Continuous Models for Polymerization

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Calculations for chemical reactor design in which a very large number of reactions take place, as in polymerization, have not been extensively carried out in the literature. Some work has been done. Recently (*7*) addition and copolymerization reactions were considered for continuous stirred tank reactors and batch reactors by solving a large number of differential equations on a computer. Since for polymerization reactions the number of reactions is conceptually infinite, the truncation required for a computer demands an approximation to a finite system. Because of the limitation of the memory in a digital computer the number of differential equations and hence of reactions which can be considered can be predicted. For polymerization reactions in which the degree of polymerization is great the truncated system may or may not be a good approximation. The use of the generating function (*4, 8*) has also been considered, and while this enables one to compute the concentration of any *n*-mer in a system without calculating the concentration of all of its precursors, it has not been sufficiently exploited to understand its range of applicability. The interesting facet of the generating function is that its use enables one to reduce rigorously an infinite system of equations to a finite system. Some infinite systems can be made to reduce to finite systems as shown in the treatment of polymerization reactor stability (*6, 10*). It must be noted however that the polymerization systems treated thus far have been idealized to quite simple models, and it may be necessary to solve the equations for the models as they stand for real systems, since the reductions mentioned above may not be possible. Goodrich (*4*) has shown how the method of steepest ascent may be used for a wide class of problems.

In the present paper a different technique will be presented for treating the same systems. Again the models will be idealized ones, and this paper should be considered as a tentative and introductory one for the method. In any mathematical system involving an infinite number of discrete variables the attempt is usually made to approximate the discrete problem by a continuous one. Thus in this case it will be convenient to think of concentration of a particular species of polymer P_j not as a function of the discrete variable j but of a continuous variable, as $P(j)$. It will then be shown that the infinite set of mass conservation equations for P_j will reduce to an ordinary differential equation for a continuous stirred tank reactor and a partial differential equation for the batch reactor. Now there are various ways of performing this transition from the discrete to the continuous model. For example this transition could be carried out as was done for a distillation problem (*1*). However the technique to be used here seems to be closer to the physical model than some others that have been considered by the authors.

THE CONTINUOUS VARIABLE TECHNIQUE

The propagation mechanism for addition polymerization may be represented by

$$P_j + M_1 \rightarrow P_{j+1}$$

with velocity constant k_{pj}. The symbols P_j, M_1, etc. stand for molecular species as well as their concentrations. The rate of formation r_{pj} of active polymer of length j (j monomer units) by propagation is

$$r_{pj} = k_{p,\,j-1}\, M_1\, P_{j-1} - k_{pj}\, M_1\, P_j$$

One may now define a function $P(j)$ such that $P(j) = P_j$ for integral values of j and for intermediate values by a suitable interpolation formula on P_j. In actual fact this will not be necessary, for calculations made later will only be at integral values of j. Similar statements hold for k_{pj}. If one now assumes that $k_p(j-1)\ P(j-1)$ may be expanded into a Taylor series $k_p(j-1)\ P(j-1) = k_p(j)\ P(j) -$

$$\frac{d}{dj}\left[k_p(j)\ P(j)\right] +$$

terms of higher order

and one neglects the higher order terms, then

$$r_p(j) = -M_1 \frac{d}{dj}\left[k_p(j)\ P(j)\right]$$

Note that this procedure is analogous to that used in obtaining the equation for the vibrating string as a limit of the set of equations for a set of connected discrete particles (*9*).

In what follows the total polymer concentration P_T plays a significant role. The Euler-Maclaurin summation formula (*5*) may be used to give

$$P_T = \sum_{j=1}^{\infty} P_j = \int_1^{\infty} P(j)\ dj + \frac{1}{2} P(1) + \frac{1}{2} P(\infty) +$$

terms of higher order

The first three terms on the right-hand side may be obtained as a first approximation from the area under the step function P_j when plotted against j. For very large j, P_j is zero so that

$$P_T = \sum_{1}^{\infty} P_j = \int_1^{\infty} P(j)\ dj + \frac{P_1}{2}$$

may be taken as a good approximation. Note that $P_1 = P(1)$.

MECHANISMS OF LINEAR ADDITION POLYMERIZATION

For a single monomer one may assume the following mechanism:

Initiation:

$$M_1 \xrightarrow{k_i} P_1$$

Propagation:

$$P_j + M_1 \xrightarrow{k_{pj}} P_{j+1}, \quad j = 1, 2, 3, \ldots$$

Monomer transfer:

$$P_j + M_1 \xrightarrow{k_{tfj}} P_1 + M_j, \; j = 1, 2, 3, \ldots$$

Termination steps:

Monomer:

$$P_j + M_1 \xrightarrow{k_{tj}} M_{j+1}, \quad j = 1, 2, 3, \ldots$$

Spontaneous:

$$P_j \xrightarrow{k_{tj}} M_j, \quad j = 1, 2, 3, \ldots$$

Disproportionation:

$$P_j + P_i \xrightarrow{k_{tj}} M_j + M_i, \; j, i = 1, 2, 3, \ldots$$

Combination:

$$P_j + P_i \xrightarrow{k_{tj}} M_{i+j}, \; j, i = 1, 2, 3, \ldots$$

If there are two monomers A and B then one possible mechanism for linear addition copolymerization is

Initiation:

$$A_1 \xrightarrow{k_{ai}} P_1$$

$$B_1 \xrightarrow{k_{bi}} Q_1$$

Propagation:

$$P_j + A_1 \xrightarrow{k_{paaj}} P_{j+1}, \quad j = 1, 2, 3, \ldots$$

$$P_j + B_1 \xrightarrow{k_{pabj}} Q_{j+1}, \quad j = 1, 2, 3, \ldots$$

$$Q_j + A_1 \xrightarrow{k_{pbaj}} P_{j+1}, \quad j = 1, 2, 3, \ldots$$

$$Q_j + B_1 \xrightarrow{k_{pbbj}} Q_{j+1}, \quad j = 1, 2, 3, \ldots$$

Spontaneous termination:

$$P_j \xrightarrow{k_{taj}} A_j, \quad j = 1, 2, 3, \ldots$$

$$Q_j \xrightarrow{k_{tbj}} B_j, \quad j = 1, 2, 3, \ldots$$

where P_j is the concentration of active polymer with an active end group A and with an obvious interpretation for the other symbols.

ADDITION POLYMERIZATION IN A STIRRED TANK REACTOR

Consider a stirred tank reactor with influent and effluent rates q and with a volume V. Suppose also the only feed to the reactor is monomer solution and catalyst. The special case of monomer termination with no chain transfer will be considered. The steady state equations are

$$M_1^{(o)} - M_1 \left[1 + k_i \theta + \theta \sum_1^{\infty} k_{pj} P_j + \theta \sum_1^{\infty} k_{tj} P_j \right] = 0$$

$$- P_1 [1 + \theta k_{p1} M_1 + \theta k_{t1} M_1] + \theta k_i M_1 = 0$$

$$- P_T + k_i \theta M_1 - \theta M_1 \sum_1^{\infty} k_{tj} P_j = 0$$

$$- M_j + \theta M_1 k_{t,\, j-1} P_{j-1} = 0, \qquad j = 2, 3, \ldots$$

$$- P_j - \theta M_1 (k_{pj} P_j - k_{p,\, j-1} P_{j-1}) - \theta M_1 k_{tj} P_j = 0, \qquad j = 2, 3, \ldots$$

These equations, in the transition to a continuous distribution of species, become

$$M_1^{(o)} - M_1 \left[1 + k_i \theta + \theta \int_1^{\infty} k_p(j)\, P(j)\, dj + \theta \int_1^{\infty} k_t(j)\, P(j)\, dj + \frac{\theta}{2} (k_{t1} + k_{p1})\, P(1) \right] = 0 \quad (1)$$

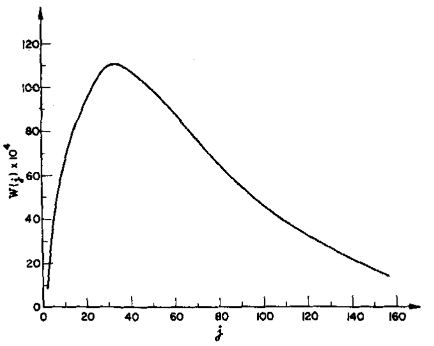

Fig. 1. Weight distribution of polymers in a stirred tank.

$$P(1) = \frac{\theta k_i M_1}{1 + \theta(k_{p1} + k_{t1})\, M_1} \quad (2)$$

$$P_T = k_i \theta M_1 - \theta M_1 \int_1^{\infty} k_t(j)\, P(j)\, dj - \frac{1}{2} \theta M_1 k_{t1} P(1) \quad (3)$$

$$M_j = \theta M_1 k_t(j-1)\, P(j-1), \quad j \geqslant 2 \quad (4)$$

$$\frac{d}{dj} [k_p(j)\, P(j)] + \frac{1 + \theta M_1 k_t(j)}{\theta M_1} P(j) = 0, \quad j \geqslant 2 \quad (5)$$

where $P_T = \int_1^{\infty} P(j)\, dj + \frac{1}{2} P_1$. Equation (5) may be integrated if the substitution $S(j) = k_p(j)\, P(j)$ is made with the result

$$P(j) = \frac{k_{p1}}{k_p(j)} P(1) \exp\left[- \int_1^j \alpha(j)\, dj \right], \quad j \geqslant 1$$

where (6)

$$\alpha(j) = \frac{1 + \theta M_1 k_t(j)}{\theta M_1 k_p(j)}$$

M_j may be obtained from Equation (4):

$$M(j) = \theta M_1 P(1)\, k_{p1} \frac{k_t(j-1)}{k_p(j-1)} \exp\left[- \int_1^{j-1} \alpha(j)\, dj \right], \quad j \geqslant 2 \quad (7)$$

In order that Equations (6) and (7) may be useful it is necessary to obtain M_1 and $P(1)$. If one substitutes $P(j)$ from Equation (6) and $P(1)$ from Equation (2) into Equation (1), a complicated equation in M_1 will be obtained which may be solved. $P(1)$ will then follow from Equation (2).

The system takes a particularly simple form when the rate constants are assumed to be independent of j. The equations for this case are

$$M_1^{(o)} - M_1 [1 + k_i \theta + \theta (k_p + k_t)\, P_T] = 0$$

$$P(1) = \frac{\theta k_i M_1}{1 + \theta (k_p + k_t)\, M_1}$$

$$P_T = \frac{k_i \theta M_1}{1 + \theta k_t M_1}$$

$$M(j) = \theta k_t M_1 P(1)\, e^{-\alpha(j-2)}, \qquad j \geqslant 2$$

$$P(j) = P(1)\, e^{-\alpha(j-1)}, \qquad j \geqslant 1$$

$$\alpha = \frac{1 + \theta k_t M_1}{\theta k_p M_1}$$

With this simplification M_1 is readily found as the solution of a quadratic equation.

The weight distribution function $W(j)$ is defined by

$$W(j) = \frac{\text{weight of active plus dead polymer of length } j}{\text{total weight of polymer}}$$

$$= \frac{j\, [P(j) + M(j)]}{M_1^{(o)} - M_1}$$

$$= \frac{P(1)}{M_1^{(o)} - M_1} j \left\{ \frac{k_p(1)}{k_p(j)} \exp\left[- \int_1^j \alpha(j)\, dj \right] + \frac{k_p(1)}{k_p(j-1)} \theta M_1 k_t(j-1) \exp\left[- \int_1^{j-1} \alpha(j)\, dj \right] \right\}$$

for the general case and for the case in which k_p and k_t are independent of j:

$$W(j) = \frac{P(1)}{M_1^{(o)} - M_1} [j\, e^{-\alpha(j-1)}]\, [1 + \theta k_t M_1 e^{\alpha}]$$

Differentiating $W(j)$ and setting it equal to zero one gets a value of j which is the most probable degree of polymerization. Thus $j_p = \alpha^{-1}$.

In order to illustrate the ideas presented here consider the following numerical example:

$M_1^{(o)} = 1$ g. mole/liter
$\theta = 1$ hr.
$k_i = 0.03$ hr.$^{-1}$
$k_p = 100$ liter/g. mole hr.
$k_t = 1.0$ liter/g. mole hr.

With this choice of parameters

$$\begin{aligned}
M_1 &= 0.493 \text{ g. moles/liter}\\
P(1) &= 2.93 \times 10^{-4} \text{ g. moles/liter}\\
P_T &= 0.989 \times 10^{-2} \text{ g. moles/liter}\\
P(j) &= 2.93 \times 10^{-4} \exp\,[-0.0304\,(j-1)],\ j \geqslant 1\\
M(j) &= 1.44 \times 10^{-4} \exp\,[-0.0304\,(j-2)],\ j \geqslant 2\\
W(j) &= 8.73 \times 10^{-4} \exp\,[-0.0304\,(j-1)],\ j \geqslant 1\\
j_p &= 32.9
\end{aligned}$$

Figure 1 shows a plot of $W(j)$ vs. j for the above example.

Mechanisms other than the one chosen for illustration may be handled in a similar manner. In the case of copolymerization six algebraic equations and two coupled differential equations must be solved. Table 1 contains the function $W(j)$ for several mechanisms of addition polymerization in a continuous stirred tank reactor. All rate constants in this table are assumed to be independent of j, and in the case of copolymerization it is assumed that $k_{paa} = k_{pba}$ and $k_{pbb} = k_{pab}$.

ADDITION POLYMERIZATION IN A SERIES OF CONTINUOUS WELL-AGITATED REACTORS

Consider a system of R well-agitated continuous reactors in which the feed to the first is a solution of monomer in concentration $M_1^{(o)}$ moles per liter in an amount of q liters per unit of time. It may be supposed that the temperature of each reactor and the volume of same is different but specified. For the sake of definiteness the rate constants will be taken independent of j, the termination step will be spontaneous, and there is no chain transfer. The mass balances for deactivated polymer, active monomer, and total active polymer in the rth reactor are

$$M_1^{(r-1)} = M_1^{(r)}\,[1 + k_{tr}\,\theta_r + \theta_r\,k_{pr}\,P_T^{(r)}] + k_{tr}\,\theta_r\,P^{(r)}(1), \quad r = 1 \text{ to } R \qquad (8)$$

$$P^{(r)}(1) = \frac{P^{(r-1)}(1) + \theta_r\,k_{tr}\,M_1^{(r)}}{1 + k_{tr}\,\theta_r + \theta_r\,k_{pr}\,M_1^{(r)}};$$

$$P^{(o)}(1) = 0, \quad r = 1 \text{ to } R \qquad (9)$$

$$P_T^{(r)} = \frac{P_T^{(r-1)} + \theta_r\,k_{tr}\,M_1^{(r)}}{1 + \theta_r\,k_{tr}};$$

$$P_T^{(o)} = 0, \quad r = 1 \text{ to } R \qquad (10)$$

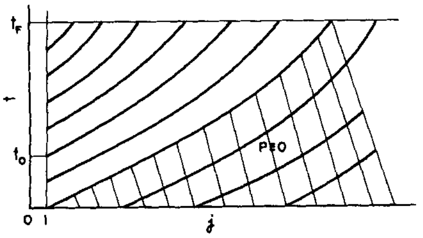

Fig. 2. Characteristic curves for active polymer distributions for linear addition polymerization in a batch reactor with monomer termination assumed.

These are simple algebraic equations which may be solved from reactor to reactor; in fact substitution of Equations (9)and (10) into Equation (8) gives a cubic equation in $M_1^{(r)}$, on the assumption that $M_1^{(r-1)}$, etc. are known.

The mass balances on the deactivated and active polymer distributions are

$$M^{(r)}(j) = \theta_r\,k_{tr}\,P^{(r)}(j) + M^{(r-1)}(j); \quad j \geqslant 2, \quad r = 1 \text{ to } R \qquad (11)$$

$$M_j^{(o)} = 0, \quad j \geqslant 2$$

$$\frac{dP^{(r)}(j)}{dj} + \alpha_r\,P^{(r)}(j) = \gamma_r\,P^{(r-1)}(j) \qquad (12)$$

$$\alpha_r = \frac{1 + \theta_r\,k_{tr}}{k_{pr}\,\theta_r\,M_1^{(r)}};\ \gamma_r = \frac{1}{\theta_r\,k_{pr}\,M_1^{(r)}}$$

$$P^{\circ}(j) = 0$$

$P^{(r)}(1)$ is calculated from Equations (8), (9), and (10). Equation (12) is a set of linear simultaneous first-order differential equations which may be written in matrix form as

$$\frac{d\bar{P}(j)}{dj} + \bar{\bar{A}}\,\bar{P}(j) = 0 \qquad (13)$$

where

$$\bar{P}(j) = \begin{bmatrix} P^{(1)}(j)\\ P^{(2)}(j)\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ P^{(R)}(j)\end{bmatrix}; \quad \bar{\bar{A}} = \begin{bmatrix} \alpha_1 & 0 & 0 & \cdots & \cdots & 0\\ -\gamma_2 & \alpha_2 & 0 & \cdots & \cdots & 0\\ 0 & -\gamma_3 & \alpha_3 & 0 & \cdots & 0\\ \cdot & & & & & \\ \cdot & & & & & \\ \cdot & & & & & \\ \cdot & & & & & \\ 0 & \cdots & \cdots & \cdots & -\gamma_r & \alpha_R\end{bmatrix}$$

and with the initial condition

$$\bar{P}(1) = \begin{bmatrix} P^{(1)}(1)\\ P^{(2)}(1)\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ P^{(R)}(1)\end{bmatrix}$$

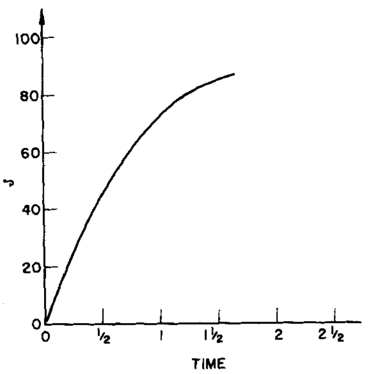

Fig. 3. Rate of growth of active polymers w monomer termination assumed.

The solution of Equation (13) is

$$\bar{P}(j) = \sum_{k=1}^{R} \frac{\bar{y}_k^{\,T}\,\bar{P}(1)}{\bar{y}_k^{\,T}\,\bar{x}_k}\,\bar{x}_k\,e^{-\lambda_k(j-1)}$$

where λ_k is an eigenvalue of the matrix $\bar{\bar{A}}$ and $\bar{x}_k$ and $\bar{y}_k^{\,T}$ are modal columns and modal rows of the matrix $adj[\bar{\bar{A}} - \lambda_k\,\bar{\bar{I}}]$. The eigenvalues of $\bar{\bar{A}}$ are $\lambda_k = \alpha_k$ and $\bar{x}_k$ and $\bar{y}_k$ may be taken as

$$\bar{x}_k = \begin{bmatrix} \prod_{i=2}^{R} (\alpha_i - \alpha_k)\\ \gamma_2 \prod_{i=3}^{R} (\alpha_i - \alpha_k)\\ \gamma_2\ \gamma_3 \prod_{i=4}^{R} (\alpha_i - \alpha_k)\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ \gamma_2\ \gamma_3 \cdots\cdots \gamma_R\end{bmatrix}; \quad \bar{y}_k = \begin{bmatrix} \gamma_2\ \gamma_3 \cdots \gamma_R\\ (\alpha_1 - \alpha_k)\ \gamma_3\ \gamma_4 \cdots \gamma_R\\ (\alpha_1 - \alpha_k)(\alpha_2 - \alpha_k)\gamma_4 \cdots \gamma_R\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ \prod_{i=1}^{R-2} (\alpha_i - \alpha_k)\ \gamma_R\\ \prod_{i=1}^{R-1} (\alpha_i - \alpha_R)\end{bmatrix}$$

$$\gamma_i \prod_{i=1}^{R}{}' (\alpha_i - \alpha_k)$$

$$.1) \prod_{i=l+1}^{R} \gamma_i \prod_{j=1}^{l-1} (\alpha_i - \alpha_k)$$

$$_t = \begin{bmatrix} \theta_1 \; k_{t1} & 0 & \dots\dots & 0 \\ 0 & \theta_2 \; k_{t2} & \dots\dots & \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ 0 & \dots\dots & \dots\dots & \theta_r \; k_{tr} \end{bmatrix}$$

The vector $\overline{P}(j)$ may then be written. As an example for $R = 2$

$$P^{(2)}(j) = \frac{\gamma_2 P^{(1)}(1)}{\alpha_2 - \alpha_1} e^{-\alpha_1(j-1)} + \frac{\gamma_2 P^{(1)}(1) + (\alpha_1 - \alpha_2) P_1^{(2)}}{\alpha_1 - \alpha_2} e^{-\alpha_2(j-1)}$$

The vector $\overline{M}(j)$ may be found easily, since Equation (11) in matrix form is

$$\overline{\overline{J}}\,\overline{M}(j) = \overline{\overline{k}}_t \overline{P}(j)$$

where

$$; \quad \overline{\overline{J}} \begin{bmatrix} 1 & 0 & 0 \dots\dots\dots & 0 \\ -1 & 1 & 0 \dots\dots\dots & 0 \\ 0 & -1 & 1 \dots\dots\dots & 0 \\ \cdot & & & \\ \cdot & & & \\ 0 & 0 & 0 \dots -1 & 1 \end{bmatrix}$$

and so since the inverse of $\overline{\overline{J}}$ may be easily found:

$$M^{(r)}(j) = \sum_{i=1}^{r} \theta_i \, k_{ti} \, P^{(i)}(j)$$

TABLE 1. MOLECULAR WEIGHT DISTRIBUTION FUNCTION $W(j)$ FOR SEVERAL TERMINATION MECHANISMS OF LINEAR ADDITION POLYMERIZATION WITH RATE CONSTANTS INDEPENDENT OF j

MECHANISM	W(j)
monomer termination $k_{tf} = 0$	$j\, e^{-\alpha(j-1)} \left[1 + \Theta\, k_t\, M_1\, e^{\alpha}\right] \frac{P(1)}{M_1^{(o)} - M_1}$ $\alpha = \frac{1 + \Theta\, k_t\, M_1}{\Theta\, k_p\, M_1}$
monomer termination $k_{tf} \neq 0$	$j\, e^{-\alpha(j-1)} \left[1 + \Theta\, k_{tf}\, M_1 + \Theta\, k_t\, M_1\, e^{\alpha}\right] \frac{P(1)}{M_1^{(o)} - M_1}$ $\alpha = \frac{1 + \Theta(k_t + k_{tf})\, M_1}{\Theta\, k_p\, M_1}$
spontaneous termination $k_{tf} = 0$	$j\, e^{-\alpha(j-1)} \left[1 + \Theta\, k_t\right] \frac{P(1)}{M_1^{(o)} - M_1}$ $\alpha = \frac{1 + \Theta\, k_t}{\Theta\, k_p\, M_1}$
disproportionation termination $k_{tf} = 0$	$j\, e^{-\alpha(j-1)} \left[1 + \Theta\, k_t\, P_T\right] \frac{P(1)}{M_1^{(o)} - M_1}$ $\alpha = \frac{1 + \Theta\, k_t\, P_T}{\Theta\, k_p\, M_1}$
combination termination $k_{tf} = 0$	$j\, e^{-\alpha(j-1)} \left[1 + \frac{\Theta\, k_t\, P(1)}{2} (j-1)\, e^{\alpha}\right] \frac{P(1)}{M_1^{(o)} - M_1}$ $\alpha = \frac{1 + \Theta\, k_t\, P_T}{\Theta\, k_p\, M_1}$
Copolymerization spontaneous termination $k_{tf} = 0$ $k_{paa} = k_{pba}$ $k_{pbb} = k_{pab}$	$\frac{j\, e^{-\gamma(j-1)} \left[P(1)\,(1 + \Theta\, k_{ta}) + Q(1)\,(1 + \Theta\, k_{tb})\right]}{\left[A_1^{(o)} + B_1^{(o)} - A_1 - B_1\right]}$ $\gamma = \frac{(\alpha\beta - 1)}{(2 + \alpha + \beta)}$ $\alpha = \left[\frac{1}{\Theta\, k_{paa}\, A_1} + \frac{k_{ta}}{k_{paa}\, A_1} + \frac{k_{pbb}\, B_1}{k_{paa}\, A_1}\right]$ $\beta = \left[\frac{1}{\Theta\, k_{pbb}\, B_1} + \frac{k_{tb}}{k_{pbb}\, B_1} + \frac{k_{paa}\, A_1}{k_{pbb}\, B_1}\right]$

LINEAR ADDITION POLYMERIZATION IN A BATCH REACTOR

In this section a batch reactor initially charged with monomer of concentration $M_1^{(o)}$ will be considered. For the special case of monomer termination an analytical solution for the active polymer distribution $P(j, t)$ is possible. When one assumes no chain transfer and rate constants independent of j, the unsteady state batch reaction conservation equations for $M_1(t)$, $P_1(t)$ $P_T(t)$, $M_j(t)$ and $P_j(t)$ are for the discrete case

$$\frac{dM_1}{dt} = -k_i\, M_1 - (k_p + k_t)\, P_T\, M_1; \quad M_1(0) = M_1^{(o)} \tag{14}$$

$$\frac{dP_1}{dt} = k_i\, M_1 - (k_p + k_t)\, P_1\, M_1; \quad P_1(0) = 0 \tag{15}$$

$$\frac{dP_T}{dt} = k_i\, M_1 - k_t\, P_T\, M_1; \quad P_T(0) = 0 \tag{16}$$

$$\frac{dM_j}{dt} = k_t\, M_1\, P_{j-1}; \quad j = 2 \text{ to } \infty; \quad M_j(0) = 0 \tag{17}$$

$$\frac{dP_j}{dt} = -k_p\, M_1\,(P_j - P_{j-1}) - k_t\, P_j; \quad j = 2 \text{ to } \infty; \quad P_j(0) = 0 \tag{18}$$

Equations (17) and (18) may be transformed to

$$\frac{\partial M(j, t)}{\partial t} = k_t\, M_1\, P(j-1, t), \quad j \geqslant 2, \quad M(j, o) = 0 \tag{19}$$

$$\frac{\partial P(j, t)}{\partial t} = -k_p\, M_1 \frac{\partial P(j, t)}{\partial j} - k_t\, M_1\, P(j, t); \quad j \geqslant 2 \tag{20}$$

$$P(j, 0) = 0$$

$$P(1, t) = P_1(t)$$

Note that Equations (14), (15), and (16) may be solved easily, since

$$\frac{dM_1}{-k_i - (k_p + k_t)\, P_T} = \frac{dP_1}{k_i - (k_p + k_t)\, P_1} = \frac{dP_T}{k_i - k_t\, P_T}$$

so that Equations (14), (15), and (16) reduce to simple uncoupled first-order ordinary differential equations. Therefore one assumes that $M_1(t)$, $P_1(t)$, and $P_T(t)$ are available as functions of the time. In order to solve Equation (20) the change of variable

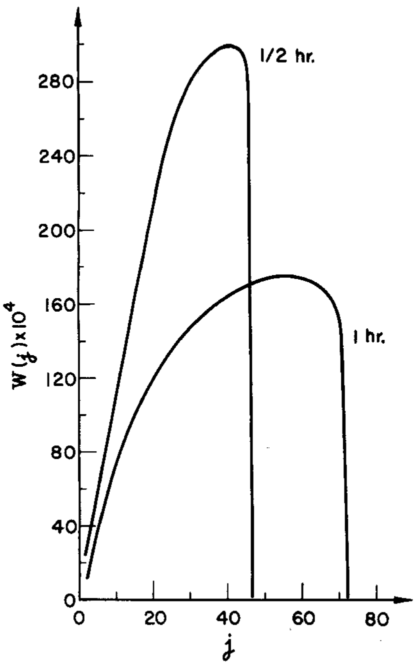

Fig. 4. Weight distribution of polymers produced in a batch reactor with monomer termination assumed.

$$\tau = \int_o^t M_1(\xi)\ d\xi \text{ or } t = f(\tau)$$

transforms it to

$$\frac{\partial P}{\partial \tau} = -k_p \frac{\partial P}{\partial j} - k_t P; \quad j \geqslant 2$$

with boundary conditions

$$P = 0, \quad \tau = 0$$
$$P = P_1[f(\tau)], \quad j = 1$$

The solution of this system obtained by the Laplace transformation is

$$P(j,t) = P_1\left[f \left(\int_o^t M_1(\xi)\ d\xi - \frac{j-1}{k_p} \right) \right] e^{-k_t/k_p\ (j-1)}, \quad \tau > \frac{j-1}{k_p}$$

$$P(j,t) = 0 \qquad \tau < \frac{j-1}{k_p}$$

The vanishing of the distribution $P(j,t)$ for $\tau < \dfrac{j-1}{k_p}$ quantitatively defines a finite time lag T_J which must elapse before a molecule of length J is grown, as

$$J = 1 + k_p\ \tau_J = 1 + k_p \int_o^{T_J} M_1(\xi)\ d\xi$$

The idea of time lag is consistent with the physical concept that an arbitrarily long molecule cannot be grown in an arbitrarily short period of time. It is suggested that the concept of a time lag should make one question the range of validity $t > 0$ of the set of ordinary differential equations usually written as a model for a batch reactor. In fact the whole concept of a rate expression for the formation of a very large molecule probably needs re-examination from a theoretical point of view. The equations arising from the application of the continuous variable technique may be considered as a model which is consistent with an improved range of validity, $t > T_J$.

The application of the Laplace transformation in the solution for $P(j,t)$ resulted from the fact that the monomer concentration occurred in the equations in a special way. In general for any other termination step a numerical method of solution must be used. The method of characteristics appears to be the best choice and will be briefly described. Equation (20) may be written

$$\frac{\partial P}{\partial t} + k_p M_1 \frac{\partial P}{\partial j} = -k_t M_1 P =$$
$$\left(\frac{dP}{dS}\right)_\phi = \left(\frac{dt}{dS}\right)_\phi \frac{\partial P}{\partial t} +$$
$$\left(\frac{dj}{dS}\right)_\phi \frac{\partial P}{\partial j}$$

where $\left(\dfrac{dP}{dS}\right)_\phi$ is the directional derivative of $P(j,t)$ along a set of curves ϕ in the (j,t) plane. In this case

$$\left(\frac{dt}{dS}\right)_\phi = 1 \quad \text{and}$$
$$\left(\frac{dj}{dS}\right)_\phi = k_p M_1(t)$$

so that the characteristic curves are defined by

$$\left(\frac{dj}{dt}\right)_\phi = k_p M_1(t) \qquad (21)$$

and Equation (20) becomes

$$\left(\frac{dP}{dt}\right)_\phi = -k_t M_1(t) P \qquad (22)$$

The characteristic curves are indicated in schematic form in Figure 2. It is apparent that $P(j,t)$ is identically zero along all characteristics emanating from the abscissa, since P is identically zero there. The characteristic curve emanating from the point $(1,0)$ gives the relationship between the length of the largest polymer grown and the time t. Quantitatively this relationship is obtained by integrating Equation (21) from $(1,0)$ to (J,t). Along the line $j = 1$, P has the value $P_1(t)$, and therefore by integrating Equation (22) along characteristics emanating from $(1,t)$ one obtains $P(j,t)$ for the entire space bounded by the lines $j = 1$ and $t = t_f$. These integrations give

$$j(t) = 1 + k_p \int_{t_o}^t M_1(\xi)\ d\xi$$

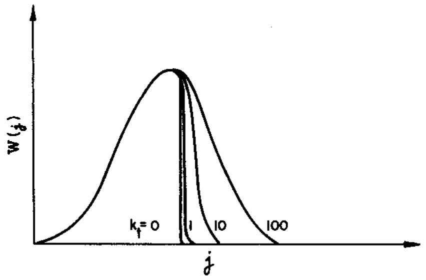

Fig. 5. Weight distribution of polymers as a function of termination rate k_t, with combination termination assumed.

$$P(j(t),t) = P_1(t_o)\ e^{-k_t \int_{t_o}^t M_1(\xi)\ d\xi}$$

The above methods may be extended to the case where the rate constants are not independent of j. The pertinent conservation equations, with monomer termination assumed, are for the continuous case

$$\frac{dM_1}{dt} = -M_1 \left[k_t + \int_1^\infty k_p(j)\ P(j,t)\ dj + \int_1^\infty k_t(j)\ P(j,t)\ dj + \frac{k_{p1} P_1}{2} + \frac{k_{t1} P_1}{2} \right] \qquad (23)$$

$$\frac{dP_1}{dt} = k_t M_1 - (k_{p1} + k_{t1})\ P_1 M_1 \qquad (24)$$

$$\frac{dP_T}{dt} = M_1 \left[k_t - \int_1^\infty k_t(j)\ P(j,t)\ dj - \frac{k_t P_1}{2} \right] \qquad (25)$$

$$\frac{\partial M(j,t)}{\partial t} = M_1 k_t (j-1)\ P(j-1),t) \quad j \geqslant 2 \qquad (26)$$

$$\frac{\partial P(j,t)}{\partial t} + M_1 \frac{\partial}{\partial j}[k_p(j)\ P(j,t)] + k_t(j)\ M_1 P(j,t) = 0 \quad j \geqslant 2 \qquad (27)$$
$$P(j,0) = 0$$
$$P(1,t) = P_1(t)$$

For monomer termination application of the Laplace transform is still valid, yielding

$$P(j,t) = P_1\left[f \left(\int_o^t M_1(\xi)\ d\xi - \int_1^j \frac{dj}{k_p(j)} \right) \right] \frac{k_{p1}}{k_p(j)}\ e^{-\int_1^j \frac{k_t(j)}{k_p(j)} dj}$$

TABLE 2. DIFFERENTIAL AND INTEGRAL RELATIONS ALONG CHARACTERISTIC CURVES FOR SEVERAL MECHANISMS OF BATCH REACTOR LINEAR ADDITION POLYMERIZATION WITH RATE CONSTANTS INDEPENDENT OF j

Mechanism	Characteristic Curves	Differential Relations	Integral Relations
monomer termination	$\left(\frac{dj}{dt}\right)_\phi = k_p M_1(t)$	$\left(\frac{dP}{dt}\right)_\phi = -k_t M_1(t) P$	$j = 1 + k_p \int_{t_o}^t M_1(\xi)\, d\xi$; $P(t) = P_1(t_o)\, e^{-k_t \int_{t_o}^t M_1(\xi)\, d\xi}$
spontaneous termination	↓	$\left(\frac{dP}{dt}\right)_\phi = -k_t P$	↓ $P(t) = P_1(t_o)\, e^{-k_t (t-t_o)}$
disproportionation termination or combination termination	↓	$\left(\frac{dP}{dt}\right)_\phi = -k_t P_T(t) P$	↓ $P(t) = P_1(t_o)\, e^{-k_t \int_{t_o}^t P_T(\xi) d\xi}$
co-polymerization spontaneous termination $k_{paa} = k_{pba}$ $k_{pbb} = k_{pab}$	$\left(\frac{dj}{dt}\right)_{\phi_1} = 0$ $\left(\frac{dj}{dt}\right)_{\phi_2} = k_{paa} A_1(t) + k_{pbb} B_1(t)$	$\frac{k_{pbb} B_1}{k_{paa} A_1} \left(\frac{dP}{dt}\right)_{\phi_1} = \left(\frac{dQ}{dt}\right)_{\phi_1} - \left[k_{tb} + k_{paa} A_1 + k_{pbb} B_1\right] Q$ $+ \left[\frac{k_{pbb} B_1}{k_{paa} A_1} k_{ta} + \frac{k_{pbb}^2 B_1^2}{k_{paa} A_1} + k_{pbb} B_1\right] P = 0$ $\left(\frac{dP}{dt}\right)_{\phi_2} + \left(\frac{dQ}{dt}\right)_{\phi_2} + k_{ta} P + k_{tb} Q = 0$	

$$\tau > \int_1^j \frac{dj}{k_p(j)}$$

$$P(j, t) = 0, \quad \tau < \int_1^j \frac{dj}{k_p(j)}$$

The method of characteristics solution is facilitated by use of the substitution $S(j) = k_p(j)\ P(j, t)$. The characteristic curves are defined by

$$\left(\frac{dj}{dt}\right)_\phi = k_p(j)\ M_1(t)$$

and Equation (27) becomes

$$\left(\frac{dS}{dt}\right)_\phi = -k_t(j)\ M_1(t)\ S$$

Integrating these relations one gets

$$\int_1^{j(t)} \frac{dj}{k_p(j)} = \int_{t_o}^t M_1(\xi)\ d\xi$$

$$P(j(t),t) = \frac{k_{p1} P_1(t_o)}{k_p(j(t))}\ e^{-\int_{t_o}^t k_t(j(\xi))\, M_1(\xi)\, d\xi}$$

Since the above integrations and integration of Equations (23), (24), and (25) are coupled, an iterative procedure is suggested.

1. Obtain initial approximations $M_1^{(o)}(t)$ and $P_1^{(o)}(t)$ by integrating Equations (23), (24), and (25) under the initial approximation

$$\left[\int_1^\infty k_p(j)\ P(j)\ dj\right]^{(o)} = k_{p1} P_T - \frac{k_{p1}\ P_1}{2}$$

$$\left[\int_1^\infty k_t(j)\ P(j, t)\ dj\right]^{(o)} = k_{t1} P_T - \frac{k_{t1}\ P_1}{2}$$

2. Use $M_1^{(o)}(t)$ and $P_1^{(o)}(t)$ to obtain an initial approximation $P^{(o)}(j, t)$ by the method of characteristics.
3. Use $P^{(o)}(j, t)$ to get second approximations $\left[\int_1^\infty k_p(j)\ P(j, t)\ dj\right]^{(1)}$ and $\left[\int_1^\infty k_t(j)\ P(j, t)\ dj\right]^{(1)}$.

Mechanisms other than the one chosen for illustration may be handled in a similar manner. In the case of copolymerization one must solve six ordinary differential equations and two coupled first-order partial differential equations. Application of the method of characteristics yields two families of characteristic curves along which simultaneous numerical integration of two coupled differential expressions must be carried out. Table 2 tabulates the pertinent relations along characteristic curves for several mechanisms of linear addition polymerization. All rate constants in this table are assumed to be independent of j.

Consider now a numerical example in which the same pertinent parameters are used as in the previous example. For purposes of illustration the termination is again assumed to be monomer. Figure 3 gives the largest polymer grown as a function of time. Notice that the largest polymer which can ever be produced is of length 93.

The weight distribution at two values of time is shown in Figure 4. Notice that the distributions fall off rather rapidly indicating that the concentration of active polymers of length j rises rapidly to its steady state value.

It should be pointed out that the continuous variable method gives weight distributions which fall off rapidly only if the prevailing mode of termination is assumed to be monomer, spontaneous, or disproportionation. For the case of combination termination the weight distributions fall off more and more gradually as the value of k_t is increased, as shown schematically in Figure 5. Since experimentally observed distributions also fall off gradually, it seems highly unlikely that any termination besides combination ever prevails in real situations. This is consistent with the conclusions of previous workers (2, 3).

NOTATION

A_j, B_j = jth polymers and concentrations of same
j = degree of polymerization
k (with various subscripts) = reaction velocity constants for initiation, propagation, or termination
M_j = dead polymer and concentration of same
P_j, $P(j)$ = concentration of active polymer
P_T = total polymer concentration
t = time

Greek Letters

α, γ = parameters defined in text
θ = holding time for stirred reactor
τ = pseudo time variable for batch reactor
ϕ = characteristic curves for batch reactor
λ_j = eigenvalue of a matrix

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