Stochastic Modeling of Polymerization in a Continuous Flow Reactor

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Synopsis

A stochastic approach, namely, a continuous time Markov chain (Markov process), is employed to analyze and model, in a unified fashion, both polymerization and dispersive mixing in a continuous flow reactor. Results include the distribution of numbers of active and dead polymers with chain length j both inside the reactor and at the exit. This approach can be extended to the determination of the degree of polymerization of a copolymer. Expressions are derived for the mean and variance of the number of monomers of a given type in a copolymer chain. The model can be applied to both the time homogeneous and heterogeneous processes.

INTRODUCTION

Stochastic approaches, predominantly Markov chains, have been widely employed to determine the distribution of the degree of polymerization in terms of the chain length or the number of monomer units in a polymer, or the composition distribution of a polymer when several kinds of monomers are involved in the polymerization process.[1-8] Saidel and Katz[9] and Katz et al.[10] have used a Markov process to model the molecular weight distribution for polymerization in a two-phase system. All earlier works, however, appear to have dealt only with polymerization in closed systems or batch reactors. Industrially, polymerization reactions are often carried out in open systems or continuous flow chemical reactors rather than in batch reactors. When a continuous flow chemical reactor is employed, we should be concerned not only with stochastic transitions of each chemical species as in a batch reactor, but also with the stochastic transition of each chemical species between the interior and exterior of the reactor.[11] Hence, the results from the stochastic treatment of polymerization in a batch reactor are not directly applicable to a flow reactor.
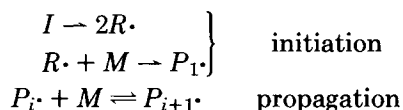
The process of polymerization is continuous in time and discrete in state which denotes the degree of polymerization of the polymer under consideration; hence, it is advantageous to analyze or model it as a Markov process (continuous time Markov chain) rather than a Markov chain. In this work, the theory of the Markov process is employed to examine the degree of polymerization and the composition of copolymers in a continuous flow chemical reactor. This model is sufficiently general so that it can be applied to unsteady as well as steady flow reactors.

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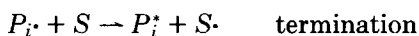
HOMOPOLYMERIZATION

Consider polymerization of monomers of one type (homopolymerization) in a continuous flow reactor which contains solvent and (nonactive) monomers initially. Let $x_1(s)$ $(s > 0)$ denote the rate of active monomers, in terms of the number, entering the reactor with the feed stream, which contains both active and nonactive monomers. We assume that the active monomers react independently of one another in chain propagation and that the rate of chain propagation is not limited by the insufficient availability of nonactive monomers. Furthermore, we assume that the mode of mixing of the reacting mixture is on the microscopic scale (mixing of individual molecules) so that the diffusional effect is negligible.

Let A_i denote the state where a polymer chain in a flow reactor is composed of i monomers; in other words, the degree of polymerization corresponding to state A_i is i $(i = 1, 2, \ldots, l)$. We assume that the degree of polymerization of a chain cannot exceed the maximum number l and a chain at any state A_i can terminate or exit from the reactor. In parlance of stochastic processes, states $A_1, A_2, \ldots, A_l$ are transient states, and both termination and exit can be viewed as leading to the absorbing states; collectively, these processes are analogous to the so-called illness–death process.[12] Furthermore, we assume that the transition is constrained so that it occurs only between state A_i and state A_{i+1} or A_{i-1}. The former is the forward process of adding one monomer at a time to the end of a polymer chain, and the latter is the reverse process of removing one monomer from the end of a chain.

In free radical polymerization, e.g., polymerization of styrene or ethylene, free radicals $R\cdot$ for chain initiation are produced by an initiator I, such as benzoyl peroxide, either photochemically or thermally. A free radical attacks a monomer M to form an active monomer $P_1\cdot$. The active monomers thus formed interact with the nonactive monomers to propagate polymer chains. The reactions can be depicted as[13–16]

$$\left.\begin{array}{l} I \rightarrow 2R\cdot \\ R\cdot + M \rightarrow P_1\cdot \end{array}\right\} \quad \text{initiation}$$

$$P_i\cdot + M \rightleftharpoons P_{i+1}\cdot \quad \text{propagation}$$

Chain termination is assumed to be irreversible and can occur through the interaction of an active polymer $P_i\cdot$ with another molecule, e.g., a solvent molecule S, causing a transfer of the free electron to the solvent molecule, i.e.,

$$P_i\cdot + S \rightarrow P_i^* + S\cdot \quad \text{termination}$$

where P_i^* denotes a dead polymer of chain length i. Such termination stops the growth of the chain without affecting its degree of polymerization. In ionic polymerization of monomer molecules, e.g., isobutylene molecules, the active species for chain initiation is an unstable ion, and the process proceeds essentially in the same manner as free radical polymerization.

For a polymer chain, transition from one state to another, termination, and exit from the reactor are governed by the intensities of transition k_{ij}, the intensities of termination η_i, and the intensities of exit μ_i. They are defined as follows:

$$k_{ij}\Delta t + o(\Delta t) = \text{Pr \{a chain in state } A_i \text{ at time } t \text{ will be in state}$$
$$A_j \ (j = i \pm 1) \text{ at time } t + \Delta t\}, \quad (1)$$

$\eta_i \Delta t + o(\Delta t) = $ Pr {a chain in state A_i at time t will terminate at time

$$t + \Delta t\}, \quad (2)$$

$\mu_i \Delta t + o(\Delta t) = Pr$ {a chain in state A_i at time t will exit from the

$$\text{reactor at time } t + \Delta t\} \quad (3)$$

We define

$$k_{ii} = -(k_{i,i-1} + k_{i,i+1} + \eta_i + \mu_i) \quad (4)$$

so that

$1 + k_{ii}\Delta t + o(\Delta t) = $ Pr {a chain in state A_i at time t will remain in the

$$\text{same state at time } t + \Delta t\} \quad (5)$$

If the reacting conditions, e.g., temperature, remain constant throughout the reactor over the entire time period, the intensity of transition of a polymer chain from state A_i to state A_j, k_{ij}, and the intensity of termination of a polymer chain in state A_i, η_i, may be assumed to be dependent on state A_i, or the chain length of the polymer i, but independent of time. Furthermore, the intensities of exit are also assumed to be independent of time, which is the case of a continuous stirred tank flow reactor.[11] Let

$P_{ij}(t - s) = $ transition probability that a chain in state A_i at

time s will be in state A_j (inside the reactor) at time t, $i, j = 1, 2, \ldots, l$. (6)

It can be shown that the transition probabilities $\{p_{ij}(t - s)\}$ satisfy the following Kolmogorov forward differential equations[12,17]:

$$\frac{d}{dt} p_{ij}(t - s) = \sum_{m=1}^{l} p_{im}(t - s) k_{mj} \quad (7)$$

with the initial conditions

$$p_{ij}(0) = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases} \quad (7')$$

In matrix notation, eqs. (7) and (7') can be rewritten, respectively, as

$$\frac{d}{dt} \mathbf{P}(t - s) = \mathbf{P}(t - s)\mathbf{K} \quad (8a)$$

and

$$\mathbf{P}(0) = \mathbf{I} = \text{identity matrix} \quad (8b)$$

where

$$\mathbf{K} = [k_{ij}] \quad (9)$$

and

$$\mathbf{P}(t - s) = [p_{ij}(t - s)] \quad (10)$$

Equation (7) or (8) is a first-order differential equation whose solution is well known.[12,18]

We assume that the eigenvalues, $\rho_1, \rho_2, \ldots, \rho_l$, of the matrix $\mathbf{K}$ defined by its characteristic equation

$$|\rho\mathbf{I} - \mathbf{K}| = 0 \quad (11)$$

are real and distinct. The characteristic matrix $\mathbf{B}(m)$ is

$$\mathbf{B}(m) = (\rho_m \mathbf{I} - \mathbf{K}), \quad m = 1, 2, \dots, l \tag{12}$$

The column vector $\mathbf{Q}_m(r)$ defined as

$$\mathbf{Q}_m(r) = \begin{bmatrix} B_{r1}(m) \\ B_{r2}(m) \\ \vdots \\ B_{rl}(m) \end{bmatrix}$$

then is the eigenvector of $\mathbf{K}$ corresponding to the eigenvalue ρ_m; it is the rth column of the adjoint matrix (or the matrix of cofactor) of $\mathbf{B}(m)$. The solution to eq. (8) is given as

$$\mathbf{P}(t - s) = \mathbf{Q}(r)\mathbf{W}(t - s)\mathbf{Q}^{-1}(r) \tag{13}$$

where

$$\mathbf{Q}(r) = \begin{bmatrix} B_{r1}(1) & B_{r1}(2) & \cdots & B_{r1}(l) \\ B_{r2}(1) & B_{r2}(2) & \cdots & B_{r2}(l) \\ \vdots & \vdots & \ddots & \vdots \\ B_{rl}(1) & B_{rl}(2) & \cdots & B_{rl}(l) \end{bmatrix} \tag{14}$$

and

$$\mathbf{W}(t - s) = \begin{bmatrix} e^{\rho_1(t-s)} & 0 & \cdots & 0 \\ 0 & e^{\rho_2(t-s)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & e^{\rho_m(t-s)} \end{bmatrix} \tag{15}$$

By expanding eq. (13), we obtain

$$p_{ij}(t - s) = \sum_{m=1}^{l} B_{ri}(m) \frac{Q_{jm}(r)}{|\mathbf{Q}(r)|} e^{\rho_m(t-s)} \tag{16}$$

where $Q_{jm}(r)$ is the cofactor of the element $B_{rj}(m)$ of the matrix $\mathbf{Q}(r)$ and $|\mathbf{Q}(r)|$ is the determinant of $\mathbf{Q}(r)$.

Equation (16) states that given a polymer with chain length i at time s, the probability that the chain length will be j ($j = 1, 2, \dots, l$) at time t is $p_{ij}(t - s)$. We assume that at time s the chain is in state A_1 (active monomer or initiating species). Each of the $x_1(s)$ active monomers (in state A_1 at time s) must be in one of the l states ($A_1, A_2, \dots, A_l$) or in the state of death due to termination or exit from the reactor at time t. For example, an active monomer will be in state A_5 if it undergoes stepwise propagation by the addition of four monomers to become an active polymer with chain length 5. Hence,

$$x_1(s) = \sum_{j=1}^{l} N_j(t) + \sum_{j=1}^{l} D_j(t) + \alpha(t) \tag{17}$$

where

$N_j(t)$ = random variable representing the number of active or unterminated polymers with degree of polymerization j in the reactor at time t

$D_j(t)$ = random variable representing the number of dead or terminated polymers with degree of polymerization j in the reactor at time t

$\alpha(t)$ = random variable representing the number of all polymers that exited

from the reactor during the time interval (s,t)

The probability that a polymer chain with degree of polymerization j will terminate in the interval (s,t) can be expressed as

$$\int_s^t p_{1j}(\tau - s)\eta_j d\tau \tag{18}$$

From the theory of the pure death process,[19] once a chain terminates at time τ, the probability that it will remain in the reactor until time t is equal to

$$e^{-(t - \tau)\mu_j}, \qquad s \leq \tau \leq t \tag{19}$$

The probability that a chain with degree of polymerization j will terminate and remain in the reactor during the time interval (s,t) is, from eqs. (18) and (19),

$$q_{1j}(t - s) = \int_s^t p_{1j}(\tau - s)\eta_j e^{-(t - \tau)\mu_j} d\tau \tag{20}$$

With $p_{1j}(t - s)$ and $q_{1j}(t - s)$ known, it is seen that the probability distribution of the degree of polymerization in the reactor at time t, arising from $x_1(s)$ active monomers, is multinomial.[20] Thus,

$$\Pr[N_1(t) = n_1(t), \ldots, N_l(t) = n_l(t); D_1(t) = d_1(t),$$
$$\ldots, D_l(t) = d_l(t)|x_1(s)]$$

$$= \frac{x_1(s)!}{\prod\limits_{j=1}^{l} n_j(t)! \prod\limits_{j=1}^{l} d_j(t)! \left[x_1(s) - \sum\limits_{j=1}^{l} n_j(t) - \sum\limits_{j=1}^{l} d_j(t)\right]!}$$

$$\times \prod_{j=1}^{l} [p_{1j}(t - s)]^{n_j(t)} \prod_{j=1}^{l} [q_{1j}(t - s)]^{d_j(t)}$$

$$\times \left[1 - \sum_{j=1}^{l} p_{1j}(t - s) - \sum_{j=1}^{l} q_{1j}(t - s)\right]^{\{x_1(s) - \sum_{j=1}^{l} n_j(t) - \sum_{j=1}^{l} d_j(t)\}} \tag{21}$$

The expected number and the variance of polymers with degree of polymerization j in the reactor at time t are, respectively,

$$E[N_j(t) + D_j(t)] = \int_0^t x_1(s) [p_{1j}(t - s) + q_{1j}(t - s)] ds \tag{22}$$

and

$$\text{Var}[N_j(t) + D_j(t)]$$
$$= \text{Var}[N_j(t)] + \text{Var}[D_j(t)] + 2 \text{Cov}[N_j(t), D_j(t)]$$

$$= \int_0^t x_1(s) \{p_{1j}(t - s)[1 - p_{1j}(t - s)] + q_{1j}(t - s)[1 - q_{1j}(t - s)]$$

$$- 2p_{1j}(t - s)q_{1j}(t - s)\}ds \tag{23}$$

The integrals in eqs. (22) and (23) arise because the active monomers enter the reactor in a continuous manner and at the rate $x_1(s)$ $(0 < s < t)$.

The probability that an unterminated polymer with degree of polymerization j will exit from the reactor in the time interval $(t, t + \Delta t)$ is

$$p_{1j}(t - s)\mu_j \Delta t \tag{24}$$

Also, the probability that a terminated polymer with degree of polymerization j will exit from the reactor in the time interval $(t, t + \Delta t)$ is

$$q_{1j}(t - s)\mu_j \Delta t \tag{25}$$

Let $Y_j(t)$ and $Z_j(t)$ be random variables representing, respectively, the numbers of unterminated and terminated polymers, both with degree of polymerization j, exiting from the reactor in the time interval $(t, t + \Delta t)$. Then, the distribution of $Y_j(t)$ and $Z_j(t)$ are binomial, i.e.,

$$\Pr[Y_j(t) = y_j(t)|x_1(s)] = \text{binomial } [x_1(s), p_{1j}(t - s)\mu_j \Delta t]$$

$$= \frac{x_1(s)!}{y_j(t)![x_1(s) - y_j(t)]!} [p_{1j}(t - s)\mu_j \Delta t]^{y_j(t)}$$

$$\times [1 - p_{1j}(t - s)\mu_j \Delta t]^{\{x_1(s) - y_j(t)\}} \tag{26}$$

and

$$\Pr[Z_j(t) = z_j(t)|x_1(s)] = \text{binomial } [x_1(s), q_{1j}(t - s)\mu_j \Delta t]$$

$$= \frac{x_1(s)!}{z_j(t)![x_1(s) - z_j(t)]!} [q_{1j}(t - s)\mu_j \Delta t]^{z_j(t)}$$

$$\times [1 - q_{1j}(t - s)\mu_j \Delta t]^{\{x_1(s) - z_j(t)\}} \tag{27}$$

The mean and variance of $Y_j(t)$ are obtained by making use of the known formulae of the binomial distribution.[20] Thus, we have, from eq. (26),

$$E[Y_j(t)] = \int_0^t x_1(s)[p_{1j}(t - s)\mu_j \Delta t]ds \tag{28}$$

and

$$\text{Var}[Y_j(t)] = \int_0^t x_1(s)[p_{1j}(t - s)\mu_j \Delta t][1 - p_{1j}(t - s)\mu_j \Delta t]ds \tag{29}$$

Similarly, from eq. (27), the mean and variance of $Z_j(t)$ are obtained, respectively, as

$$E[Z_j(t)] = \int_0^t x_1(s)[q_{1j}(t - s)\mu_j \Delta t]ds \tag{30}$$

and

$$\text{Var}[Z_j(t)] = \int_0^t x_1(s)[q_{1j}(t - s)\mu_j \Delta t][1 - q_{1j}(t - s)\mu_j \Delta t]ds \tag{31}$$

In addition, suppose that $Y_j^*(t)$ and $Z_j^*(t)$ denote the random variables representing, respectively, the numbers of unterminated and terminated polymers with degree of polymerization j, which exit from the flow reactor during the time interval $(0, t)$. Then, from eqs. (28) and (30), the expected numbers of $Y_j^*(t)$ and $Z_j^*(t)$ are, respectively,

$$E[Y_j^*(t)] = \int_0^t x_1(s) \int_s^t p_{1j}(\tau - s)\mu_j d\tau ds \tag{32}$$

and

$$E[Z_j^*(t)] = \int_0^t x_1(s) \int_s^t q_{1j}(\tau - s)\mu_j d\tau ds \tag{33}$$

It is of practical interest to study the steady state behavior of a flow reactor or the performance of the reactor after the reactor has been in operation for a sufficiently long time, when the feed rate is fixed at x_1. The steady state behavior of the reactor may be obtained from the unsteady state results by letting t approach infinity. For instance, the expected number of polymers with degree of polymerization j in the steady state reactor is, from eq. (22),

$$\lim_{t \to \infty} E[N_j(t) + D_j(t)] = \lim_{t \to \infty} x_1 \int_0^t [p_{1j}(t-s) + q_{1j}(t-s)]ds \quad (34)$$

In practice, the initial number of active monomers may not be constant. If, for instance, active monomers are initiated photochemically, we might assume that the number of active monomers in the feed stream is distributed in a Poisson form, i.e.,

$$\Pr[X_1(s) = x_1(s)] = \frac{\lambda^{x_1(s)}e^{-\lambda}}{x_1(s)!} \quad (35)$$

When $x_1(s)$ is the outcome of a random variable, all of the expressions derived earlier must be viewed as conditional on $[X_1(s) = x_1(s)]$. Unconditional expressions can be obtained by considering the distribution of $X_1(s)$. For example, when $X_1(s)$ is a random variable, $E[Y_j(t)]$ in eq. (28) is conditional on $[X_1(s) = x_1(s)]$. The unconditional mean is then obtained as

$$E[Y_j(t)] = \int_0^t E[X_1(s)p_{1j}(t-s)\mu_j \Delta t]ds$$

$$= \int_0^t E[X_1(s)]p_{1j}(t-s)\mu_j \Delta t \, ds \quad (36)$$

The stochastic model described so far can also be applied to a batch polymerization reactor. Let us consider a batch reactor containing initially $n_1(0)$ active monomers, a sufficient amount of nonactive monomers, and/or solvent. The system corresponds to the following condition:

$$\mu_i = 0, \qquad i = 1, 2, \ldots, l$$

$$k_{ii} = -\left(\sum_{j \neq i} k_{ij} + \eta_i\right)$$

Analogous to eq. (17), we have

$$n_1(0) = \sum_{j=1}^l N_j(t) + \sum_{j=1}^l D_j(t) \quad (37)$$

Thus, corresponding to eq. (22), the expected number of polymers with degree of polymerization j in the reactor at time t is

$$E[N_j(t) + D_j(t)] = n_1(0)[p_{1j}(t) + q_{1j}(t)] \quad (38)$$

Similarly, the variance of polymers with degree of polymerization j in the reactor at time t can be expressed as

$$\text{Var}[N_j(t) + D_j(t)] = n_1(0)\{p_{1j}(t)[1 - p_{1j}(t)] + q_{1j}(t)[1 - q_{1j}(t)]$$
$$- 2p_{1j}(t)q_{1j}(t)\} \quad (39)$$

which is analogous to eq. (23).

If no reaction occurs in a continuous flow polymerization reactor, we have

$$k_{ij} \neq 0, \qquad i = j = 1 \; \rbrace$$
$$\quad = 0, \qquad \text{otherwise} \rbrace$$
$$\eta_i = 0, \qquad i = 1, 2, \ldots, l$$
$$\mu_i \neq 0, \qquad i = 1 \qquad\qquad \rbrace$$
$$\quad = 0, \qquad i = 2, 3, \ldots, l \rbrace$$

According to eq. (4), k_{11} can be related to the intensity of exit, μ_1, as

$$k_{11} = -\mu_1 \tag{40}$$

The probability that a molecule, which may be a tracer molecule, will remain in the reactor from time 0 to time t can be evaluated from eq. (7) as

$$p_{11}(t) = \exp(k_{11}t) \tag{41}$$

Substitution of eq. (40) into eq. (41) yields

$$p_{11}(t) = \exp(-\mu_1 t) \tag{42}$$

Assume that $x_1(0)$ tracer molecules are instantaneously injected into the reactor, i.e., the time dependence of the rate of tracer molecules supply to the reactor is of the delta function. Then the expected number of tracer molecules in the reactor at time t can be evaluated from eq. (22) as

$$E[N_1(t)] = x_1(0) \exp(-\mu_1 t) \tag{43}$$

where μ_1 is the reciprocal of the mean residence time. This is the known result obtained from the deterministic mass balance approach for a completely homogeneous flow reactor.[11,21]

COPOLYMERIZATION

Simultaneous polymerization of two or more monomers by chain-growth polymerization is referred to as copolymerization.[14-16] An initial system of different types of monomers will produce polymer chains of various lengths and various compositions. Thus, both the degree of polymerization and the compositional distribution of a copolymer, containing any numbers of different monomers, are of practical importance. It will be shown that the theory derived in the previous section can be extended to the case of copolymerization.

Assume that there are λ different types of monomers $M_r, r = 1, 2, \ldots, \lambda$, in a continuous flow reactor. A free radical attacks a monomer (from any of λ different types) to form an active monomer. With λ different monomers in existence, we can assume that there will be λ different active monomers, one corresponding to each type of monomers. A polymer chain starting with any active monomer is propagated by the addition of one monomer (from any of λ different types) at each transition. Here, we assume that the transition is only from state A_i to state A_{i+1}. In other words, a polymer chain cannot come back to its original state once it leaves it. In the continuous time Markov chain (Markov process) under consideration, the polymer chain sojourns in a given state A_i for a random length of time (duration of stay), which has an exponential density function according to the pure death process[19] [also see eq. (19)]. After leaving state A_i, the polymer chain enters state A_{i+1}. The process is essentially a Markov chain (discrete time) except that the transition occurs after a random

length of time rather than after a fixed time period. Let us consider a copolymer with degree of polymerization j or a copolymer in state A_j at time t. The co-polymer with chain length j indicates that $j - 1$ transitions have taken place among the λ states $\{M_r; r = 1, 2, \ldots, \lambda\}$. If we study the process at the time of transitions, we have the so-called imbedded Markov chain.[22] For this Markov chain, the growing polymer chain is said to be in state M_m if its terminal unit is a monomer of type m; it undergoes a transition to state M_r upon addition of a monomer of type r.

As a polymer chain grows from a solution containing monomers, a monomer unit attaches itself to the active end of the chain (assuming, as usual, that there is only one). We assume that only the terminal units affect the rate of addition of the next monomer unit.[5] Let h_{mr} denote the probability that a polymer, with a monomer of type m as the end unit, adds a monomer of type r. Thus, h_{mr} can be related to the corresponding rate constants and intensities by[23]

$$h_{mr} = \frac{a_{mr} C_r}{\sum\limits_{r=1}^{\lambda} a_{mr} C_r + \eta_m^* + \mu_m^*} \tag{44}$$

where

a_{mr} = rate constant for adding a monomer of type r to a chain ending in a monomer of type m

η_m^* = intensity of termination of a polymer chain ending in a monomer of type m

μ_m^* = intensity of exit of a polymer ending in a monomer of type m

C_r = concentration of the monomers of type r in the reactor

Note that C_r may be considered as a constant, if the availability of nonactive monomers of type r is not limited. Furthermore, the transition probability matrix for the imbedded Markov chain may be written as

$$\mathbf{H} = [h_{mr}], \qquad m, r = 1, 2, \ldots, \lambda \tag{45}$$

This $\lambda \times \lambda$ matrix, $\mathbf{H}$, includes only the transient states of the process.

Let $h_r(1)$ denote the initial probability of an active monomer to be in state M_r. The initial probability vector $\mathbf{h}(1)$ is a row vector of λ elements, i.e.,

$$\mathbf{h}(1) = [h_1(1)\ h_2(1) \cdots h_r(1) \cdots h_\lambda(1)] \tag{46}$$

If the polymerization is initiated only with active monomers of type w, then the initial probability vector $\mathbf{h}(1)$ is a row vector of 1 (the wth element) and 0's (all the others). From the theory of the Markov chain with stationary transition probabilities, we have

$$\mathbf{h}(j) = \mathbf{h}(1)\ \mathbf{H}^{j-1} \tag{47}$$

such that

$$\mathbf{h}(j) = [h_1(j)\ h_2(j) \cdots h_r(j) \cdots h_\lambda(j)] \tag{48}$$

where $h_r(j)$ denotes the probability that a polymer with degree of polymerization j has a monomer of type r ($r = 1, 2, \ldots, \lambda$) as the end unit.

The intensities of transition k_{ij}, defined in eq. (1) for homopolymerization must

be modified to take into account the fact that monomers of λ different types participate in the process of copolymerization. It is readily seen that for λ different monomers, the probability of transition from state A_i at time t to state A_{i+1} at time $t + \Delta t$ becomes

$$k_{i,i+1}\Delta t + o(\Delta t) = \left[\sum_{m=1}^{\lambda} \sum_{r=1}^{\lambda} h_m(i)h_{mr} \right] \Delta t + o(\Delta t) \tag{49}$$

Also, for the case of λ different monomers, the intensity of termination of a polymer chain with degree of polymerization i, η_i, in eq. (2) should be expressed as

$$\eta_i = \sum_{m=1}^{\lambda} h_m(i)\eta_m^* \tag{50}$$

Similarly, the intensity of exit of a polymer chain with degree of polymerization i, μ_i, in eq. (3) may be written as

$$\mu_i = \sum_{m=1}^{\lambda} h_m(i)\mu_m^* \tag{51}$$

Since we assume that the transition is only from state A_i to state A_{i+1}, i.e.,

$$k_{ij} = 0 \quad \text{for} \quad j \neq i \quad \text{or} \quad i + 1,$$

eq. (4) reduces to

$$k_{ii} = -(k_{i,i+1} + \eta_i + \mu_i) \tag{52}$$

The transition probabilities $\{p_{ij}(t - s)\}$ are then readily obtained by following the same procedures presented in the previous section. Thus, the mean and variance of the number of copolymers with degree of polymerization j in the reactor at any time t may be obtained, respectively, from eqs. (22) and (23).

It is of interest to compute the mean and variance of the number of monomers of a certain type in a chain with degree of polymerization j. At time t, $p_{1j}(t)$ gives the probability of obtaining a copolymer containing j monomers. From the transition probability matrix $\mathbf{H}$ we can compute the mean and variance of the number of visits to any state M_r starting from any state M_m. Let $_mU_r$ be the number of visits to state M_r in $j - 1$ steps starting from state M_m, i.e.,

$$_mU_r = \sum_{n=0}^{j-1} I_n^r \tag{53}$$

where

$$I_n^r = \begin{cases} 1, & \text{if the polymer chain is in state } M_r \text{ after } n \text{ steps} \\ 0, & \text{otherwise} \end{cases}$$

The expected number of visits to state M_r in $j -1$ steps starting from state M_m is then

$$\begin{aligned} E[_mU_r] &= E\left[\sum_{n=0}^{j-1} I_n^r \right] \\ &= \sum_{n=0}^{j-1} E[I_n^r] \\ &= \sum_{n=0}^{j-1} [(1 - h_{mr}^n) \cdot 0 + h_{mr}^n \cdot 1] \\ &= \sum_{n=0}^{j-1} h_{mr}^n \end{aligned} \tag{54}$$

where h_{mr}^n is an n-step transition probability. Since M_m can be one of the λ states, we see that for all states [see eqs. (44) and (45)]

$$[E(_mU_r)] = \sum_{n=0}^{j-1} \mathbf{H}^n = \frac{\mathbf{I} - \mathbf{H}^j}{\mathbf{I} - \mathbf{H}} = \mathbf{T}_j, \qquad m, r = 1, 2, \ldots, \lambda \qquad (55)$$

Starting with the initial probability vector $\mathbf{h}(1)$ given by eq. (46), we have

$$\mathbf{h}(1)\mathbf{T}_j = [T_1 T_2 \cdots T_r \cdots T_k]_j \qquad (56)$$

where T_r is the expected number of monomers of type r in a copolymer with chain length j. The corresponding variance is

$$\mathrm{Var}[_mU_r] = E[(_mU_r)^2] - (E[_mU_r])^2, \qquad m, r = 1, 2, \ldots, \lambda \qquad (57)$$

for a large value of j,

$$E[(_mU_r)^2] \cong \sum_{w=1}^{\lambda} h_{mw}[E(_wU_r + \delta_{mr})^2]$$

$$= \sum_{w=1}^{\lambda} h_{mw}[E(_wU_r)^2 + 2 E(_wU_r)\delta_{mr} + \delta_{mr}] \qquad (58)$$

where δ_{mr} is the Kronecker delta. Since M_m is one of the λ states, we have for all states $(m, r = 1, 2, \ldots, \lambda)$ that

$$[E(_mU_r)^2] = \mathbf{H}[E(_mU_r)^2] + 2(\mathbf{HT}_j)_{\mathrm{diagonal}} + (\mathbf{HJ})_{\mathrm{diagonal}}$$

and, therefore,

$$[E(_mU_r)^2] = [\mathbf{I} - \mathbf{H}]^{-1} [2(\mathbf{HT}_j)_{\mathrm{diagonal}} + (\mathbf{HJ})_{\mathrm{diagonal}}] \qquad (59)$$

where $\mathbf{J}$ is a $\lambda \times \lambda$ matrix with 1 as its elements. Hence, in matrix notation, eq. (57) can be rewritten as

$$[\mathrm{Var}(_mU_r)] = [E(_mU_r)^2 - \{E(_mU_r)\}^2]$$

$$= \mathbf{V}_j, \qquad j = 1, 2, \ldots, l \qquad (60)$$

Substitution of eqs. (55) and (59) into eq. (60) yields

$$\mathbf{V}_j = [\mathbf{I} - \mathbf{H}]^{-1}[2(\mathbf{HT}_j)_{\mathrm{diagonal}} + (\mathbf{HJ})_{\mathrm{diagonal}}] - \mathbf{T}_j^{(\mathrm{sq})} \qquad (61)$$

where $\mathbf{T}_j^{(\mathrm{sq})}$ is obtained from $\mathbf{T}_j$ by squaring each elements. Starting with the initial probability vector $\mathbf{h}(1)$, we have

$$\mathbf{h}(1)\mathbf{V}_j = [V_1 V_2 \cdots V_r \cdots V_\lambda]_j$$

where V_r is the variance of the number of monomers of type r $(r = 1, 2, \ldots, \lambda)$ in a polymer chain with degree of polymerization j.

TIME HETEROGENEOUS PROCESS

In the preceding sections, the intensities of transition, termination, and exit are assumed to be independent of time (time homogeneous process). However, the intensities of transition, k_{ij}, and intensities of termination, η_i, may not be time independent if, for instance, there are spatial and/or temporal variations

of the temperature or monomer concentrations in the reactor. Even for constant k_{ij} and η_i, the intensities of exit, μ_i, may be a function of age or duration of stay of a polymer chain in the reactor. This is especially true for a reactor where the composition is not uniform throughout it.

If the elements of the matrix $\mathbf{K}$ in eq. (9) are continuous functions of time (time heterogeneous process), a unique solution to the differential equation (8) is obtainable; but it may not be in closed form.[16] In general, it is in the form of

$$\mathbf{P}(t - s) = \mathbf{G}(t - s) = \mathbf{I} + \int_s^t \mathbf{G}(\tau - s)\mathbf{K}(\tau - s)d\tau \qquad (62)$$

The matrix $\mathbf{G}(t - s)$ is unique and can be obtained by iteration according to the matrix sequence

$$\mathbf{G}_0 = \mathbf{I} = \text{identity matrix}$$

$$\mathbf{G}_{m+1} = \mathbf{I} + \int_s^t \mathbf{G}_m \mathbf{K}(\tau - s)d\tau, \qquad m = 0, 1, \ldots \qquad (63)$$

It can be shown that $\mathbf{G}_{m+1}$ converges uniformly to $\mathbf{G}(t - s)$. With $\mathbf{P}(t - s)$ obtained here, all the previous results obtained for the time homogeneous process are also applicable to the time heterogeneous process. However, μ_j and η_j have to be expressed as functions of time. For example, eqs. (18) and (19) are rewritten as, respectively,

$$\int_s^t p_{ij}(\tau - s)\eta_j(\tau)d\tau \qquad (18')$$

and

$$e^{-\int_\tau^t \mu_j(\xi)d\xi} \qquad (19')$$

Naturally, eq. (62) should also be applicable to a time homogeneous process in which the intensity matrix $\mathbf{K}$ is not a function of time. By iterating eq. (62) for the time homogeneous process, we finally obtain

$$\mathbf{P}(t - s) = \mathbf{P}(0) \exp[(t - s)\mathbf{K}]$$

$$= \sum_{n=0}^{\infty} \frac{(t - s)^n K^n}{n!} \qquad (64)$$

which is an alternative form of eq. (13).[12]

In the previous section on copolymerization, we assume that the concentration of each type of monomer is constant. Then, the transition probability h_{mr} given in eq. (44) is approximately independent of time. However, in general, if the concentrations of monomers vary with time, h_{mr} would be time-dependent. For time-dependent intensity functions, eq. (47) becomes

$$\mathbf{h}(j) = \mathbf{h}(1) \prod_{n=1}^{j-1} \mathbf{H}_n \qquad (65)$$

The mean and variance of the number of monomers of a certain type in a copolymer j, given by eqs. (56) and (61), remain the same except that $[E(_mU_r)]$ or $\mathbf{T}_j$ in eq. (55) is now expressed as

$$\mathbf{T}_j = \sum_{n=0}^{j-1} \prod_{i=0}^{n} \mathbf{H}_i \qquad (66)$$

DISCUSSION AND CONCLUSIONS

It is well known that a chemical reaction, e.g., polymerization, is essentially a stochastic process. It is also well known that the flows in continuous flow reactors are often chaotic and stochastic in nature. Therefore, the present unified stochastic approach is more fundamental than the deterministic or partially stochastic approaches in analyzing the complex mechanisms of polymerization occuring in a flow chemical reactor. A variety of information (such as the polymer size distribution and the copolymer composition distribution), which are extremely difficult to obtain by means of deterministic approaches, can be obtained from the present unified stochastic approach.

The present stochastic model can be extended in a straightforward manner to a flow system with a complex geometry, e.g., a system containing n totally interconnected well-mixed tanks, or a reactor with a complex flow pattern, e.g., an incompletely mixed tank reactor or a multiphase reactor. The intensity matrix $\mathbf{K}$ given in eq. (9) and the corresponding performance equations for such a system can be modified without much difficulty.

To examine the validity and applicability of the model, estimates of the intensities of transition, k_{ij}, and termination, η_i, must be obtained. This can be accomplished with a batch reactor as long as the patterns of local mixing in the batch and the flow reactor are the same. The exit age distribution or the density function of the residence times of polymers, $f(t)$, in an arbitrary reactor may be obtained from the concentration-time function by injecting a specified quantity of polymers into the reactor in the form of a delta function. The probability of the residence time of a polymer, T (which is considered to be a random variable), being in the interval $(t, t + dt)$ is equal to the probability of the polymer being in the reactor with age t multiplied by the probability of exiting from the reactor during the interval $(t, t + dt)$, i.e.,

$$\Pr[t < T < t + dt] = \Pr[T > t]\mu(t)dt$$

or

$$f(t)dt = \left[1 - \int_0^t f(\tau)d\tau\right]\mu(t)dt \tag{67}$$

Thus, once the exit age distribution is determined through a tracer experiment, the intensity of exit, $\mu(t)$, is obtained as

$$\mu(t) = \frac{f(t)}{1 - \int_0^t f(\tau)d\tau} \tag{68}$$

provided that hydrodynamic conditions in the reactor for this tracer experiment can be maintained similar to those in a flow reactor with chemical reaction. When the maximum degree of polymerization l is large, the effort required for calculations makes the machine computation necessary. However, the computation may be facilitated by the fact that the matrix $\mathbf{K}$ is either a bidiagonal or a tridiagonal matrix.

A continuous time Markov chain (Markov process) is employed to model a polymerization process in a continuous flow chemical reactor. Expressions are derived for the distributions of the degree of polymerization of active and dead

polymers at any time t in the reactor as well as at the exit. It is possible to extend the treatment in a rigorous manner both to the determination of the degree of polymerization of a copolymer and the compositional distribution for any type of monomers in it. The mean and variance of the number of monomers of a given type in a copolymer chain are derived. The model can also be applied when the reactivity of the growing chains is influenced by a limited number of monomers preceding the active end. In this case, it is expected that the intensities of transition will be functions of time for which the theory in the preceding section would apply. It is worth emphasizing again that the present stochastic model is general and is applicable also to situations where the input rate of active monomers, $x_1(s)$, the intensities of exit, μ_i, the intensities of termination, η_i, and/or the intensities of transition, k_{ij}, are not constant, but are functions of time (time heterogeneous processes). In spite of their practical importance, time heterogeneous processes have received little attention in the literature.

NOMENCLATURE

A_i	state of a polymer, i indicating its degree of polymerization
a_{mr}	rate constant for adding a monomer of type r to a chain ending in a monomer of type m
C_r	concentration of the monomer of type r
$D_j(t)$	random variable representing the number of terminated polymers with degree of polymerization j at time t inside the reactor
$f(t)$	density function of the residence time or exit age distribution
$\mathbf{h}(1)$	initial probability vector
h_{mr}	probability that a polymer having a monomer of type m as an end unit will add a monomer of type r
$\mathbf{H}$	transition probability matrix for the imbedded Markov chain
I	initiator
k_{ij}	intensity of transition of a polymer chain from state A_i to state A_j
$\mathbf{K}$	intensity matrix as defined in eq. (9)
l	maximum number of monomers in a polymer
M	monomer
$N_j(t)$	random variable representing the number of unterminated polymers with degree of polymerization j at time t
$p_{ij}(t-s)$	probability that a chain in state A_i at time s will be in state A_j at time t
$\mathbf{P}(t-s)$	transition probability matrix as defined in eq. (10)
$P_i\cdot$	unterminated (active) polymer with degree of polymerization i
P_i^*	terminated (dead) polymer with degree of polymerization i
$Q_{jm}(r)$	cofactor of the element $B_{rj}(m)$ of the matrix $\mathbf{Q}(r)$
$q_{1j}(t-s)$	probability that a polymer with chain length j will terminate and remain in the reactor during the interval (s, t)
$R\cdot$	free radicals
S	solvent molecule
T_r	the expected number of monomers of type r in a copolymer with chain length j
$_mU_r$	the number of visits to state M_r in $j-1$ steps starting from state M_m
V_r	variance of the number of monomers of type r in a copolymer with chain length j
$x_1(s)$	rate of active monomers, in terms of the number, entering the reactor at time s
$Y_j(t)$	random variable representing the number of unterminated polymers with degree of polymerization j exiting from the reactor in the interval $(t, t + \Delta t)$
$Y_j^*(t)$	random variable representing the number of unterminated polymers with degree of polymerization j exiting from the reactor during the inverval $(0, t)$
$Z_j(t)$	random variable representing the number of terminated polymers with degree of polymerization j exiting from the reactor in the interval $(t, t + \Delta t)$
$Z_j^*(t)$	random variable representing the number of terminated polymers with degree of polymerization j exiting from the reactor during the interval $(0, t)$

Greek Symbols

$\alpha(t)$ random variable representing the number of polymers that exited from the reactor during the interval (s, t)

δ_{wr} Kronecker delta

η_i intensity of termination of a polymer chain with degree of polymerization i

η_m^* intensity of termination of a copolymer chain ending in a monomer of type m

μ_i intensity of exit of a polymer chain in state A_i from the reactor

μ_m^* intensity of exit of a copolymer chain ending in a monomer of type m

ρ_i eigenvalue of the intensity matrix $\mathbf{K}$

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