

A STATISTICAL THEORY OF POLYMER
COMPOSITIONS BASED ON ABSORBING
MARKOV CHAINS

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ABSTRACT

A STATISTICAL THEORY OF POLYMER COMPOSITIONS BASED ON ABSORBING MARKOV CHAINS

by George G. Lowry

Absorbing Markov chain theory has been applied to the problem of describing the composition of polymers with the use of matrix formalism to simplify the mathematics involved.

In each system studied, the states of the system were defined in such a manner that a finished polymer molecule corresponds to an absorbing state. Then each of the other states is transient and is defined in such a manner that the probability of transition from any state to any other state is easily written in terms of physical parameters. The result is a very compact formalism that permits computation of several aspects of polymer composition easily.

Linear addition and linear condensation polymer systems have been analyzed to obtain the distribution, and its moments, of the degree of polymerization. Addition polymer systems involved termination by combination, disproportionation, chain transfer, or any combination, and biradical initiation as well. Condensation polymer systems involved

those with a single monomer (with and without monofunctional molecules present), and those with two monomers, as in nylon 66.

Results obtained for linear addition copolymers include, in addition to DP distributions, the mean composition of the copolymer in terms of its component monomer units for a real, finite DP distribution. Also the formulation for obtaining the composition of the copolymer in terms of various types of monomer sequences of fixed length was given.

Possible extensions of the theory to new systems, to refinements of systems already considered, and to the attainment of new information about systems, are discussed.

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BASED ON ABSORBING MARKOV CHAINS

by

George G. Lowry

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VITA

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I. INTRODUCTION

As early as 1871, Hlasiwetz and Habermann advanced the idea that proteins and carbohydrates are polymeric and that they include a large variety of isomeric and polymeric species differing primarily in their degree of molecular condensation, (1) as opposed to a colloidal "state" of matter with varying degrees of physical condensation. However, it was not until the work of Staudinger in 1920 (2) and subsequently that chemists became generally convinced of the validity of this concept, not only for carbohydrates and proteins but also for a host of other natural and synthetic substances now known as polymers.

Staudinger pointed out the fact, long disputed because it was unpalatable to those steeped in the philosophy of determinism, that these macromolecules or polymers were not all of the same size or shape but consisted of a large range of molecular species for each "individual" polymeric substance. Once the scientific world began to accept this concept, theoreticians began to attempt to answer the questions about how such molecules came to be, and about how they could be described mathematically, if they were not such definite entities as chemists were accustomed to working with. In 1930 Kuhn published the first paper involving the application of the methods of statistics to the field of polymer

science. (3) Since then, most of the useful theories about polymers have involved statistics in one manner or another.

There are three distinct, but related, areas of investigation that might be considered for a theory of polymerization. They are:

1. the nature of individual mechanistic steps, their rates, and their relation to structure of reactants, products, and transition states;

2. overall rates of appearance and disappearance of different types of species as related to the rates of the mechanistic steps;

3. the nature of the products formed as determined by the kinetics and thermodynamics of the reactions involved.

It has been found through long experience that the nature of the individual mechanistic steps for both condensation polymers (4) and presumably also addition polymers (5) does not differ materially from that of lower molecular weight analogs. This area of investigation has been of more interest to synthetic chemists than to theoretical chemists, although in recent years several papers have been published dealing with the molecular orbital theory of polymerization. (6)

The overall rates of reaction have not been treated for polymerization reactions by stochastic process theory for two principal reasons. Although the equations describing polymerization reactions as a stochastic process can be set down in much the same manner as for small molecule

systems, (7) they involve second order differential-difference equations which are difficult or impossible to solve in closed form. Secondly, a more-or-less deterministic approach coupled with statistical averaging formulas has been very successful in describing the aspects of polymerization reactions that are of interest in practical problems, (8) so that the effort necessary to handle the stochastic treatment successfully has not appeared worthwhile.

However the makeup of the products formed by polymerization reactions lends itself admirably to a stochastic process theory, and it is this area that is considered in this thesis.

In considering the specific type of mathematical model to be selected, we may consider some aspects of theories in general. A theory may be viewed as an abstraction of a physical system to a mathematical model which may then be manipulated to obtain relationships which can be related back to the physical system. In this sense then, a theory or mathematical model cannot be spoken of in terms of correctness, but rather should be evaluated in terms of its usefulness.

Evidently the value of a theory or model is a function of the usefulness of the predictions obtainable therefrom, and, to extend the pragmatic basis of value judgment, is also a function of the simplicity and ease of application of the theory. Therefore, as a generality, it may be stated that the best theory for a particular situation is

that one which yields the desired relationships to the degree of accuracy required with the least expenditure of effort on the part of the investigator.

While some useful information about polymer composition may be obtained from kinetic relationships (sometimes combined with combinatoric formulas of statistics) by using deterministic models, stochastic models have usually proven more useful. The particular stochastic model developed here is especially easy to apply, and has the added advantage of unifying several seemingly unrelated subjects into one basic theory. The usefulness of the theory is shown not only by the ease with which some relationships have been obtained, but also by the fact that some new relationships (difficult to obtain with earlier formalisms) have been developed.

To illustrate the differences between a deterministic and a stochastic model in this field of investigation, the degree of polymerization of a linear addition polymer will be obtained by each method.

In the deterministic approach, we may say that the rate of polymerization is simply designated by $-d[M]/dt = R_p$; i.e., the rate of disappearance of monomer, or the rate of addition of monomer molecules to the growing chain, is a constant. Also, the rate at which new chains are formed, assumed equal to the rate at which chains are terminated (cease to grow) is simply $-d[F]/dt = R_t$.

It is apparent that the rate of disappearance of

monomer with respect to the rate of appearance of terminated polymer chains is numerically equal to the number of monomer units per chain, termed "degree of polymerization" and usually abbreviated DP. Thus,

$$DP = \frac{-d[M]/dt}{-d[P]/dt} = R_p/R_t .$$

In this deterministic approach, the two rates are real-valued, essentially-continuous functions of time, and their quotient, the DP, is also real-valued and continuous. Further, once the values of R_p and R_t have been established, the value of the DP has been determined absolutely.

In the stochastic model, we assume the "random variable" (9) denoting DP is integer-valued, i.e., a polymer chain may not contain a fractional monomer unit. In this sense, the stochastic model seems closer to physical reality, but the deterministic model may be just as useful for some purposes.

We assume that, once a polymer molecule is initiated (starts to grow), one of three things may be true within any small time increment Δt :

1. no reaction may occur;
2. one monomer molecule may be added, with probability p ;
3. the growing polymer molecule may be terminated, with probability q .

We further choose Δt small enough that the probability of two of these occurrences during Δt is immeasurably small.

Further, since only the second and third events affect DP (although the first would affect other quantities, such as the overall rate of disappearance of monomer) we restrict our analysis to the set of all intervals of length Δt during which either of the last two events occurs, and call each such interval a "step," so that $p+q=1$.

The values of p and q may be estimated from measurable quantities by using the commonly applied relations between "probabilities" and frequencies. (10) Thus, we say that the probability of adding a monomer molecule is numerically equal to the relative frequency (rate) of the monomer addition reaction, and q has a similar relation to the termination reaction. Thus we write $p=1-q=R_p/[R_p+R_t]$.

A little reflection on this system shows that the probability of a finished polymer molecule having a DP of n (i.e., its formation requires n steps of types two and three following initiation) is simply $P_{DP}(n) = p^{n-1}q$ for $n = 1, 2, 3, \dots$. Thus, from the stochastic model we do not obtain a single absolute value of DP, but rather a probability distribution which assigns a probability to the occurrence of polymer molecules of any positive integral-valued DP. From this probability distribution we may calculate an average DP (first absolute moment of the distribution) which is essentially the same as the DP obtained deterministically.

Thus, the first approach described the mean DP while the second takes into consideration random fluctuations

about this mean, which can be described statistically in terms of higher moments of the probability distribution. For many purposes in polymer science the higher moments are as important as the mean value. For example, the degrees of polymerization measured by various experimental methods are ratios of different moments of the distribution. For such purposes then, the stochastic model is superior to the deterministic model.

The stochastic approach illustrated above was used very early in polymer theory, (11) but it soon met with difficulties. If we are dealing with a mechanistically more complicated polymerization system, the writing of a probability distribution function in such an intuitive manner becomes very difficult, if not impossible. Also, the evaluation of the sums involved in determining higher moments of distributions becomes extremely difficult, if not impossible, for systems even slightly more complicated than the present one. Scanlan overcame this problem to some extent by the use of moment generating functions (sometimes using Laplace transforms as limiting case treatments) to obtain the moments of more complicated distributions. (12) This approach did not give him the distribution functions directly, even though they could be approximated from the moments by use of Gram-Charlier series (13) or other techniques.

Bamford and Tompa were able to calculate still more complex systems by using Laplace transforms for moments and

Laguerre polynomials for the distributions. (14) However, the use of Laplace transforms involves the replacement of a summation by an integral, which obviously is not valid if the polymerization under consideration yields polymer of low average DP. Also, they found that the transforms were not available for some of the systems they studied and were forced to resort to numerical calculations.

In the field of copolymerizations, Wall was the first to utilize a stochastic process approach to the problems of DP distribution and composition of the copolymer in terms of the relative amounts of the different monomers incorporated in the macromolecule. (15) However, his treatment was rather limited in that it treated only a few special cases that simplified the mathematics considerably.

Simha and Branson published a very extensive and rather complete treatment of statistics of copolymerization (16) but many of the results were stated in such complex formulations that they were difficult or impossible to apply directly. Stockmayer then interpreted some of Simha and Branson's results by utilizing the common "tricks" of replacing summations by integrals and factorials by Stirling's approximation, together with mathematical insight and judgment. (17) The results he obtained were valid for copolymers in the limit of infinite DP but were of limited value, particularly for low average degree of polymerization, for real systems.

A. Markov Chains

The simplest stochastic model to apply is the first order Markov chain. (18) This model assumes that if a system (molecule) is in a given state on a particular step, the probability of its being in the same or in any other state on the next step depends only on the two states involved and is independent of the states occupied on any previous step or of the number of previous steps. These restrictions are not considered to introduce serious aberrations into the model and the mathematics involved is simple compared to the extensive results obtained.

Price published a Markov chain treatment of copolymerization systems which utilized the simplifications available with the formalisms of matrix theory. (19) Unfortunately, his theory is valid only for the limit of infinite DP, and had few new results, although the means of obtaining the results was somewhat more elegant than previous methods. Then Peller published a matrix treatment of copolymerization which is not restricted to infinite DP limiting cases, (20) but he failed to utilize the full simplification available with the matrix notation of Markov chains, and his results are sufficiently complex in appearance as to be difficult to follow.

In this thesis, a matrix notation of Markov chain theory is utilized which, once developed, is simple, compact, and neat to use. In addition, one basic theory

applies to obtaining DP distributions and moments for addition polymers, condensation polymers, and copolymers, as well as to obtaining composition of copolymers for real, finite DP distributions as well as for the limiting case of infinite DP. The key to this consolidation and simplification is in the use of absorbing Markov chain theory (21) by careful definition of states and transition probabilities, as will be demonstrated in the following pages.

II. FORMALISM OF ABSORBING MARKOV CHAIN THEORY

A. Notation

The theory expounded in this thesis is formally a matrix treatment of a probabilistic model. The rudiments of both matrix theory and probability theory are generally known to scientists, so they will not be reviewed here.

However, these fields have the common difficulty of lacking uniformity in notation from one writer or investigator to another. In fact, it appears unlikely that any two writers in either of these fields use exactly the same notation for the same relationships or operations.

In this section are set down the generalities of the notation to be used throughout the text. Occasionally a new specific notation will be defined elsewhere, but most will be found together here in compact form.

1. Matrices and vectors

A matrix will be denoted by a bold face capital Roman letter (**M**, **A**, etc.). A vector will be denoted by a bold face lower case Roman letter (**v**, **b**, etc.). Whether a vector is a $1 \times n$ (row) vector or an $n \times 1$ (column) vector will be evident from context.

The elements of a matrix will be denoted by subscripted lower case Roman letters corresponding to the particular

matrix involved. Thus, the elements of a matrix \mathbf{M} are m_{ij} , where i is the row and j is the column in which m_{ij} occurs. The principle exception to this correspondence between the letters denoting matrices and those denoting their matrix elements is in the case of the identity matrix, \mathbf{I} , the square matrix whose elements are the Kronecker deltas, δ_{ij} , defined by the relationships

$$\delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j. \end{cases}$$

The elements of a vector will be denoted by subscripted lower case Roman letters corresponding to the particular vectors involved. Thus, the elements of a vector \mathbf{v} are v_k where k is the position in which the element v_k occurs. Since matrix elements possess double subscripts and vector elements possess only single subscripts, no confusion should arise on this account.

Alternatively, a matrix or vector will be written sometimes as the set of its own elements. Thus, $\mathbf{M} = \{m_{ij}\}$ and $\mathbf{v} = \{v_k\}$.

A null matrix, all of whose elements are zero, will be denoted by \mathbf{Z} .

Matrix operations and relationships will be indicated by the following notation. \mathbf{AB} is the usual row-by-column product of the two matrices (this applies to pairs of vectors or vectors and matrices also, provided they have the necessary dimensional relationships). \mathbf{A}^{-1} is the inverse of \mathbf{A} , i.e., $\mathbf{AA}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{I}$. \mathbf{A}^n is the n 'th power of \mathbf{A}

defined as $\mathbf{A}\mathbf{A}\mathbf{A}\dots\mathbf{A}$ (n times) and $\mathbf{A}^r\mathbf{A}^s = \mathbf{A}^s\mathbf{A}^r = \mathbf{A}^{r+s}$.

One specific vector is particularly useful. Define $\mathbf{s} = \{s_k\}$, where $s_k = 1$ for all k , to be a column vector. If \mathbf{s} is an $n \times 1$ vector and \mathbf{A} is an $m \times n$ matrix, then $\mathbf{A}\mathbf{s} = \mathbf{v}$, where \mathbf{v} is an $n \times 1$ column vector and the v_k are the row sums of the elements of \mathbf{A} .

One additional specific matrix requiring definition is \mathbf{A} . This notation violates our rule of denoting matrices by Roman letters, but this is done to conform to one of the few widely accepted notations of matrix theory. The "characteristic equation" of a square matrix is defined as $|\mathbf{A} - \lambda\mathbf{I}| = 0$, where $|\mathbf{A}|$ is the general symbol for the determinant of any matrix \mathbf{A} . Then if \mathbf{A} is $n \times n$, $\lambda_1, \lambda_2, \dots, \lambda_n$ are the n characteristic roots of the characteristic equation and are usually called eigenvalues of the matrix \mathbf{A} . Then \mathbf{A} has the block diagonal form

$$\mathbf{A} = \begin{pmatrix} \mathbf{J}_1 & & \\ & \mathbf{J}_2 & \\ & & \ddots \end{pmatrix}$$

where each \mathbf{J}_i is a square matrix corresponding to a given eigenvalue, with dimension equal to the degeneracy of the eigenvalue (i.e., the multiplicity of the characteristic root). Thus, the sum of the dimensions of the \mathbf{J}_i equals the dimension of \mathbf{A} . Specifically, for each \mathbf{J}_i , every diagonal element is λ_i and every superdiagonal element is either one or zero, with zeros elsewhere.

This form of \mathbf{A} is known variously as the "Jordan Canonical Form" (which term will be used here), the "Weierstrass-Jordan Canonical Form" or the "Classical Canonical Form" of the matrix \mathbf{A} . Note that for degeneracy of one (i.e., distinct root of the characteristic equation) $\mathbf{J}_i = \{\lambda_i\}$ and if all roots have degeneracy of one, $\mathbf{A} = \{\lambda_i \delta_{ij}\}$.

2. Probabilities

If X is a real-valued function defined over the points of a sample space with a probability measure, then X is called a random variable. If a sample space contains a finite or countably infinite number of sample points it is said to be discrete, and a random variable defined over such a sample space is termed a discrete random variable.

The symbol $\Pr\{A\}$ is read "probability that the event A occurs," so that $\Pr\{X = h\}$ is the "probability that the random variable X assumes the value h ."

The function $P_X(h) = \Pr\{X = h\}$ for each real number h is called the probability distribution function of the random variable X . The function $F_X(h) = \Pr\{X \leq h\}$ for each real number h is called the cumulative distribution function of the random variable X . For a discrete, integral-valued random variable X , $P_X(h) = F_X(h) - F_X(h-1)$.

The mathematical expectation, or mean value, of a function $f(X)$ of the random variable X is $\langle f(X) \rangle = \sum P_X(h) f(h)$, where the summation is over all values of h for which $P_X(h)$ is defined, provided that the series

converges absolutely. In particular, the r 'th absolute moment of the random variable X is $\langle X^r \rangle$.

Finally we have the terminology of conditional probability. The "probability that the event A occurs, given that the event B occurs with certainty" is written $\Pr\{A|B\}$. Then the "probability that events A and B both occur" is $\Pr\{A \cap B\} = \Pr\{B\}\Pr\{A|B\}$.

B. Introduction to Markov Chain Theory

As stated in the introduction, a mathematical model is a first order Markov chain (to which we shall confine our attention, and therefore will call simply "Markov chain") if the probability of a system being in a given state on a particular step is dependent only on that state and the state of the immediately preceding step. For the present the terms "system," "state," and "step" shall remain undefined.

In order to obtain some of the basic relationships and methods of Markov chain theory, it is convenient to restate the properties of Markov chains in symbols. Let $\underline{E}^{(n)}$ mean "the state of the system immediately after n steps," so that $\underline{E}_i^{(n)}$ means "the system is in state i after exactly n steps." The symbolic definition of Markov chains states that $\underline{E}^{(n)} = f[\underline{E}^{(n-1)}]$, and $\underline{E}^{(n)} \neq f[n, \underline{E}^{(n-2)}, \dots, \underline{E}^{(0)}]$.

From the basic properties of conditional probability we have $\Pr\{\underline{E}_i^{(n)} \cap \underline{E}_j^{(n+1)}\} = \Pr\{\underline{E}_i^{(n)}\}\Pr\{\underline{E}_j^{(n+1)}|\underline{E}_i^{(n)}\}$. While this statement is unambiguous, it is cumbersome, so the

following simplified notation is introduced. Define $p_i^{(n)} = \Pr\{\underline{E}_i^{(n)}\}$ and $p_{ij} = \Pr\{\underline{E}_j^{(n+1)} | \underline{E}_i^{(n)}\}$. Note that it would be redundant to write $p_{ij}^{(n)}$, because $p_{ij} \neq f(n)$. Then by application of Bayes' Theorem of conditional probability, we have simply

$$p_j^{(n+1)} = \sum_i p_i^{(n)} p_{ij} \quad (2.1)$$

where the summation is over all the states available to the system. (22)

From inspection, it is evident that the set of all equations (2.1), i.e., for all j , is formally equivalent to the multiplication of a row vector by a square matrix to yield another row vector, thus,

$$\mathbf{p}^{(n+1)} = \mathbf{p}^{(n)} \mathbf{P} \quad (2.2)$$

where $\mathbf{p}^{(x)} = \{p_i^{(x)}\}$ and $\mathbf{P} = \{p_{ij}\}$. In the remainder of the thesis relations of the type of (2.1) will be stated in the form of (2.2) so that the powerful simplifications of matrix theory will be directly applicable. The vectors $\mathbf{p}^{(x)}$ represent the probability of the system occupying, after the x 'th step, each of the various states available; the sum of the elements of $\mathbf{p}^{(x)}$ is therefore unity, and all $p_i^{(x)} \geq 0$. The matrix \mathbf{P} is commonly called a "transition matrix" and its elements are the "transition probabilities" of the Markov chain. \mathbf{P} has the properties:

1. it is a square matrix;
2. all elements are non-negative, real, with the upper bound of unity;

3. all row sums are unity.

The first property signifies that all states of the system are mathematically available on every step, even though some transition probabilities may be 0; the second is a requirement if p_{ij} are to be probabilities; the third states that the system must exist in some allowed state at all times. Any matrix possessing these properties is termed a "stochastic matrix," or sometimes a "Markov matrix," whether it is being used in Markov chain problems or not.

Particularly important probability vectors include $\mathbf{p}^{(0)}$, the initial distribution of states of the system, and $\mathbf{p}^{(\infty)}$, the equilibrium distribution of states of the system. The latter comes from one of the most important theorems of Markov chain theory which says that, for an aperiodic Markov chain, $\lim_{n \rightarrow \infty} \mathbf{p}^{(n)}$ is an equilibrium vector which, for convenience, we denote $\mathbf{p}^{(\infty)}$.

We know that $\mathbf{p}^{(0)}\mathbf{P} = \mathbf{p}^{(1)}$, and hence $\mathbf{p}^{(2)} = \mathbf{p}^{(1)}\mathbf{P} = \mathbf{p}^{(0)}\mathbf{P}\mathbf{P} = \mathbf{p}^{(0)}\mathbf{P}^2$; by induction it is easily seen that $\mathbf{p}^{(r)}\mathbf{P}^s = \mathbf{p}^{(r+s)}$. This is known as the Chapman-Kolmogorov equation. Then $\mathbf{P}^s = \mathbf{P}^{(s)}$ is called an s-step transition matrix and $p_{ij}^{(s)}$ are s-step transition probabilities, since

$$\begin{aligned} \Pr\{\underline{E}_i^{(r)} \cap \underline{E}_j^{(r+s)}\} &= \Pr\{\underline{E}_i^{(r)}\} \Pr\{\underline{E}_j^{(r+s)} \mid \underline{E}_i^{(r)}\} \\ &= p_i^{(r)} p_{ij}^{(s)}. \end{aligned}$$

From these relations the entire matrix treatment of Markov chains has evolved. (18)

C. Linear Addition Polymerization

1. Systems

A "system" generally will be considered to be either a polymer molecule or a potential polymer molecule. E.g., in addition polymerization, a single monomer activated by an initiation reaction is capable of adding more monomer molecules and becoming a polymer. A single activated monomer molecule can hardly be called a polymer molecule before it adds at least one more monomer molecule, but it still may be a system by our definition because it is potentially a polymer molecule. Other differences between systems and polymer molecules will be brought out in the section on definition of states.

With complete generality, each polymer molecule comes from one and only one system.

"System" in this sense really is a mathematical rather than a chemical concept, though the two are related. However, it might be considered to be an open chemical (micro) system -- open because both energy and matter traverse the "boundary" between the system and the surroundings.

2. Steps

In systems describing addition polymers, a "step" corresponds to a simple reaction, i.e., it is a "mechanistic step." It may be the addition of a monomer molecule or of a group of molecules to yield a larger growing molecule,

or it may be a termination process of some type to yield a finished polymer molecule lacking growth potential.

The important feature is that a step corresponds to the system participating in some reaction rather than no reaction. Thus, "n steps have occurred" means that "the system has reacted n times" rather than "n time intervals have passed."

3. States

When labelling states symbolically, it is convenient to number them serially beginning with state 1. Then $p_k^{(n)}$ is the probability the system is in the state k after exactly n steps as well as being the k'th element in the vector $\mathbf{p}^{(n)}$. Similarly, p_{ij} is the transition probability from state i to state j as well as being the element in the i'th row and j'th column of the transition matrix \mathbf{P} .

In all addition systems treated here we shall define state 1 as finished, or kinetically dead, polymer molecule. Under no circumstances will a system in state 1 ever have a composition other than it had when it first entered state 1. Thus $p_{1j} = \delta_{1j}$. In Markov chain theory any state i for which $p_{ij} = \delta_{ij}$ is called an absorbing state. A Markov chain which includes one or more absorbing states is called an absorbing Markov chain. (18, 21)

If $p_{il}^{(n)} > 0$ for all i and some n in such a system, then $p_{ii}^{(m)}$ ($i \neq 1$) approaches zero as m increases without bound. Such a state is called transient. (18) The relative

residence "times" (numbers of steps) in each of the transient states prior to absorption determine the composition of the polymer molecules. We can therefore obtain all the desired results by considering only the set of transient states and their inter-relationships, even though a complete description of each system also includes state 1. That is, the properties of state 1 are actually obtained from those of the other states by difference in this stochastic matrix description.

a. Single chain termination, first approximation.--

The term "linear addition polymerization" refers to the following process. The polymerization is initiated by the formation of a reactive site on a low molecular weight molecule. The reactive site may be a free radical, a carbanion, a carbonium ion, or an analogous entity involving an atom other than carbon. The initiating species may be either a fragment of an initiator in the system or the product of addition of such a fragment to a single monomer molecule, or it may be a fragment produced by a unimolecular or bimolecular (possibly even termolecular) decomposition of monomer molecules.

Initiation is followed by propagation, in which additional monomer molecules add (with rate R_p) singly to the reactive site in an orderly fashion, the reactive site being shifted to the new end of the polymer backbone chain with each addition.

Finally the reactive site is deactivated, or terminated, by some reaction (with rate R_t), normally bimolecular, never to be restored to active polymerization.

This is addition polymerization, which is linear if no other reaction occurs to cause formation of a branch point in the backbone of the polymer molecule.

To translate this description into the language of absorbing Markov chains, we say there are only two states in the system. State 1 is, as always, finished polymer molecule; state 2 is a molecule with a reactive site at one end. [The definitions of states for this and other linear addition homopolymerization systems are summarized together in TABLE I for reference.]

Then initiation is represented by $\mathbf{p}^{(0)} = (0 \ 1)$, for if $p_1^{(0)}$ were non-zero, it would imply a positive probability of a system never becoming a potential polymer molecule which is a contradiction. Propagation is represented by the transition $\underline{E}_2^{(n)} \longrightarrow \underline{E}_2^{(n+1)}$ with probability p_{22} . Termination is represented by the transition $\underline{E}_2^{(n)} \longrightarrow \underline{E}_1^{(n+1)}$ with probability p_{21} . This system is defined completely by

$$\mathbf{p}^{(0)} = (0 \ 1)$$

and

$$\mathbf{P} = \begin{pmatrix} 1 & 0 \\ p_{21} & p_{22} \end{pmatrix}$$

To obtain values for the elements of \mathbf{P} , we again use the numerical equivalence of relative frequencies to probabilities so that $p_{22} = 1 - p_{21} = R_p / [R_p + R_t]$.

TABLE I. Summary of definitions of states for various linear addition homopolymerization systems

System	State 1	State 2	State 3	State 4
3a	Dead polymer	Actively growing polymer molecule	-----	-----
3b	Dead polymer	Active monomer species	Actively growing molecule of $DP \geq 2$	-----
3c	Dead polymer	Molecule actively growing at first end	Molecule actively growing at second end, after first end has terminated	-----
3d	Dead polymer	First actively growing molecule	Second and final actively growing molecule	-----
3e	Dead polymer	Active monomer species	First actively growing polymer molecule if double chain termination	Final actively growing molecule

b. Second approximation.-- The results obtained from the system described above are in agreement with those obtained by previous workers using different approaches. (11,12,14) However, there is one shortcoming of such a system which seems to have been overlooked previously. This is the fact that we have mathematically given the name "polymer" to material with $DP = 1$ if it has suffered initiation and termination reactions, even though it may be chemically identical to monomer that has never undergone such reactions.

This doesn't lead to significant error if $\langle DP \rangle$ is high, but it can be a major source of error if $\langle DP \rangle$ is low, say of the order of 1-10. Primarily, it seems basically unsatisfactory to define one of two identical molecules as polymer and the other as monomer simply because the one had a different history than the other. Therefore it is desirable to require that a molecule have $DP \geq 2$ before it is counted as a polymer molecule.

In order to achieve this refinement, we simply define state 2 as "active monomer species" and state 3 as "actively polymerizing molecule of $DP \geq 2$." Then, to assure counting only polymer molecules, we set $p_{21} = 0$ and $p_{23} = 1$, and in addition we have $p_{22} = p_{32} = 0$, $p_{33} = 1 - p_{31} = R_p / [R_p + R_t]$, yielding

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ p_{31} & 0 & p_{33} \end{pmatrix}$$

An interesting feature of this description is the increased generality available. If we wish to consider molecules of $DP = 1$ as polymer, we may bypass state 2 by letting $\mathbf{p}^{(0)} = (0 \ 0 \ 1)$. If we wish to count only molecules with $DP \geq 2$ as polymer, we let $\mathbf{p}^{(0)} = (0 \ 1 \ 0)$.

With the present formalism $\mathbf{p}^{(0)}$ is applied after all the extensive manipulations have been performed (on \mathbf{P}), so that results are obtained just about as easily for one basis of counting as for the other.

c. Double-site initiation.-- It is possible in some cases to have two reactive sites on a single initiating species. Following initiation, the polymer molecule may grow outward in two directions independently.

Although in such a system both ends of the active species are simultaneously engaged in propagation reactions, it is convenient to assume mathematically that the reactions occur in the following sequence:

1. initiation occurs;
2. the first end propagates;
3. the first end terminates;
4. the second end propagates;
5. the second end terminates.

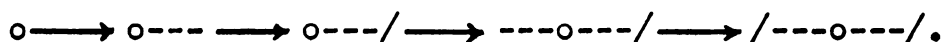
For illustration, we may use a symbolic representation, which may clarify some systems. Let

o represent initiation,

--- represent the set of all propagation reactions from a single initial reactive site, and

/ represent termination of one reactive site.

Then the five stages described above may be represented as follows:



Now we may define the states of this system and set up the transition matrix and initial probability vector. State 1 is dead polymer molecule; state 2 is a molecule with an actively polymerizing reactive site at the first end; state 3 is a molecule with an actively polymerizing reactive site at the second end, after the first end has terminated. Then the system is fully defined by

$$\mathbf{p}^{(0)} = (0 \quad 1 \quad 0) \quad (2.3)$$

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & p_{22} & p_{23} \\ p_{31} & 0 & p_{33} \end{pmatrix} \quad (2.4)$$

In this system, we assume both active sites are equally reactive so $p_{22} = p_{33} = 1 - p_{23} = 1 - p_{31} = R_p / [R_p + R_t]$. Since $p_{21} = 0$ and $p_3^{(0)} = 0$, we are assured that only molecules of $DP \geq 2$ are counted.

One possible physical interpretation of the mathematical system described by $\mathbf{p}^{(0)}$ and \mathbf{P} is:

1. $\mathbf{p}^{(0)}$ corresponds to formation of the initiating species with two reactive sites (o);

2. p_{22} is the probability of adding monomer to the first reactive site (o---);

3. p_{23} is the probability of terminating the first reactive site and, since it corresponds to one step in the

system which will eventually be counted in the DP distribution, simultaneously adding one monomer unit to the second reactive site (-o---/);

4. p_{33} is the probability of adding more monomer to the second reactive site (---o---/);

5. p_{31} is the probability of terminating the second reactive site (/---o---/).

Thus, the smallest sequence of reactions available to a system with this description is initiation, termination of the first reactive site without propagation, addition of one monomer molecule to the second reactive site, and termination of the second reactive site. For such a minimum sequence $DP = 2$.

d. Single-site initiation, double chain termination.--

In some systems, termination occurs in such a manner that two growing polymer chains join together to form a single finished polymer chain rather than two finished polymer chains. Such a reaction is called, not surprisingly, "termination by combination." As we have defined it, one system consists of the two chains which ultimately become one. This is another example of the non-identity of a polymer molecule and a system. In this instance though, the difference is that a growing polymer molecule is not a system but a portion of a system.

To set up the vector-matrix description of this process, let us translate it into the type of description

used in section c. We can say mathematically that:

1. the first chain is initiated;
2. the first chain propagates;
3. the first chain terminates and is "held in temporary storage condition;"
4. the second chain is initiated;
5. the second chain propagates; and
6. the second chain terminates and at the same

time joins onto the first chain. Symbolically, these stages may be written as



A different, but mathematically equivalent representation might be



These two equivalent schemes are described by equations (2.3) and (2.4). State 1 is dead polymer molecule; state 2 is the first actively growing polymer molecule; state 3 is the second and final actively growing polymer molecule. Then p_{22} is the probability of propagation of the first active chain, p_{23} is the probability that the first active chain is terminated and the second is initiated, p_{33} is the probability of propagation of the second active chain, and p_{31} is the probability that the second active chain is terminated and at the same time is connected to the first chain to yield the finished molecule.

The minimum reaction sequence in this system yields $DP = 2$, as is required physically.

e. Single-site initiation, any termination.-- We have encountered systems with two different types of termination, and it is now possible to demonstrate how both types of system may be described by a single transition matrix simply by varying the initial probability vector.

For compactness, let us define "single chain termination" as a termination reaction in which one actively growing polymer chain becomes one finished polymer chain. Denote the rate of this reaction R_{t1} . Then "double chain termination" is a termination reaction in which two actively growing polymer chains join together upon termination to yield a single finished polymer chain, with rate R_{t2} . We may still use $R_t = R_{t1} + R_{t2}$ as the overall rate of termination.

In section d we showed that a system with double chain termination was described by equations (2.3) and (2.4). Observe that if equation (2.4) is used together with $\mathbf{p}^{(0)} = (0 \ 0 \ 1)$, we have a description of a system with single chain termination. By this simple expedient we are able to bypass state 2 so that our system (i.e., potential polymer molecule) never consists of more than one actively polymerizing molecule.

However we are still counting molecules with $DP = 1$ as polymer molecules. This may be avoided, or used as seems fit, by writing a still more general transition matrix:

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & p_{33} & p_{34} \\ p_{41} & 0 & 0 & p_{44} \end{pmatrix} \quad (2.5)$$

where $p_{33} = p_{44} = 1 - p_{34} = 1 - p_{41} = R_p / [R_p + R_t]$. Then we may use any of three different initial probability vectors depending on the system of interest. For double chain termination, $\mathbf{p}^{(0)} = (0 \ 0 \ 1 \ 0)$. For single chain termination, counting all molecules of $DP \geq 1$ as polymer, $\mathbf{p}^{(0)} = (0 \ 0 \ 0 \ 1)$. For single chain termination, counting only molecules of $DP \geq 2$ as polymer, $\mathbf{p}^{(0)} = (0 \ 1 \ 0 \ 0)$.

The utility of such a general transition matrix is forcibly demonstrated by considering a more complex situation. In some polymerization reactions, single chain termination and double chain termination both occur. For such reactions, let F_1 = fraction of polymer molecules arising from single chain termination = probability that a system involves single chain termination. Then F_2 = fraction of polymer molecules arising from double chain termination = probability that a system involves double chain termination. Then we may utilize equation (2.5) with either of two different initial probability vectors. If we wish to count all molecules with $DP \geq 1$ as polymer,

$$\mathbf{p}^{(0)} = (0 \ 0 \ F_2 \ F_1) ; \quad (2.6)$$

if we wish to count only molecules with $DP \geq 2$ as polymer,

$$\mathbf{p}^{(0)} = (0 \ F_1 \ F_2 \ 0) . \quad (2.7)$$

To evaluate F_1 and F_2 we proceed as follows. Let f be the fraction of active polymer chains that undergo single chain termination so that $1-f$ is the fraction that undergo double chain termination. Specifically, $f = R_{t1}/R_t$.

Then if N is the total number of active polymer chains in the reaction, the number of finished polymer chains arising from single chain termination is $Nf = N_1$. The number of finished polymer chains arising from double chain termination is $N(1-f)/2 = N_2$. Normalizing these to obtain fractions, we have

$$\begin{aligned} N_1/(N_1+N_2) &= F_1 = 2f/(1+f) \\ N_2/(N_1+N_2) &= F_2 = (1-f)/(1+f). \end{aligned}$$

In terms of reaction rates, these become

$$F_1 = 1-F_2 = 2R_{t1}/(2R_{t1}+R_{t2}). \quad (2.8)$$

f. Binary copolymerization.-- All the systems discussed above have involved only one monomer species; even so, evaluation of transition probabilities and initial probabilities became slightly complicated.

A large portion of polymerization reactions of interest to polymer chemists involve copolymerization of two or more monomer species. (23) In such cases the complexities in evaluation are greatly multiplied, but in principle, and sometimes in practice, they are amenable to treatment by the formalism being developed here.

In this section a simple binary copolymerization (two monomer species only) with single chain termination will

be described in vector-matrix notation. The evaluation of the elements for this system will be treated in the section on applications to specific systems. Expansion to more complicated copolymerization systems (e.g., more than two monomers, double chain termination, etc.) is straightforward, though cumbersome, and will be considered in the same section.

For generality call the two monomer species in the reaction A and B. State 1 is dead polymer molecule. State 2 is actively growing polymer molecule whose unit at the reactive end is derived from monomer A; state 3 is a similar species derived from monomer B.

Since either A or B may be involved in an initiation reaction,

$$\mathbf{p}^{(0)} = (0 \quad p_2 \quad p_3) . \quad (2.9)$$

As a first approximation p_2 and p_3 are proportional to the molar concentrations of monomers A and B in the reaction, although in a few cases data are available to allow a slightly better estimation of p_2 and p_3 , as will be demonstrated.

States 2 and 3 may each react with either monomer, and both states are capable of termination so that the transition matrix is

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{pmatrix} \quad (2.10)$$

From this system we can obtain DP distribution and moments, relative amounts of the two monomers incorporated in the copolymer, and relative amounts of the different types of sequences (of any length desired) of the two monomers incorporated in the copolymers. For the last of these types of information it is necessary to utilize augmented matrices and vectors, to be discussed later, which increase the amount of computations but do not introduce any new conceptual difficulties.

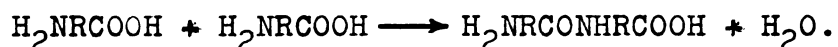
As a special type of copolymerization, homopolymerizations of mono-substituted ethylenes (vinyl compounds) have two different stereoconfigurations possible for each monomer unit in the chain and may be considered as copolymerizations of d- and l-enantiomers. (24) The relative amounts of various types of d,l-sequences can be analyzed using the same formalism. Thus we have an approach to the analysis of microstructures of the stereospecific polymers that have become increasingly important in recent years.

D. Linear Condensation Polymers

Condensation polymerization is quite different from addition polymerization. While the latter is a chain reaction process resulting in chain molecules, the former is a series of individual reactions resulting in a chain molecule.

In condensation polymerization a monomer normally consists of a small molecule containing two reactive

groups, such as carboxylic acid, amino, alkanol, etc. In the simplest case, every monomer molecule is identical and each contains one of each of two groups capable of reacting together to yield a new functional group in a larger molecule plus a small simple molecule. E.g., if the monomer is an amino acid, a single reaction of two monomer molecules results in an amide molecule and a molecule of water:



It has been shown that, unless R is only a very few carbon atoms in length, the functional groups on the new dimer molecule have essentially the same reactivity as those on the monomer. (4) The tendency is for more dimerization reactions to occur until the monomer concentration is depleted and dimer concentration is increased to a significant level. The obvious result is that monomer concentration drops precipitously during the early stages of the reaction before polymer of any appreciable DP has appeared.

This is a very complex reaction to describe statistically because a given polymer molecule arises from a very large number of possible precursor species, but useful results still can be obtained.

1. Systems

It is convenient to consider a "system" as a polymer molecule after the reaction is completed, and not as a potential polymer molecule.

2. Steps

Assume that the process described by the Markov chain is a counting process rather than a reaction process. Thus, we count the number of monomer units of which each polymer molecule consists. A step may be considered to be the movement from one monomer unit to the next, across the condensed functional group (ester, amide, etc.).

3. States

Define state 2 as the presence of a monomer unit in the chain on a given step and state 1 as the absence of a monomer unit. Then the counting process is described as follows. Initiation ($\mathbf{p}^{(0)}$) corresponds to beginning a count at a terminal monomer unit. Propagation (p_{22}) corresponds to finding the next functional group attached to another monomer unit, and termination (p_{21}) corresponds to not finding the next functional group attached to another monomer unit, i.e., the count is terminated. When the count is terminated, it obviously cannot be re-initiated for the same polymer molecule, so $p_{12} = 0$.

The mathematical description of the system is then

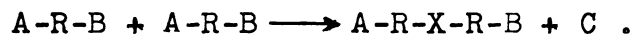
$$\mathbf{p}^{(0)} = (0 \quad 1)$$

$$\mathbf{P} = \begin{pmatrix} 1 & 0 \\ p_{21} & p_{22} \end{pmatrix}$$

and it remains merely to evaluate $p_{22} = 1 - p_{21}$ for specific cases.

We shall consider four different cases, but all correspond to linear (straight chain) polymers. Branched condensation polymers may be made simply by using some k -functional ($k \geq 3$) monomer species in the original mixture, but such cases will not be considered here.

a. Single monomer, two different functional groups.-- In this case, every molecule in the initial monomer "mixture" is identical and is of the type A-R-B where R is a chemically inert group (e.g., alkylene, phenylene, etc.) and A and B are different functional groups capable of reacting as



If all the functional groups were to react (except, perhaps, for one of each type) the result would be a single polymer molecule with DP equal to the number of monomer molecules present initially. However, the reaction usually ceases before complete reaction has occurred, and it is on this basis that we may analyze the system to obtain finite DP distributions.

Each monomer molecule contains two reactive functional groups, but each time a reaction occurs, two reactive functional groups are destroyed. It is then reasonable to define the degree of conversion, α , as the fraction of reactive functional groups initially present that have reacted. This, by our usual method of evaluation, leads to the conclusion that the probability a particular reactive

functional group has reacted is simply α , so we have

$$p_{22} = 1 - p_{21} = \alpha.$$

Note that here, unlike addition polymerization systems, we are content to allow monomer molecules to be counted as polymer. For condensation polymers this appears reasonable on two counts. First, a more or less philosophical reason, is the fact that a monomer molecule does not undergo a reaction and ultimately remain a monomer molecule (barring reversible reactions, of course). Second, the concentration of monomer practically vanishes in the early stages of a condensation polymerization, unlike the situation with addition polymerization, and it is desirable to have some indication of the degree to which this has occurred. If it is desired to count only molecules with $DP \geq 2$, this extension of the system is treated in exactly the manner it was for addition polymerization.

b. Equal amounts of two monomers.-- We may have a reaction in which two monomers are present initially in equal amounts, and in which one of the monomers contains two identical reactive groups of one type and the other monomer contains two identical reactive groups of a second type capable of reacting with the first type. For example, we may have a dibasic acid such as adipic acid, and a diamine such as hexamethylene diamine; the resulting polymer is a polyamide, known commercially as nylon 66.

In this case the definition of degree of conversion and of the transition probabilities are the same as in section a.

c. Single monomer, two different functional groups, in presence of monofunctional reactant.-- This case is chemically the same as that in part a, except for the presence of some monofunctional molecule such as a monobasic acid, a monohydric alcohol, a monoamine, etc. Whenever a monofunctional molecule reacts we may say that the polymer molecule is "capped" or incapable of further reaction at that end.

Designate the difunctional monomer as A-R-B and the monofunctional diluent as A-R'. Then every molecule of any DP will have a structure A---B or A---R'. It is convenient always to begin counting with the unit terminated by an A group, so that we automatically count every possible molecule. Then the propagation probability p_{22} corresponds to another unit following the one just counted. The termination probability p_{21} is the probability that the unit just counted has an unreacted B group or is derived from A-R' so that it is incapable of further reaction.

Let α be the fraction of B groups originally present that have reacted. This is numerically equal to the probability that a given B group has reacted. Then let ϕ be the mole fraction of A-R-B present initially, so that ϕ is the probability of propagation (of the count) at $\alpha = 1$,

i.e., where further reaction is impossible because of complete reaction of B groups. [Labelling is arbitrarily chosen in such a manner that the concentration of A groups always exceeds that of B groups.] From the definition of conditional probability, we have $p_{22} = 1 - p_{21} = \phi\alpha$, so that

$$\mathbf{P}^{(0)} = \begin{pmatrix} 0 & 1 \end{pmatrix} \quad (2.11)$$

$$\mathbf{P} = \begin{pmatrix} 1 & 0 \\ 1 - \alpha\phi & \alpha\phi \end{pmatrix} \quad (2.12)$$

d. Unequal amounts of two monomers.-- If the two monomers are represented by A-R-A and B-R'-B, with A-R-A chosen arbitrarily as that which is in excess initially, the system is conveniently treated as a binary copolymerization. State 2 represents the presence of an A unit on a given step (count) and state 3 represents the presence of a B unit on a given step (count).

Define α (degree of conversion) as the fraction of B groups initially present that have reacted and r as the mole ratio of B-R'-B to A-R-A present initially. Then it is easily shown that

$$\mathbf{P}^{(0)} = \begin{pmatrix} 0 & \frac{1-r\alpha}{1+r(1-2\alpha)} & \frac{r(1-\alpha)}{1+r(1-2\alpha)} \end{pmatrix} \quad (2.13)$$

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 \\ 1 - \alpha r & 0 & \alpha r \\ 1 - \alpha & \alpha & 0 \end{pmatrix} \quad (2.14)$$

If we let $r=1$, then we have another description of case b, as expected.

E. Matrix Relationships to Polymer Composition

The composition of a polymer is determined completely by the order in which the system occupies the various transient states prior to absorption in state 1. To study this, we work only with the inter-relationships among the transient states and/or with the absorption (termination) probabilities.

For instance, if we wish to know the probability distribution function for the degree of polymerization of the system described by equations (2.3) and (2.4), we need merely determine the probability that the system resides in states two and three for a total of exactly n steps, for each allowed value of n . It turns out that this may be determined entirely by use of a vector and a matrix which describe only these two states. (21) In general, if the dimension of the transition matrix \mathbf{P} is \underline{r} , we need perform all operations with a matrix of dimension $\underline{r}-1$ only, which results in a material reduction of the labor involved.

Partition \mathbf{P} as follows:

$$\mathbf{P} = \left(\begin{array}{c|c} \mathbf{I} & \mathbf{Z} \\ \hline \mathbf{R} & \mathbf{Q} \end{array} \right) \quad (2.15)$$

In our systems, if \mathbf{P} is an $s \times s$ matrix, \mathbf{I} is a 1×1 identity matrix, \mathbf{Z} is a $1 \times (s-1)$ null matrix, \mathbf{R} is an $(s-1) \times 1$ matrix which we call the "absorption matrix" and \mathbf{Q} is an $(s-1) \times (s-1)$ matrix which is the "propagation

matrix" since it describes what happens to the system during propagation.

Similarly the probability vector \mathbf{p} accompanying \mathbf{P} is a $1 \times s$ vector whose elements sum to unity. If we truncate \mathbf{p} to contain only its last $(s-1)$ components, which are the probabilities of occupancy of the transient states, we label the truncated vector \mathbf{q} and call it a "transient state vector."

1. Properties of the propagation matrix

The n -step elements of the transition matrix \mathbf{P} were labelled $p_{ij}^{(n)}$. In like manner, we label the n -step elements of the partitioned transition matrix

$$\mathbf{P}^{(n)} = \left(\begin{array}{c|c} \mathbf{I}^{(n)} & \mathbf{Z}^{(n)} \\ \mathbf{R}^{(n)} & \mathbf{Q}^{(n)} \end{array} \right)$$

and we desire simple evaluations of each of these symbols.

We showed previously that $\mathbf{P}^{(n)} = \mathbf{P}^n$, and from the rules for block multiplication (25) of matrices $\mathbf{I}^{(n)} = \mathbf{I}$ and $\mathbf{Q}^{(n)} = \mathbf{Q}^n$. Since \mathbf{Z} and \mathbf{R} are not square matrices, \mathbf{Z}^n and \mathbf{R}^n are undefined. However the application of the rules for block multiplication of matrices yields $\mathbf{Z}^{(n)} = \mathbf{Z}$.

Since \mathbf{P} is stochastic, $\mathbf{R} + \mathbf{Q}\mathbf{s} = \mathbf{I}\mathbf{s}$ from the definition of stochastic matrices. Further, any power of a stochastic matrix is stochastic also, so we obtain $\mathbf{R}^{(n)} + \mathbf{Q}^{(n)}\mathbf{s} = \mathbf{I}\mathbf{s}$ which gives us finally $\mathbf{R}^{(n)} = (\mathbf{I} - \mathbf{Q}^{(n)})\mathbf{s}$. [A column vector composed entirely of ones is denoted \mathbf{s} .] To summarize, we have

$$\begin{aligned}
\mathbf{P}^{(n)} &= \mathbf{P}^n \\
\mathbf{I}^{(n)} &= \mathbf{I} \\
\mathbf{Z}^{(n)} &= \mathbf{Z} \\
\mathbf{Q}^{(n)} &= \mathbf{Q}^n \\
\mathbf{R}^{(n)} &= (\mathbf{I} - \mathbf{Q}^n)\mathbf{s}
\end{aligned}$$

A few sums of power series of \mathbf{Q} will be useful and are given here. From the definition of transient states, it is obvious that $\lim_{n \rightarrow \infty} q_{ij}^{(n)} = 0$ for all i, j . This

implies that $\lim_{n \rightarrow \infty} \mathbf{Q}^n = \mathbf{Z}$. It can be shown (25) that for a matrix with these properties

$$\sum_{k=0}^{\infty} \mathbf{Q}^k = (\mathbf{I} - \mathbf{Q})^{-1},$$

where $\mathbf{Q}^0 = \mathbf{I}$, and we shall denote this sum the matrix \mathbf{N} .

If we define $x\mathbf{Q} = \mathbf{W}$, $0 \leq x \leq 1$, x a scalar, it is clear that

$$\sum_{k=0}^{\infty} x^k \mathbf{Q}^k = \sum_{k=0}^{\infty} \mathbf{W}^k = (\mathbf{I} - \mathbf{W})^{-1}. \quad (2.16)$$

Finally, we have

$$\sum_{k=0}^{n-1} \mathbf{Q}^k = (\mathbf{I} - \mathbf{Q}^n)\mathbf{N}$$

since

$$\begin{aligned}
(\mathbf{I} - \mathbf{Q}^n)\mathbf{N} &= (\mathbf{I} - \mathbf{Q}^n)(\mathbf{I} + \mathbf{Q} + \mathbf{Q}^2 + \dots) \\
&= \mathbf{I} + \mathbf{Q} + \mathbf{Q}^2 + \dots \\
&\quad - \mathbf{Q}^n - \mathbf{Q}^{n+1} - \dots \\
&= \mathbf{I} + \mathbf{Q} + \mathbf{Q}^2 + \dots + \mathbf{Q}^{n-2} + \mathbf{Q}^{n-1} \\
&= \sum_{k=0}^{n-1} \mathbf{Q}^k.
\end{aligned}$$

2. Degree of polymerization

The absorption matrix $\mathbf{R}^{(n)}$ has special significance for our systems. The element $r_{i1}^{(n)}$ is the probability that a system in the i 'th state initially has experienced absorption on or before the n 'th step. Thus $\mathbf{q}^{(0)}\mathbf{R}^{(n)}$ is the probability that the system was absorbed on or before the n 'th step, i.e., $\mathbf{q}^{(0)}\mathbf{R}^{(n)} = \text{Pr}\{\text{DP} \leq n\}$ which is the definition of the cumulative distribution function.

Therefore,

$$F_{\text{DP}}(n) = \mathbf{q}^{(0)}(\mathbf{I}-\mathbf{Q}^n)\mathbf{s} \text{ for } n=1,2,3,\dots \quad (2.17)$$

Since DP is an integral-valued discrete random variable, we have

$$\begin{aligned} P_{\text{DP}}(n) &= F_{\text{DP}}(n) - F_{\text{DP}}(n-1) \\ &= \mathbf{q}^{(0)}(\mathbf{I}-\mathbf{Q}^n)\mathbf{s} - \mathbf{q}^{(0)}(\mathbf{I}-\mathbf{Q}^{n-1})\mathbf{s} \\ &= \mathbf{q}^{(0)}(\mathbf{I}-\mathbf{Q}^n - \mathbf{I} + \mathbf{Q}^{n-1})\mathbf{s} \\ &= \mathbf{q}^{(0)}\mathbf{Q}^{n-1}(\mathbf{I}-\mathbf{Q})\mathbf{s} \text{ for } n=1,2,3,\dots \quad (2.18) \end{aligned}$$

For some purposes it is desirable to know the moment generating function of the distribution, $M_X(t)$, which is defined as the mathematical expectation of e^{tX} . [The dummy variable t has no physical significance.] It can be shown that the r 'th moment of a probability distribution of the random variable DP is simply

$$\langle \text{DP}^r \rangle = [d^r M_{\text{DP}}(t)/dt^r]_{t=0} .$$

For the integral-valued discrete random variable DP we have the moment generating function

$$M_{\text{DP}}(t) = \sum_{n=1}^{\infty} e^{tn} P_{\text{DP}}(n).$$

Now, with equation (2.18) for $P_{DP}(n)$ we write

$$\begin{aligned} M_{DP}(t) &= \sum_{n=1}^{\infty} e^{tn} \mathbf{q}^{(0)} \mathbf{Q}^{n-1} (\mathbf{I}-\mathbf{Q}) \mathbf{s} \\ &= e^t \mathbf{q}^{(0)} \left[(\mathbf{I}-\mathbf{Q}) \sum_{k=0}^{\infty} e^{tk} \mathbf{Q}^k \right] \mathbf{s} . \end{aligned} \quad (2.19)$$

Since $0 \leq e^t \leq 1$ for values of $t \leq 0$, and the value of ultimate interest here is $t=0$, the series in (2.19) converges, and using the evaluation of equation (2.16) we obtain

$$M_{DP}(t) = \mathbf{q}^{(0)} e^t (\mathbf{I}-\mathbf{Q}) (\mathbf{I}-\mathbf{Q}e^t)^{-1} \mathbf{s} .$$

For some purposes, it is desirable to know the cumulant generating function of a distribution. This is defined simply as

$$K_{DP}(t) = \log_e M_{DP}(t).$$

The r 'th cumulant, κ_r is obtained in a manner analogous to that for the r 'th moment, (26), i.e.,

$$\kappa_r = [d^r K_{DP}(t)/dt^r]_{t=0} .$$

The utility of cumulants comes from the fact that cumulants are additive for joint distributions and moments are not. Also, the first few derivatives of $K_{DP}(t)$ are frequently more easily obtained than are the same derivatives of $M_{DP}(t)$. Then the moments are obtained from the cumulants by use of a simple set of relationships. (13)

Although expressions for $M_{DP}(t)$ and $K_{DP}(t)$ are included for their interest and possible utility, there is a simpler way of obtaining the DP moments of our systems. Thus, Kemeny and Snell have shown (21) that

$$DP = \mathbf{q}^{(0)} \mathbf{N} \mathbf{s}$$

and

$$DP^2 = \mathbf{q}^{(0)} (2\mathbf{N}-\mathbf{I}) \mathbf{N} \mathbf{s} .$$

We simply extend their derivation in the following manner.

Let

$$\langle DP^n \rangle = \mathbf{q}^{(0)} \mathbf{t}_n, \quad (2.20)$$

so that

$$\mathbf{t}_1 = \mathbf{Ns}. \quad (2.21)$$

Then we obtain the recursion formula

$$\mathbf{t}_n = \mathbf{t}_1 + (\mathbf{N}-\mathbf{I}) \sum_{k=1}^{n-1} \binom{n}{k} \mathbf{t}_k \quad (2.22)$$

where $\binom{n}{k}$ is the binomial coefficient defined as

$\binom{n}{k} = n!/k!(n-k)!$ We thus have a simple means of obtaining all integral moments of the DP distributions.

Polymer chemists normally use ratios of moments for characterization. The four most common of these "averages" are defined below: (27)

$$\text{number average DP} = \langle DP \rangle_n = \langle DP \rangle \quad (2.23)$$

$$\text{weight average DP} = \langle DP \rangle_w = \langle DP^2 \rangle / \langle DP \rangle \quad (2.24)$$

$$\text{"z" average DP} = \langle DP \rangle_z = \langle DP^3 \rangle / \langle DP^2 \rangle \quad (2.25)$$

$$\text{"z+1" average DP} = \langle DP \rangle_{z+1} = \langle DP^4 \rangle / \langle DP^3 \rangle \quad (2.26)$$

The value obtained from colligative property measurements (cryoscopic and ebullioscopic methods, osmometry, etc.) is $\langle DP \rangle_n$. The value normally obtained from light scattering experiments is $\langle DP \rangle_w$, although $\langle DP \rangle_n$ is also obtainable in theory (and sometimes in practice) if the DP distribution is reasonably broad and if a complete Zimm plot is determined accurately. From ultracentrifuge studies it is possible to obtain all four of the above averages and, in theory, higher averages. The average obtained from dilution viscometry (not an absolute method yet) is usually called

simply the viscosity average, $\langle DP \rangle_v$; for many systems $\langle DP \rangle_n < \langle DP \rangle_v < \langle DP \rangle_w$, but it may be possible to have $\langle DP \rangle_v > \langle DP \rangle_w$.

A parameter frequently used to indicate the breadth of a molecular weight distribution is the ratio $\langle MW \rangle_w / \langle MW \rangle_n = \langle DP \rangle_w / \langle DP \rangle_n$. When this ratio is unity the sample contains all molecules of identical DP; the distribution of molecular chain lengths broadens as the ratio increases.

It is instructive to investigate this ratio in statistical parameters more directly descriptive of the distribution. Thus, from equations (2.23) and (2.24) we have $\langle DP \rangle_w / \langle DP \rangle_n = \langle DP^2 \rangle / \langle DP \rangle^2$. Now if we define a "polydispersity index"

$$\Delta = \left[\frac{\langle DP \rangle_w}{\langle DP \rangle_n} - 1 \right]^{1/2}$$

we have $\Delta^2 = \frac{\langle DP^2 \rangle - \langle DP \rangle^2}{\langle DP \rangle^2}$. But the numerator of this

expression is the variance of the degree of polymerization. Then Δ is simply the ratio of the standard deviation of the DP distribution to the number average DP. The relationship between Δ and the usual ratio is illustrated in Figure 1 for $\Delta \leq 1$.

The convenience of a parameter such as Δ compared with $\langle DP \rangle_w / \langle DP \rangle_n$ is evident when we consider synthetic polymers having rather narrow DP distributions. Such polymers usually arise either from fractionation of polymers having initially broader distributions or from reactions

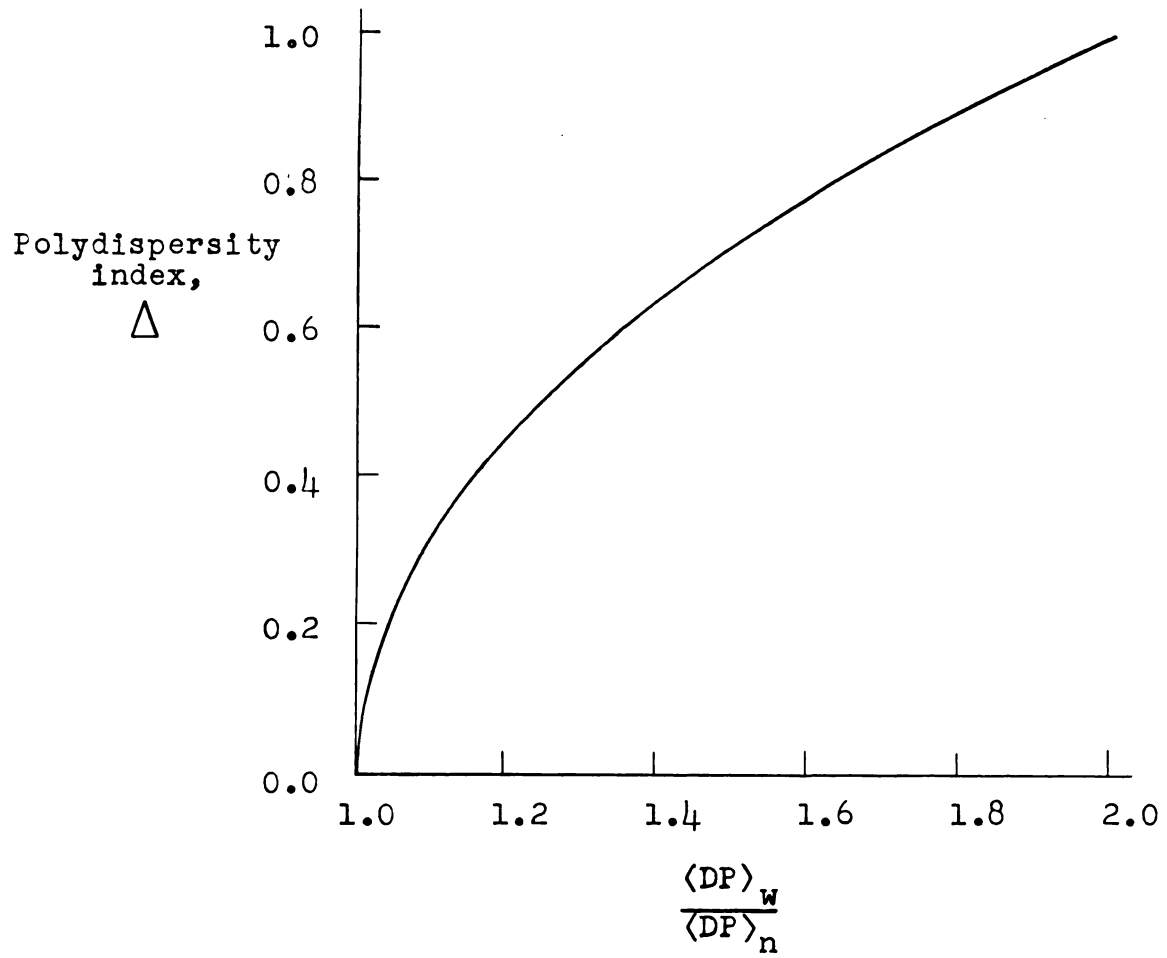


Figure 1. Breadth of DP distribution as represented by the ratio of weight average DP to number average DP

which theoretically should yield polymers with a Poisson distribution of DP. (28) In either case, the distribution can be closely approximated by a normal (Gaussian) distribution curve. Then for such polymers we may say that approximately two-thirds of the molecules have DP within the range $\langle DP \rangle_n \pm \Delta \langle DP \rangle_n$. Such an observation is not easily achieved merely by considering the ratio $\langle DP \rangle_w / \langle DP \rangle_n$.

The degree of success in obtaining a polymer with a Poisson distribution is also conveniently indicated by the value of Δ . The variance of a Poisson distribution is always the same as the first moment, (9) so that

$\Delta = \langle DP \rangle^{-1/2}$, which is easily compared with the experimentally determined value of Δ .

3. Composition of binary copolymers

For a simple binary copolymer, there are three different types of information (other than DP distributions) that may be of interest. The most common of these is the gross composition, or the fraction of all monomer units in the copolymer that are derived from each of the two monomers.

The second most common in recent years is the relative concentrations of different types of monomer sequences in the copolymer. If the two monomers involved are A and B, then an analysis of monomer pairs would yield the relative concentrations of AA, AB, BB, and BA pairs. Concentrations of the eight binary triples, sixteen binary quadruples, etc. may be obtained if desired also.

Finally, it may be desirable to know the lengths and fluctuations of lengths of homopolymer sequences within the copolymer, i.e., the lengths of sequences of all one type of monomer unit.

All these types of composition information are obtained more easily by a Markov chain approach than by a deterministic approach, even where the latter is applicable.

a. Gross composition, infinite DP limit.-- The usual deterministic approach assumes that an active copolymer chain undergoes only the four propagation reactions of adding each of the two monomers to each of the two types of active ends, and that termination is insignificant with respect to propagation. (23)

This assumption can be applied to the absorbing Markov chain approach simply by assuming that $p_{21} = p_{31} = 0$. Then \mathbf{Q} becomes stochastic, denoted \mathbf{Q}_s to indicate its special nature, and may be rewritten

$$\mathbf{Q}_s = \begin{pmatrix} (q_s)_{11} & 1-(q_s)_{11} \\ 1-(q_s)_{22} & (q_s)_{22} \end{pmatrix} \quad (2.27)$$

Since \mathbf{Q}_s is stochastic, \mathbf{Q}_s^n reaches an equilibrium value, and

$$\mathbf{q}^{(\infty)} = \mathbf{q}^{(0)} \mathbf{Q}^{(\infty)} .$$

In this case, it is easily shown that

$$\mathbf{q}^{(\infty)} = \begin{pmatrix} \frac{1-(q_s)_{22}}{2-(q_s)_{11}-(q_s)_{22}} & \frac{1-(q_s)_{11}}{2-(q_s)_{11}-(q_s)_{22}} \end{pmatrix} \quad (2.28)$$

which gives the gross copolymer composition assuming

infinite DP. When $(q_s)_{11}$ and $(q_s)_{22}$ are evaluated in terms of kinetic parameters, the results are identical to those obtained deterministically.

b. Gross composition, finite DP.--- In order to determine the gross copolymer composition without using the restriction of infinite DP, we proceed as follows:

Let $\mathbf{q}^{(h)}$ represent the expected composition for a molecule having DP exactly equal to h . Then if \mathbf{q} is the composition of copolymer having a real DP distribution,

$$\mathbf{q} = \sum_{h=1}^{\infty} \mathbf{q}^{(h)} P_{DP}(h) .$$

The value of $P_{DP}(h)$ is obtained from equation (2.18), and

$$\mathbf{q}^{(h)} = \frac{\mathbf{q}^{(0)}}{h} \sum_{k=0}^{h-1} \mathbf{q}_s^k .$$

This last sum is easily evaluated in the following manner.

Since \mathbf{q}_s is stochastic, we know that the limit $\lim_{n \rightarrow \infty} \mathbf{q}_s^{(n)} = \mathbf{q}_s^{(\infty)}$.

Then decompose \mathbf{q}_s into $\mathbf{q}_s^{(\infty)} + \mathbf{E}$ and $\mathbf{q}_s^n = \mathbf{q}_s^{(\infty)} + \mathbf{E}^{(n)}$.

As will be seen in the section on applications to specific systems, if we assume equal termination probabilities for both active states $\mathbf{E}^{(n)}$ can be written in the form

$$\mathbf{E}^{(n)} = \frac{A^n}{1-A} \mathbf{M} \quad (2.29)$$

where A is a constant with absolute value no greater than unity. Then

$$\sum_{n=0}^{h-1} \mathbf{E}^{(n)} = \frac{1-A^h}{(1-A)^2} \mathbf{M}$$

which leads to

$$\mathbf{q}^{(h)} = \mathbf{q}_s^{(\infty)} + \frac{1}{(1-A)^2} \left[\frac{1}{h} - \frac{A^h}{h} \right] \mathbf{q}^{(0)} \mathbf{M}$$

with the result that

$$\mathbf{q} = \mathbf{q}_s^{(\infty)} + \frac{1}{(1-A)^2} \left[\sum_{h=1}^{\infty} \frac{1}{h} P_{DP}(h) - \sum_{h=1}^{\infty} \frac{A^h}{h} P_{DP}(h) \right] \mathbf{q}^{(0)} \mathbf{M} \quad (2.30)$$

c. Analysis of monomer sequences of fixed length.--

Suppose we wish to know relative concentrations of AA, AB, BA, and BB pairs in the binary copolymer. Then we illustrate the use of an augmented matrix here; in the same manner, but with greatly increased amount of computation, we may also obtain concentrations of triples, quadruples, etc.

The simple transition matrix for a binary copolymer system is given by equation (2.10). Now, to form the augmented matrix we redefine the states as follows:

State 1 = dead polymer;

State 2 = active polymer with AA at end;

State 3 = active polymer with AB at end;

State 4 = active polymer with BA at end;

State 5 = active polymer with BB at end.

The new transition matrix is 5 x 5. If the rate of a propagation or termination reaction is independent of the penultimate monomer unit at the active chain end, we have $p_{22} = p_{42}$, $p_{23} = p_{43}$, $p_{34} = p_{54}$, $p_{35} = p_{55}$, $p_{21} = p_{41}$ and $p_{31} = p_{51}$. Also, it is obvious that a terminal active AA pair cannot be transformed into a terminal active pair

of either type BA or type BB in a single step, so

$p_{24} = p_{25} = 0$. By entirely similar reasoning we have

$p_{32} = p_{33} = p_{44} = p_{45} = p_{52} = p_{53} = 0$. Thus the transition matrix for this system is

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ p_{21} & p_{22} & p_{23} & 0 & 0 \\ p_{31} & 0 & 0 & p_{34} & p_{35} \\ p_{41} & p_{42} & p_{43} & 0 & 0 \\ p_{51} & 0 & 0 & p_{54} & p_{55} \end{pmatrix} \quad (2.31)$$

Also, if the initial vector of equation (2.9) is designated as $\mathbf{u}^{(0)}$, then for the present system we have

$$\mathbf{p}^{(0)} = \left(0 \quad u_2^{(0)} p_{22} \quad u_2^{(0)} p_{23} \quad u_3^{(0)} p_{34} \quad u_3^{(0)} p_{35} \right).$$

It is a simple matter to obtain the infinite DP limit of sequence compositions for this case, as Price has shown. (19) In principle, the composition may be obtained for copolymers of finite DP distribution, but the computations become tedious for such cases. In such an analysis, the value of DP to be used in equation (2.30) would be the number of pairs in a polymer chain, i.e., one less than the actual DP of the polymer.

d. Homopolymer sequences in copolymers.-- For this analysis we define state 2 as a monomer of the type being considered, say A, on the active chain end, and state 1 is either dead polymer or the first unit in a sequence of the other type. The matrix description is then

$$\mathbf{p}^{(0)} = \begin{pmatrix} 0 & 1 \end{pmatrix} \quad (2.32)$$

$$\mathbf{P} = \begin{pmatrix} 1 & 0 \\ p_{21} & p_{22} \end{pmatrix} \quad (2.33)$$

with p_{22} representing addition of another A molecule to an A end, and p_{21} representing either termination or addition of a B monomer to an A end. The case for sequences of B is identical except for the numerical values of p_{21} and p_{22} .

The distribution and moments of the sequence lengths are obtained from the matrix using equations (2.18) and (2.20-2.22).

III. APPLICATIONS TO SPECIFIC SYSTEMS

In applying the Markov chain formalism to specific systems, the general solutions for different types of systems will be obtained first. Then numerical solutions will be given for arbitrary, but reasonable, values of the various initial and transition probabilities. Finally numerical solutions will be obtained for some actual physical systems for which the required constants are available.

A. Linear Addition Homopolymers

It is simplest to solve only the general system described in section II-C-3-e, which then can be easily particularized to any type of linear addition homopolymer.

1. General solutions

The transition matrix was given in equation (2.5). We may assign to the propagation probability the value

$\theta = p_{33} = p_{44}$. Then the propagation matrix is

$$\mathbf{Q} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & \theta & 1-\theta \\ 0 & 0 & \theta \end{pmatrix}$$

which may be shown to be equal to the product of three matrices (known as a similarity transformation) as given at the top of the next page:

$$\mathbf{Q} = \mathbf{SAS}^{-1} = \begin{pmatrix} 1 & 0 & \frac{1}{\theta(1-\theta)} \\ 0 & 1 & \frac{-1}{1-\theta} \\ 0 & 0 & \frac{1}{1-\theta} \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & \theta & 1 \\ 0 & 0 & \theta \end{pmatrix} \begin{pmatrix} 1 & 0 & -\frac{1}{\theta} \\ 0 & 1 & 1 \\ 0 & 0 & 1-\theta \end{pmatrix}$$

The determination of the matrix \mathbf{S} which satisfies the above relationships is a difficult task where degenerate eigenvalues exist. The problem is treated in a number of books and reviews on the subject of matrix theory. (29)

Since $\mathbf{Q}^n = \mathbf{SA}^n\mathbf{S}^{-1}$, we have

$$\mathbf{Q}^n = \begin{pmatrix} 0 & 0 & \theta^{n-1} \\ 0 & \theta^n & n\theta^{n-1}(1-\theta) \\ 0 & 0 & \theta^n \end{pmatrix}$$

and

$$\mathbf{N} = (\mathbf{I} - \mathbf{Q})^{-1} = \begin{pmatrix} 1 & 0 & 1/(1-\theta) \\ 0 & 1/(1-\theta) & 1/(1-\theta) \\ 0 & 0 & 1/(1-\theta) \end{pmatrix}$$

From these results, the various quantities of interest are:

$$F_{DP}(n) = \mathbf{q}^{(0)} \begin{pmatrix} 1 - \theta^{n-1} \\ 1 - n\theta^{n-1} + (n-1)\theta^n \\ 1 - \theta^n \end{pmatrix}$$

$$P_{DP}(n) = \mathbf{q}^{(0)} \begin{pmatrix} \theta^{n-2}(1-\theta) \\ (n-1)\theta^{n-2}(1-\theta)^2 \\ \theta^{n-1}(1-\theta) \end{pmatrix}$$

$$\langle DP \rangle = \frac{\mathbf{q}^{(0)}}{1-\theta} \begin{pmatrix} 2-\theta \\ 2 \\ 1 \end{pmatrix}$$

$$\langle DP^2 \rangle = \frac{\mathbf{q}^{(0)}}{(1-\theta)^2} \begin{pmatrix} 4-3\theta+\theta^2 \\ 4+2\theta \\ 1+\theta \end{pmatrix}$$

$$\langle DP^3 \rangle = \frac{\mathbf{q}^{(0)}}{(1-\theta)^3} \begin{pmatrix} 8-5\theta+4\theta^2-\theta^3 \\ 8+14\theta+2\theta^2 \\ 1+4\theta+\theta^2 \end{pmatrix}$$

$$\langle DP^4 \rangle = \frac{\mathbf{q}^{(0)}}{(1-\theta)^4} \begin{pmatrix} 16+\theta+11\theta^2-5\theta^3+\theta^4 \\ 16+66\theta+36\theta^2+2\theta^3 \\ 1+11\theta+11\theta^2+\theta^3 \end{pmatrix}$$

For the general case, $\mathbf{q}^{(0)} = (F_1 \ F_2 \ 0)$, where $F_1 = 1 - F_2 = 2f/(1+f)$. Using this vector we obtain:

$$F_{DP}(n) = 1 - \frac{n(1-f)+2f}{1+f} \theta^{n-1} + \frac{(n-1)(1-f)}{1+f} \theta^n \quad \text{for } n=2,3,\dots$$

$$P_{DP}(n) = \frac{(1-\theta)\theta^{n-2}}{1+f} [2f+(1-f)(n-1)(1-\theta)] \quad \text{for } n=2,3,4,\dots$$

$$\langle DP \rangle_n = \frac{2+2f(1-\theta)}{(1-\theta)(1+f)}$$

$$\langle DP \rangle_w = \frac{2+\theta+f(2-4\theta+\theta^2)}{(1-\theta)[1+f(1-\theta)]}$$

$$\langle DP \rangle_z = \frac{4+7\theta+\theta^2+f(4-12\theta+3\theta^2-\theta^3)}{(1-\theta)[2+\theta+f(2-4\theta+\theta^2)]}$$

$$\langle DP \rangle_{z+1} = \frac{8+33\theta+18\theta^2+\theta^3+f(8-32\theta-7\theta^2-6\theta^3+\theta^4)}{(1-\theta)[4+7\theta+\theta^2+f(4-12\theta+3\theta^2-\theta^3)]}$$

$$\frac{\langle DP \rangle_w}{\langle DP \rangle_n} = \frac{(1+f)[2+\theta+f(2-4\theta+\theta^2)]}{2[1+f(1-\theta)]^2}$$

At the two limits of f , this ratio becomes

$$\frac{\langle DP \rangle_w}{\langle DP \rangle_n} = \begin{cases} \frac{2+\theta}{2} & \text{for } f = 0 \\ \frac{4-3\theta+\theta^2}{4-4\theta+\theta^2} & \text{for } f = 1 \end{cases}$$

The values one usually sees published for this ratio are $3/2$ at $f = 0$ and 2 at $f = 1$, which correspond to the limiting values at $\theta = 1$, i.e., at infinite DP. To illustrate the effect of θ and f on the value of the ratio, a three-dimensional surface is shown in Figure 2.

As further illustrations of some of the relationships found above, TABLE II gives representative values of $\langle DP \rangle_n$, TABLE III gives $\langle DP \rangle_w / \langle DP \rangle_n$, and TABLE IV gives the fraction of polymer molecules having degree of polymerization within $\pm 10\%$ of $\langle DP \rangle_n$. The last of these tables is easily computed with the use of the expression for the cumulative distribution function, and is another indication of the breadth of the distributions involved. All three of these tables give the values as functions of both θ and of f .

2. Relationship of probabilities to kinetic constants

All the remarks here apply to free radical-initiated vinyl polymerizations, but the extension to polymerizations initiated by other agents is not difficult, merely lengthy if all possibilities are to be considered in detail.

Two simplifying assumptions are used, although they could be avoided in a more comprehensive treatment. First, it is assumed that all radicals in a given system are equally reactive. Second, it is assumed that the total

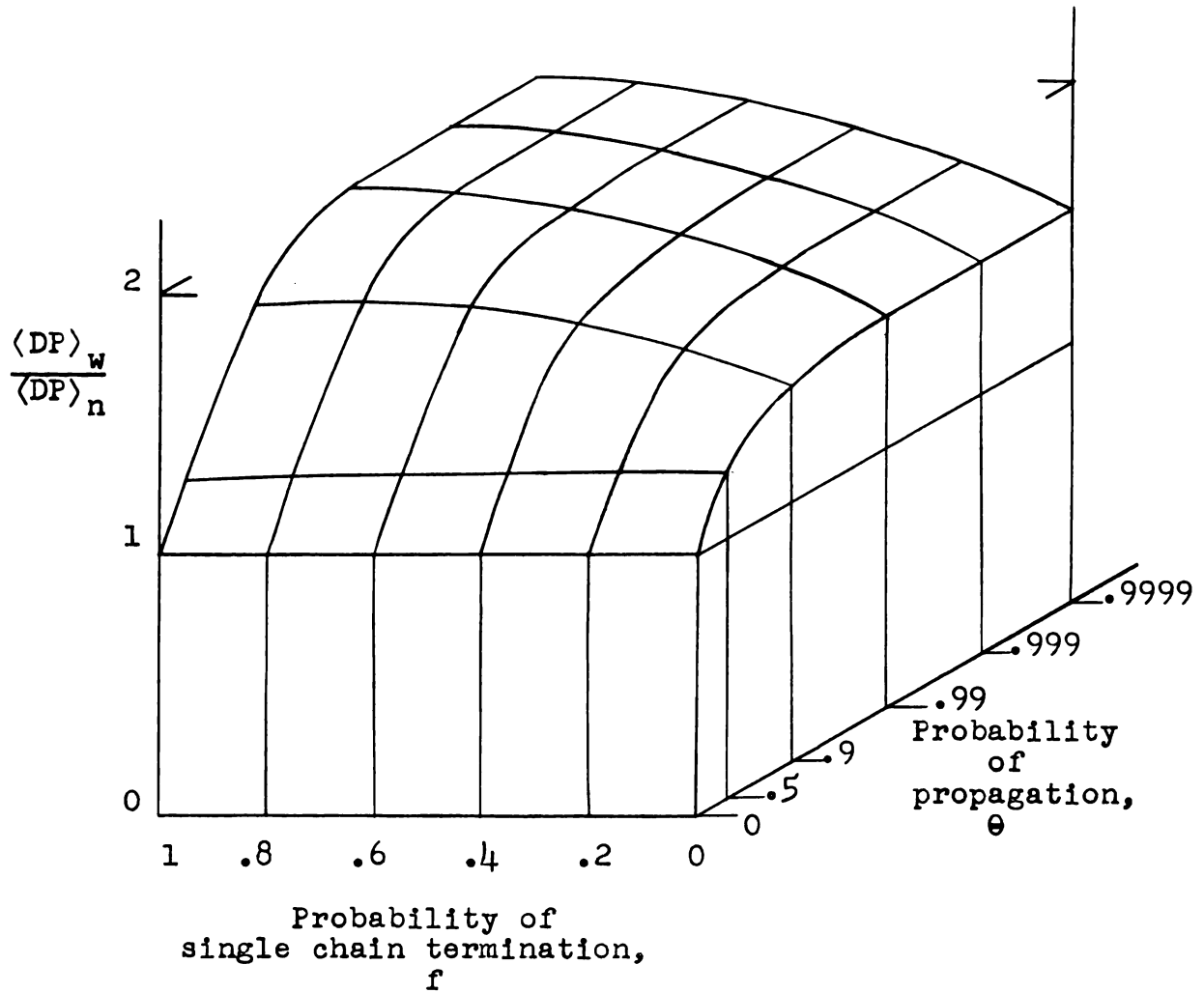


Figure 2. Surface of ratio of weight average DP to number average DP as a function of f and of θ for linear addition homopolymers

TABLE II. Number average degree of polymerization for linear addition homopolymers

θ	f					
	0	.2	.4	.6	.8	1
.5000	4	4	3	3	3	3
.9000	20	17	15	13	12	11
.9900	200	167	143	126	112	101
.9990	2,000	1,667	1,429	1,251	1,112	1,001
.9999	20,000	16,670	14,290	12,500	11,110	10,000

TABLE III. Ratio of weight average degree of polymerization to number average degree of polymerization for linear addition homopolymers

θ	f					
	0	.2	.4	.6	.8	1
.5000	1.25	1.26	1.26	1.25	1.24	1.22
.9000	1.45	1.58	1.67	1.73	1.75	1.74
.9900	1.50	1.67	1.80	1.90	1.95	1.97
.9990	1.50	1.68	1.82	1.92	1.98	2.00
.9999	1.50	1.68	1.82	1.92	1.98	2.00

TABLE IV. Number fraction of polymer molecules having degree of polymerization within $\pm 10\%$ of number average degree of polymerization for linear addition homopolymers

θ	f					
	0	.2	.4	.6	.8	1
.5000	.1875	.2083	.2232	.2344	.2431	.2500
.9000	.1111	.1234	.1322	.1388	.1439	.1480
.9900	.1086	.0983	.0910	.0855	.0812	.0778
.9990	.1088	.0972	.0890	.0828	.0780	.0741
.9999	.1117	.0990	.0899	.0830	.0777	.0735

concentration of reactive species and the concentration of each individual reactive species remain constant. This is valid during the time required for the growth of any individual polymer molecule except those initiated during the first few seconds of the reaction.

a. Initiation reactions.-- For the purposes of this treatment, the rate of appearance of reactive molecules may be taken as simply R_i . However, the magnitude of R_i may be estimated if the nature of the initiating reaction(s) is known, although in many cases the detailed nature of this step is the least well understood aspect of the overall mechanism. By way of illustration, three general types of initiation reactions are considered:

1. One initiator molecule decomposes by some (unimolecular) reaction to form one active site which continues to add monomer molecules until termination occurs. If $[C]$ is the initiator concentration and $[R^*]$ is the concentration of active molecules,

$$R_i = k_i[C] = d[R^*]/dt.$$

2. One initiator molecule decomposes by some (unimolecular) reaction to form two active sites which continue to add monomer molecules until termination occurs.

Then

$$R_i = 2k_i[C] = d[R^*]/dt.$$

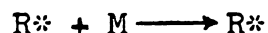
3. Two monomer molecules react (bimolecularly) to form two active sites which continue to add monomer

molecules until termination occurs. In this case,

$$R_i = 2k_i[M]^2 = d[R^*]/dt.$$

In addition, there are other less frequently encountered modes of initiation which have rate laws different from those above. (8)

b. Propagation reactions.-- For the purposes of this treatment the terms "propagation" and "termination" refer to a single growing molecule rather than to the usual kinetic chain. We shall assume that only one propagation reaction occurs, with only one rate law, viz.,

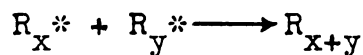


$$R_p = -d[M]/dt = k_p[R^*][M].$$

c. Termination reactions.-- Two general types of molecular chain termination reactions are important, and they may be designated by their kinetic terms -- chain termination and chain transfer. In both cases, a molecular chain is terminated, so that for purposes of a description of polymer composition the sum of the probabilities of both types of reaction is the appropriate parameter. For rate expressions, however, a kinetic chain ceases to exist after a chain termination reaction, but after a chain transfer reaction the kinetic chain continues even though the original molecular chain is completed.

1. In chain termination by combination, two growing polymer chains simply join together forming a single molecular chain with length equal to the sum of the lengths

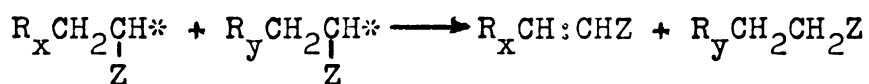
of the two chains that joined:



$$R_{tc} = k_{tc} [R^*]^2.$$

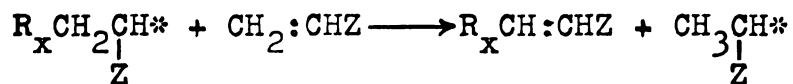
Thus the unpaired (radical) electrons on each of the growing chains "pair up" to form a normal covalent bond. This is the only termination reaction which fits our previous description of "double chain termination" reaction; the others are all "single chain termination" reactions.

2. In chain termination by disproportionation an atom or group (usually hydrogen atom) transfers from one growing polymer chain to the other. The result is two polymer chains with the same lengths as before the reaction, one being a saturated molecule and the other having a double bond at the end:



$$R_{td} = k_{td} [R^*]^2.$$

3. In chain transfer to monomer, a monomer molecule reacts with a growing active polymer chain resulting in a non-ionic, non-radical polymer molecule and a small, active radical that can undergo further polymerization. For example,



$$R_{trm} = k_{trm} [R^*][M].$$

Thus, the term "chain transfer" comes quite naturally from the fact that the kinetic chain is "transferred"

from one growing molecule to another, so that in a kinetic sense the reaction is unaffected but in a molecular composition sense the reaction is terminated.

4. In chain transfer to "solvent" the mechanism is identical to the preceding except that the transferring entity is a "solvent" or any other foreign reagent rather than monomer. For example,



$$R_{trs} = k_{trs}[R^1H][R^*].$$

d. Evaluation of θ generally. Since only propagation and termination are allowed explicitly in our model, the propagation probability θ may be taken simply as the rate of propagation divided by [the rate of propagation plus the rate of molecular chain termination]. Thus,

$$\theta = R_p / [R_p + R_{tc} + R_{td} + R_{trm} + R_{trs}].$$

All the rate expressions contain $[R^*]$ in some form, which is essentially an immeasurably small quantity, even with electron paramagnetic resonance methods, in most free radical-initiated polymerizations. The usual way to avoid this problem is to invoke the steady-state approximation so that $d[R^*]/dt = -d[R^*]/dt$.

This leads to

$$R_i = (k_{tc} + k_{td})[R^*]^2$$

because the steady-state approximation assumes that the

rate of initiation is the same as the rate of kinetic chain termination. Therefore,

$$[R^*] = R_i^{1/2} (k_{tc} + k_{td})^{-1/2}.$$

e. Evaluation of f generally.-- We defined f as the fraction of active polymer chains that undergo single chain termination. Then

$$f = [R_{td} + R_{trm} + R_{trs}] / [R_{td} + R_{trm} + R_{trs} + R_{tc}].$$

f. Parameters for methyl methacrylate polymerization at 60°C.-- From data of several different workers (30) we write the following approximate rate constants and the rates, assuming monomer concentration of nine moles per liter. The value of k_i is in considerable doubt, but this example is for illustration only, so the k_i value is used.

$k_i = 10^{-15}$ l/m/sec.	$[R^*] = 6.07 \times 10^{-11}$ m/l.
$k_p = 734$ l/m/sec.	$R_p = 4.01 \times 10^{-7}$ m/l/sec.
$k_{trm} = 4.6 \times 10^{-4}$ l/m/sec.	$R_{trm} = 2.51 \times 10^{-13}$ m/l/sec.
$k_{td} = 3.74 \times 10^7$ l/m/sec.	$R_{td} = 1.38 \times 10^{-13}$ m/l/sec.
$k_{tc} = 6.5 \times 10^6$ l/m/sec.	$R_{tc} = 2.40 \times 10^{-14}$ m/l/sec.
$k_{trs} = 0$	

From these values we obtain

$$\theta = .99999897$$

$$f = .942$$

Then

$$\langle DP \rangle_n = 9.9987 \times 10^5$$

$$\langle DP \rangle_w = 1.9981 \times 10^6$$

$$\langle DP \rangle_z = 2.9947 \times 10^6$$

$$\langle DP \rangle_{z+1} = 3.9899 \times 10^6$$

$$\langle DP \rangle_w / \langle DP \rangle_n = 1.9983$$

$$\text{Standard Deviation of DP} = 9.9903 \times 10^5$$

B. Linear Condensation Polymers

Condensation polymers result from either of two systems: single monomer with two different functional groups; or two difunctional monomers capable of reacting together.

1. Single monomer

From equations (2.11) and (2.12), the initial transient state vector and the propagation matrix are:

$$\mathbf{q}^{(0)} = (1)$$

$$\mathbf{Q} = (\alpha\phi)$$

Then we also have

$$\mathbf{q}^n = (\alpha^n \phi^n)$$

and

$$\mathbf{N} = \left(\frac{1}{1-\alpha\phi} \right).$$

From these results we obtain the various quantities of interest as follows:

$$F_{DP}(n) = 1 - (\alpha\phi)^n \quad \text{for } n=1,2,3,\dots \quad (3.1)$$

$$P_{DP}(n) = (\alpha\phi)^{n-1} (1-\alpha\phi) \quad \text{for } n=1,2,3,\dots \quad (3.2)$$

$$\langle DP \rangle = \frac{1}{1-\alpha\phi} \quad (3.3)$$

$$\langle DP^2 \rangle = \frac{1+\alpha\phi}{(1-\alpha\phi)^2} \quad (3.4)$$

$$\langle DP^3 \rangle = \frac{1+4\alpha\phi+(\alpha\phi)^2}{(1-\alpha\phi)^3} \quad (3.5)$$

$$\langle DP^4 \rangle = \frac{1+11\alpha\phi+11(\alpha\phi)^2+(\alpha\phi)^3}{(1-\alpha\phi)^4} \quad (3.6)$$

Finally we obtain

$$\langle DP \rangle_n = \frac{1}{1-\alpha\phi} \quad (3.7)$$

$$\langle DP \rangle_w = \frac{1+\alpha\phi}{1-\alpha\phi} \quad (3.8)$$

$$\langle DP \rangle_z = \frac{1+4\alpha\phi+(\alpha\phi)^2}{1-(\alpha\phi)^2} \quad (3.9)$$

$$\langle DP \rangle_{z+1} = \frac{1+11\alpha\phi+11(\alpha\phi)^2+(\alpha\phi)^3}{(1-\alpha\phi)[1+4\alpha\phi+(\alpha\phi)^2]} \quad (3.10)$$

$$\langle DP \rangle_w / \langle DP \rangle_n = 1+\alpha\phi \quad (3.11)$$

As an illustration, TABLE V gives $\langle DP \rangle_n$ and the fraction of molecules having DP within $\pm 10\%$ of $\langle DP \rangle_n$, both as functions of $(\alpha\phi)$. The value of $\langle DP \rangle_w / \langle DP \rangle_n$ increases linearly with $(\alpha\phi)$, ranging from one to two.

TABLE V. Degrees of polymerization of condensation polymer from single difunctional monomer

$\alpha\phi$	$\langle DP \rangle_n$	Number fraction of polymer molecules having DP within $\pm 10\%$ of $\langle DP \rangle_n$
.5000	2	.2500
.9000	10	.0737
.9900	100	.0737
.9990	1,000	.0737
.9999	10,000	.0734

2. Two monomers

From equations (2.13) and (2.14) the initial transient state vector and the propagation matrix are found to be

$$\mathbf{q}^{(0)} = \left(\frac{1-r\alpha}{1+r(1-2\alpha)} \quad \frac{r(1-\alpha)}{1+r(1-2\alpha)} \right)$$

$$\mathbf{Q} = \begin{pmatrix} 0 & r\alpha \\ \alpha & 0 \end{pmatrix}$$

The propagation matrix may be written as the product

$$\mathbf{Q} = \frac{1}{2} \begin{pmatrix} 1 & r^{1/2} \\ r^{-1/2} & -1 \end{pmatrix} \begin{pmatrix} \alpha r^{1/2} & 0 \\ 0 & -\alpha r^{1/2} \end{pmatrix} \begin{pmatrix} 1 & r^{1/2} \\ r^{-1/2} & -1 \end{pmatrix}$$

From this we obtain

$$\mathbf{Q}^n = \alpha^n r^{n/2} \begin{pmatrix} \frac{1+(-1)^n}{2} & \frac{1-(-1)^n}{2} r^{1/2} \\ \frac{1-(-1)^n}{2} r^{-1/2} & \frac{1+(-1)^n}{2} \end{pmatrix}$$

and

$$\mathbf{N} = \frac{1}{1-r\alpha^2} \begin{pmatrix} 1 & r\alpha \\ \alpha & 1 \end{pmatrix}$$

From these results we obtain the various quantities of interest as follows:

$$F_{DP}(n) = \begin{cases} 1 - \alpha^n r^{n/2} & \text{for } n=2,4,6,\dots \\ 1 - \alpha^n r^{(n+1)/2} \left(\frac{2-\alpha-\alpha r}{1+r-2\alpha r} \right) & \text{for } n=1,3,5,\dots \end{cases}$$

$$P_{DP}(n) = \begin{cases} \alpha^{n-1} r^{(n-1)/2} \left[\left(\frac{2-\alpha-\alpha r}{1+r-2\alpha r} \right) - \alpha r^{1/2} \right] & \text{for } n=2,4,6,\dots \\ \alpha^{n-1} r^{(n-1)/2} \left[1 - \alpha r \left(\frac{2-\alpha-\alpha r}{1+r-2\alpha r} \right) \right] & \text{for } n=1,3,5,\dots \end{cases}$$

The peculiar nature of these expressions arises from the cyclic nature of the Markov chain under consideration. That is, for a given starting state the system moves through the states in a definite order, returning to the starting state after an even number of steps, as long as it remains in the set of transient states. Likewise, in this chain of period 2, the system is in the other state after an odd

number of steps as long as it remains in the set of transient states. This property does not have a marked effect on the DP distribution except at very low DP.

This is another illustration of the preferability of a stochastic model over a deterministic model, as the latter does not result in a periodic expression, even though Flory recognized and pointed out the existence of this type of situation. (31)

Further results are:

$$\langle DP \rangle = \frac{1+r}{1+r-2r\alpha}$$

$$\langle DP^2 \rangle = \frac{(1+r\alpha)^2 + r(1+\alpha)^2}{(1-r\alpha^2)(1+r-2r\alpha)}$$

$$\langle DP^3 \rangle = \frac{1+r+12r\alpha+10r\alpha^2+10r^2\alpha^2+12r^2\alpha^3+r^2\alpha^4+r^3\alpha^4}{(1-r\alpha^2)^2(1+r-2r\alpha)}$$

$$\langle DP^4 \rangle =$$

$$\frac{1+r+28r\alpha+47r\alpha^2+47r^2\alpha^2+136r^2\alpha^3+47r^2\alpha^4+47r^3\alpha^4+28r^3\alpha^5+r^3\alpha^6+r^4\alpha^6}{(1-r\alpha^2)^3(1+r-2r\alpha)}$$

$$\langle DP \rangle_n = \frac{1+r}{1+r-2r\alpha}$$

$$\langle DP \rangle_w = \frac{(1+r\alpha)^2 + r(1+\alpha)^2}{(1-r\alpha^2)(1+r)}$$

$$\langle DP \rangle_z = \frac{1+r+12r\alpha+10r\alpha^2+10r^2\alpha^2+12r^2\alpha^3+r^2\alpha^4+r^3\alpha^4}{(1-r\alpha^2)[(1+r\alpha^2)+r(1+\alpha)^2]}$$

$$\langle DP \rangle_{z+1} =$$

$$\frac{1+r+28r\alpha+47r\alpha^2+47r^2\alpha^2+136r^2\alpha^3+47r^2\alpha^4+47r^3\alpha^4+28r^3\alpha^5+r^3\alpha^6+r^4\alpha^6}{(1-r\alpha^2)(1+r+12r\alpha+10r\alpha^2+10r^2\alpha^2+12r^2\alpha^3+r^2\alpha^4+r^3\alpha^4)}$$

$$\frac{\langle DP \rangle_w}{\langle DP \rangle_n} = \frac{(1+r)[1+r(1+\alpha)^2 - 2r^2\alpha^3 + r^2\alpha^2] - 8r^2\alpha^2}{(1-r\alpha^2)(1+r)^2}$$

TABLE VI gives $\langle DP \rangle_n$, TABLE VII gives $\langle DP \rangle_w / \langle DP \rangle_n$, and TABLE VIII gives the fraction of polymer molecules having DP within $\pm 10\%$ of $\langle DP \rangle_n$. All three tables are given for a range of values of both α and r .

For the value $r=1$, we have the results for systems with initial concentrations of both monomers the same. These results are identical to those for condensation polymers from one difunctional monomer in the absence of monofunctional reactants (i.e., for $\phi=1$ in equations (3.1)-(3.11)).

For the value $\alpha=1$, we have the systems at complete conversion with or without excess of one monomer. For this limiting case we have

$$F_{DP}(n) = \begin{cases} 1-r^{n/2} & \text{for } n=2,4,6,\dots \\ 1-r^{(n+1)/2} & \text{for } n=1,3,5,\dots \end{cases}$$

$$P_{DP}(n) = \begin{cases} r^{(n-1)/2}(1-r^{1/2}) & \text{for } n=2,4,6,\dots \\ r^{(n-1)/2}(1-r) & \text{for } n=1,3,5,\dots \end{cases}$$

$$\langle DP \rangle_n = \frac{1+r}{1-r}$$

$$\langle DP \rangle_w = \frac{(1+r)^2 + 4r}{(1-r)(1+r)}$$

$$\langle DP \rangle_z = \frac{(1+r)(1+22r+r^2)}{(1-r)[(1+r)^2+4r]}$$

$$\langle DP \rangle_{z+1} = \frac{1+76r+230r^2+76r^3+r^4}{(1-r)(1+r)(1+22r+r^2)}$$

$$\frac{\langle DP \rangle_w}{\langle DP \rangle_n} = \frac{(1+r)^2 + 4r}{(1+r)^2}$$

TABLE VI. Number average degree of polymerization for linear condensation polymers from two monomers

α	r				
	.9000	.9900	.9990	.9999	1
.5000	1.90	1.99	2	2	2
.9000	6.79	9.57	10	10	10
.9900	16.10	66.78	95	99	100
.9990	18.66	166.1	167	952	1,000
.9999	18.97	195.1	1,667	6,667	10,000
1.0000	19.00	199.0	1,999	19,999	-----

TABLE VII. Ratio of weight average degree of polymerization to number average degree of polymerization for linear condensation polymers from two monomers

α	r				
	.9000	.9900	.9990	.9999	1
.5000	1.48	1.50	1.50	1.50	1.50
.9000	1.87	1.90	1.90	1.90	1.90
.9900	1.98	1.98	1.99	1.99	1.99
.9990	2.00	2.00	2.00	2.00	2.00
.9999	2.00	2.00	2.00	2.00	2.00
1.0000	2.00	2.00	2.00	2.00	2.00

TABLE VIII. Number fraction of polymer molecules having degree of polymerization within $\pm 10\%$ of number average degree of polymerization for linear condensation polymers from two monomers

α	r				
	.9000	.9900	.9990	.9999	1
.5000	.5000	.2466	.2500	.2500	.2500
.9000	.0624	.0819	.0818	.0818	.1168
.9900	.0861	.0726	.0741	.0744	.0778
.9990	.0819	.0718	.0736	.0735	.0741
.9999	.0388	.0718	.0735	.0734	.0735
1.0000	.0388	.0704	.0734	.0734	-----

3. Evaluation of parameters

Unlike the case of addition polymerization, the transition probabilities are not obtained from kinetic parameters for condensation polymers.

The value of α is determined entirely by the degree of conversion obtained, which may be determined by how soon the reaction is arrested or by the amount of side reactions (presumably unknown) that prevent complete conversion. In this sense, α is related to kinetic parameters but such aspects as rate of removal of the resultant small molecules (water, ammonia, etc.) have an effect which depends on the reactor geometry and other conditions too complex to evaluate properly.

The values of ϕ and r are determined entirely by the makeup of the initial reaction mixture. Attainment of $\phi=1$ is achieved "simply" by careful purification of the single monomer involved, and values of ϕ less than unity are best achieved by adding known amount of monofunctional compounds to rigorously purified monomer.

It is generally very difficult or impossible to obtain $r=1$ exactly. However, in some cases it can be done by use of a stoichiometric salt which can be purified by recrystallization or other standard methods. An example of this is the formation of hexamethylenediammonium adipate ("nylon salt") in the production of nylon 66.

C. Linear Addition Copolymers

When dealing with linear addition copolymerizations, the problem of evaluating transition probabilities is a great deal more complex than it is for the corresponding homopolymerizations. However, with a few simplifying assumptions the probabilities may be evaluated to a reasonable degree of accuracy.

1. Limiting case of no termination reaction

The matrix treatment of the Markov chain approach to this limiting case has been given adequately by F. P. Price, (19) but some of the important features and results will be given briefly here as a preview to the more general treatment. In this case, the propagation matrix is stochastic and is given by equation (2.27); Q_s^n reaches an equilibrium value of

$$Q_s^{(\infty)} = \frac{1}{2 - (q_s)_{11} - (q_s)_{22}} \begin{pmatrix} 1 - (q_s)_{22} & 1 - (q_s)_{11} \\ 1 - (q_s)_{22} & 1 - (q_s)_{11} \end{pmatrix}$$

To evaluate the various $(q_s)_{ij}$ we examine the various possible propagation reactions and their rates (23), viz.,

<u>Reaction</u>	<u>Rate</u>
$\sim A^* + A \longrightarrow \sim A^*$	$R_{11} = k_{11}[\sim A^*][A]$
$\sim A^* + B \longrightarrow \sim B^*$	$R_{12} = k_{12}[\sim A^*][B]$
$\sim B^* + A \longrightarrow \sim A^*$	$R_{21} = k_{21}[\sim B^*][A]$
$\sim B^* + B \longrightarrow \sim B^*$	$R_{22} = k_{22}[\sim B^*][B]$

By utilizing the usual numerical equivalence of probability

and frequency, we see that $(q_s)_{11} = R_{11}/(R_{11}+R_{12})$ and $(q_s)_{22} = R_{22}/(R_{21}+R_{22})$.

The concentrations of $\sim A^*$ and $\sim B^*$ are seen to cancel in these expressions, but we still are left with four kinetic rate constants in addition to monomer concentrations. These normally are incorporated into "monomer reactivity ratios" defined as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. As a result, we have only two unknown parameters to be determined from the gross copolymer composition, assuming the validity of the limitation of no termination reaction. In terms of monomer reactivity ratios and monomer concentrations, we have

$$(q_s)_{11} = \frac{r_1[A]}{r_1[A]+[B]} \quad \text{and} \quad (q_s)_{22} = \frac{r_2[B]}{r_2[B]+[A]}$$

a. Gross composition, arbitrary parameters.-- To illustrate the gross composition of binary addition copolymers predicted by this approach, two systems are illustrated in TABLE IX. These are the systems having reactivity ratios of $r_1 = r_2 = 0.1$ and $r_1 = 0.1, r_2 = 5.0$.

b. Concentrations of sequences of length two.--

In this case, our stochastic propagation matrix is given by equation (2.31). Then we find that

$$\mathbf{P}^{(\infty)} = \frac{1}{2-p_{11}-p_{22}} \begin{pmatrix} p_{11}p_{21} & p_{12}p_{21} & p_{12}p_{21} & p_{22}p_{12} \end{pmatrix}$$

where the various $(q_s)_{ij}$ have been replaced by p_{ij} for the sake of compactness, since the matrix is stochastic

anyway. This result, too, has been shown by Price. (19)
The concentrations of these various pair sequences for the same two systems as above are given in TABLE X.

TABLE IX. Gross composition of linear binary addition copolymers for two hypothetical systems

[A]	$r_1 = r_2 = 0.1$			$r_1 = 0.1, r_2 = 5.0$		
[A]+[B]	$(q_s)_{11}$	$(q_s)_{22}$	$(q_s)_1^{(\infty)}$	$(q_s)_{11}$	$(q_s)_{22}$	$(q_s)_1^{(\infty)}$
0.1	.0110	.4737	.3473	.0110	.9783	.0215
0.2	.0244	.2857	.4227	.0244	.9524	.0465
0.4	.0625	.1304	.4812	.0625	.8824	.1115
0.6	.1304	.0625	.5188	.1304	.7692	.2097
0.8	.2857	.0244	.5773	.2857	.5556	.3836
0.9	.4737	.0110	.6527	.4737	.3571	.5498

TABLE X. Composition of sequence pairs in linear binary addition copolymers for two hypothetical systems, limiting case of infinite DP

[A]	$r_1 = r_2 = 0.1$			$r_1 = 0.1, r_2 = 5.0$		
[A]+[B]	$p_1^{(\infty)}$	$p_2^{(\infty)} = p_3^{(\infty)}$	$p_4^{(\infty)}$	$p_1^{(\infty)}$	$p_2^{(\infty)} = p_3^{(\infty)}$	$p_4^{(\infty)}$
0.1	.0038	.3435	.3092	.0002	.0213	.9572
0.2	.0103	.4124	.1649	.0011	.0454	.9081
0.4	.0301	.4511	.0677	.0070	.1045	.7840
0.6	.0677	.4511	.0301	.0274	.1824	.6079
0.8	.1649	.4124	.0103	.1096	.2740	.3425
0.9	.3092	.3435	.0038	.2604	.2894	.1608

c. Homopolymer sequence lengths within the copolymer.--

The matrix description was given by equations (2.32) and (2.33). For sequences of monomer A, $p_{22} = r_1[A]/(r_1[A]+[B])$ and for sequences of monomer B, $p_{22} = r_2[B]/(r_2[B]+[A])$.

Sequence length analyses have not received much attention from polymer chemists. However, Rice and Nagasawa (32) have pointed out that the distribution of sequence lengths is essential in the evaluation of the free energy of a polyampholyte in a solution. Thus, it is reasonable that any general theory of the statistical thermodynamics of mixing of copolymers with solvents will require such information also.

If we let the random variable M refer to the length of a sequence, then the properties most likely to be of interest are found to be:

$$P_M(n) = p_{21}p_{22}^{n-1} \quad \text{for } n=1,2,3,\dots$$

$$\langle M \rangle = 1/p_{21}$$

$$\langle M^2 \rangle = (1+p_{22})/(p_{21})^2$$

$$\text{Var}(M) = p_{22}/(p_{21})^2$$

Wall has also obtained these expressions for $\langle M \rangle$ and $P_M(n)$ (15). The values of $P_M(n)$ and $\langle M \rangle$ for the same two systems previously treated are given in TABLE XI.

d. Characterization of stereoregularity in vinyl polymers.-- Miller and Nielsen, (33) and Price (19) have pointed out that stereoregularity in vinyl polymers can be analyzed by considering it as a copolymerization of the d- and l-stereoisomers of the same monomer unit in the chain. (24)

The quantities usually desired are the relative concentrations of sequences of length three in the copolymer,

TABLE XI. Homopolymer sequence length distributions within linear binary addition copolymers for two hypothetical systems

[A]	A sequences		B sequences	
[A]+[B]	$P_M(n)$	$\langle M \rangle$	$P_M(n)$	$\langle M \rangle$
$r_1 = r_2 = 0.1$				
0.1	$.0111x(.0110)^n$	1.011	$.9000x(.4737)^n$	1.900
0.2	$.0250x(.0244)^n$	1.025	$.4000x(.2857)^n$	1.400
0.4	$.0667x(.0625)^n$	1.067	$.1500x(.1304)^n$	1.150
0.6	$.1500x(.1304)^n$	1.150	$.0667x(.0625)^n$	1.067
0.8	$.4000x(.2857)^n$	1.400	$.0250x(.0244)^n$	1.025
0.9	$.9000x(.4737)^n$	1.900	$.0111x(.0110)^n$	1.011
$r_1 = 0.1, r_2 = 5.0$				
0.1	$.0111x(.0110)^n$	1.011	$45.00 x (.9783)^n$	46.00
0.2	$.0250x(.0244)^n$	1.025	$20.00 x (.9524)^n$	21.00
0.4	$.0667x(.0625)^n$	1.067	$7.50 x (.8823)^n$	8.50
0.6	$.1500x(.1304)^n$	1.150	$3.33 x (.7692)^n$	4.33
0.8	$.4000x(.2857)^n$	1.400	$1.25 x (.5556)^n$	2.25
0.9	$.9000x(.4737)^n$	1.900	$.56 x (.3571)^n$	1.56

as these may be analyzed by nuclear magnetic resonance spectroscopy. (34) In this case, the stochastic propagation matrix is 8×8 , and the solutions are given and discussed by Price. The details of the analysis will not be repeated here, but, in essence, the problem simplifies to the case of $r_1 = r_2$ and $[A] = [B]$. The result is that $[AAA] = [BBB]$, $[ABA] = [BAB]$, and $[ABB] = [BAA] = [AAB] = [BBA]$.

2. Copolymers having finite DP distributions

The most difficult problems in analysis of real copolymer systems are the evaluation of termination probabilities and the complexity of the algebra involved in a solution of a completely general system.

The first of these two problems will be treated in more detail in part b. The latter problem can be handled easily if we restrict our hypothetical system slightly, and in principle it can be handled without restriction if one considers the results worthwhile in view of the cumbersome algebra involved.

a. Analysis of hypothetical case.--- The restrictions we shall use for the sake of tractability are:

1. assume the relative termination rate, and hence the termination probability, is the same for systems in both of the transient states; and

2. assume the values of the elements of the initial transient state vector are proportional to the concentrations of the two monomers.

Neither of these limiting assumptions introduces serious error, particularly if the termination rate is very small compared to the propagation rate, which will be true of most systems of interest. Thus, if the termination rate is very small, differences among the various termination rates possible become even less important in terms of the overall system. Also, if the termination rate is very small, the

DP is large, and the influence of the initial vector becomes vanishingly small. We shall apply the formalism to systems for which the assumptions are only moderately good, but shall retain them for convenience.

Utilizing these assumptions, we may describe the system in the following manner.

$$\mathbf{p}^{(0)} = \begin{pmatrix} 0 & \frac{[A]}{[A]+[B]} & \frac{[B]}{[A]+[B]} \end{pmatrix}$$

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 \\ 1-\theta & p_{11}\theta & p_{12}\theta \\ 1-\theta & p_{21}\theta & p_{22}\theta \end{pmatrix}$$

Application of the usual formalism to these yields the probability distribution function, which is independent of the value of $p_2^{(0)}$ and $p_3^{(0)}$:

$$P_{DP}(n) = (1-\theta)\theta^{n-1} \quad \text{for } n=1,2,3,\dots$$

Since, by letting $\theta = \alpha\phi$, this is the same probability distribution function as that obtained for linear condensation polymers from a single monomer, the moments and average DP's are the same also. The extension of these results to count only polymer with $DP \geq 2$ or to consider double chain termination as well as single chain termination is a simple matter, even though the algebra becomes increasingly complex.

To obtain the gross copolymer composition we apply equations (2.29) and (2.30). To this end, we obtain

$$\mathbf{q}^n = \frac{1}{2-p_{11}-p_{22}} \begin{pmatrix} p_{21}+p_{12}(p_{22}+p_{11}-1)^n & p_{12}-p_{12}(p_{22}+p_{11}-1)^n \\ p_{21}-p_{21}(p_{22}+p_{11}-1)^n & p_{12}+p_{21}(p_{22}+p_{11}-1)^n \end{pmatrix}$$

which may be rewritten $\mathbf{q}^{(n)} = \mathbf{q}^{(\infty)} + \mathbf{E}^{(n)}$, where $\mathbf{E}^{(n)}$ is given by equation (2.29) with

$$A = p_{22} + p_{11}^{-1}$$

$$\mathbf{M} = \begin{pmatrix} p_{12} & -p_{12} \\ -p_{21} & p_{21} \end{pmatrix}$$

From these relationships it is possible to obtain the final desired results of the gross composition of a copolymer having finite DP distribution under the limiting assumptions used. Since $P_{DP}(h) = (1-\theta)\theta^{h-1}$, equation (2.30) becomes

$$\mathbf{q} = \mathbf{q}_s^{(\infty)} + \frac{(1-\theta)}{\theta(1-A)^2} \ln \frac{1-A\theta}{1-\theta} \mathbf{q}^{(0)} \mathbf{M} \quad (3.12)$$

The results of application of equation (3.12) to the two hypothetical polymers analyzed previously are given in TABLE XII for three values of θ , of which $\theta = 1$ corresponds to the limiting case of infinite DP.

TABLE XII. Gross composition of linear binary addition copolymers for two hypothetical systems, given as fraction of monomer A in the copolymer

[A] [A]+[B]	$r_1 = r_2 = 0.1$			$r_1 = 0.1, r_2 = 5.0$		
	$\theta=.5$	$\theta=.9$	$\theta=1$	$\theta=.5$	$\theta=.9$	$\theta=1$
0.1	.1968	.2987	.3473	.0758	.0414	.0215
0.2	.2923	.3819	.4227	.1522	.0852	.0465
0.4	.4348	.4670	.4812	.3085	.1829	.1115
0.6	.5652	.5330	.5188	.4729	.3039	.2097
0.8	.7077	.6181	.5773	.6601	.4808	.3836
0.9	.8032	.7013	.6527	.7817	.6311	.5498

These results are shown also as copolymer composition surfaces in Figures 3 and 4.

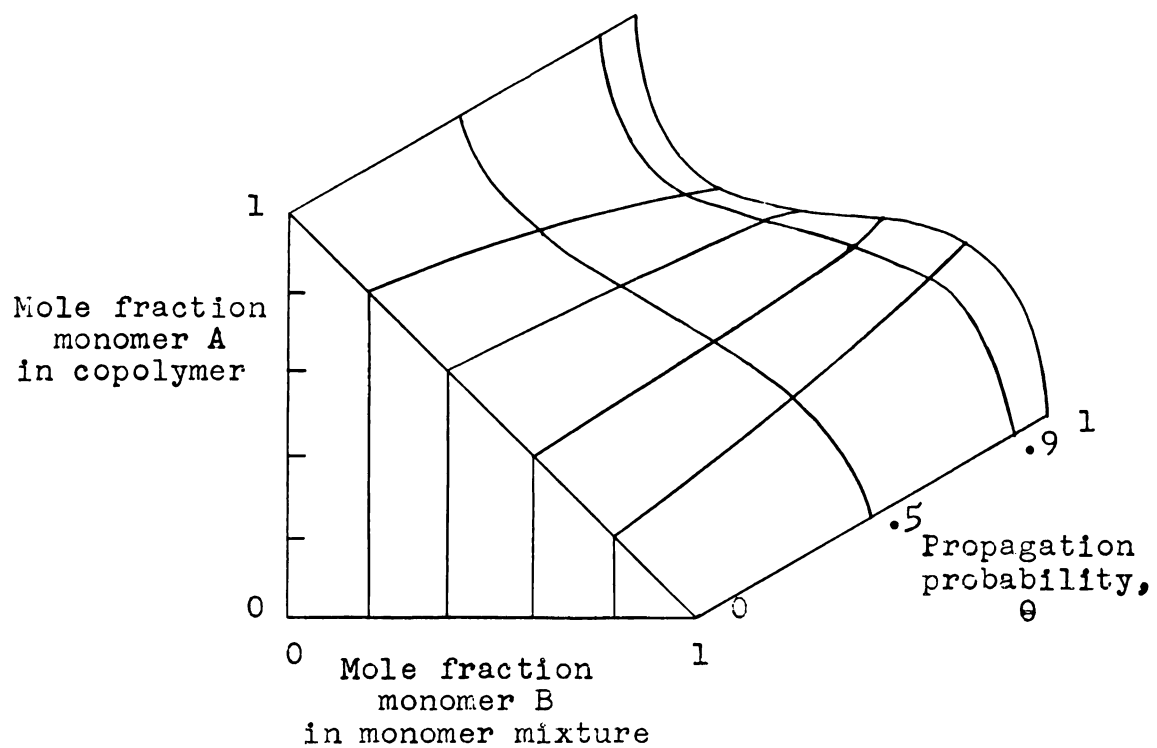


Figure 3. Copolymer composition as a function of θ for the hypothetical system: $r_1 = r_2 = 0.1$

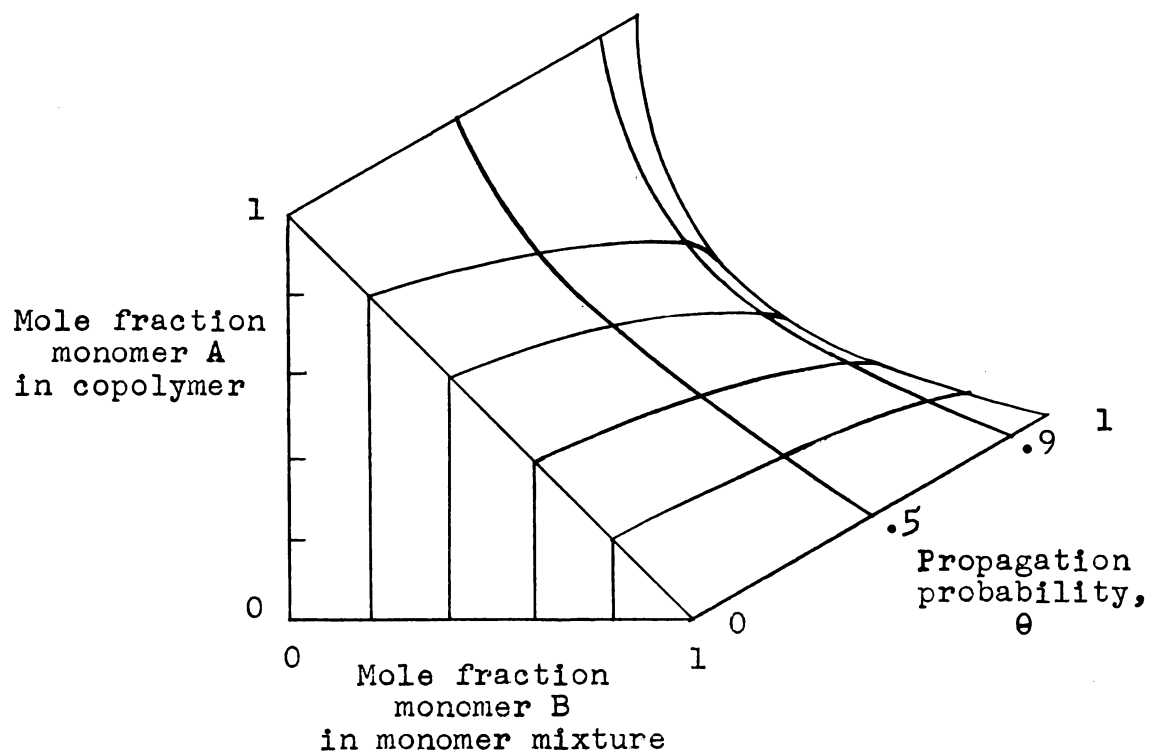


Figure 4. Copolymer composition as a function of θ for the hypothetical system: $r_1 = 0.1$, $r_2 = 5.0$

b. Analysis of "real" case.-- As an example of the application of this theory to a real copolymer case, one of the most widely studied copolymer systems is used. Monomer A is methyl methacrylate and monomer B is styrene. Then the copolymer reactivity ratios at 60°C are approximately $r_1 = .45$, $r_2 = .50$. (35)

Copolymerizations of this type usually are carried out with the addition of free radical initiator, so that the values of termination rate constants depend on the catalyst used and the amount of it as well as the temperature of polymerization. Alfrey, Bohrer, and Mark have pointed out in some detail the difficulty of estimating the rates of all the possible termination reactions. (23) For this analysis, then, we simply assume $\theta = .999$, since this would, for this copolymer, correspond to a number average molecular weight of the order of 10^5 , which is of the same order of magnitude as is the molecular weight of commercial copolymers of this type.

We shall further assume that the copolymerization is initiated by 2,2'-azobis(2-methylpropionitrile). It has been found that the relative initiation efficiencies of these two monomers with this initiator at 60°C are such (36) that the initial transient state vector is

$$\mathbf{q}^{(0)} = \begin{pmatrix} \frac{.49[A]}{.49[A]+.51[B]} & \frac{.51[B]}{.49[A]+.51[B]} \end{pmatrix}$$

The gross composition of this copolymer under these

assumed values of parameters using equation (3.12) is given in TABLE XIII for both $\theta = .999$ and $\theta = 1$.

TABLE XIII. Gross composition of methyl methacrylate-styrene copolymers with finite and infinite DP distributions.

$\frac{[A]}{[A]+[B]}$	Fraction of MMA in copolymer	
	$\theta = .999$	$\theta = 1.0$
0.1	.172553	.172885
0.2	.286213	.286624
0.4	.442984	.443213
0.6	.589733	.589603
0.8	.729766	.729483
0.9	.840010	.839695

Upon comparing the values in the two columns of TABLE XIII, we see that the usual assumption of infinite DP in the computation of gross copolymer composition is good to within the usual experimental error involved for this system with its usual rather high DP distribution. However, as can be seen from TABLE XII and Figures 3 and 4, such an assumption would lead to considerable error if copolymers of very low DP distribution were studied.

IV. SUMMARY AND CONCLUSIONS

Absorbing Markov chain theory has been applied to the problem of describing the composition of polymers with the use of matrix formalism to simplify the mathematics involved.

In each system studied, the "states" of the system were carefully defined in such a manner that state 1 is absorbing (i.e., once a system enters state 1, it never leaves) so that it corresponds to finished polymer molecule. Then each of the other states is transient (i.e., as the number of steps taken by the system in the process under consideration increases without bound, the probability of occupancy of the transient states vanishes), and is defined in such a manner that the probability of transition from any state to any other state is easily written in terms of physical parameters (rate constants, composition of reaction mixtures, etc.). The result is a very compact formalism that permits computation of several aspects of polymer composition easily.

Linear addition and linear condensation polymer systems have been analyzed to obtain the distribution and moments of the degree of polymerization and the first four "average" degrees of polymerization measured by physical methods, viz., number average, weight average, "z" average,

and " $z+1$ " average degree of polymerization. Included in the addition polymer systems were those involving termination by combination, by disproportionation, by chain transfer, or by any combination of these, as well as a system involving biradical initiation with termination by disproportionation or chain transfer or both. Included in the condensation polymer systems were those involving a single monomer of type A-R-B, with or without the presence of a monofunctional molecule of type A-R', as well as those involving two monomers of types A-R-A and B-R'-B, not necessarily in equimolar amounts, such as are involved in the synthesis of nylon 66, Dacron, and similar substances.

Linear addition copolymers have been analyzed to obtain the distribution and moments of degree of polymerization in exactly the manner used for homopolymers, and to obtain the distribution and moments of the lengths of sequences of either monomer alone within the copolymer. Also obtained for the first time is an expression yielding the mean composition of the copolymer in terms of its component monomer units for a real, finite DP distribution rather than merely for the limiting case of infinite degree of polymerization. Also the mathematical formulation for obtaining the composition of the copolymer in terms of various types of monomer sequences of fixed length was outlined, but not solved explicitly.

Some of the problems, particularly the more complicated ones involving copolymers, were not solved algebraically

in detail. They can be easily solved for numerical results (ultimately desired anyway) for either hypothetical or actual cases by use of computers, or even desk calculators. This would not involve approximate methods, but would simply utilize the ease of working with matrices composed of numbers rather than algebraic symbols.

There are many directions in which this work could be extended to obtain needed or desired results as well as perhaps new insight into some systems which have previously defied analysis. The first category of these extensions involves the careful definitions of states of new systems. Some systems in this category include inter-intramolecular polymerization (i.e., formation of small ring structures concurrently with polymerization), termination of polymerization by formation of macro-ring structures, ring-chain transition polymerization (e.g., epoxide polymerization, silicone polymerization, etc.), "living polymer" systems (28), branched and cross-linked polymer formation, polypeptide and protein formation, reversible and equilibrium polymerization systems.

The second category of extensions involves generalization of the transition probabilities used with the present formalism together with systems already defined as well as the possible extensions given above. Thus, in addition polymerization systems, the values of the transition probabilities are functions of the degree of conversion of the reaction (because of depletion of initiator and

monomer, viscosity increase causing diffusion-controlled mechanisms, etc.) and of temperature. In the present analysis these are tacitly assumed constant but their variability could be included in the numerical computation of the results for real systems.

Finally, the formalism might be extended to give additional information. For example, Stockmayer has concluded (37) that fluctuations in copolymer composition (i.e., relative amounts of monomers in copolymer) must be known in order to properly analyze light scattering results for copolymers. He has concluded (17) that in the limit of infinite DP the copolymer composition distribution is an immeasurably narrow Gaussian distribution, but apparently no estimate of the composition fluctuations has ever been made for finite DP distributions. Kemeny and Snell have indicated that such a problem is essentially intractable because of the unavailability of the values of some infinite sums in general terms. (21) However, it may be possible to obtain reasonable estimates by use of a computer approximation together with an extension of the present formalism.

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