

Applications of generating functions to polymerization kinetics. 3. General procedure illustrated for propagation with monomer conversion

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The derivation of the product distribution function for the catalytic polymerization mechanism involving propagation with monomer conversion is used to illustrate the general procedure for obtaining the exact discrete distribution arising from a polymerization mechanism. The coupled differential equations arising from the polymerization mechanism are integrated using a generating function substitution. Due to the stepwise growth of polymer chains, this approach is generally applicable to problems in polymerization kinetics. The integrated rate law for the mechanism under consideration is similar to the Poisson distribution, except for a time dependent parameter which suppresses chain growth as time passes. This distribution function has a limiting value as time approaches infinity determined by the ratio of initial monomer and catalyst. The number-average and weight-average degrees of polymerization are also derived using an elementary technique involving generating functions. Catalytic polymerizations frequently give rise to chemical kinetics problems which are difficult to solve due to difficulty in integrating the coupled rate equations. The procedures outlined in this paper permit these problems to be overcome in many cases.

1. Introduction

Man made polymers are not synthesized as a single molecular species, but rather as a distribution of structurally related molecules. A specific product distribution is obtained for a given polymerization mechanism and set of reaction conditions. The relationship between the product distribution and the reaction mechanism is a typical chemical kinetics problem. Since the product distribution plays a major role in controlling the physical properties of a polymer, controlling the product distribution is of considerable industrial importance.

In spite of the importance of the product distribution in polymer chemistry, a

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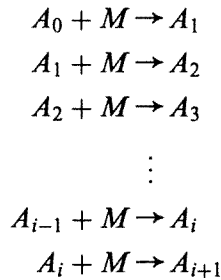
general approach to deriving such distributions from a polymerization mechanism is missing even in advanced texts in chemical kinetics and polymer chemistry [1–5]. The only product distributions which are derived are the Poisson distribution for “living” polymers, and the Schulz–Flory distribution for condensation polymerizations [1–3]. The procedure for obtaining each is usually the one originally employed by Flory and is not generally applicable to any other type of mechanistic scheme [6]. In fact, the procedure for deriving the Poisson distribution requires the concentration of the reactants be held constant, a condition not usually encountered in the laboratory. In the field of catalytic polymerizations (e.g., ionic and Ziegler–Natta catalyzed polymerization of alkenes) the polymerization mechanism can involve several steps which influence the product distribution [7,8]. The reaction conditions also introduce factors which are known to modify the product distribution [9–13]. It is very rare to see any of these factors included in a polymerization kinetics study, which starts from a mechanistic scheme and leads to the product distribution [7,8]. Clearly, polymerization reactions are an important class of reactions which provide a set of mathematical problems which has retarded the advancement of this field of chemical kinetics [14,15].

The simplest polymerization mechanism involves propagation only. To illustrate the general procedure for solving chemical kinetics problems for polymerization reactions, the problem of propagation with concomitant conversion of reactant into polymer is treated. When a fully activated catalyst is exposed to a polymerizable reactant, called a monomer, the reactants add one at a time to the growing polymer chain attached to the catalyst. In the absence of any elimination, transfer or termination reactions, the polymer chain continues to grow until the monomer is completely consumed or the reaction mixture is quenched by some species which almost instantly interrupts the catalytic cycle. The chemical kinetics of this type of reaction can be tracked by following the disappearance of the monomer or the formation of the distribution of polymer molecules. The latter data provide a much richer source of information for testing a proposed reaction mechanism and is vital to controlling the physical properties of the polymer.

The product distribution function, for the catalytic polymerization of a monomer by a fully activated catalyst, involving propagation only and with a constant concentration of monomer was first solved by Flory [16]. The product distribution function for this one case of a “living” polymerization was found to be the Poisson distribution

$$A_i = F_0 e^{-kMt} \frac{(kMt)^i}{i!},$$

where A_i is the number of polymer chains composed of i monomers, the number of monomers is designated by M , F_0 is the number of catalyst sites, the rate constant for propagation is given by k , and t represents the polymerization time. The basic mechanism for this reaction is shown in scheme 1.



Scheme 1.

For a constant reaction volume, the terms M and A_i may be defined as the concentration of monomer and growing polymer chains composed of i monomers, respectively. The rate constant k is assumed to be independent of chain length. Though this assumption is commonly made for polymerization reactions, it is not necessary using the procedure outlined in this paper.

A more general procedure for obtaining the product distribution function for this mechanism was published in 1963, using a technique from control systems called the Z -transform [17]. This was simply a method involving generating functions taken from combinatorics and applied to a series of coupled differential equations [7,15]. The set of reactions given in scheme 1 gives rise to the following series of differential equations:

$$\begin{aligned}
 \frac{dA_0}{dt} &= -kMA_0, \\
 \frac{dA_1}{dt} &= kMA_0 - kMA_1, \\
 &\vdots \\
 \frac{dA_i}{dt} &= kMA_{i-1} - kMA_i.
 \end{aligned} \tag{2}$$

The general form of this differential equation is given by the recursion formula shown for the i th case. This paper describes the derivation of the simple, but previously unreported procedure for obtaining the product distribution function and its averages when the monomer concentration decreases as polymer is formed, as it would under most realistic reaction conditions, for the elementary mechanism governing "living" polymerizations [1].

2. Distribution function

In order to integrate the series of coupled differential equations arising from scheme 1, it is convenient to define the following generating function:

$$F = \sum_{i=0}^{\infty} A_i Y^i. \quad (3)$$

The time derivative of F yields an expression involving dA_i/dt ,

$$\frac{dF}{dt} = \sum_{i=0}^{\infty} \left(\frac{dA_i}{dt} \right) Y^i. \quad (4)$$

Using the expression for dA_i/dt resulting from eq. (2) gives rise to the following equation:

$$\frac{dF}{dt} = kMY \sum_{i=0}^{\infty} A_{i-1} Y^{i-1} - kM \sum_{i=0}^{\infty} A_i Y^i. \quad (5)$$

Since M is decreasing with time according to the simple rate equation shown in eq. (6),

$$-\frac{dM}{dt} = kMF_0, \quad (6)$$

eq. (6) must be integrated,

$$M = M_0 e^{-kF_0 t} \quad (7)$$

and the resulting function for M substituted into eq. (5). Note that M_0 is the concentration of monomer at $t = 0$. Substituting F back into eq. (5), as well, yields the following, elementary integral:

$$\int_{F_0}^F \frac{dF}{F} = (Y - 1)kM_0 \int_0^t e^{-kF_0 t} dt. \quad (8)$$

Upon integration, F is found to be defined in terms of kinetic parameters and Y ,

$$F = F_0 \exp\left(-\frac{M_0}{F_0} (1 - e^{-kF_0 t})(1 - Y)\right). \quad (9)$$

F_0 is the value of F at $t = 0$, which is required by the reaction conditions to also be the total catalyst concentration. Expanding eq. (9) into a power series of Y leads to an expression possessing the same form as the original generating function,

$$F = \sum_{i=0}^{\infty} \left(\frac{F_0 e^{-Q} Q^i}{i!} \right) Y^i, \quad (10)$$

where

$$Q = \frac{M_0}{F_0} (1 - e^{-kF_0 t}). \quad (11)$$

A term-by-term comparison of eqs. (3) and (10) gives the product distribution function for a catalytic polymerization when the monomer concentration decreases due to conversion,

$$A_i = F_0 e^{-Q} \frac{Q^i}{i!} \tag{12}$$

Note that eq. (11) is a Poisson distribution with a time dependent function Q in place of kMt in eq. (1). Fig. 1 illustrates how the product distribution arising from eq. (11) is similar to that of eq. (1) except for the slower rate of growth at longer polymerization times. In fact, eqs. (11) and (12) represent the general form of the Poisson distribution originally derived by Flory for the special case of Q being a constant.

3. Average molecular weight functions

The number-average and weight-average molecular weights of a polymer are obtained by multiplying the number-average (X_n) and weight-average (X_w) degree of polymerizations by the molecular weight of the repeat unit and correcting for the end-groups when they are present. These average degrees of polymerization are defined as follows:

$$X_n = \frac{\sum_{i=0}^{\infty} iA_i}{\sum_{i=0}^{\infty} A_i} \tag{13}$$

and

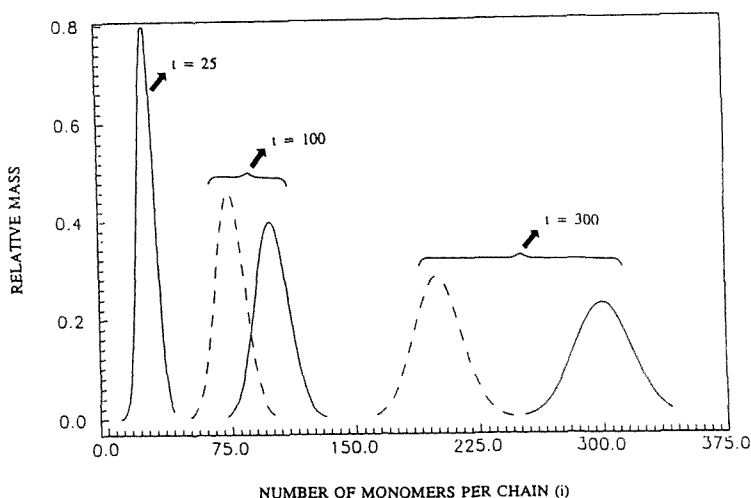


Fig. 1. The product distribution functions at three polymerization times are shown for the case of propagation with conversion (---), and with monomer held constant (—), for $k = 1$, $F_0 = 1$ and $M_0 = 300$.

$$X_w = \frac{\sum_{i=0}^{\infty} i^2 A_i}{\sum_{i=0}^{\infty} i A_i}. \quad (14)$$

The sums can be carried out from $i = 1$ to ∞ by simply subtracting out the first term of the series, if that is desired. Three sums are necessary to evaluate these two important molecular parameters: $\sum A_i$, $\sum i A_i$, and $\sum i^2 A_i$. These sums are readily obtained from the definition of the generating function by taking the derivative of F with respect to Y , multiplying by Y , and then repeating the process, followed by letting Y equal one,

$$F = \sum_{i=0}^{\infty} A_i Y^i = \sum_{i=0}^{\infty} A_i, \quad (15)$$

$$\left(Y \frac{d}{dY} \right) F = \sum_{i=0}^{\infty} i A_i Y^i = \sum_{i=0}^{\infty} i A_i, \quad (16)$$

$$\left(Y \frac{d}{dY} \right)^2 F = \sum_{i=0}^{\infty} i^2 A_i Y^i = \sum_{i=0}^{\infty} i^2 A_i. \quad (17)$$

Since F was obtained as a function of kinetic parameters and Y (eq. (9)). X_n and X_w may be obtained by substituting the expression for F from eq. (9) directly into eqs. (15)–(17) and the subsequent results directly into eqs. (13) and (14),

$$X_n = \frac{M_0}{F_0} (1 - e^{-kF_0 t}) \quad (18)$$

and

$$X_w = 1 + \frac{M_0}{F_0} (1 - e^{-kF_0 t}). \quad (19)$$

The so-called polydispersity index X_w/X_n is given by

$$\frac{X_w}{X_n} = 1 + \left(\frac{M_0}{F_0} (1 - e^{-kF_0 t}) \right)^{-1}. \quad (20)$$

The time dependent behavior of these averages for the chain length of the polymer are illustrated in fig. 2.

4. Conclusions

A general procedure for deriving the product distribution and molecular weight averages for catalytic polymerizations has been applied to the case of propagation with monomer conversion. This simple result clearly illustrates the method for deriving product distributions directly from a polymerization mechanism. The resulting distribution function is a Poisson distribution which slows its rate of

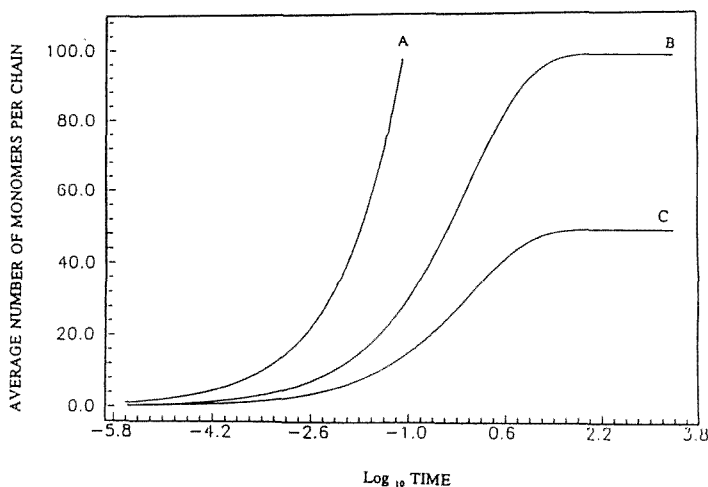


Fig. 2. The number-average chain length (X_n) is shown for (A) the case of monomer concentration held constant at $M/F_0 = 100$, (B) the case for $M_0/F_0 = 100$, and (C) the case for $M_0/F_0 = 50$; in all three cases $k = 1$.

growth as a time dependent function of monomer concentration. The limiting number-average degree of polymerization (i.e. the average number of monomers per chain) is set by the initial ratio of monomer to catalyst. This more realistic and more general case approaches as a limiting case the original product distribution function derived by Flory [16].

The ability to quantitatively analyze and experimentally test the product distribution for a given polymerization mechanism requires a knowledge of the distribution function. The procedure necessary to solve these types of problems to obtain a product distribution from a polymerization mechanism is as follows:

- (1) write down the general form of the rate equation from the reaction mechanism,
- (2) define the necessary generating function(s),
- (3) substitute the rate equation into the time derivative of the generating function,
- (4) integrate with respect to the generating function,
- (5) expand the integrated rate law with respect to the variable Y ,
- (6) obtain the distribution by a term-by-term comparison with the original generating function.

The easiest way of checking the validity of a proposed mechanism is by a graphical comparison of the experimental and theoretically predicted product distributions. In the simple case treated here, the rate at which the Poisson distribution shifts to higher molecular weights can now be quantitatively checked.

Perhaps the most important application of the results obtained here is in the analysis of more complex mechanisms, particularly those associated with Ziegler-Natta catalysis. For any reaction in which the catalyst is fully activated at the time

polymerization starts, the growing polymer chains which have yet to terminate or transfer must obey the product distribution function reported here. The application of this procedure to more complex mechanisms, use of the general form of the Poisson distribution to these systems, and their comparison to experimental results is currently under investigation.

Acknowledgement

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References

- [1] H.R. Allcock and F.W. Lampe, *Contemporary Polymer Chemistry* (Prentice Hall, Englewood Cliffs, 1990).
- [2] P.C. Hiemenz, *Polymer Chemistry* (Dekker, New York, 1984).
- [3] G. Odian, *Principles of Polymerization* (Wiley-Interscience, New York, 1991).
- [4] J.W. Moore and R.G. Pearson, *Kinetics and Mechanism* (Wiley, New York, 1981).
- [5] S.W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960).
- [6] P.J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, 1953).
- [7] K.W. McLaughlin and C.A.J. Hoeve, *Stud. Phys. Theor. Chem.* 63 (1989) 317.
- [8] J. Largo-Cabrero and J. Guzman, *Macromolecules* 12 (1979) 526.
- [9] E. Peacock-Lopez and K. Lindenberg, *J. Phys. Chem.* 88 (1984) 2270.
- [10] E. Peacock-Lopez and K. Lindenberg, *J. Phys. Chem.* 90 (1986) 1725.
- [11] K.W. McLaughlin, D.D. Latham, C.E. Hoyle and M.A. Trapp, *J. Phys. Chem.* 93 (1989) 3643.
- [12] C.E. Hoyle, M.A. Trapp, C.H. Chang, D.D. Latham and K.W. McLaughlin, *Macromolecules* 22 (1989) 35.
- [13] H.-K. Mahabadi, *Macromolecules* 24 (1991) 606.
- [14] H. Tompa, in: *Free-Radical Polymerisation*, *Comprehensive Chemical Kinetics*, Vol. 14A, eds. C.H. Bamford and C.F.H. Tipper (Elsevier, Amsterdam, 1976) Ch. 7.
- [15] F.C. Goodrich, *Polymer Fractionation*, ed. M.J.R. Cantow (Academic Press, New York, 1967) Ch. F.
- [16] P.J. Flory, *J. Am. Chem. Soc.* 62 (1940) 1561.
- [17] W.H. Abraham, *I & EC Fundamentals* 2 (1963) 221.