-1}^A, F_1^B, F_2^B, \dots, F_{n-1}^B, k_i, k_r, k_3, k_4, k_5) \quad (6)$$

where C is a constant and $H'(F_i^A, F_i^B, k_i)$ is a quadratic function in the F_i^A 's; $i < n$.

Since the final molecular weight distribution is known to be the most probable one, these equations may be separated into steady-state and transient parts by substituting

$$\begin{aligned}
 F_n^A &= F_n^A(p) + f_n^A \\
 F_n^B &= F_n^B(p) + f_n^B
 \end{aligned}$$

where $F_n^A(p)$, $F_n^B(p)$ denote most probable distributions and f_n^A , f_n^B are deviations from most probable distributions.

The transient equations then take the form as follows

$$\begin{aligned}
 df_n^A &= -Cf_n^A \\
 &+ H[F^A(p), F^B(p), f_1^A, f_2^A, \dots, f_{n-1}^A, f_1^B, f_2^B, \dots, f_{n-1}^B, k_t, k_r, k_3, k_4, k_5] \quad (7)
 \end{aligned}$$

Equation (7) can also be written as

$$df_n^A/dt = -Cf_n^A + H(t, k_i) \quad (8)$$

where $H(t, k_i)$ is some function of time and reaction rate constants. Taking the Laplace transform of eq. (8) yields

$$Sf_n^A(s) - (f_n^A)_{t=0} = -Cf_n^A(s) + L[H(t, k_i)] \quad (9)$$

$$(S + C)f_n^A(s) = (f_n^A)_{t=0} + L[H(t, k_i)] \quad (10)$$

$$f_n^A(s) = (f_n^A)_{t=0} \frac{1}{S - C} + \frac{1}{S + C} L[H(t, k_i)] \quad (11)$$

taking the inverse Laplace of eq. (11) yields

$$f_n^A = e^{-Ct}(f_n^A)_{t=0} + L^{-1}[L(e^{-Ct})L(H)] \quad (12)$$

Since

$$L^{-1}[L(e^{-Ct})L(H)] = e^{-Ct} * H(t, k_i) \text{ i.e.,}$$

denotes a convolution of e^{-Ct} and $H(t, k_i)$

$$\int_0^t H(\tau, k_i) e^{-C(t-\tau)} d\tau$$

thus

$$f_n^A = {}^0f_n^A e^{-Ct} + \int_0^t H(\tau) e^{-C(t-\tau)} d\tau \quad (13)$$

where ${}^0f_n^A$ denotes the initial value of f_n^A .

In principle, each f_n^A and f_n^B may be calculated in succession by this recursion formula beginning with

$$f_1^A = {}^0f_1^A e^{-2[k_t B + k_r \phi + k_3(A+M)]t} \quad (14)$$

$$f_1^B = {}^0f_1^B e^{-2[k_t A + k_r \phi + k_4(B+M)]t} \quad (15)$$

At best, however, eq. (13) is a very tedious solution to evaluate exactly. This form for the solution is well suited for numerical analysis, however. The starting information required for such a calculation would be the following: initial molecular weight distribution, ${}^0f_1^A$ and ${}^0f_1^B$; the steady values of A , B , M , and ϕ ; rate constants, k_t , k_3 , k_4 , k_5 (note k_r is not needed since the equilibrium constant is known from the statement above).

Even without a formal solution available some general conclusions may be drawn about the molecular weight distribution variations.

(1) Ester exchange reactions are not necessary to observe molecular weight distribution changes with no change in the degree of polymerization. The forward and reverse reactions are sufficient to produce the effect. This can be explained by the following thought experiment. Assume that we have initially a molecular weight distribution which is not the most probable one and where $k_{fT_1}(A)(B) \neq k_{rT_1}(\phi)(M)$. Suddenly we change the temperature of the mixture so that equilibrium will be reached with respect to the degree of polymerization, that is, $k_{fT_2}(A)(B) = k_{rT_2}(\phi)(M)$. Now before the mixture reaches equilibrium with respect to each species, that is, $dA_i/dt = 0$ and $dB_j/dt = 0$, a rearrangement of molecular weight distribution must take place as a direct consequence of total equilibrium in the system. Quite often this fact is overlooked, and any change in molecular weight distribution is blamed on ester interchange reactions.

(2) In every case it is observed that ester exchange reactions hasten the approach to the most probable distribution.

CONCLUSIONS

It has been found that the overall rate expression for condensation polymerization may be integrated readily and used as a framework for batch experiments to determine the validity of the kinetic model. If the model is appropriate, the same data may be used to compute the reaction rate constants.

Molecular weight distributions for batch reactors may be determined by integrating an infinite set of ordinary differential equations one at a time. This initial value nature of the molecular weight distribution calculations is very convenient bonus in the choice of the model.

APPENDIX

Analysis of Adiabatic Experiments

The equal reactivity model in the form of eq. (4) of Part I¹ will now be used as a framework in analyzing adiabatic batch experiments. The temperature will change according to the following expression.

$$C_p W \frac{dT}{dt} = (-\Delta H) V_r (k_t AB - k_r M \phi) \quad (\text{A-1})$$

where C_p is the specific heat (constant), W is the weight of reactor charge, V_r is the volume of the reactor, and ΔH is the heat of reaction.

This may be combined with eq. (4) of Part I to give

$$\frac{dT}{dt} = - \frac{(-\Delta H)}{\rho C_p} \frac{dA}{dt} = + \frac{(-\Delta H)^0 A}{\rho C_p} \frac{dp}{dt} \quad (\text{A-2})$$

where ρ is W/V_r .

If the heat of reaction is assumed to be constant, it may be calculated from ΔT and Δp .

$$(-\Delta H) = \frac{\rho C_p \Delta T}{{}^0 A \Delta p} \quad (\text{A-3})$$

Then the forward rate constant can be evaluated from the initial rate of temperature rise:

$$k_t = \frac{C_p \rho \alpha}{(-\Delta H)^0 A^2} \left(\frac{dT}{dt} \right)_0 \quad (\text{A-4})$$

The equilibrium constant would be evaluated as before.

References

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