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### Stochastic Formulation of the General Differential Difference Equation for Addition-Growth Kinetic Processes—Example of Anionic Polymerization

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NEW INTERPRETATIONS

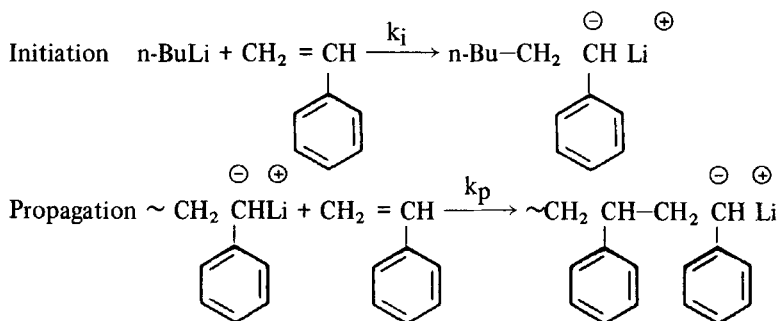
**Stochastic Formulation of the General  
Differential Difference Equation for  
Addition-Growth Kinetic Processes—  
Example of Anionic Polymerization**

**SUMMARY**

In an effort to lend some insight into the probabilistic nature of step-growth kinetic processes, the differential rate expression for anionic polymerization with one rate constant is derived from stochastic theory.

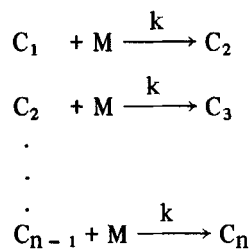
**INTRODUCTION**

A typical addition-growth process is the anionic polymerization of styrene with n-butyllithium in 1,2-dimethoxyethane [1]. The reaction is characterized by a very fast rate of initiation followed by stepwise addition of monomer to growing chains (propagation). If scrupulous care is taken to eliminate impurities, no termination of the active chains occurs. The product of such a reaction is thus termed "living polymer." The mechanism is depicted below.



For this example,  $k_i$  is much greater than  $k_p$  so that initiation is essentially complete before polymer growth proceeds.

Anionic polymerization in which each growth step is governed by a single rate constant is defined by the mechanism below:



where  $C_n$  is the molar concentration as a function of time of polymer containing  $n$  units, and  $M$  is the molar concentration of monomer as a function of time. The rate expression for  $C_n$  is obtained by assuming that the reaction rate of each step in the mechanism is proportional to the first power of the product of the concentrations of each species reacting in that step.

$$\frac{dC_n}{dt} = kMC_{n-1} - kMC_n; n \geq 2 \quad (1)$$

This rate expression was solved many years ago [1] to yield a Poisson distribution for  $C_n$ .

One purpose of this paper is to relate the formal assumptions of stochastic theory to the assumptions of the classical kinetic approach. For example, Eq. (1) was obtained by assuming each step in the mechanism was a second-order reaction. This assumption is interpretable through the stochastic approach and arises because each step in the polymerization model involves a bimolecular reaction of molecules which have statistically independent reaction paths.

There exists a large body of literature on stochastic processes describing, for example, population growth, reactions of small numbers of small molecules, and various chain reactions. The stochastic formalism introduced here for the simplest chain reaction will perhaps serve as an introduction to this literature.

## STOCHASTIC FORMULATION

Let us define an event as the process of adding one monomer unit to the end of a growing polymer chain in an anionic polymerization characterized by a single rate constant  $k$ .

We can completely define this anionic polymerization by three assumptions:

- (1) Anionic polymerization is a process occurring in time in which events (defined in the first paragraph) occur randomly.
- (2) The probability of occurrence of an event in an interval of time is not a function of time. That is, the probability of occurrence of a single event in the interval  $(t, t + \Delta t)$ , is:

$$P_1 [t, t + \Delta t] = \lambda_1 \Delta t + O(\Delta t) \quad (2)$$

The parameter  $O(\Delta)$  (read "order of  $\Delta t$ ") means a function which is of smaller order of magnitude than  $\Delta t$ , that is,

$$\lim_{\Delta t \rightarrow 0} \frac{O(\Delta t)}{\Delta t} = 0$$

We require only that  $\lambda$  be a positive constant. The relation between  $\lambda$  and the rate constant for propagation,  $k$ , is discussed later.

- (3) The probability of a total of two or more events occurring in the time period  $(t, t + \Delta t)$  is  $O(\Delta t)$ .

The probability of  $n$  occurrences in the interval  $(0, t)$  is the probability of forming a polymer chain of  $n$  links after the polymerization has proceeded for a time  $t$ . We call this probability  $P_n(t)$ . Furthermore,

$$P_n(t) = \frac{C_n(t)}{\sum_{i=1}^{\infty} C_i(t)}$$

where  $C_n(t)$  = concentration of polymer containing  $n$  monomer units in moles/liter at a time  $t$ .

$$\sum_{i=1}^{\infty} C_i(t) = I^0 - I,$$

where  $I^0$  is the initiator concentration at zero time and  $I$  is the initiator

concentration at any subsequent time. Since we assumed instantaneous initiation

$$\sum_{i=1}^{\infty} C_i(t) = I^0$$

We set out to obtain an expression for  $P_n(t)$ . In a very general setting we can write that

$$P_n(0, t + \Delta t) = \sum_{k=0}^n \text{Prob. [k occurrences in (t, t + \Delta t), n - k occurrences in (0, t)]} \quad (3)$$

Assumption (1) requires that the occurrence probabilities in Eq. (3) must be statistically independent. Therefore,

$$P_n(0, t + \Delta t) = \sum_{k=0}^n \text{Prob. [k occurrences in (t, t + \Delta t)]} \times \text{Prob. [n - k occurrences in (0, t)]} \quad (4)$$

To evaluate all the terms in the sum in Eq. (4) we need Eq. (2) and a formal statement of assumption 3.

$$P_1(t, t + \Delta t) = \lambda \Delta t + O(\Delta t) \quad (2)$$

where  $P_1(t, t + \Delta t)$  is the probability of adding one monomer unit to the growing chain in the time interval  $\Delta t$ .

$$P_2 \text{ or more } (t, t + \Delta t) = O(\Delta t) \quad (5)$$

where  $P_2 \text{ or more } (t, t + \Delta t)$  is the probability of adding two or more monomer units to the growing chain in the time interval  $\Delta t$ .

$$P_0(t, t + \Delta t) = 1 - P_1(t, t + \Delta t) - P_2 \text{ or more } (t, t + \Delta t) \quad (6)$$

where  $P_0(t, t + \Delta t)$  is the probability of adding zero monomer units in the time interval  $\Delta t$ .

$$P_0(t, t + \Delta t) = 1 - \lambda \Delta t - O(\Delta t) \quad (7)$$

The left-hand side of Eq. (4) is the probability that polymer with  $n$  links is present in the system at time  $t + \Delta t$ . This could have been accomplished by having polymer with  $n$  links at time  $t$  and no monomer addition in  $\Delta t$ , polymer with  $n - 1$  links at time  $t$  and one monomer addition in  $\Delta t$ , or polymer with  $n - k$  ( $k \geq 2$ ) links at time  $t$  and  $k$  monomer additions in  $\Delta t$ . The right-hand side of Eq. (4) can thus be easily expanded as follows:

$$\begin{aligned}
 P_n(0, t + \Delta t) &= P_0(t, t + \Delta t) \times P_n(t) \\
 &+ P_1(t, t + \Delta t) \times P_{n-1}(t) \\
 &+ P_{2 \text{ or more}}(t, t + \Delta t) \times \sum_{k=2}^n \text{Prob. } [n - k \text{ occurrences in } (0, t)]
 \end{aligned}
 \tag{8}$$

Substituting the definitions for  $P_1(t, t + \Delta t)$ ,  $P_{2 \text{ or more}}(t, t + \Delta t)$ , and  $P_0(t, t + \Delta t)$  from Eqs. (2), (5), and (7) into Eq. (8) yields:

$$\begin{aligned}
 P_n(t + \Delta t) &= [1 - \lambda\Delta t + O(\Delta t)] P_n(t) + [\lambda\Delta t + O(\Delta t)] P_{n-1}(t) \\
 &+ O(\Delta t) \sum_{k=2}^n \text{Prob. } [n - k \text{ occurrences in } (0, t)]
 \end{aligned}
 \tag{9}$$

The terms involving  $O(\Delta t)$  in Eq. (9) are grouped together for convenience

$$\begin{aligned}
 P_n(t + \Delta t) &= (1 - \lambda\Delta t) P_n(t) + \lambda\Delta t P_{n-1}(t) \\
 &+ O(\Delta t)[P_n(t) - P_{n-1}(t)] + O(\Delta t) \sum_{k=2}^n \text{Prob. } [n - k \text{ occurrences in } (0, t)]
 \end{aligned}
 \tag{10}$$

Next we transpose  $P_n(t)$  to the left side of Eq. (10) and divide both sides by  $\Delta t$ .

$$\begin{aligned} \frac{P_n(t + \Delta t) - P_n(t)}{\Delta t} &= \frac{-\lambda \Delta t P_n(t) + \lambda \Delta t P_{n-1}(t)}{\Delta t} \\ &+ \frac{O(\Delta t)}{\Delta t} [P_n(t) - P_{n-1}(t)] \\ &+ \frac{O(\Delta t)}{\Delta t} \sum_{k=2}^n \text{Prob. } [n - k \text{ occurrences in } (0,t)] \end{aligned} \quad (11)$$

When one takes the limit as  $\Delta t \rightarrow 0$  of both sides of Eq. (11), the left side thus obtained is recognizable as the definition of a derivative from the calculus. The  $\Delta t$  term cancels the first term on the right-hand side, and the other two terms vanish since

$$\lim_{\Delta t \rightarrow 0} \frac{O(\Delta t)}{\Delta t} = 0.$$

The differential difference equation thus obtained is shown in Eq. (12).

$$\frac{dP_n(t)}{dt} = -\lambda P_n(t) + \lambda P_{n-1}(t) \quad (12)$$

If we identify the parameter  $\lambda$  as:

$$\lambda = kM \quad (13)$$

where  $k$  is the rate constant for propagation and  $M$  is the monomer concentration (assumed to be independent of time), then Eq. (12) represents the rate expression for anionic polymerization with constant monomer concentration.

If the reduced time  $\tau$  is defined as:

$$\tau = \int_0^t M(t) dt \quad (14)$$

then the stochastic formalism developed earlier can be cast in terms of  $\tau$ , and one obtains the differential difference equation:

$$\frac{dP_n(\tau)}{d\tau} = -\lambda'P_n(\tau) + \lambda'P_{n-1}(\tau) \quad (15)$$

where

$$\lambda' = k \quad (16)$$

Equation (15) represents the general rate expression for anionic polymerization with a single rate constant.

Solution of Eqs. (12) or (15) by induction [2] or a generating function [3] yields the Poisson distribution in  $t$  or  $\tau$ , respectively.

### DISCUSSION

The assumptions used to obtain Eq. (12) are those required to define a Poisson process in time, so called because the solution of Eq. (12) leads, as we have seen, to a Poisson distribution in time. Other examples of Poisson processes are radioactive decay and the simple birth model for population genetics [4].

The stochastic formalism is not often taught in a chemical kinetics course. The details of this simple addition-growth kinetic scheme have been presented here as an illustration of the probabilistic origin of simple-rate expressions.

### ACKNOWLEDGMENTS

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- [4] Examples of time-dependent processes which are Poisson in nature are discussed in: A. T. Bharucha-Reid, *Elements of the Theory of Markov Processes and their Applications*, McGraw-Hill, New York, 1960; and N. T. J. Bailey, *The Elements of Stochastic Processes with Applications to the Natural Sciences*, Wiley, New York, 1964. These authors also set up the differential difference equations for more complex time-dependent systems.

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