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Kinetic Modeling of Polymerization Reactions

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INTRODUCTION

A polymer is a high molecular weight material; polymerization is the series of reactions leading to the formation of polymers from low molecular weight material (called monomers). These can be broadly classified as step growth and chain growth polymerizations [1, 2]. In the former, the growth of molecules occurs through the reaction of reactive groups, e.g., —COOH, —NH_2, —OH, located on the molecules. Polymer formation can occur through this mechanism only when the starting monomer has at least two reactive groups, when there are more than two of them in the monomer, the resultant polymer is either branched or crosslinked in structure. As opposed to this, linear polymers are formed by the polymerization of bifunctional monomers. In chain growth polymerization there are growth centers in the reaction mass, to which monomers add on successively until either all monomers are consumed or some external agent terminates the polymerization.

Depending on the nature of these growth centers, chain growth polymerization can be further classified into radical, cationic, anionic, and stereoregular polymerizations [1–8]. It has been found that different mechanisms of polymerization have different characteristics. As an example, in step growth polymerization, the weight average molecular weight of polymer formed increases with the reaction time, whereas for chain growth polymerization it reaches a certain maximum value only.

Like all other reactions in nature, polymerization is reversible. However, in almost all the studies, it is assumed to be irreversible in order to simplify the analysis. In reversible polymerization, the overall conversion is limited by equilibrium; in practice, the reverse step is suppressed by applying high vacuum and higher temperatures. Unlike reactions of low molecular weight compounds, in polymerization there is a formation of several homologs which are chemically the same but differ in their molecular weights. The reaction mass can thus be characterized by a molecular weight distribution (MWD). This is nothing but a plot of the concentration of oligomer of chain length n (denoted by $[P_n]$) versus n. The different physical properties of the polymers are to a large extent dependent upon MWD and a given MWD can be equivalently represented by its moments. For polymeric systems, only the first three moments can be experimentally measured [1, 3], and they have been shown to characterize the MWD completely. The general definition of moments is given by

$$\lambda_K = \sum_{n=1} n^K [P_n]; \qquad K = 0,1,2, \ldots \tag{1}$$

where $[P_n]$ is the concentration of P_n species of chain length n in the reaction mass. The number and the weight average chain lengths μ_n and μ_w are the polydispersity index ρ of the polymer are defined in terms of these moments as

$$\mu_n = \frac{\lambda_1}{\lambda_0} \tag{2a}$$

$$\mu_w = \frac{\lambda_2}{\lambda_1} \tag{2b}$$

$$\rho = \frac{\mu_w}{\mu_n} \tag{2c}$$

In Eq. 2c, ρ measures the breadth of the MWD and is equal to 1 for monodisperse material. On multiplying μ_n and μ_w with the molecular weight of the repeat unit, one obtains the number average molecular weight $\bar{M}_n$ and the weight average molecular weight $\bar{M}_w$. These are known to determine the physical properties of the polymers. For example, the viscosity of molten polymers is proportional to the weight average molecular weight and above a certain value of M_w, the viscosity usually varies [3] as $\bar{M}_w$ [3, 4]. This is important in estimating the power requirements for pumping the reaction mass, say, through a tubular reactor, a spinnerette to obtain fibers, or extruders and molds. In another example, the aliphatic polyester formed from ω-hydroxydecanoic acid has little strength or spinnability when μ_n is about 25 but it gives long, extremely weak fibers that can be cold-drawn when μ_n is about 55 [2]. However, for μ_n above 100, it can be spun easily and cold-drawn to strong fibers. In the following section we present the analysis of batch reactors forming polymers through the reversible step growth and radical mechanisms.

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STEP GROWTH POLYMERIZATION [1–3]

Step growth polymerization occurs through reaction of two or more reactive groups. If the starting monomer is bifunctional, the resulting polymer is linear in structure; otherwise the polymer is branched. The following analysis of batch reactors is presented for both cases.

Kinetic Model of Reversible Linear Step Growth Polymerization

It is assumed that the starting monomer is an ARB type where A and B are the reacting functional groups. On polymerization, larger chains are formed but no matter what the chain length, it has one unreacted A and one unreacted B at its ends. The growth of the polymer can be schematically written as

$$P_m + P_n \underset{k_p'}{\overset{k_p}{\rightleftharpoons}} P_{m+n} + W, \qquad m, n = 1, 2, \ldots \tag{3}$$

where W is the condensation product and P_m is a polymer chain having m repeat units. It is observed that polymerization is represented by a set of infinite elementary reactions given in Eq. 3 and it is desired to model these kinetically to determine the MWD of the polymer as a function of time. Based on the experiments of Bhide and Sudborough, Flory proposed the equal reactivity hypothesis in which the reactivity of the reactive groups is independent of the chain length of the polymer. This serves as the most basic assumption in the modeling of step growth polymerization and is described below.

A chemical reaction can occur only when the reacting molecules collide. The rate of reaction, R, can thus be written in terms of the product of the collision frequency, $\omega_{m,n}$, between P_m and P_n and the probability of their reaction, $Z_{m,n}$. Therefore,

$$R = \alpha\omega_{m,n}Z_{m,n} \tag{4}$$

where α is a constant of proportionality. From the equal reactivity hypothesis [1], the probability of reaction, $Z_{m,n}$, is independent of m and n. Thus, if Z is the probability of reaction between two reacting groups and P_m and P_n can react in s distinct ways, $Z_{m,n}$ would be equal to sZ. Additionally, the collision frequency $\omega_{m,n}$ between two dissimilar molecules is proportional to $[P_m][P_n]$, whereas that between P_m and P_n is proportional to $[P_m]^2/2$. Consequently, if k_p is the rate constant associated with the reaction of functional groups, the kinetic model under the equal reactivity hypothesis can be written as

$$k_{p,mn} = \frac{R}{[P_m][P_n]} = sk_p, \qquad m \neq n;\ m, n = 1, 2, \ldots \tag{5a}$$

$$= \frac{R}{[P_m]^2} = \frac{sk_p}{2}, \qquad m = n;\ m = 1, 2, \ldots \tag{5b}$$

For linear chains, the reacting functional groups are always located at the end of the chain. This means that in Eq. 5, s is always 2, as seen in Figure 1. Any polymer species P_n ($n \geq 2$) is formed in the forward step by reacting a P_r ($r < n$, $r = 1,2 \ldots$) with a P_{n-r}. In the reverse reaction, it is formed by the attack of the condensation product, W, on the bonds of the polymer chain. W can react on any position of the chain but there are two locations on it which would give a small chain of the same length. For a linear polymer, P_n, the total number of bonds is $(n - 1)$. Consequently, the mole balance relation for P_n in a batch reactor is given by

$$\frac{d[P_1]}{dt} = 2k_p[P_1]\sum_{i=1}^{\infty}[P_i] + 2k_p'[W]\sum_{n=2}^{\infty}[P_n] \tag{6a}$$

$$\frac{d[P_n]}{dt} = -2k_p[P_n]\sum_{m=1}^{\infty}[P_m] + k_p\sum_{r=1}^{n-1}[P_r][P_{n-r}]$$

$$+2k_n'[W]\sum_{m=n+1}^{\infty}[P_m] - k_p'(n-1)[P_n][W], \qquad n \geq 2 \tag{6b}$$

where k_p and k_p' are the forward and the reverse reaction rate constants, respectively. The relation for the kth moment can be derived by multiplying the preceding mole balance relations for P_n by n^k ($k = 0,1,2$) and summing the various terms appropriately. The ultimate moment generation relates are given by [10]

$$\frac{d\lambda_0}{dt} = -k_p\lambda_0^2 + k_p'[W](\lambda_1 - \lambda_0) \tag{7a}$$

$$\frac{d\lambda_1}{dt} = 0 \tag{7b}$$

$$\frac{d\lambda_2}{dt} = 2k_p\lambda_1^2 + \frac{k_p'}{3}[W](\lambda_1 - \lambda_3) \tag{7c}$$

To be able to solve Eq. 6, the MWD of the feed to the batch reactor must be known. Let us assume that at $t = 0$ it is given by

$$[P_n]\Big|_{t=0} = [P_n]_0, \qquad n = 1, 2, 3, \ldots \tag{8}$$

Correspondingly, its moments can be found and are assumed to be given by

$$\lambda_k\Big|_{t=0} = \sum_{n=1}^{\infty} n^k[P_n]_0 = \lambda_k^0, \qquad k = 0,1,2 \tag{9}$$

Equation 7b is the easiest to integrate and it shows that the first moment λ_1 is time invariant, equal to λ_1^0. It may be observed that the first moment is the same as the total count of repeat units, which is time invariant during polymerization. Equation 7c gives λ_2 but it involves λ_3 and can be integrated only when some information about it is known. However, if the moment generation relation for λ_3 is written, it is found that it involves λ_4

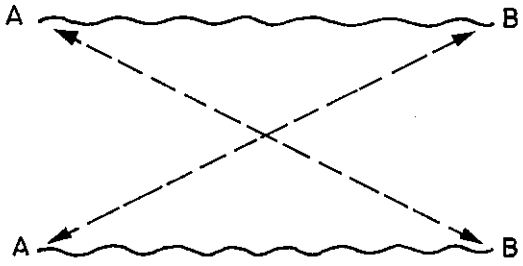

Figure 1 Schematic representation of reaction between linear chains.

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$$\sum_{i=n+1}^{\infty}[P_i] = \lambda_0 - [P_n] -$$

By using Eq. 11, the MWD re

$$\frac{d[P_1]}{dt} = -2k_p[P_1]\left(\frac{\lambda_0 + k}{k_p}\right.$$

$$\frac{d[P_n]}{dt} = -2k_p[P_n]\lambda_0 + k_p$$

$$+ 2k_p'[W]\Big\{\lambda_0 -$$

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and the moment generation relation for λ_4 involves λ_5, and so on. This hierarchy of relation has been broken by using a suitable closure relation. This approximate closure relation for the bifunctional step growth polymerization was proposed in the literature by assuming the MWD to be given by the Schulz–Zimm relation for which λ_3 is related to λ_0, λ_1, and λ_2 by the following relation [11, 12]:

$$\lambda_3 \cong \frac{\lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)}{\lambda_1\lambda_0} \tag{10}$$

In the literature, computations of moments have been made and results have been compared with those found from the exact MWD [11, 13–17]. The match between the two has been good and the approximation given in Eq. 10 yields satisfactory results in the entire range of computation.

The major difficulty of computing the MWD of reversible ARB polymerization lies in the fact that the chain growth step consists of an infinite number of elementary reactions as written in Eq. 6. The various mole balance relations for species P_i for any i in batch reactors are highly nonlinear and coupled differential equations. Computationally one solves an arbitrarily large number (say N) of these equations such that the concentration of P_N is close to zero. However, some truncation error is introduced in the repeat count variable because higher chain length species are neglected. In actual practice, one would like to determine the first three moments of the distribution—λ_0, λ_1, and λ_2—and the concentrations of the first few oligomers, which cannot be determined without solving the entire MWD. It is possible to decouple these equations using the following transformation [18]:

$$\sum_{i=n+1}^{\infty} [P_i] = \lambda_0 - [P_n] - \sum_{i=1}^{n-1} [P_i] \tag{11}$$

By using Eq. 11, the MWD relations given in Eq. 6 can be modified:

$$\frac{d[P_1]}{dt} = -2k_p[P_1]\left(\frac{\lambda_0 + k_p'[W]}{k_p}\right) + 2k_p'[W]\lambda_0 \tag{12a}$$

$$\frac{d[P_n]}{dt} = -2k_p[P_n]\lambda_0 + k_p \sum_{r=1}^{n-1} [P_r][P_{n-r}] - 2k_p'[P_n][W](n+1) + 2k_p'[W]\left\{\lambda_0 - \sum_{i=1}^{n-1} [P_i]\right\}, \qquad n \geq 2 \tag{12b}$$

and at $t = 0$;

$$[P_n] = [P_n]_0; \qquad n = 1,2,3, \ldots \tag{12c}$$

Equations 12 are now in the decoupled form and the concentration of any species can be determined sequentially by first determining the zeroth moment of distribution, λ_0, through Eq. 7a and the problem of truncation error is completely eliminated.

To illustrate the method outlined above, formation of polyethylene terephthalate (PET) in batch reactors is analyzed with ethylene glycol (EG) evaporating [19–21]. If it is assumed that the polymer formed cannot be evaporated and the vapor–liquid equilibrium is governed by Raoult's law, then

$$p_r = p_r^*(T)\,\frac{[W]}{[W] + \lambda_0} \tag{13}$$

where p_r and $p_r^*(T)$ are the pressure applied on the reactor and the vapor pressure of the condensation product and [W] is the concentration of the condensation product. Experiments have shown that PET has an equilibrium constant $K(= k_p/k_p')$ of 0.5, which is independent of temperature, and conversion of 99% is needed to obtain fiber-grade polymer. In order to push the polymerization in the forward direction, high vacuum and temperature are applied. The effect of the polymerization pressure and the temperature can be evaluated through the use of Eqs. 7, 12, and 13 as follows. To obtain the solution of Eqs. 12 and 13, they are written in the nondimensional form using the following variables [18]:

$$P_n = \frac{[P_n]}{\lambda_1^0} \tag{14a}$$

$$\beta = \frac{k_p'}{k_p} \equiv \frac{1}{K} \tag{14b}$$

$$t' = k_p \lambda_1^0 t \tag{14c}$$

$$w = \frac{[W]}{\lambda_1^0} \tag{14d}$$

where

$$\lambda_1^0 = \sum_1^\infty n[P_n]_0 \tag{14e}$$

It is assumed that the feed to the batch reactor has its MWD given by Flory's distribution with conversion p_A of functional groups as 0.3; i.e., at $t = 0$,

$$p_n = (1 - 0.3)(0.3)^n$$

The moment equations can be derived; they are

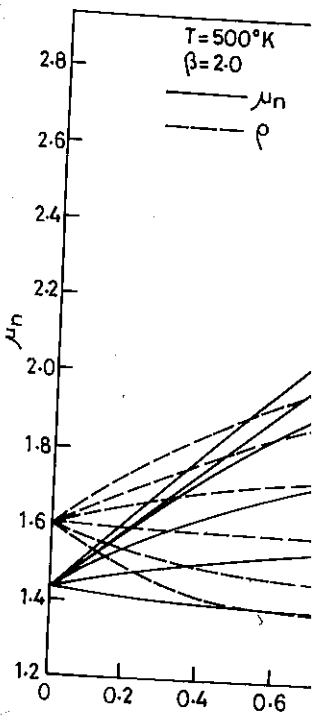
$$\frac{d\lambda_0}{dt} = -\lambda_0^2 + \beta W(\lambda_1 - \lambda_0) \tag{15a}$$

$$\frac{d\lambda_1}{dt} = 0 \tag{15b}$$

$$\frac{d\lambda_2}{dt} = 2\lambda_1^2 + \frac{\beta}{3} W(\lambda_1 - \lambda_3) \tag{15c}$$

These can be solved using the closure relation given in Eq. 10. Once the pressure and the temperature are specified, λ_0, λ_2. P_1, and P_2 can be found from Eqs. 15 and 16 using the Runge–Kutta numerical technique. The concentration of the condensation product W is obtained from Eq. 13 assuming the escaping vapors and the liquid are in thermodynamic equilibrium.

By using the computation method outlined here, it is possible to determine λ_0, λ_2, P_1, and P_2 as a function of the dimensionless reaction time and the μ_n and ρ are computed using Eq. 2. At low pressures, a large amount of EG is evaporated and μ_n and ρ increase continuously with time (as shown in Fig. 2). This implies that the polymers formed at low reaction pressures are highly polydispersed long-chain species. As opposed to this, at high pressures, the situation is found to be just the opposite. The dimensionless concentrations of the first two species P_1 and P_2 are presented in Figure 3 at different system pressures.



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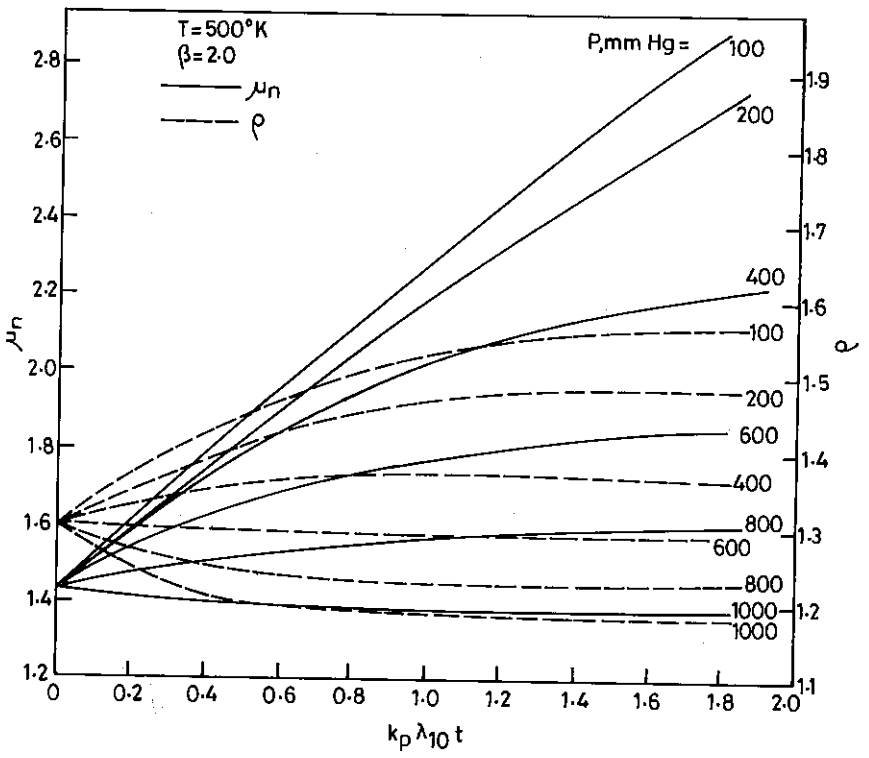


Figure 2 Number average chain length, μ_n, and polydispersity index, ρ, versus time, for various values of reaction pressures (T = 500 K, β = 2.0).

As the reaction proceeds the monomer, P_1, converts into the higher oligomers. The consumption of the monomer depends on the extent of the forward reaction. It is thus seen that the reactor pressure affects the consumption of P_1 in the reaction mass. Similarly, the concentration of the dimer, P_2, increases with the residence time of the reactor. The equilibrium point is specified when the concentration of any species does not change with time. We thus see from Figure 3 that the equilibrium is delayed as the system's pressure is reduced.

When the temperature of the reactor is increased, the vapor pressure p^* in Eq. 13 goes up, thus reducing the reaction mass. This in turn reduces the effect of the reverse step in step growth polymerization. In PET reactors, it is seen that the equilibrium constant, K, is unaffected by the temperature. Figures 4 and 5 present data for P_1, P_2, μ_n, and ρ with the reaction times for different temperatures. It is found that at high temperatures, higher chain length species are formed and the polymer mass is also highly polydispersed. The effect of higher temperature is similar to that of the reduction of the total pressure and the equilibrium is delayed.

In the analysis presented above, it was assumed that the functional groups of various oligomers have the same reactivity, independent of the chain length, n, of the molecules they are located on. The comparison of computed results with the assumption of equal reactivity with experimental data has sufficiently indicated that the overall polymerization

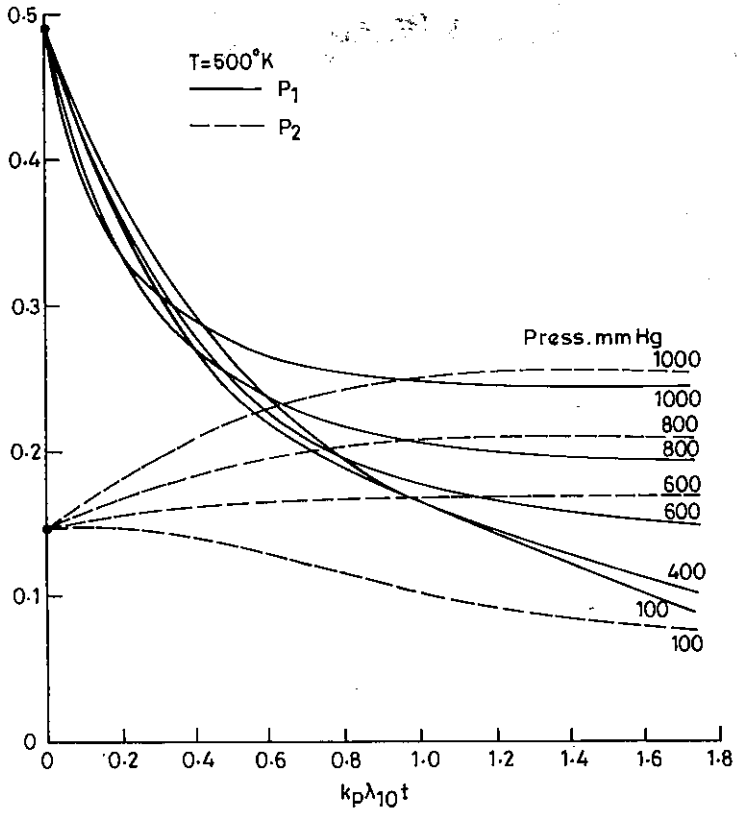


Figure 3 Effect of reactor pressure on concentrations of P_1 and P_2. $P_{10} = 0.49$, $P_{20} = 0.143$.

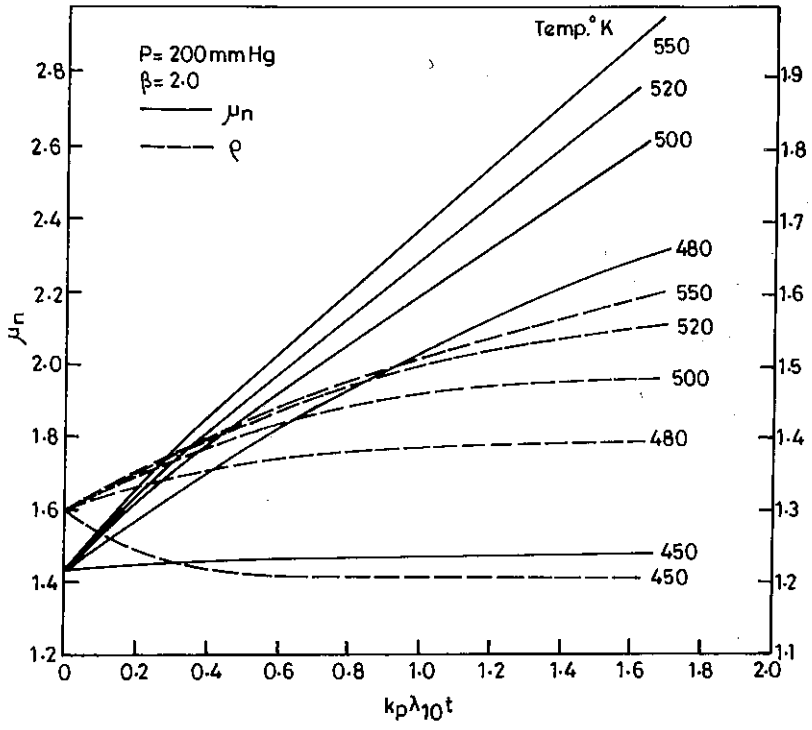
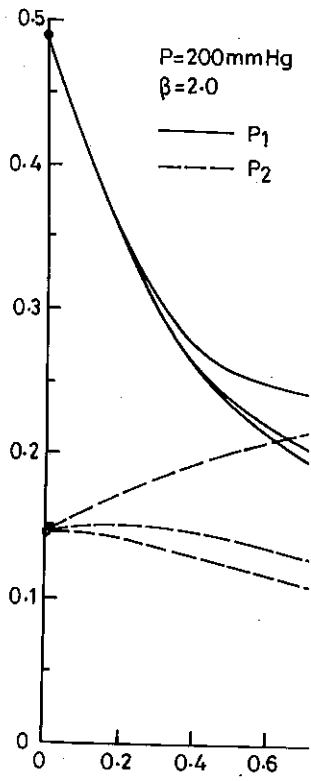


Figure 4 Number average chain length, μ_n, and polydispersity index, ρ, versus time, t, for various values of reaction temperatures (P = 200 mm Hg, β 2.0).



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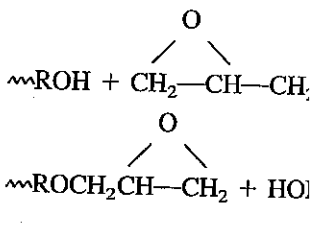


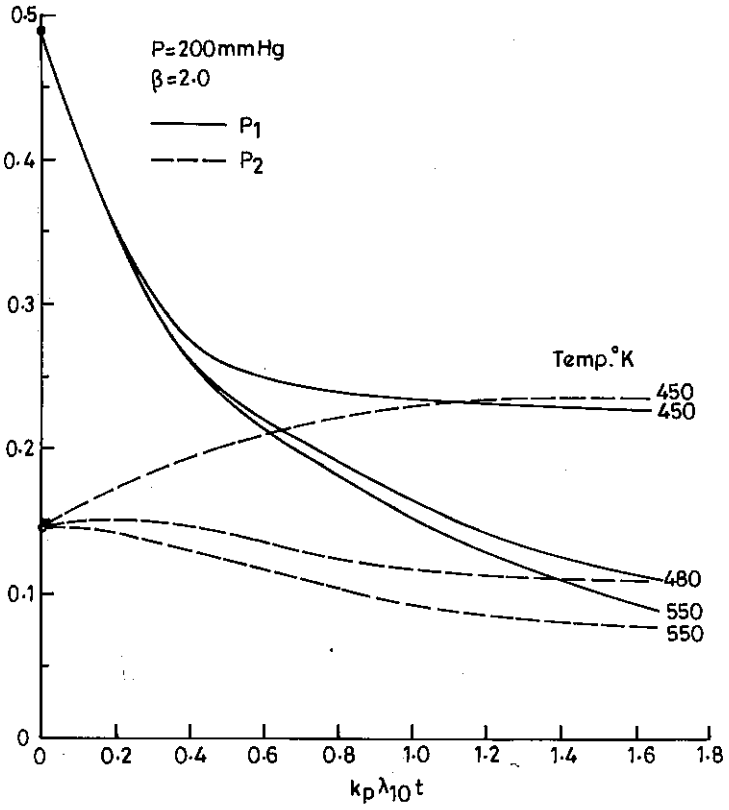
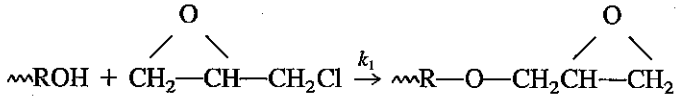


Figure 5 Effect of reactor temperature on concentration of P_1 and P_2.

is far more complex and the assumption of equal reactivity is a considerable simplification [22]. In addition, as the polymerization progresses, the viscosity of the reaction mass increases several fold and the overall reaction, at some stage depending on the reactor used, becomes mass transfer controlled [13, 23–25].

In the reaction-controlled region, unequal reactivity of functional groups is commonly observed. This can arise when the reacting groups are not kinetically equivalent, as in the polymerization of a diacid with a glycol having primary and secondary OH groups which have different reactivities. These asymmetric monomers are usually represented symbolically as the polymerization of (AA + BC) monomers where functional groups B and C react with A with different rate constants. The ring-opening reaction, as found in anhydrides, generates two functional groups which particpate in the chain-building process and these two steps generally have different reactivities. The formation of epoxy resins can be represented by the following equations:



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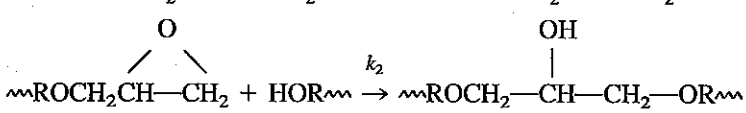

(16b)

where k_1 and k_2 are the different rate constant values. In urethane polymerization, the unequal reactivity is explained by examining the effect of charge densities of the isocyanate groups on the phenyl diisocyanate monomer, OCN—⬡—NCO. As one of the isocyanate group reacts, the positive charge on the phenyl group reduces from its initial value and the reactivity of the second —NCO group falls. This phenomenon is known as induced asymmetry and can be modeled kinetically as

$$BB + AA \xrightarrow{k_a} A + B \tag{17a}$$

$$\sim\!B + AA \xrightarrow{k_a} A\!\sim \tag{17b}$$

$$\sim\!B + A\!\sim \xrightarrow{k_b} \sim\!BA\!\sim \tag{17c}$$

where AA represents the diisocyanate. Case analyzed various situations of asymmetry and induced asymmetry and derived the molecular weight distribution in terms of the probabilities of reaction of the various functional groups [26].

There is another class of unequal reactivity polymerization in which the rate constants of the various oligomers are dependent on their chain lengths. This is chain length dependent reactivity [16, 27–36], which is found, for example, in the polymerization of sodium-*p*-fluorothiophenoxide [37]. In this, the reaction mass has more unreacted monomer than that predicted by the equal reactivity hypothesis. This observation suggests that the monomer has a lower reactivity. In the formation of polyamides, on the other hand, polymer molecules are found to have lower reactivity [38].

Kinetic Model for Reversible Nonlinear Step Growth Polymerization

Nonlinear step growth polymerization takes place with monomers RY_f having functionality, $f > 2$. In this Y is the reactive group which on reaction gives rise to chemical bonds. There are several industrially important nonlinear step growth polymerization systems and some of these are polyesters from adipic acid or phthalic anhydride and glycerol or pentacrythritol (alkyl resins), curing of epoxy propolymers with diamines, curing of phenol formaldehyde polymers with hexamethylene tetramine, etc. In this class of polymerization, branched molecules are formed at low conversions of reactive groups. At a well-defined conversion [$= 1/(f - 1)$], some of these branched molecules are found to combine into an infinite network structure of macroscopic dimensions, called a gel [1]. This phenomenon occurs long before the reactive groups are completely consumed, and the point at which this occurs is referred to as the critical or gel point. Experimentally, the gel point is recognized as the state when the viscosity of the reaction mass becomes infinite and "gas bubbles" fail to rise through the reaction mass.

The study of nonlinear step growth polymerization is more complex than that of the linear case, and several approaches have been taken by different workers in this area to model the nonlinear. Flory [1, 39, 40] and Stockmayer [41–44] have approached this problem by determining the probabilities of finding various branched molecular structures in the reaction mass. Thereafter, they used these probability distributions to compute the number and weight average molecular weights of the polymer before gelation. Their approach, however, becomes exceedingly complex for systems of industrial importance. Other workers [45–47] have attempted to derive the average molecular weights directly, without first obtaining the detailed distributions. However, the kinetic approach presented in this section is more advantageous than the other approaches because it can be used easily to predict the behavior of nonlinear polymerization in homogeneous continuous

stirred tank reactors (HC
intramolecular reactions.

The analysis using the
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The reverse step to this i
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because when W reacts with
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6*b*, P_{10} is assumed to be of
figure it is seen that a star
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P_{14}, P_{15}, and P_{16} can be form
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found that

$$\left.\begin{aligned}\delta_{r\to i} &= \delta_{r\to(r-i)} = b + 2\\ \delta_{r\to i} &= 0\\ &= 2\end{aligned}\right\}$$

where $m = 1,2, \ldots$

stirred tank reactors (HCSTRs). In addition, it can be more easily adapted to account for intramolecular reactions.

The analysis using the kinetic approach of the self-polymerization of RY_f monomers, with Y functional group reacting with Y, is presented in this section. It is assumed that P_n represents an n-mer in the reaction mass. If there are no intramolecular reactions, there are $nf - 2(n - 1)$ unreacted Y groups on P_n since every bond in the molecule is formed by reaction of two Y groups. Similar to the linear step growth polymerization, kinetic analysis has been made for the reversible nonlinear step growth polymerization with the monomer of functionality, f. In the forward reaction of step growth polymerization, two functional groups of different molecules react to give higher molecular weight species. When the reactive groups of the same molecule react, cyclic molecules are formed. The modeling of the intramolecular reaction is extremely complex and is still an active area of research [58–70]. Jacobson and Stockmayer [64] analyzed the formation of intramolecular bonds and observed that two reacting groups in a given chain must turn around and lie within a small volume, V_s, of each other. However, it has been shown that this represents only a crude description of the cyclization process. Mutter, Sater, and Flory [71] used the theory of chain statistics to describe this process. In this model they accounted for the presence of bond angle restrictions as well as steric hindrance. In addition, they included the cyclization constraints that the bonds of reacting sides must approach each other so that they are parallel to each other.

The reverse step to this involves the reaction of the bonds of a macromolecule with the molecules of the condensation product, W. In multifunctional polymerization, the polymer chains are in general branched and as a result of this the modeling of the reverse reaction becomes considerably more complex [72–74] compared to those for linear chains because when W reacts with any on the bonds of the polymer chain, it forms oligomers of small chains. Let us now consider the reverse reaction of a P_{10} molecule with W. Regardless of its structure, it has nine bonds where W can react. If P_{10} is linear, there are two equivalent sites on it which would form P_1, P_2, up to P_9 when W reacts with it (see Fig. 6*a*). It is thus seen through this example that the number of sites forming species of lower molecular weight out of the higher ones is independent of the chain structure in linear polymers. However, for branched molecules this is not found to be so and the reverse step is found to be chain structure–dependent as demonstrated below. In Figure 6*b*, P_{10} is assumed to be of the star type with four branches of equal length. From the figure it is seen that a star P_{17} cannot break to form P_5 to P_{12}. However, it has four equivalent sites where, by the reverse reaction, smaller molecules P_1, P_2, P_3, P_4, P_{13}, P_{14}, P_{15}, and P_{16} can be formed. In Figure 6*c*, a general branched molecule is shown with one branch at a given branch point of the chain backbone. It is assumed that there exists an equal number of repeat units between the two branch points in this structure. Suppose this molecule has a total of r repeat units and we wish to determine the number of sites on it where P_n will be formed on reaction with W. A term $\delta_{r\to n}$ is defined which gives the number of sites on P_r that would give P_n (where $n < r$) through the reverse reaction. This term accounts for the structural effects; for linear polymers it is equal to 2 for all feasible n. If in Figure 6*c*, P_r has b branch points with each segment having x repeat units, it is found that

$$\delta_{r\to i} = \delta_{r\to(r-i)} = b + 2 \qquad \text{if } k \le x \tag{18a}$$

$$\left.\begin{aligned}\delta_{r\to i} &= 0\\ &= 2\end{aligned}\right\} \qquad \begin{aligned}&\text{if } (mx + 1) \le i \le (m + 1)x\\ &\text{if } 1 + (m + 1)x \le i \le (m + 2)x\end{aligned} \tag{18b, 18c}$$

where $m = 1,2, \ldots$

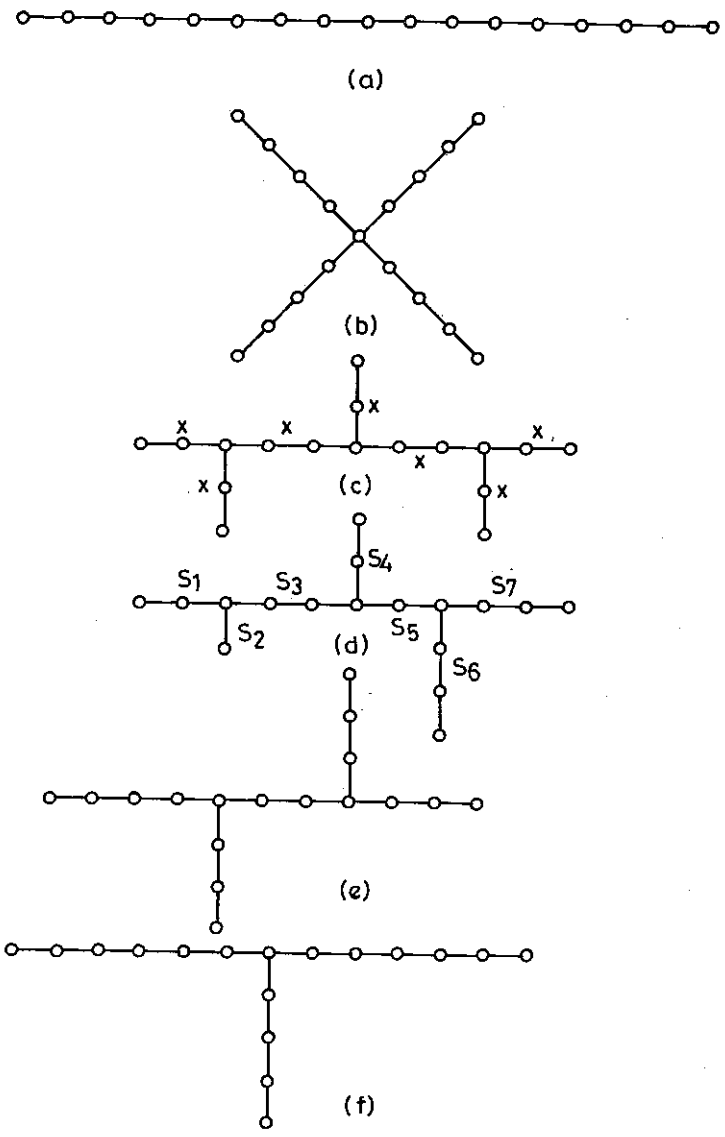

Figure 6 Structures of branched polymer chains.

The structure shown in Figure 6*c* can be further generalized by assuming unequal lengths of the segments. For any general chain structure, to find $\delta_{r\to n}$, the (a) location, number, and lengths of various branches and (b) chain length of the molecule must be known. It is then possible to work out the length of the backbone and determine $\delta_{r\to n}$ using a computer program as follows.

We first characterize any branched molecule by dividing it into different segments in Figure 6*d* where the molecule is divided into seven segments s_1 to s_7. If each branch is

treated as one of the seg
The total number of seg

$$n_s = 2b + 1$$

Since the segments leng
n_B, and the location of b

$$n_B = r - \sum_{i=1}^{b} s_{2i}$$

$$K_m = K_{m-1} + s_{2m-1}$$

For example, in Figure 6*d*
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To find $\delta_{r\to n}$, backbon
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Figure 6*d*, if the chain scis
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To avoid the counting of th
both ends up to its midpoin

$$N_{1/2} = \frac{r}{2}, \qquad r \text{ eve}$$

$$= \frac{r-1}{2}, \qquad r \text{ odd}$$

It is evident that the number
$P_{r\to n}$ out of P_r is equal and

$$\delta_{r\to n} = \delta_{r\to(r-n)}$$

The algorithm presented
branches are scanned to find
the forward and reverse dire
generated from various chain
For all branched molecule

$$\sum_{n=1}^{r-1} \delta_{r\to n} = 2(r-1)$$

$$\sum_{n=1}^{r-1} n\delta_{r\to n} = r(r-1)$$

treated as one of the segments, it is then observed that every alternate segment is a branch. The total number of segments, n_s, and the number of branches, b, are related by

$$n_s = 2b + 1 \tag{19}$$

Since the segments lengths s_i ($i = 1,2, \ldots, n_s$) are known, the backbone chain length, n_B, and the location of branch points K_m ($m = 1,2, \ldots, b$) in P_r are related by

$$n_B = r - \sum_{i=1}^{b} s_{2i} \tag{20a}$$

$$K_m = K_{m-1} + s_{2m-1} + 1, \qquad K_0 = 0, \quad m = 1,2, \ldots, b \tag{20b}$$

For example, in Figure 6*d*, $s_1 = 2$, $s_2 = 1$, $s_2 = 2$, $s_4 = 2$, $s_5 = 1$, $s_6 = 3$, and $s_7 = 3$. For this case backbone chain length n_B is 11 and branch point locations K_m are positions 3, 6, and 8 on the backbone.

To find $\delta_{r\to n}$, backbone indices I_p and I'_q for the forward and the reverse directions are defined. These specify the number of repeat units if the backbone is broken at the pth and qth positions from the forward and reverse directions respectively. As an example, in Figure 6*d*, if the chain scission occurs at the seventh bond of the backbone, molecule P_{10} is formed from this end, and which gives $I_7 = 10$ in the forward direction. As opposed to this, in the reverse direction, the same bond breakage gives P_7 and the corresponding index $I'_4 = 7$. For symmetric chains, the values of I_p and I'_q for same p and q are identical; otherwise they are not. The flow chart for generating these indices is given in Table 1. The information so generated is used to find $\delta_{r\to n}$; the algorithm for this is given in Table 2. To avoid the counting of the available sites twice, scanning of the molecule is done from both ends up to its midpoint, $N_{1/2}$ given by

$$N_{1/2} = \frac{r}{2}, \quad r \text{ even}; \qquad = \frac{r-1}{2}, \quad r \text{ odd} \tag{21}$$

It is evident that the number of possible sites for forming P_n ($n = 1,2, \ldots, r-1$) and P_{r-n} out of P_r is equal and

$$\delta_{r\to n} = \delta_{r\to(r-n)} \tag{22}$$

The algorithm presented in Table 2 is divided into two major sections. In the first, branches are scanned to find $\delta_{r\to n}$. In the second, scanning of the backbone is done from the forward and reverse directions. Results for $\delta_{17\to n}$ ($n = 1,2, \ldots, 16$) have been generated from various chain structures seen in Figure 6 and summarized in Table 3.

For all branched molecules, the following two relations are found to hold always:

$$\sum_{n=1}^{r-1} \delta_{r\to n} = 2(r-1) \tag{23a}$$

$$\sum_{n=1}^{r-1} n\delta_{r\to n} = r(r-1) \tag{23b}$$

Table 1 Generation of the Forward and Reverse Backbone Indices

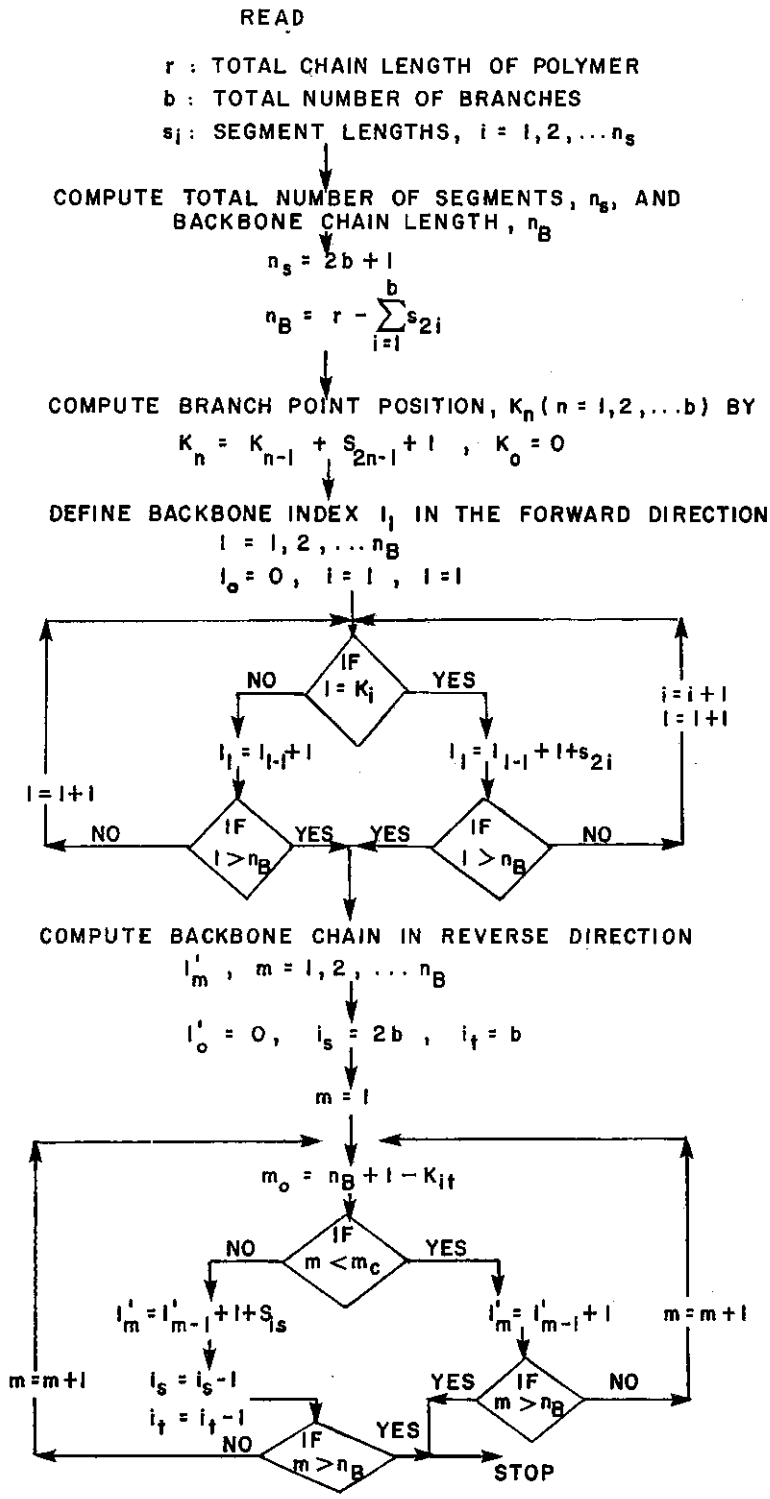

Table 2 Calculation of $\delta_{r\to n}$

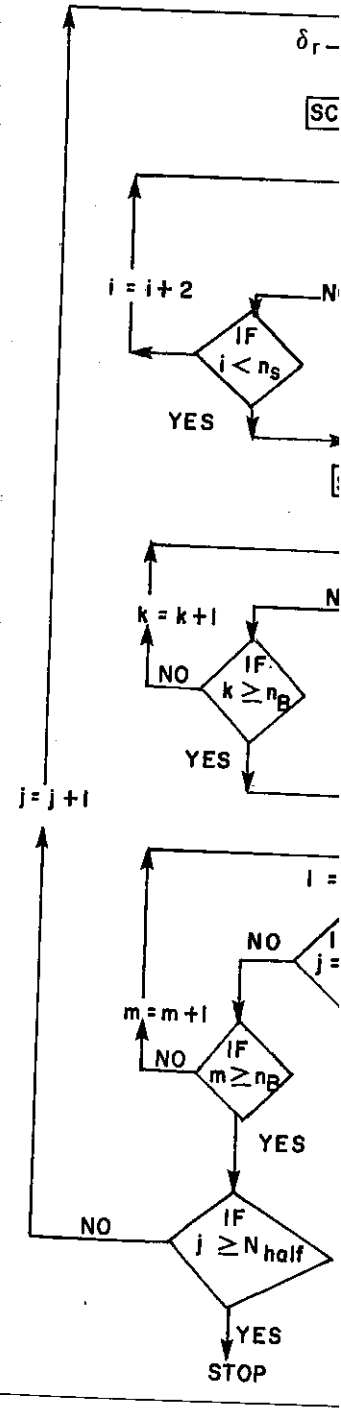

Table 2 Calculation of $\delta_{r\to n}$ from the Knowledge of Backbone Indices Generated from Table 1

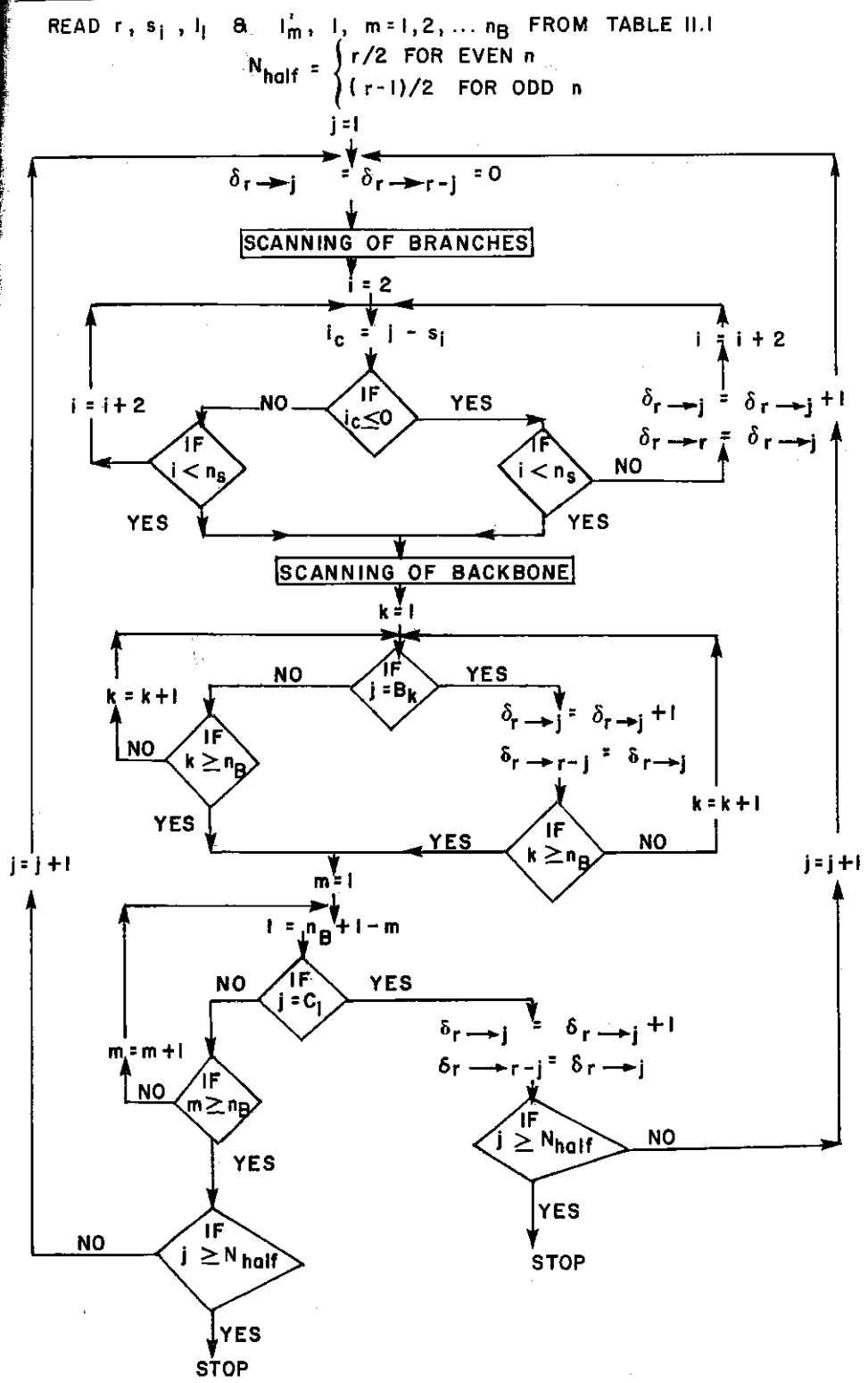

Table 3 Value of $\delta_{r\to n}$ for Different Branched Structures Seen in Figure 6

n	$\delta_{17\to n}$ for Fig 6*a*	$\delta_{17\to n}$ for Fig 6*b*	$\delta_{17\to n}$ for Fig 6*c*	$\delta_{17\to n}$ for Fig 6*d*	$\delta_{17\to n}$ for Fig 6*e*	$\delta_{17\to n}$ for Fig 6*f*
1	2	4	5	5	4	3
2	2	4	5	4	4	3
3	2	4	0	2	4	3
4	2	4	0	1	1	3
5	2	0	2	1	0	2
6	2	0	2	1	0	2
7	2	0	2	1	1	0
8	2	0	0	1	2	0
9	2	0	0	1	2	0
10	2	0	2	1	1	0
11	2	0	2	1	0	2
12	2	0	2	1	0	2
13	2	4	0	1	1	3
14	2	4	0	2	4	3
15	2	4	5	4	4	3
16	2	4	5	5	4	3

However, the summation $\sum_{n=1}^{r-1} n^2\delta_{r\to n}$ depends on the structure. If the chain structure is that given in Figure 6*c*, then

$$\sum_{n=1}^{r-1} n^2\delta_{r\to n} = A_1 r^3 + A_2 r^2 + A_3 r + A_4 \tag{24}$$

where

$$A_1 = \frac{(20b^3 + 24b^2 + 14b + 2)}{3(2b + 1)^3} \tag{25a}$$

$$A_2 = -\frac{(8b^4 + 64b^3 + 88b^2 + 32b + 6)}{6(2b + 1)^3} \tag{25b}$$

$$A_3 = \frac{(16b^4 + 30b^3 + 26b^2 + 16b + 2)}{6(2b + 1)^3} \tag{25c}$$

$$A_4 = -\frac{(2b^4 + 9b^3 + b^2)}{6(2b + 1)^3} \tag{25d}$$

It is observed that the relations given in Eqs. 25 are independent of the functionality f of the starting monomer. If there are no intramolecular reactions, there would be $nf - 2(n - 1)$ unreacted Y groups on P_n because for every bond formed, two Y groups are consumed. Two reacting molecular species P_n and P_m have $f_1 = [nf - 2(n - 1)]$ and $f_2 = [mf - 2(m - 1)]$ unreacted functional groups on them. When they undergo reaction, there are $f_1 f_2/2$ distinct ways by which they can react. The factor of 1/2 is included because the reactive groups Y are identical. For any general species P_n produced according to Eq. 3

the mole balance relatio
be derived as

$$\frac{d[P_1]}{dt} = 2k_p(a + 1)$$

$$\frac{d[P_n]}{dt} = k_p \sum_{r=1}^{n-1} (ar$$

$$-2k_p(an +$$

$$-k_p'[P_n][W]$$

$$a = \frac{f - 2}{2}$$

Equations 26 involve the
reacting polymer chains.
the chain structure.

A functional group app
polymer in the reaction
collision of two oligomer
them. Whenever reactive
branch is produced at that
of a hexafunctional mono
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In the functional group
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and is the same to the mon
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to G very conveniently.

Various forward and re

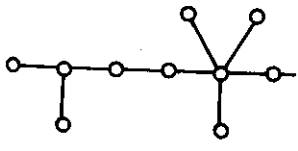

Figure 7 General structure o

in Figure 6

	$\delta_{17\to n}$ for Fig 6e	$\delta_{17\to n}$ for Fig 6f
	4	3
	4	3
	4	3
	1	3
	0	2
	0	2
	1	0
	2	0
	2	0
	1	0
	0	2
	0	2
	1	3
	4	3
	4	3
	4	3

ture. If the chain structure is

(24)

(25a)

(25b)

(25c)

(25d)

ent of the functionality f of there would be $nf - 2(n -$ vo Y groups are consumed. $2(n - 1)]$ and $f_2 = [mf -$ ndergo reaction, there are /2 is included because the oduced according to Eq. 3

the mole balance relation for the step growth polymerization in the batch reactor can now be derived as

$$\frac{d[P_1]}{dt} = 2k_p(a + 1)[P_1]\left\{\sum_{m=1}^{\infty}(am + 1)[P_m]\right\} + k_p'[W]\sum_{r=2}^{\infty}\delta_{r\to 1}[P_r] \tag{26a}$$

$$\frac{d[P_n]}{dt} = k_p\sum_{r=1}^{n-1}(ar + 1)\{a(n - r) + 1\}[P_r][P_{n-r}] - 2k_p(an + 1)[P_n]\sum_{m=1}^{\infty}(am + 1)[P_m] - k_p'[P_n][W](n - 1) + k_p'[W]\sum_{r=n+1}^{\infty}\delta_{r\to n}[P_r] \qquad \text{for } n \leq 2 \tag{26b}$$

$$a = \frac{f - 2}{2} \tag{26c}$$

Equations 26 involve the term $\delta_{r\to n}$, which is dependent on the number of branches in the reacting polymer chains. This implies that Eqs. 26 cannot be solved without knowledge of the chain structure.

A functional group approach is now discussed in order to find the average branching of polymer in the reaction mass. Consider a hexafunctional monomer ($f = 6$). At every collision of two oligomers, two reactive groups are eliminated to form a bond between them. Whenever reactive groups in the middle of the chain undergo chemical reaction, a branch is produced at that point. A general chain structure produced by the polymerization of a hexafunctional monomer is shown in Figure 7. It is possible to follow the course of polymerization through the functional group approach, which is a generalization of Flory's analysis of bifunctional step growth polymerization.

In the functional group approach, one defines ($f + 1$) functional group species in order to follow the polymerization of RY_f monomers. As an example, one would require seven species A to G as shown in Figure 8. These differ from each other in terms of the number of unreacted reactive groups Y on them. For example, A has all reactive groups unreacted and is the same to the monomer while B has one reacted reactive group, C has two, and so on. As species B has only one of its reactive group reacted, it can be situated only at chain ends. Species C forms the linear part of the chain, while the other species lead to branching. It is possible to represent the chain structure of Figure 7 in terms of species B to G very conveniently.

Various forward and reverse reactions leading to polymer formation involving these

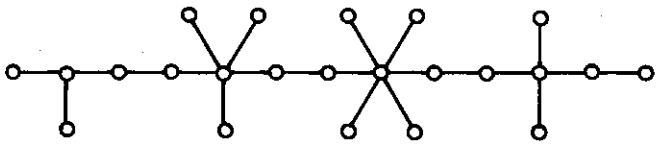

Figure 7 General structure of polymer chain in the polymerization of hexafunctional monomer.

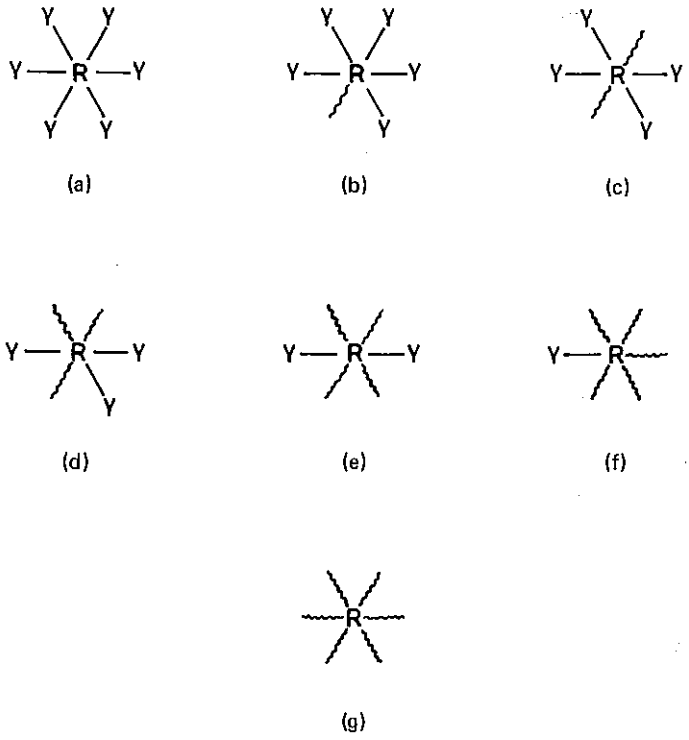

Figure 8 Structures of functional group species.

functional group species can be easily written and are summarized in Table 4. In writing these, it has been assumed that all species are available for chemical reaction with equal likelihood. It is assumed that species A reacts with C. There is a chemical reaction of reactive groups Y on species A with those of species C; when this occurs, species A would become B because one of its reactive group is reacted while C becomes D for the same reason. In view of this, the forward step of the reaction between species A and C can be represented as

$$A + C \xrightarrow{k_3} D + (B) + W \tag{27}$$

on the right-hand side B appears in parentheses to indicate that B is not free but is in the combined state as B–D.

To determine the reactivity k_3 (see Table 4), it is observed that reaction between any two species occurs only when they collide. If the collision frequency between species A and C is represented Z_{AC} and Q_{AC} as the probability of reaction between A and C, then rate $\mathcal{R}_{AC}$ is given as

$$\mathcal{R}_{AC} = \alpha Z_{AC} Q_{AC} \tag{28}$$

where α is the constant of proportionality. For equal reactivity of reactive groups Y, Z_{AC} would be given by $[(6 \times 4)/2Z]$ where Z is the probability of reaction between Y's of the two species A and C. The factor $(6 \times 4)/2$ arises because species A has six and species C

Table 4 Various Reactions of

Forward Reactions

$A + A \xrightarrow{k_1} B + (B) + W,$

$A + B \xrightarrow{k_2} C + (B) + W,$

$A + C \xrightarrow{k_3} D + (B) + W,$

$A + D \xrightarrow{k_4} E + (B) + W,$

$A + E \xrightarrow{k_5} F + (B) + W,$

$A + F \xrightarrow{k_6} G + (B) + W,$

$B + B \xrightarrow{k_7} G + (C) + W,$

$B + C \xrightarrow{k_8} D + (C) + W,$

$B + D \xrightarrow{k_9} E + (C) + W,$

$B + E \xrightarrow{k_{10}} F + (C) + W,$

$B + F \xrightarrow{k_{11}} G + (C) + W,$

$C + C \xrightarrow{k_{12}} D + (D) + W,$

$C + D \xrightarrow{k_{13}} E + (D) + W,$

$C + E \xrightarrow{k_{14}} F + (D) + W,$

$C + F \xrightarrow{k_{15}} G + (D) + W,$

$D + D \xrightarrow{k_{16}} E + (E) + W,$

$D + E \xrightarrow{k_{17}} F + (E) + W,$

$D + F \xrightarrow{k_{18}} G + (E) + W,$

$E + E \xrightarrow{k_{19}} F + (F) + W,$

$E + F \xrightarrow{k_{20}} G + (F) + W,$

Table 4 Various Reactions of Species A to G

Forward Reactions

$$A + A \xrightarrow{k_1} B + (B) + W, \qquad k_1 = \frac{6 \times 6}{2} k$$

$$A + B \xrightarrow{k_2} C + (B) + W, \qquad k_2 = \frac{6 \times 5}{2} k$$

$$A + C \xrightarrow{k_3} D + (B) + W, \qquad k_3 = \frac{6 \times 4}{2} k$$

$$A + D \xrightarrow{k_4} E + (B) + W, \qquad k_4 = \frac{6 \times 3}{2} k$$

$$A + E \xrightarrow{k_5} F + (B) + W, \qquad k_5 = \frac{6 \times 2}{2} k$$

$$A + F \xrightarrow{k_6} G + (B) + W, \qquad k_6 = \frac{6 \times 1}{2} k$$

$$B + B \xrightarrow{k_7} G + (C) + W, \qquad k_7 = \frac{5 \times 5}{2} k$$

$$B + C \xrightarrow{k_8} D + (C) + W, \qquad k_8 = \frac{5 \times 4}{2} k$$

$$B + D \xrightarrow{k_9} E + (C) + W, \qquad k_9 = \frac{5 \times 3}{2} k$$

$$B + E \xrightarrow{k_{10}} F + (C) + W, \qquad k_{10} = \frac{5 \times 2}{2} k$$

$$B + F \xrightarrow{k_{11}} G + (C) + W, \qquad k_{11} = \frac{5 \times 1}{2} k$$

$$C + C \xrightarrow{k_{12}} D + (D) + W, \qquad k_{12} = \frac{4 \times 4}{2} k$$

$$C + D \xrightarrow{k_{13}} E + (D) + W, \qquad k_{13} = \frac{4 \times 3}{2} k$$

$$C + E \xrightarrow{k_{14}} F + (D) + W, \qquad k_{14} = \frac{4 \times 2}{2} k$$

$$C + F \xrightarrow{k_{15}} G + (D) + W, \qquad k_{15} = \frac{4 \times 1}{2} k$$

$$D + D \xrightarrow{k_{16}} E + (E) + W, \qquad k_{16} = \frac{3 \times 3}{2} k$$

$$D + E \xrightarrow{k_{17}} F + (E) + W, \qquad k_{17} = \frac{3 \times 2}{2} k$$

$$D + F \xrightarrow{k_{18}} G + (E) + W, \qquad k_{18} = \frac{3 \times 1}{2} k$$

$$E + E \xrightarrow{k_{19}} F + (F) + W, \qquad k_{19} = \frac{2 \times 2}{2} k$$

$$E + F \xrightarrow{k_{20}} G + (F) + W, \qquad k_{20} = \frac{2 \times 1}{2} k$$

Table 4 (*Continued*)

$F + F \xrightarrow{k_{21}} G + (G) + W,$	$k_{21} = \frac{1 \times 1}{2} k$

Reverse Reactions

$B + (B) + W \xrightarrow{k'_1} A + A,$	$k'_1 = \frac{[B]}{XX} k'$
$B + (C) + W \xrightarrow{k'_2} A + B,$	$k'_2 = \frac{[C]}{XX} k'$
$B + (D) + W \xrightarrow{k'_3} A + C,$	$k'_3 = \frac{[D]}{XX} k'$
$B + (E) + W \xrightarrow{k'_4} A + D,$	$k'_4 = \frac{[E]}{XX} k'$
$B + (F) + W \xrightarrow{k'_5} A + E,$	$k'_5 = \frac{[F]}{XX} k'$
$B + (G) + W \xrightarrow{k'_6} A + F,$	$k'_6 = \frac{[G]}{XX} k'$
$C + (C) + W \xrightarrow{k'_7} B + B,$	$k'_7 = 2\frac{[C]}{XX} k'$
$C + (D) + W \xrightarrow{k'_8} B + C,$	$k'_8 = 2\frac{[D]}{XX} k'$
$C + (E) + W \xrightarrow{k'_9} B + D,$	$k'_9 = 2\frac{[E]}{XX} k'$
$C + (F) + W \xrightarrow{k'_{10}} B + E,$	$k'_{10} = 2\frac{[F]}{XX} k'$
$C + (G) + W \xrightarrow{k'_{11}} B + F,$	$k'_{11} = 2\frac{[G]}{XX} k'$
$D + (D) + W \xrightarrow{k'_{12}} C + C,$	$k'_{12} = 3\frac{[D]}{XX} k'$
$D + (E) + W \xrightarrow{k'_{13}} C + D,$	$k'_{13} = 3\frac{[E]}{XX} k'$
$D + (F) + W \xrightarrow{k'_{14}} C + E,$	$k'_{14} = 3\frac{[F]}{XX} k'$
$D + (G) + W \xrightarrow{k'_{15}} C + F,$	$k'_{15} = 3\frac{[G]}{XX} k'$
$E + (E) + W \xrightarrow{k'_{16}} D + D,$	$k'_{16} = 4\frac{[E]}{XX} k'$
$E + (F) + W \xrightarrow{k'_{17}} D + E,$	$k'_{17} = 4\frac{[F]}{XX} k'$
$E + (G) + W \xrightarrow{k'_{18}} D + F,$	$k'_{18} = 4\frac{[G]}{XX} k'$

Table 4 (*Continued*)

$F + (F) + W \xrightarrow{k'_{19}} E + E,$	
$F + (G) + W \xrightarrow{k'_{20}} E + F,$	
$G + (G) + W \xrightarrow{k'_{21}} F + F,$	

Note: XX = [B] + [C] + [D] + [

has four reactive groups and
$(6 \times 4)/2$. Since the collisi
[A][C], it implies that the rea

$$k_3 = \frac{6 \times 4}{2} k$$

where k is the reactivity of
forward steps have been deriv

The reverse reaction in m
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ity arises because we must ha
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A, but simultaneously D woul
even though in reality it is only
reaction of any given functiona
be available. The reverse react

$$B + (D) + W \xrightarrow{k'_3} A + C$$

The rate constant for this step i
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condensation product W. To d
species B has only one reacte
reverse rate $\mathcal{R}'_{B(D)}$ is given by

$$\mathcal{R}'_{B(D)} = k'[B][W]P_{B(D)}$$

where $P_{B(D)}$ is the probability o
species can be found adjacent t

$$P_{B(D)} = \frac{[D}{[B] + [C] + [D] +}$$

With this background and the ki
mole balance relations for thes
given by

Table 4 (*Continued*)

$F + (F) + W \xrightarrow{k'_{19}} E + E,$	$k'_{19} = 5\,\frac{[F]}{XX}\,k'$
$F + (G) + W \xrightarrow{k'_{20}} E + F,$	$k'_{20} = 5\,\frac{[G]}{XX}\,k'$
$G + (G) + W \xrightarrow{k'_{21}} F + F,$	$k'_{21} = 6\,\frac{[G]}{XX}\,k'$

Note: XX = [B] + [C] + [D] + [E] + [F] + [G].

has four reactive groups and the distinct combinations of two Y groups between them is $(6 \times 4)/2$. Since the collision frequency between species A and C is proportional to [A][C], it implies that the reactivity k_3 for this step is given by

$$k_3 = \frac{6 \times 4}{2}\,k \tag{29}$$

where k is the reactivity of Y groups. Using similar logic the rate constants of all the forward steps have been derived and included in Table 4.

The reverse reaction in multifunctional polymerization involves the reaction of the bonds in functional group species with the condensation product, W. However, complexity arises because we must have knowledge of the neighborhood species. For example, one considers bond B–D reacting with W. In the reverse reaction step, B would become A, but simultaneously D would become C. Thus it appears to be a trimolecular reaction even though in reality it is only bimolecular in nature. If attention is focused on the reverse reaction of any given functional group species, knowledge of the connecting species must be available. The reverse reaction step can be written as

$$B + (D) + W \xrightarrow{k'_3} A + C \tag{30}$$

The rate constant for this step in Table 4 has been shown to be k'_3 and it is desired to write this in terms of the reverse rate constant k' between given reaction Y group and the condensation product W. To do so, the reaction is taken as that between B and W. Since species B has only one reacted bond in it, its reactivity would therefore be k' and the reverse rate $\mathcal{R}'_{B(D)}$ is given by

$$\mathcal{R}'_{B(D)} = k'[B][W]P_{B(D)} \tag{31}$$

where $P_{B(D)}$ is the probability of finding D adjacent to species B. If it is assumed that any species can be found adjacent to B, this probability term can be approximated as

$$P_{B(D)} = \frac{[D]}{[B] + [C] + [D] + [E] + [F] + [G]} \tag{32}$$

With this background and the kinetic scheme given in Table 4, it is possible to write the mole balance relations for these functional group species in batch reactors. These are given by

$$\frac{d[A]}{dt} = -3k[A][M[+ k'[B][M] \tag{33a}$$

$$\frac{d[B]}{dt} = 3k[A][M] - \frac{5}{2}k[B][M] + 2k'[C][W] - k'[B][W] \tag{33b}$$

$$\frac{d[C]}{dt} = \frac{5}{2}k[B][M] - 2k[C][M] + 3k'[D][W] - 2k'[C][W] \tag{33c}$$

$$\frac{d[D]}{dt} = 2k[C][M] - \frac{3}{2}k[D][M] + 4k'[E][W] - 3k'[D][W] \tag{33d}$$

$$\frac{d[E]}{dt} = \frac{3}{2}k[D][M] - k[E][M] + 5[F][W] - 4k'[E][W] \tag{33e}$$

$$\frac{d[F]}{dt} = k[E][M] - \frac{k}{2}[F][M] + 6k'[G][W] - 5k'[F][W] \tag{33f}$$

$$\frac{d[G]}{dt} = \frac{k}{2}[F][M] - 6k'[G][W] \tag{33g}$$

$$\frac{d[W]}{dt} = k[M]\left\{\frac{3}{2}[A] + \frac{5}{4}[B] + [C] + \frac{3}{4}[D] + \frac{[E]}{2} + \frac{[F]}{4}\right\} - k'[W]\left\{\frac{[B]}{2} + [C] + \frac{3}{2}[D] + 2[E] + \frac{5}{2}[F] + 3[G]\right\} \tag{33h}$$

where

$$[M] = 6[A] + 5[B] + 4[C] + 3[D] + 2[E] + [F] \tag{33i}$$

Once the concentrations of the functional group species are known the average branches present in the reaction mass can be determined in the following way. Species D, E, F, and G have 1, 2, 3, and 4 branches, respecitvely. The average number of branches present in the reaction mass can be given by

$$\bar{b} = \frac{[D] + 2[F] + 3[F] + 4[G]}{\sum_{n=1}^{\infty}[P_n]} \tag{34}$$

Computations have shown that in multifunctional polymerization, the concentration of the higher functional group species E to G are present in negligible concentrations compared to B to D all the way up to the gel point. Thus an average structure (as shown in Fig. 6*c*) can be assumed without introducing any error in computations.

In multifunctional polymerization one is mainly interested in the moments of the distribution instead of the entire MWD. Equation 21 can be added according to Eq. 1 for all n to obtain the moment generation results. With the help of Eq. 47, the following relations are derived:

$$\frac{d\lambda_0}{dt} = k(a\lambda_1 + \lambda_0)^2 + k'[W](\lambda_1 - \lambda_0) \tag{35a}$$

$$\frac{d\lambda_1}{dt} = 0 \tag{35b}$$

$$\frac{d\lambda_2}{dt} = 2k(a\lambda_2 + \lambda_1)^2 + k'[W]\{(A_2 + 1)\lambda_2 + A_3\lambda_1 + A_4\lambda_0\} + k'[W](A_1 - 1)\lambda_3 \tag{35c}$$

Equation 35c is dependent o
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Using the computer algo
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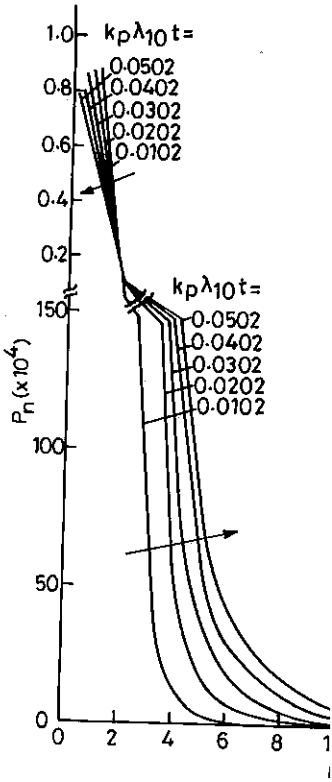

Figure 9 Dimensionless concentra

Equation 35c is dependent on the higher moment λ_3 and can be solved only after assuming some moment closure relation as is done for linear polymerization.

Using the computer algorithm for $\delta_{r\to n}$, r was fixed at 17. This was calculated for various n ($n = 1,2, \ldots, 16$), and results are presented in Table 3 for different chain structures. The table shows an extreme sensitivity to the chain structure. Since the mole balance relations involve $\delta_{r\to n}$, the MWD of the polymer is expected to be greatly affected by the branching. The computation technique outlined here has been demonstrated for the batch polymerization of hexafunctional monomers. For this we need seven functional group species (Fig. 8); their numerical solution shows that the total branching is small for the conversion of reactive groups below the gel point. With the information on average branching so generated, it is now possible to determine the MWD of the polymer. In Figure 9, concentrations of P_n species versus chain length n were plotted with the time of polymerization t' as a parameter.

Examination of Figure 9 reveals that as the reaction time t' increases, the MWD becomes broader. This is expected with increasing time, higher oligomers are formed in larger concentrations and both the average chain length and the polydispersity index ρ are expected to increase. In Figure 10, the MWD of a given time of polymerization is plotted for different equilibrium constants, K. As K is increased, the reaction is closer to irreversible polymerization and for a given time of polymerization, a higher conversion of reactive groups is achieved. This would in turn imply that the MWD would become

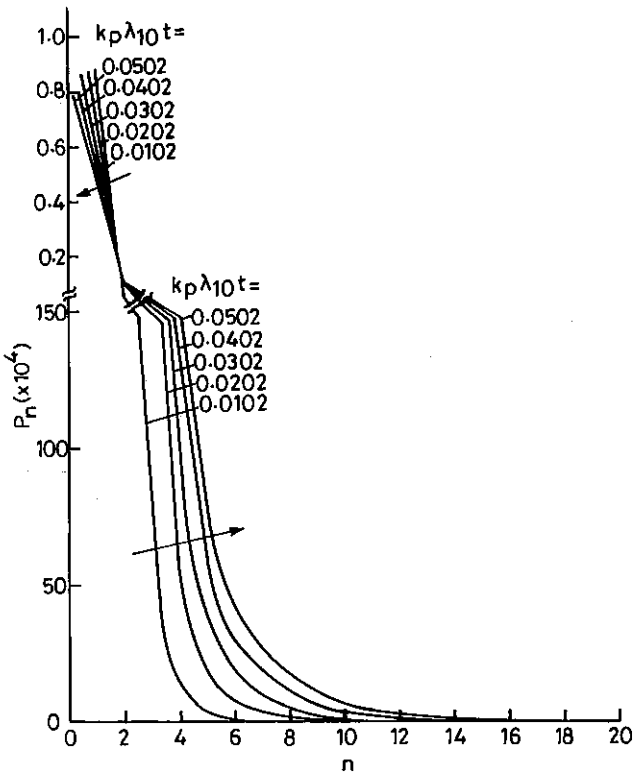

Figure 9 Dimensionless concentration of P_n species versus n (t varies from 0.0102 to 0.0502).

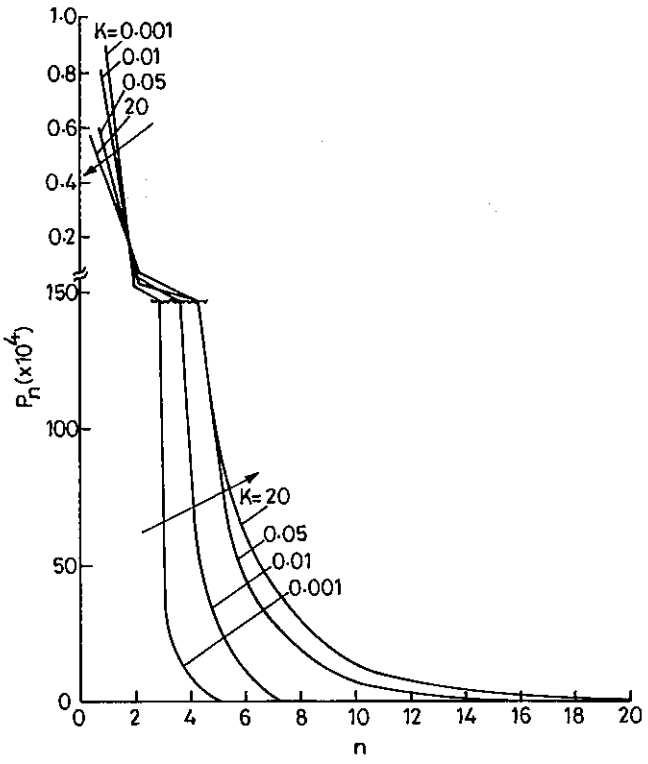

Figure 10 Dimensionless concentration of P_n species versus n (K varies from 0.0 to 20).

broader for increasing K, which is indeed seen in this figure. From the MWD results, it is possible to calculate the moments λ_0 and λ_2 (defined in Eq. 1). Theoretically (also found computationally), the first moment λ_1 is time invariant; thus the number and weight average chain lengths μ_n and μ_w and the polydispersity index ρ can be determined. It is found that the overall polymerization is limited by equilibrium conversion, which increases with increasing K. It is further observed from Eqs. 18 that for a given r, $\delta_{r\to n}$ is $(b + 2)$ for small n, which implies that as the degree of branching b increases, smaller chains (and therefore large chains due to symmetry) are formed preferentially. This would give rise to a higher polydispersity index compared to those formed from irreversible polymerization at the same conversion of reactive groups. An an example, for $K = 0.1$, at conversion of 13.87% the polydispersity index is 2.10; for the same conversion for irreversible polymerization it is 1.89.

In deriving an expression for $\sum_{n=1}^{r-1} n^2\delta_{r\to n}$ in Eqs. 25, a specific chain structure as in Figure 6*c* was assumed. Computations for noninteger segment length x and noninteger number of branches were tested against wide variations of parameters. Noninteger x in actuality amounts to stating that all segment lengths are not of equal length. If the chain length r and the number of branches b (whole numbers here) are given, x can be calculated as

$$x = \frac{r - b}{2b + 1} \tag{36}$$

If x calculated this way is a noninteger (say 6.7), the lower integer value x^* of x is chosen (in this case 6) and r^* is calculated as

$$r^* = (2b + 1)x^* \tag{37}$$

The remainder $(r - r^*)$ repeat units are distributed on various chain segments. For this chain structure, $\delta_{r\to n}$ can be computed using the algorithm of Table 2. On comparing the exact $\sum_{r=1}^{n} n^2\delta_{r\to n}$ with that determined from Eq. 24, results are found to be within 1%. On similar testing for fractional branching b, the discrepancy between the exact results and those from Eq. 24 is negligible.

The generation relation for the second moment λ_2 in Eqs. 26 involves third moment λ_3. To solve it, a moment closure relation for λ_3 is needed. If the polymerization is assumed irreversible, the MWD in multifunctional self-polymerization can be solved exactly and is given by

$$\frac{[P_n]}{[P]_0} = \frac{\{n(f-1)\}!}{n!\,\{(f-2)n+2\}!} fp^{n-1}(1-p)^{n(f-2)+2} \tag{38}$$

where p is the conversion of reactive groups. From this, the third moment for the polymerization of hexafunctional monomers can be derived as

$$\lambda_3 = \frac{(1 + p - 7p^2 + 5p^3) + (1 - 5p)^2 2p\lambda_2}{(1-5p)^3} \tag{39}$$

which can serve as a moment closure approximation. From the numerical solution of the MWD relations given in Eqs. 26, one can also find λ_0, λ_1, λ_2, and λ_3 and curve-fit these results using the empirical relation

$$\ln \lambda_3 = a_1 + a_2 \ln \lambda_0 + a_3 \ln \lambda_2 \tag{40}$$

where a_1 and a_3 are the curve-fit constants to be determined. On doing this we find that

$$\lambda_3 = \frac{1.036\,\lambda_2^{1.45}}{\lambda_0^{2.67}} \tag{41}$$

With the moment closure approximations in Eqs. 39 and 41, Eq. 35c has been solved for λ_2 and its values compared with those found from the MWD results. It is found that for a given K, Eq. 41 serves as a good approximation provided the conversion is well below the gel point conversions. As the gel point conversion is approached, Eq. 39 serves as a good representation, as can be seen in Table 5.

With the developments outlined in this work, it is now possible to analyze the equilibrium in multifunctional step growth polymerization. Since at equilibrium the MWD is stationary, their moments would also be time invariant, or $d\lambda_i/dt = 0$ $(i = 1,2\ldots)$. From Eq. 35a, for the zeroth moment, we obtain

$$K = \frac{k}{k'} = \frac{[W](\lambda_1 - \lambda_0)}{(a\lambda_1 + \lambda_0)^2} \tag{42}$$

Since the condensation product does not leave the reaction mass, the stoichiometry of the polymerization for λ_0^0 moles of monomer initially present is given by

$$[W] = \lambda_0^0 - \sum_{n=1}^{\infty} [P_n] = \lambda_0^0 - \lambda_0 \tag{43}$$

Table 5 Comparison of λ_2 Values Obtained by Using Three Different λ_3 Expressions Given by Eqs. 39–41

Time	Conversion (%)	λ_2 Values: By MWD	Using Flory-Schulz relation for λ_3	Using Stockmayer relation for λ_3	Using Eq. 41 for λ_3
For $K = 0.1$					
0.0012	0.3586	1.02191	1.02191	1.02192	1.02191
0.0102	2.9600	1.20845	1.20860	1.20852	1.20841
0.0202	5.6483	1.47215	1.47379	1.47255	1.47217
0.0302	8.1048	1.81644	1.82477	1.81760	1.81718
0.0402	10.3214	2.27229	2.30387	2.27445	2.27703
0.0502	12.2970	2.87917	2.98653	2.88106	2.90465
0.0552	13.1950	3.25250	3.44561	3.24940	3.30720
0.0592	13.8720	3.58946	3.89488	3.57228	3.68610
For $K = 0.02$					
0.0012	0.358623	1.02191	1.02191	1.02192	1.02191
0.0102	2.92437	1.20550	1.20619	1.20583	1.20530
0.0202	5.40353	1.44374	1.45101	1.44552	1.44374
0.0302	7.40084	1.70129	1.73204	1.70549	1.70354
0.0402	8.92173	1.95266	2.03790	1.95538	1.96110
0.0502	10.03150	2.17232	2.35367	2.15412	2.19195
0.0602	10.81690	2.34623	2.66384	2.25357	2.37890
0.0702	11.3609	2.47397	2.95522	2.19925	2.51586
0.0802	11.7348	2.56466	3.21877	1.92928	2.60580
0.0902	11.9599	2.61093	3.44994	1.38786	2.65666
0.1052	12.1603	2.65038	3.73493	0.065054	2.67934
For $K = 0.01$					
0.0012	0.3585	1.02190	1.02191	1.02192	1.02190
0.0102	2.88118	1.20194	1.20329	1.20258	1.20155
0.0202	5.13143	1.41337	1.42601	1.41643	1.41322
0.0302	6.70479	1.60084	1.64567	1.60678	1.60344
0.0402	7.70824	1.74085	1.84022	1.74353	1.7483
0.0502	8.31215	1.83239	1.99886	1.86508	1.84459
0.0602	8.66409	1.88767	2.12117	1.89569	1.90176
0.0702	8.85234	1.91398	2.21235	1.94470	1.93246
0.0802	8.95715	1.92876	2.27917	1.90999	1.94689
0.1024	9.05435	1.94282	2.36902	1.86951	1.95117
0.1194	9.07846	1.94649	2.40623	1.64685	1.94443
For $K = 0.0025$					
0.0012	0.35802	1.02187	1.02188	1.02192	1.02183
0.0102	2.65117	1.18330	1.18779	1.18540	1.18185
0.0202	4.00993	1.29997	1.32615	1.30607	1.29796
0.0302	4.51773	1.34784	1.40186	1.35533	1.34683
0.0402	4.68372	1.36373	1.43904	1.36922	1.36377
0.0502	4.73626	1.36872	1.45737	1.36957	1.36941
0.0602	4.75310	1.37031	1.46673	1.36426	1.37150
0.0702	4.7580	1.37084	1.47167	1.35543	1.37223
0.0762	4.76011	1.37098	1.47346	1.34855	1.37243

For $\lambda_0^0 = 1$, the equilibrium

$$p_{eq} = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

The second moment λ_2 at e

$$2(a\lambda_2 + \lambda_1)^2 + \frac{\lambda_0^0 - \lambda}{K}$$

$$+ \frac{(\lambda_0^0 -}{K}$$

In Figure 11, equilibrium co reveals that it is independe increased p_{eq} is increased, gelation would occur for he

In Table 6, equilibrium two-moment closure relatio

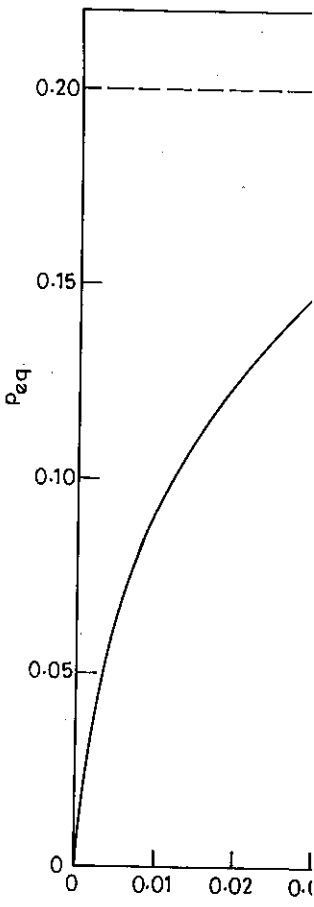

Figure 11 Equilibrium convers

ifferent λ_3 Expressions Given by

es		
	ing Stockmayer elation for λ_3	Using Eq. 41 for λ_3
	1.02192	1.02191
	1.20852	1.20841
	1.47255	1.47217
	1.81760	1.81718
	2.27445	2.27703
	2.88106	2.90465
	3.24940	3.30720
	3.57228	3.68610
	1.02192	1.02191
	1.20583	1.20530
	1.44552	1.44374
	1.70549	1.70354
	1.95538	1.96110
	2.15412	2.19195
	2.25357	2.37890
	2.19925	2.51586
	1.92928	2.60580
	1.38786	2.65666
	0.065054	2.67934
	1.02192	1.02190
	1.20258	1.20155
	1.41643	1.41322
	1.60678	1.60344
	1.74353	1.7483
	1.86508	1.84459
	1.89569	1.90176
	1.94470	1.93246
	1.90999	1.94689
	1.86951	1.95117
	1.64685	1.94443
	1.02192	1.02183
	1.18540	1.18185
	1.30607	1.29796
	1.35533	1.34683
	1.36922	1.36377
	1.36957	1.36941
	1.36426	1.37150
	1.35543	1.37223
	1.34855	1.37243

For $\lambda_0^0 = 1$, the equilibrium conversion p_{eq} can be obtained as

$$p_{eq} = \frac{\sqrt{K}}{1 + \sqrt{K}} \tag{44}$$

The second moment λ_2 at equilibrium can similarly be obtained by setting $d\lambda_2/dt = 0$, or

$$2(a\lambda_2 + \lambda_1)^2 + \frac{\lambda_0^0 - \lambda_0}{K}\{(A_2 + 1)\lambda_2 + A_3\lambda_1 + A_4\lambda_0\} + \frac{(\lambda_0^0 - \lambda_0)}{K}(A_1 - 1)\lambda_3 = 0 \tag{45}$$

In Figure 11, equilibrium conversion p_{eq} has been plotted as a function of K. Equation 44 reveals that it is independent of branching and is a monotonic function of K. As K is increased p_{eq} is increased, and for $K = 0.0625$, $p_{eq} = 0.20$, which would mean that gelation would occur for hexafunctional monomers for any k greater than this value.

In Table 6, equilibrium weight average chain length μ_{Weq} has been computed for the two-moment closure relation in Eqs. 34 and 41. This table reveals that results are ex-

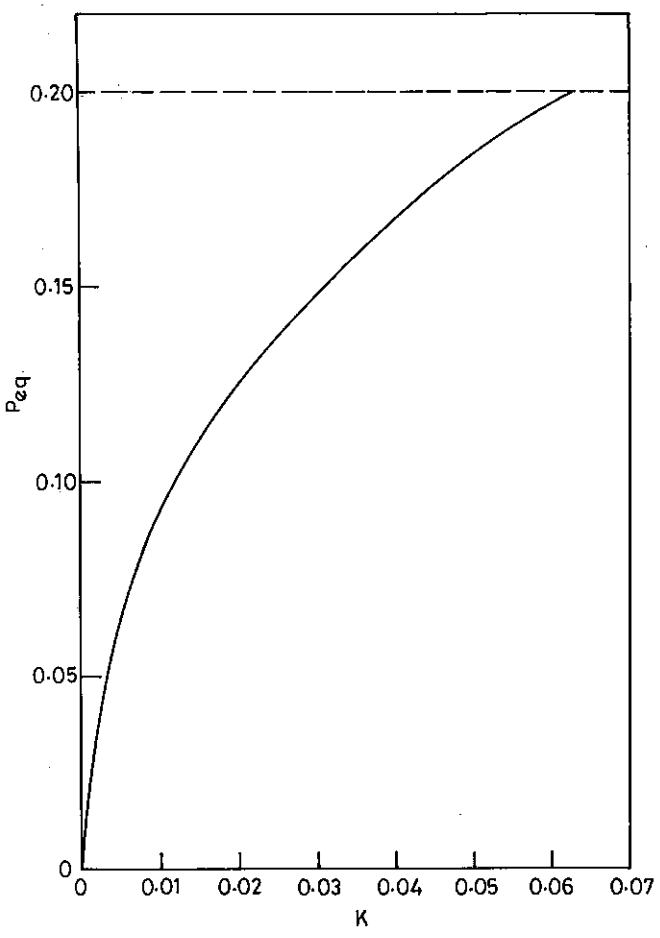

Figure 11 Equilibrium conversion, p_{eq}, versus K.

Table 6 Comparison of $\mu_{w,eq}$ Using Three Different Correlations for λ_3 Given by Eqs. 39–41

K	$\mu_{w,eq}$ using Eq. 39	$\mu_{w,eq}$ using Eq. 40	$\mu_{w,eq}$ using Eq. 41
$b = 0.02$			
0.010	2.586	−4.293	−0.661
0.012	2.933	−10.293	1.579
0.020	4.910	111.668	3.168
0.030	11.585	111.879	4.626
0.040	44.029	112.202	6.609
0.050	213.104	113.728	9.291
0.060	216.323	308.177	12.998
0.062	216.611	4470.830	13.901
$b = 0.03$			
0.010	2.652	−4.230	5.774
0.012	3.010	−10.390	5.861
0.020	5.117	75.489	6.244
0.030	12.753	75.721	6.854
0.040	20.243	76.118	7.729
0.050	275.248	78.217	9.119
0.060	277.955	302.607	12.564
0.062	278.211	4560.400	13.444
$b = 0.05$			
0.010	2.759	−4.0890	6.273
0.012	3.147	−10.4786	6.358
0.020	5.511	706.251	6.723
0.030	15.401	706.423	7.292
0.040	106.837	706.601	8.083
0.050	125.055	707.048	9.295
0.060	127.121	739.031	11.848
0.062	127.333	3491.830	12.688
$b = 0.1$			
0.010	2.947	−3.686	5.653
0.012	3.393	−10.048	5.751
0.020	6.317	114.000	6.125
0.030	24.130	114.204	6.662
0.040	92.917	114.502	7.390
0.050	99.406	115.878	8.480
0.060	100.803	289.511	10.679
0.062	100.961	4244.030	11.454

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The homolytic decom
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tremely sensitive to the closure approximation. It was observed earlier that as K approaches a value of 0.0625, for hexafunctional polymerization gelation would occur and $\mu_w \to \infty$. According to this table the moment closure in Eq. 41 gives finite μ_{Wcq} while that in Eq. 39 gives a high value. This implies that the empirical relation in Eq. 39 does not yield satisfactory results near the gel point.

RADICAL POLYMERIZATION

Unlike step growth polymerization in which the reaction occurs between the functional groups, in chain reaction polymerization the monomer polymerizes in the presence of compounds called initiators. The initiator continually generates growth centers in the reaction mass, and monomer molecules are rapidly added. It is this sequential addition of monomer molecules to growing centers which differentiates chain reactions from step growth polymerization.

The growth centers can be ionic (cationic and anionic), free radical, or coordinational in nature depending on the kind of initiator system used. Based on the nature of the growth centers, chain reaction polymerization is further classified as radical, cationic, anionic, or coordination (or stereoregular) polymerization [75]. Radical polymerization is utilized considerably more in industry and the discussion in this section is confined to radical polymerization.

Initiators for radical polymerization generate free radicals in the reaction mass. There are two types of radicals present in the reaction mass during polymerization:

1. Primary radicals, which are generated by initiator molecules directly.
2. Growing chains radicals, which are generated by the reaction between the primary radicals and the monomer molecules.

The growing chain radicals keep adding monomer molecules sequentially; this type of reaction is known as propagation. Reaction between a primary radical and a polymer radical or between two polymeric radicals makes polymer radicals unreactive by destroying their radical nature; such reactions are called termination. There are thus five kinds of species in the reaction mass at any time: initiator molecules, monomer molecules, primary radicals, growing chain radicals, and terminated polymer molecules. In order to model radical polymerization kinetically, the various reactions—initiation, propagation, and termination—must be understood.

Initiation

The molecules of initiator (denoted by I_2) can generate radicals by a homolytic decomposition of covalent bonds on absorption of energy, which can be in the form of heat, light, or high-energy radiation, depending on the initiator employed. Commercially, heat-sensitive initiators such as azo or peroxide compounds are employed. Radicals could also be generated between a pair of compounds, called redox initiators, one of which contains an unpaired electron. During the initiation, the unpaired electron is transferred to the other compound (called the acceptor), which undergoes bond dissociation. An example of redox initiators is a ferrous salt with hydrogen peroxide. In this section, however, only heat-sensitive initiators are discussed primarily because of their extensive use in industry.

The homolytic decomposition of initiator molecules can be represented schematically as

$$I_2 \xrightarrow{k_1} 2I \tag{46}$$

where I_2 is the initiator molecule and I, the primary radical. The rate of production of primary radicals, r_i' according to Eq. 46, is

$$r_i' = 2k_I[I_2] \tag{47}$$

where $[I_2]$ is the concentration of the initiator in the system at any time.

The primary radicals, I, combine with a monomer molecules, M, according to the schematic reaction

$$I + M \xrightarrow{k_1} P_1 \tag{48}$$

where P_1 is the polymer chain radical having one monomeric unit on it and k_1 is the rate constant of reaction. The rate of production, r_i, of the polymer radicals, P_1, can be written as

$$r_i = k_1[I][M] \tag{49}$$

where [I] and [M] are the concentrations of the primary radical and the monomer in the reaction mass, respectively.

Equations 47 and 49 imply that all the radicals generated by the homolytic decomposition of initiator molecules are used in generating the polymer chain radicals and no primary radicals are wasted by any other reaction. This is not true in reality and an initiator efficiency is defined to take care of the waste of primary radicals. The initiator efficiency, *f*, is the fraction of the total primary radicals produced by reaction 46 which are used in generating polymer radicals by reaction 48. Thus the rate of generation of polymer radicals is given by

$$r_i = 2fk_I[I_2] \tag{50}$$

Sometimes a solvent is added to the monomer for better temperature control. This has been shown to affect the initiator efficiency and is explained in terms of the cage theory [76, 77]. On supplying energy to initiator molecules, cleavage of a covalent bond occurs as shown in Eq. 46. According to this theory, the two dissociated fragments are surrounded by the reaction mass, which forms a sort of cage around them. The two fragments stay inside the cage for a finite amount of time during which they can recombine to give back the initiator molecule. The fragments that do not recombine diffuse, and the separated fragments are called primary radicals. If the monomer molecule is highly reactive, it can also react with a fragment inside a cage. The characteristics of the reaction medium determine how long the dissociated fragments stay inside the cage and they also affect the initiator efficiency. It is therefore expected that, if all other conditions are equal, a more viscous reaction mass would lead to a lower initiator efficiency.

Propagation Reaction

The propagation reaction is defined as the addition of monomer molecules to the growing polymer radicals. In the reaction mass there are polymer radicals of all possible sizes. In general, a polymer radical, P_n, indicates that there are *n* monomeric units joined together by covalent bonds in the chain radical. The propagation reaction can be written schematically as

$$P_n + M \xrightarrow{k_{pn}} P_{n+1},$$

where k_{pn} is the rate cons
general this would depen
increasing mathematical
As a good first approxima
in the case of polymer ra

$$k_{p1} = k_{p2} = k_{p3} = \cdots$$

Termination of Poly

The termination reaction
can occur only when a p
primary radical. The form
tion. These reactions can

$$P_m + P_n \xrightarrow{k_{t(m,n)}} M_{n+m}$$

$$P_m + I \xrightarrow{k_{t,I(m)}} M_m$$

where $m, n = 1,2,3, \ldots$
any further propagation re
chains can be formed eith
termination, two chain rad
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become inactive. These tw

$$P_m + P_n \xrightarrow{k_{tc(m,n)}} M_{m+n}$$

$$P_m + P_n \xrightarrow{k_{td(m,n)}} M_m + M_n$$

where $k_{tc(m,n)}$ and $k_{td(m,n)}$
disproportionation, respecti
to hold: all the rate constant
i.e.,

$$k_{tc(m,n)} = k_{tc}'$$

$$k_{td(m,n)} = k_{td}' \quad \text{for } m \neq$$

$$k_{tc(m,n)} = \frac{k_{tc}'}{2}$$

$$k_{td(m,n)} = \frac{k_{td}'}{2} \quad \text{for all } n$$

Various reactions occurri
[1, 3]. The intermediate spec
etc., and the mole balance e
batch reactor can be written a

$$\frac{d[I_2]}{dt} = k_I[I_2]$$

$$P_n + M \xrightarrow{k_{pn}} P_{n+1}, \qquad n = 1,2, \ldots \tag{51}$$

where k_{pn} is the rate constant for the reaction between P_n and a monomer molecule, M. In general this would depend on the size of the chain radical. It is not difficult to foresee the increasing mathematical complexity resulting from the multiplicity of the rate constants. As a good first approximation, the principle of equal reactivity is assumed to be valid even in the case of polymer radicals, which means that

$$k_{p1} = k_{p2} = k_{p3} = \cdots = k_{pn} = k_p \tag{52}$$

Termination of Polymer Radicals

The termination reaction is the one in which polymer chain radicals are destroyed. This can occur only when a polymer radical reacts with another polymer radical or with a primary radical. The former is called the mutual termintion and the latter primary termination. These reactions can be written as

$$P_m + P_n \xrightarrow{k_{t(m,n)}} M_{n+m} \tag{53a}$$

$$P_m + I \xrightarrow{k_{t,I(m)}} M_m \tag{53b}$$

where $m, n = 1,2,3, \ldots$. M_{n+m} signifies a dead polymer chain, i.e., it cannot undergo any further propagation reaction. In the case of mutual termination the inactive polymer chains can be formed either by combination or by disproportionation. In combination termination, two chain radicals just combine to give an inactive chain, whereas in disproportionation, one chain radical gives up an electron to the other and both chains become inactive. These two types of termination can be represented by

$$P_m + P_n \xrightarrow{k_{tc(m,n)}} M_{m+n} \qquad \text{(combination)} \tag{54a}$$

$$P_m + P_n \xrightarrow{k_{td(m,n)}} M_m + M_n \qquad \text{(disproportionation)} \tag{54b}$$

where $k_{tc(m,n)}$ and $k_{td(m,n)}$ are the rate constants for termination by combination and disproportionation, respectively. Once again, the principle of equal reactivity is assumed to hold: all the rate constants are independent of the chain lengths of the polymer radicals, i.e.,

$$k_{tc(m,n)} = k'_{tc} \tag{55a}$$

$$k_{td(m,n)} = k'_{td} \qquad \text{for } m \neq n \tag{55b}$$

$$k_{tc(m,n)} = \frac{k'_{tc}}{2} \tag{55c}$$

$$k_{td(m,n)} = \frac{k'_{td}}{2} \qquad \text{for all } m = n \tag{55d}$$

Various reactions occurring in radical polymerization are summarized in the Table 7 [1, 3]. The intermediate species present at the time in the reaction mass are I, P_1, P_2, P_3, etc., and the mole balance equations for each of these and the initiator molecule I_2 in a batch reactor can be written as

$$\frac{d[I_2]}{dt} = k_I[I_2] \tag{56a}$$

$$\frac{d[\mathrm{I}]}{dt} = 2fk_\mathrm{I}[\mathrm{I}_2] - k_1[\mathrm{I}][\mathrm{M}] - k_{tp}[\mathrm{I}]\sum_{m=1}^{\infty}[\mathrm{P}_m] \tag{56b}$$

$$\frac{d[\mathrm{P}_1]}{dt} = k_1[\mathrm{I}][\mathrm{M}] - k_p[\mathrm{P}_1][\mathrm{M}] - k_{tp}[\mathrm{P}_1][\mathrm{I}] - k_t'\{[\mathrm{P}_1]^2 + [\mathrm{P}_1][\mathrm{P}_2] + [\mathrm{P}_1][\mathrm{P}_3] + \cdots\} \tag{56c}$$

$$\frac{d[\mathrm{P}_n]}{dt} = k_p[\mathrm{M}][\mathrm{P}_{n-1}] - k_p[\mathrm{M}][\mathrm{P}_n] - k_{tp}[\mathrm{P}_n][\mathrm{I}] - k_t'\{[\mathrm{P}_n][\mathrm{P}_1] + [\mathrm{P}_n][\mathrm{P}_2] + \cdots + [\mathrm{P}_n]^2 + \cdots\} \tag{56d}$$

where

$$k_t' = k_{tc}' + k_{td}' \tag{56e}$$

If [P] is defined as the total concentration of polymer radicals in the reaction mass, then

$$[\mathrm{P}] = [\mathrm{P}_1] + [\mathrm{P}_2] + \cdots = \sum_{n=1}^{\infty}[\mathrm{P}_n] \tag{57}$$

and Eqs. 56c, d, and e can be added to give the rate of production of [P] as

$$\frac{d[\mathrm{P}]}{dt} = \frac{d\sum_{n=1}^{\infty}[\mathrm{P}_n]}{dt} = k_1[\mathrm{I}][\mathrm{M}] - k_{tp}[\mathrm{I}][\mathrm{P}] - k_t'[\mathrm{P}]^2 \tag{58}$$

Table 7 Reactions Occurring in Radical Polymerization

Initiation:

$$\mathrm{I}_2 \xrightarrow{k_\mathrm{I}} 2\mathrm{I}$$

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_\mathrm{I}} \mathrm{P}_1$$

Propagation:

$$\mathrm{P}_m + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{m+1} \qquad m = 1,2,\ldots$$

Termination:

Primary:

$$\mathrm{P}_m + \mathrm{I} \xrightarrow{k_{tp}} \mathrm{M}_m \qquad m = 1,2,\ldots$$

Combination:

$$\mathrm{P}_m + \mathrm{P}_n \xrightarrow{k_{tc}'} \mathrm{M}_{m+n} \qquad m \neq n, \quad m,n = 1,2,\ldots$$

$$\mathrm{P}_m + \mathrm{P}_m \xrightarrow{k_{tc}'/2} \mathrm{M}_{2m} \qquad m = 1,2,\ldots$$

Disproportionation:

$$\mathrm{P}_m + \mathrm{P}_n \xrightarrow{k_{td}'} \mathrm{M}_m + \mathrm{M}_n \; m \neq n, \quad m,n = 1,2,\ldots$$

$$\mathrm{P}_m + \mathrm{P}_m \xrightarrow{k_{td}'/2} 2\mathrm{M}_m \qquad m = 1,2,\ldots$$

The corresponding relatio

$$\frac{d[\mathrm{I}_2]}{dt} = -k_\mathrm{I}[\mathrm{I}_2]$$

$$\frac{d[\mathrm{I}]}{dt} = 2fk_\mathrm{I}[\mathrm{I}_2] - k_1[$$

The study of Eqs. 58 an equations can be derived f ization.

Initiation:

$$\mathrm{I}_2 \xrightarrow{k_\mathrm{I}} 2\mathrm{I}$$

$$\mathrm{I}_2 + \mathrm{M} \xrightarrow{k_\mathrm{I}} \mathrm{P}$$

Propagation:

$$\mathrm{P} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}$$

Termination:

$$\mathrm{P} + \mathrm{I} \xrightarrow{k_{tp}} \text{dead chains}$$

$$\mathrm{P} + \mathrm{P} \xrightarrow{k_{tc}'/2} \text{dead chains}$$

$$\mathrm{P} + \mathrm{P} \xrightarrow{k_{td}'/2} \text{dead chains}$$

The kinetic equivalence established. The replacemer each molecular species in th analogus to simplification o growth polymerization by th plifications are a direct cons

The mole balance equatio in Eqs. 58 and 59. Since t generally much higher than t

$$k_1[\mathrm{M}] \gg k_{tp}[\mathrm{P}]$$

Eq. 59b can be written as

$$\frac{d[\mathrm{I}]}{dt} \cong 2fk_\mathrm{I}[\mathrm{I}_2] - k_1[\mathrm{I}][\mathrm{M}$$

Also, in radical polymerizatio cules, and as soon as a primar Eqs. 60. Thus the concentrati

$$[\mathrm{M}] \gg [\mathrm{P}] \gg [\mathrm{I}]$$

The corresponding relation for the initiation steps can be written from Eqs. 56a and b as

$$\frac{d[I_2]}{dt} = -k_I[I_2] \tag{59}$$

$$\frac{d[I]}{dt} = 2fk_I[I_2] - k_1[I][M] - k_{tp}[I][P] \tag{59b}$$

The study of Eqs. 58 and 59 reveals that these involve only [P]. An identical set of equations can be derived from the following simplified mechanism of the radical polymerization.

Initiation:

$$I_2 \xrightarrow{k_I} 2I \tag{60a}$$

$$I_2 + M \xrightarrow{k_1} P \tag{60b}$$

Propagation:

$$P + M \xrightarrow{k_p} P \tag{60c}$$

Termination:

$$P + I \xrightarrow{k_{tp}} \text{dead chains} \tag{60d}$$

$$P + P \xrightarrow{k'_{tc}/2} \text{dead chains} \tag{60e}$$

$$P + P \xrightarrow{k'_{td}/2} \text{dead chains} \tag{60f}$$

The kinetic equivalence of the mechanisms given in Table 7 and Eqs. 60 is thus established. The replacement of a complex series of equations given in Table 7, where each molecular species in the reaction mass is distinguished by the far simpler Eqs. 60, is analogus to simplification of the complex reactions involving individual species in step growth polymerization by the reaction between reactive groups. Indeed, both these simplifications are a direct consequence of the equal reactivity hypothesis.

The mole balance equations can be simplified even beyond the simplification achieved in Eqs. 58 and 59. Since the number of monomer molecules in the reaction mass is generally much higher than the number of polymer radicals,

$$k_1[M] \gg k_{tp}[P] \tag{61}$$

Eq. 59b can be written as

$$\frac{d[I]}{dt} \cong 2fk_I[I_2] - k_1[I][M] \tag{62}$$

Also, in radical polymerization the slowest reaction is the dissociation of initiator molecules, and as soon as a primary radical is produced, it is consumed by reactions b and c of Eqs. 60. Thus the concentration of I is expected to be much less than that of P, i.e.,

$$[M] \gg [P] \gg [I] \tag{63}$$

and Eq. 58 can be rewritten as

$$\frac{d[P]}{dt} = k_1[I][M] - k_t'[P]^2 \tag{64}$$

Equations 62 and 64 imply that the primary termination step, Eq. 60d, can be neglected in the kinetic mechanism.

The rate of monomer consumption r_p for radical polymerization can now be derived from Eqs. 60b and c and approximated as

$$r_p \simeq k_p[P][M] \tag{65}$$

To find the total concentration of chain radicals, P, in the reaction mass, the steady-state approximation is used [78]. From Eq. 62,

$$\frac{d[I]}{dt} = 2fk_I[I_2] - k_1[M][I] = 0 \tag{66}$$

$$[I] = \frac{2fk_I[I_2]}{k_1[M]} \tag{67}$$

Similarly, from Eq. 64,

$$\frac{d[P]}{dt} = k_1[M][I] - k_t'[P]^2 = 0 \tag{68}$$

and from Eqs. 67 and 67,

$$[P] = \frac{2fk_I[I_2]^{1/2}}{k_t'} \tag{69}$$

The rate of propagation after some induction time is thus given by

$$r_p = k_p\left\{\frac{2fk_I[I_2]^{1/2}}{k_t'}\right\}[M] \tag{70}$$

Average Molecular Weight in Radical Polymerization

Average molecular weight in radical polymerization can be found from the kinetic model, Eqs. 60, as follows. The kinetic chain length, ν, is defined as the average number of monomer molecules reacting with a polymer chain radical during the latter's entire lifetime. This is the ratio of the rate of consumption of the monomer, to the rate of generation of polymer radicals, r_i:

$$\nu = \frac{r_p}{r_i} \tag{71}$$

From the steady-state approximation, the rate of initiation, r_i, should be equal to the rate of termination, r_t. Therefore,

$$\nu = \frac{r_p}{r_t} = \frac{k_p[M][P]}{k_t'[P]} = \frac{k_p[M]}{k_t'[P]} \tag{72}$$

On eliminating [P] with the help of Eq. 69, ν is given by

$$\nu = \frac{k_p}{(2fk_Ik_t')^{1/2}}\frac{[M]}{[I_2]^{1/2}} \tag{73}$$

Equation 73 shows that the
centration. This is expected
produced.

The quantity that is of inte
ν because μ_n gives the avera
whereas ν gives the average r
To be able to find the exact r
must be carefully analyzed.
bination, then each of the
termination occurs only by
would consist of ν monomer
then

$$\mu_n = \alpha\nu$$

where α would be between 1

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tion is one way of monitoring

Another method for contr
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represented schematically as

$$P_n + S \xrightarrow{k_{tr,S}} M_n + P_1,$$

where S is a molecule of the t

Equation 75 should be add
carried out with a transfer age
in the reaction mass, it is not r
other once again, and Eq. 75

$$P + S \xrightarrow{k_{tr,S}} M_d + P$$

Since this reaction does not
reaction mass, from Eq. 65 it
r_p. However, the kinetic chai
$k_{tr,S}$ and [S]. Equation 72 can
agents:

$$\nu = \frac{r_p}{k_t'[P]^2 + k_{tr,S}[P][S]}$$

or on taking the reciprocal

$$\frac{1}{\nu} = \frac{k_{tr,S}[S]}{k_p[M]} + \frac{(2fk_Ik_t')^{1/2}}{k_p}$$

Equation 78 predicts a decrease

Equation 73 shows that the kinetic chain length reduces with increasing initiator concentration. This is expected since an increase in $[I_2]$ would lead to more chains being produced.

The quantity that is of interest is the average chain length, μ_n. This is directly related to ν because μ_n gives the average number of monomer molecules per dead polymer chain whereas ν gives the average number of monomer molecules per growing polymer radical. To be able to find the exact relationships between the two, the mechanism of termination must be carefully analyzed. If the termination of polymer radicals occurs only by combination, then each of the dead chains would consist of 2ν monomer molecules. If termination occurs only by disproportionation, each of the inactive polymer molecules would consist of ν monomer molecules. If termination occurs by both these mechanisms, then

$$\mu_n = \alpha\nu \tag{74}$$

where α would be between 1 and 2.

As the initiator concentration is increased, the rate of polymerization goes up (Eq. 70), but ν, and therefore μ_n, goes down (Eq. 73). Therefore, control of the initiator concentration is one way of monitoring the molecular weight of the polymer.

Another method for controlling the molecular weight of the polymer is the use of a transfer agent. The polymer chain radicals react with the transfer agent and lose the capacity to add any further monomer molecules, the molecule of the transfer agent acquiring radical character in this process. The latter can grow by adding monomer molecules like any other growing chain in the reaction mass. The transfer reaction is represented schematically as

$$P_n + S \xrightarrow{k_{tr,S}} M_n + P_1, \qquad n > 1 \tag{75}$$

where S is a molecule of the transfer agent.

Equation 75 should be added to the kinetic model if radical polymerization is being carried out with a transfer agent. Since the transfer reaction occurs with equal likelihood in the reaction mass, it is not necessary to distinguish chain radicals kinetically from each other once again, and Eq. 75 can be included in the following form in Eqs. 60:

$$P + S \xrightarrow{k_{tr,S}} M_d + P \tag{76}$$

Since this reaction does not reduce or increase the total number of chain radicals in the reaction mass, from Eq. 65 it follows that the presence of a transfer agent does not affect r_p. However, the kinetic chain length, ν, changes drastically depending on the value of $k_{tr,S}$ and [S]. Equation 72 can easily be modified to account for the presence of transfer agents:

$$\nu = \frac{r_p}{k_t'[P]^2 + k_{tr,S}[P][S]} \tag{77}$$

or on taking the reciprocal

$$\frac{1}{\nu} = \frac{k_{tr,S}[S]}{k_p[M]} + \frac{(2fk_1k_t')^{1/2}}{k_p}\frac{[I_2]^{1/2}}{[M]} \tag{78}$$

Equation 78 predicts a decrease in μ_n with increasing concentration of the transfer agent.

Chain transfer reactions occur quite commonly in radical polymerization with initiator as well as monomer as follows:

With initiator:

$$P_n + I_2 \xrightarrow{k_{tr,I_2}} M_n\sim I + I \tag{79}$$

With monomer:

$$P_n + M \xrightarrow{k_{tr,M}} M_n + P_1 \tag{80}$$

These reactions can be similarly incorporated into the kinetic model and the average chain lengths can be found to be

$$\frac{1}{\alpha\mu_n} = C_M + C_S\frac{[S]}{[M]} + \frac{k_t}{k_p^2}\frac{r_p}{[M]^2} + C_I\left(\frac{k_t'}{2fk_p^2k_I}\right)\frac{r_p^2}{[M]^3} \tag{81}$$

where

$$C_M = \frac{k_{tr,M}}{k_p} \tag{82a}$$

$$C_I = \frac{k_{tr,I_2}}{k_p} \tag{82b}$$

$$C_S = \frac{k_{tr,S}}{k_p} \tag{82c}$$

Gel Effect in Radical Polymerization

The considerable increase in the rate of polymerization (as shown in Fig. 12 [75]) and the average chain length, μ_n (Figure 13 [80]) is a phenomenon common to all monomers

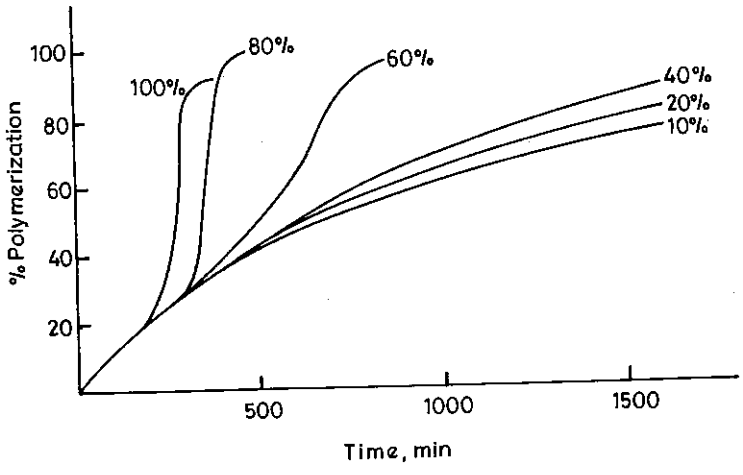

Figure 12 Polymerization of methyl methacrylate at 50°C with benzoyl peroxide initiator at various monomer concentrations (benzene as diluent).

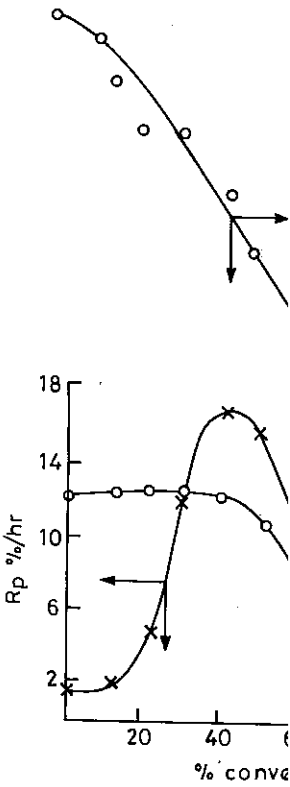

Figure 13 Average molecula
methacrylate at 60°C and 0.004
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undergoing radical polymer
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Figure 14. It is also seen th
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termination step involves th
other's proximity. Once the
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During the course of free
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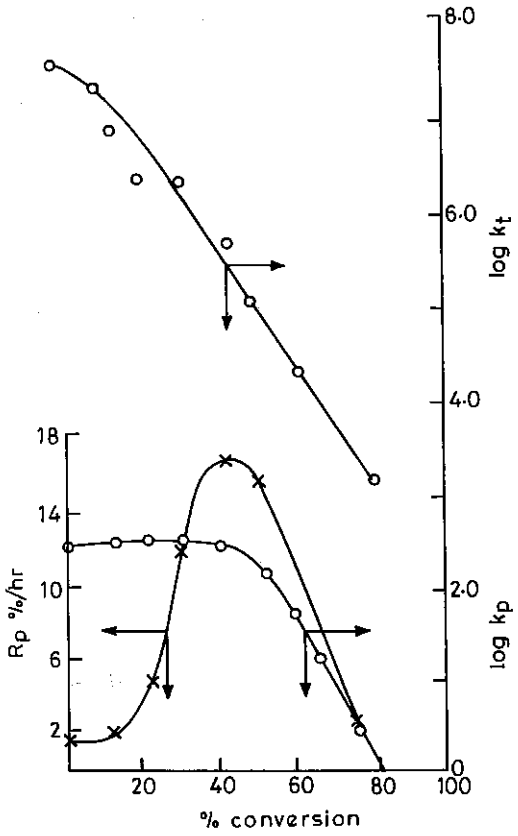

Figure 13 Average molecular weight as a function of conversion in the polymerization of methyl methacrylate at 60°C and 0.0045 mol % initiator. (Reprinted from Ref. 83, with permission of ACS, Washington.)

undergoing radical polymerization at low temperatures and is called the autoacceleration, or gel effect. This has been a subject of several studies [81–95] and has been attributed to the fall in values of the rate constants, k_p and k_t, as shown for methyl methacrylate in Figure 14. It is also seen that the rate constant k_t is affected first and falls in magnitude considerably faster than k_p. The large fall in k_t can be explained by observing that the termination step involves the diffusion of two polymer molecules from the bulk to each other's proximity. Once the proximate pair has been formed, the radical segments must undergo segmental diffusion before the termination reaction can occur. The fall in k_t occurs because the segmental diffusion becomes sluggish with the increase in the viscosity of the reaction mass. On the other hand, the propagation reaction involves the diffusion of a small molecule (i.e., monomer) from the bulk to the radical segment. There is little segmental diffusion involved in this step, thus leaving k_p unaffected up to considerably higher conversions.

During the course of free radical polymerization from the bulk monomer to complete or limiting conversion, the movement of polymer radicals toward each other goes through several regimes of changes. To demonstrate this, attention is focused on a solution consisting of dissolved, nonreacting polymer molecules. When the solution is very dilute,

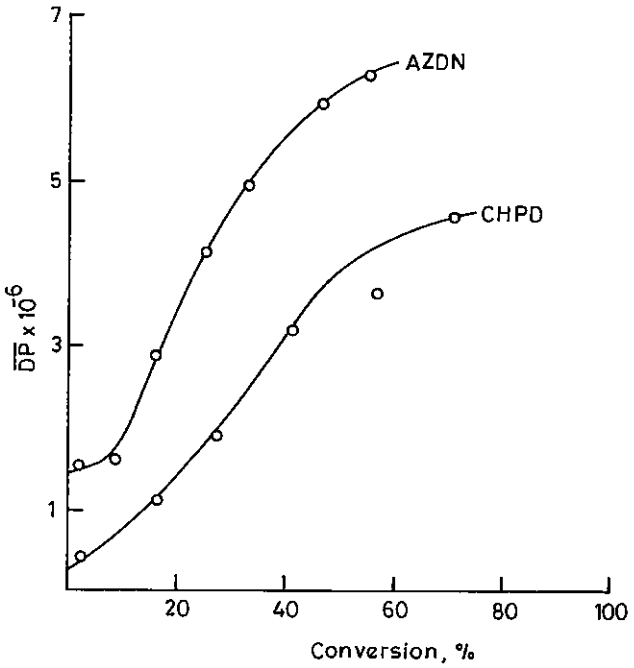

Figure 14 Bulk polymerization 25°C with AzDN initiator. The rate of initiation is 8.36×10^{-9} moles L sec^{-1}.

the polymer molecules exist in a highly coiled state and they behave like hydrodynamic spheres. In this regime, polymer molecules can undergo translational motion easily and the overall diffusion is completely governed by polymer–solvent interactions. As the polymer concentration is increased (say beyond a critical conversion C^*), the translational motion of molecule begins to be affected by the presence of other molecules. This effect, which was absent earlier, constitutes the second regime. On increasing the concentration of the polymer still further (say beyond C^{**}), in addition to the intermolecular interactions in translational motion, polymer chains begin to impose topological constraints upon the motion of surrounding molecules due to their long-chain nature. In other words, polymer molecules begin to be entangled. DeGennes modeled the motion of polymer chains in this regime through a "tube" defined by the points of entanglement. A polymer molecule can move through this only by a snakelike wriggling motion along its length; this mode of motion is sometimes called reptation. Finally, at very high concentrations (say beyond C^{***}), polymer chains begin to exert direct friction upon each other. The values of C^*, C^{**}, and C^{***} have been experimentally shown to depend on the molecular weight of the polymer.

To demonstrate the correspondence between the polymer solvent system described above and free radical polymerization, Turner [90] and Driscoll's group [82, 91–93] demonstrated that gelation starts at the polymer concentration of C^{**}. In fact, it has been shown that k_t changes continuously as the polymerization progresses [89, 95], first increasing slightly but subsequently reducing drastically at higher conversions. Tulig and Tirrell [89, 95] have argued, based on their experimental and theoretical analysis, that similar regimes for k_t must exist in the entire range of conversion.

Based upon the foregoi
Cardenas and O'Driscoll [
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grows in chain length beyc
and its termination rate co
rate constant, k_p, is not af
then by represented as follc

Initiation:

$$I_2 \xrightarrow{fk_I} 2I$$

$$I + M \xrightarrow{k_1} P_1$$

Propagation:

$$P_n + M \xrightarrow{k_p} P_{n+1}$$

$$P_{ne} + M \xrightarrow{k_p} P_{(n+1)e}$$

Termination:

$$P_m + P_n \xrightarrow{k_t} M_m + M_n$$

$$P_m + P_{ne} \xrightarrow{k_{tc}} M_m + M_n$$

$$P_{me} + P_{ne} \xrightarrow{k_{te}} M_m + M_n$$

In the above scheme, the react
been assumed to occur with r
equations for the various radic
above, and for batch reactors

$$\frac{d[P_1]}{dt} = 2fk_I[I_2] - \{k_p[M$$

$$\frac{d[P_n]}{dt} = [M][P_{n-1}] - \{k_p[$$

$$\frac{d[P_{ne}]}{dt} = k_p[M][P_{(n-1)e}] -$$

where

$$[P] = \sum_{n=1}^{n_c} [P_n]$$

$$[P_e] = \sum_{n=n_c+1}^{\infty} [P_{ne}]$$

Based upon the foregoing physical picture of the gel effect, a model was proposed by Cardenas and O'Driscoll [82, 91, 92] in which two populations of radicals are assumed to exist in the reaction mass. The first are those which are physically entangled (denoted by P_{ne}) and therefore have lower termination rate constant (k_{te}), compared to that (k_t) of the second population (denoted by P_n), which are untangled. Whenever a polymer radical grows in chain length beyond a critical value n_c, it is assumed that it becomes entangled and its termination rate constant falls from k_t to k_{te}. If it is assumed that the propagation rate constant, k_p, is not affected, the overall mechanism of radical polymerization can then by represented as follows:

Initiation:

$$I_2 \xrightarrow{fk_I} 2I \tag{83a}$$

$$I + M \xrightarrow{k_1} P_1 \tag{83b}$$

Propagation:

$$P_n + M \xrightarrow{k_p} P_{n+1} \tag{83c}$$

$$P_{ne} + M \xrightarrow{k_p} P_{(n+1)e} \tag{83d}$$

Termination:

$$P_m + P_n \xrightarrow{k_t} M_m + M_n \tag{83e}$$

$$P_m + P_{ne} \xrightarrow{k_{tc}} M_m + M_n \tag{83f}$$

$$P_{me} + P_{ne} \xrightarrow{k_{te}} M_m + M_n \tag{83g}$$

In the above scheme, the reaction between the entangled and the unentangled radicals has been assumed to occur with rate constant k_{tc} lying between k_t and k_{te}. The mole balance equations for the various radicals can be easily written from the kinetic mechanism given above, and for batch reactors

$$\frac{d[P_1]}{dt} = 2fk_I[I_2] - \{k_p[M] + 2k_t[P] + 2k_{tc}[P_e]\}[P_1] \tag{84}$$

$$\frac{d[P_n]}{dt} = [M][P_{n-1}] - \{k_p[M] + 2k_t[P] + 2k_{tc}[P_e]\}[P_n], \qquad 2 \le n \le n_c \tag{85}$$

$$\frac{d[P_{ne}]}{dt} = k_p[M][P_{(n-1)e}] - \{k_p[M] + 2k_{tc}[P] + 2k_{te}[P_e]\}[P_{ne}], \qquad n_e > n_c \tag{86}$$

where

$$[P] = \sum_{n=1}^{n_c} [P_n] \tag{87a}$$

$$[P_e] = \sum_{n=n_c+1}^{\infty} [P_{ne}] \tag{87b}$$

Since the total reaction time is usually much larger than the individual radical lifetime, the steady-state approximation can be assumed to valid here. On summing Eqs. 84 and 85 for values of n up to n_c, one gets

$$2fk_I[I_2] + k_p[M]\sum_{n=2}^{\infty}[P_{n-1}] - \{k_p[M] + 2k_t[P] + 2k_{tc}[P_e]\}\sum_{n=1}^{\infty}[P_n] = \frac{d[P]}{dt} = 0 \tag{88}$$

or

$$2fk_I[I_2] - \{2k_t[P] + 2k_{tc}[P_e]\}[P] = k_p[M][P_{nc}] \tag{89}$$

It is assumed that k_{tc} is the geometric mean of k_t and k_{te}, i.e.,

$$k_{tc} = (k_t k_{te})^{1/2} = \delta k_t \tag{90}$$

where

$$\delta = \left(\frac{k_{te}}{k_t}\right)^{1/2} \tag{91}$$

With the help of Eq. 90, Eq. 89 is simplified to

$$2fk_I[I_2] - 2k_t\{[P] + \delta[P_e]\}[P] = k_p[M][P_{nc}] \tag{92}$$

Similarly, Eq. 85 is added for all values of n above n_c assuming the steady-state approximation is valid. On doing this, the following relation is obtained:

$$k_p[M]\sum_{n=n_c+1}^{\infty}[P_{(n-1)e}] - \{k_p[M] + 2k_{tc}[P] + 2k_{te}[P_e]\}\sum_{n=n_c+1}^{\infty}[P_{ne}] = \frac{d[P_e]}{dt} = 0 \tag{93}$$

which simplifies to

$$2\delta k_t\{[P] + \delta[P_e]\} = k_p[M][P_{nc}] \tag{94}$$

Equating the left-hand sides of Eqs. 92 and 94,

$$[P] + \delta[P_e] = \left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2} \tag{95}$$

It is now necessary to define the probability of propagation to find the distribution of P_n. After a polymer chain radical is formed by the reaction between a primary radical and a monomer molecule, it can either propagate by reaction 83c and d or be terminated by transfer or mutual termination reactions 83e, f, and g. Therefore, the probability of propagation, β, for chain length less than n_c is found as

$$\beta = \frac{k_p[M]}{k_p[M] + 2k_t[P] + 2k_{tc}[P_e]} = \frac{1}{1 + \{k_t fk_I[I_2]/k_p^2[M]^2\}^{1/2}} \tag{96}$$

where the transfer reactions have been neglected. Under the steady-state approximation, $d[P_n]/dt$ is set equal to zero in Eq. 85. It is recognized that P_n is formed only when there is a propagation reaction with P_{n-1}, or

$[P_n] = \beta[P_{n-1}]$ fo

Similarly, from the steady-

$$[P_1] = \frac{2fk_I[I_2]}{k_p[M]}$$

With the help of Eqs. 97 a

$$[P_n] = \beta^n \frac{2fk_I[I_2]}{k_p[M]}$$

It is observed that β is approximated by $(\beta - 1)/\beta$

$$\beta^n = \exp(n \ln \beta) = \exp$$

where

$$\frac{1}{\nu} = 2\left\{\frac{k_t fk_I[I_2]}{k_p^2[M]^2}\right\}^{1/2}$$

and is the same as the kineti from Eq. 99 and substituted

$$[P] = \left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2}\left[1 -$$

and

$$[P_e] = \left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2}\exp\left(-$$

The rate of polymerization, r_p

$$r_p = k_p[M]\{[P] + [P_e]\} =$$

The monomer conversion, x, concentration initially present dence time, [M]. This is given

$$x = \frac{[M]_0 - [M]}{[M]_0}$$

Equation 103 can now be writt

$$r_p = \frac{dx}{dt} = k_p(1 - x)\left\{\frac{fk_I[I}{k_t}\right.$$

To solve for the rate of poly determine δ and n_c. From rheo age chain length μ_{nc} and the vol

$$K_c = \mu_{nc}^{\gamma}\phi_P$$

$$[P_n] = \beta[P_{n-1}] \qquad \text{for} \quad n \leq n_c \tag{97}$$

Similarly, from the steady-state approximation, $d[P_1]/dt$ is equal to zero and Eq. 84 gives

$$[P_1] = \frac{2fk_I[I_2]}{k_p[M]} \tag{98}$$

With the help of Eqs. 97 and 98, one finds

$$[P_n] = \beta^n \frac{2fk_I[I_2]}{k_p[M]} \tag{99}$$

It is observed that β is a quantity close to unity, which implies that ln β can be approximated by $(\beta - 1)/\beta$ and the term β^n can be rewritten as

$$\beta^n = \exp(n \ln \beta) = \exp\left\{-n\frac{(-\beta + 1)}{\beta}\right\} = \exp\left(-\frac{n}{\nu}\right) \tag{100}$$

where

$$\frac{1}{\nu} = 2\left\{\frac{k_t fk_I[I_2]}{k_p^2[M]^2}\right\}^{1/2} \tag{101}$$

and is the same as the kinetic chain length defined in Eq. 73. $[P_{n_c}]$ can now be calculated from Eq. 99 and substituted in Eqs. 94 and 95 to obtain

$$[P] = \left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2}\left[1 - \exp\left(-\frac{n_c}{\nu}\right)\right] \tag{102a}$$

and

$$[P_e] = \left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2}\exp\left(-\frac{n_c}{\nu}\right) \tag{102b}$$

The rate of polymerization, r_p, can now be determined as

$$r_p = k_p[M]\{[P] + [P_e]\} = k_p[M]\left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2}\left[1 + \frac{1 - \delta}{\delta}\exp\left(-\frac{n_c}{\nu}\right)\right] \tag{103}$$

The monomer conversion, x, as radical polymerization is defined in terms of monomer concentration initially present in the reaction mass, $[M]_0$, and that at any reaction residence time, [M]. This is given by

$$x = \frac{[M]_0 - [M]}{[M]_0} \tag{104}$$

Equation 103 can now be written in terms of the monomer conversion, x, as

$$r_p = \frac{dx}{dt} = k_p(1 - x)\left\{\frac{fk_I[I_2]}{k_t}\right\}^{1/2}\left[1 + \frac{1 - \delta}{\delta}\exp\left(-\frac{n_c}{\nu}\right)\right] \tag{105}$$

To solve for the rate of polymerization at a given conversion, x, it is necessary to determine δ and n_c. From rheological studies, the relation between critical number average chain length μ_{nc} and the volume fraction ϕ_P of polymer present in solution is given by

$$K_c = \mu_{nc}\phi_P \tag{106}$$

K_c is a constant which is (almost) independent of temperature but has different value for different polymers. In this equation γ is a constant that lies between 0.5 and 1.0, and it is found that the computed rate curves are relatively insensitive to the value of γ chosen. It is postulated that k_{te} is inversely proportional to the entanglement density d_e or

$$k_{te} = \frac{b}{d_e} \tag{107}$$

where b is a constant of proportionality and d_e is given by

$$d_e = a\left(\frac{\phi_P \mu_n}{K_c}\right) = d_e\theta\left(\frac{K_c}{\phi_P \mu_n^{\gamma}}\right)^{1/2} \tag{108}$$

Equations 106–108 can be combined to give

$$de_0 = \left(\frac{b}{ak_t}\right)^{1/2} \tag{109}$$

To be able to solve average molecular weights, the mode of termination must be known. If it is assumed that termination occurs largely by the disproportionation mechanism,

$$\frac{d[M_n]}{dt} = \{2k_t[P] + 2k_{tc}[P_e]\}[P_n], \qquad n \leq n_c \tag{110a}$$

$$\frac{d[M_n]}{dt} = \{2k_{tc}[P] + 2k_{te}[P_e]\}[P_{ne}], \qquad n > n_c \tag{110b}$$

From Eqs. 110, it is possible to derive the zeroth (λ_0), first (λ_1), and second (λ_2) moments of the inactive polymer chains as follows. For example, λ_2 is given by

$$\frac{d\lambda_2}{dt} = \sum_{n=1}^{n_c} n^2[P_n]\{2k_t[P] + 2k_{tc}[P_e]\} + \sum_{n=n_c+1}^{\infty} n^2[P_{ne}]\{2k_{tc}[P] + 2k_{te}[P_e]\} \tag{111}$$

The moments of inactive polymers are thus related to the moments of the radicals, which can now be determined by Eqs. 84–86. Assuming the steady-state approximation, it is possible to derive from these relations the following:

$$\sum_{n=1}^{n_c} n^2[P_n] = \frac{2fk_I[I_2] + k_p[M]\{2\Sigma_{n=1}^{n-1} n[P_n] + \Sigma_{n=1}^{n-1}[P_n] - n_c^2[P_{nc}]\}}{2k_t[P] + 2k_{tc}[P_e]} \tag{112a}$$

and

$$\sum_{n=n_c+1}^{\infty} n^2[P_{ne}] = \frac{k_p[M]\{2\Sigma_{n=n_c}^{\infty} n[P_{ne}] + \Sigma_{n=n_c}^{\infty}[P_{ne}] + n_c^2[P_{nc}]}{2k_{tc}[P] + 2k_{te}[P_e]} \tag{112b}$$

Substituting these in Eq. 107, one obtains

$$\frac{d\lambda_2}{dt} = k_p[M]\{[P] + [P_e]\} + 2k_p[M]\sum_{n=1}^{\infty} n[P_n] \tag{113}$$

Similarly, it can be found that

$$\frac{d\lambda_0}{dt} = 2fk_I[I_2] \tag{114}$$

and

$$\frac{d\lambda_1}{dt} = k_p[M]\{[P] + [P$$

Driscoll and coworkers [82 have solved these equation 115, the number and weigh 108, k_{te} and γ are compu conversion is obtained by i polymerization given in Ta experimental values of co theory is found to describe

Table 8 Parameters for the I Methyl Methacrylate

Parameter	
$k_p\,(fk_I/k_t)^{1/2}$	7.5 ×
k_t/k_p^2 (mol-sec L^{-1})	28
k_t (sec^{-1})	3.5 ×
K_c	8.97
α_p	1.11
$1/f$	0.159

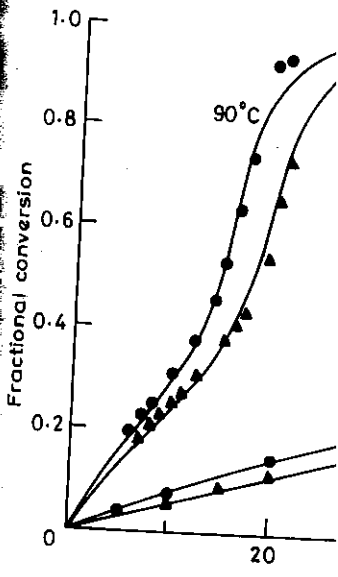

Figure 15 Experimental and pred methyl methacrylate $[I_2]_0$ for (●) 0. John Wiley and Sons, New York.)

and

$$\frac{d\lambda_1}{dt} = k_p[\mathrm{M}]\{[\mathrm{P}] + [\mathrm{P}_e]\} \tag{115}$$

Driscoll and coworkers [82] have treated K_c and $d_{e\theta}$ in Eqs. 106 and 108 as parameters and have solved these equations simultaneously. From the moments calculated by Eqs. 113–115, the number and weight average molecular weights can be found. Using Eqs. 107 and 108, k_{te} and γ are computed. On substituting these in Eq. 103, the next incremental conversion is obtained by integration. For the set of parameters for methyl methacrylate polymerization given in Table 8, these equations have been integrated and compared with experimental values of conversion and molecular weights in Figures 15 and 16. The theory is found to describe the experimental data very well.

Table 8 Parameters for the Radical Polymerization of Methyl Methacrylate

Parameter	Temperature (°C)	
	70	90
$k_p\,(fk_I/k_t)^{1/2}$	7.5×10^{-4}	3.8×10^{-3}
k_t/k_p^2 (mol-sec L^{-1})	28	16
k_I (sec^{-1})	3.5×10^{-5}	5.0×10^{-4}
K_c	8.97	5.69
α_p	1.11×10^{-1}	1.67×10^{-1}
$1/f$	0.1596	0.1731

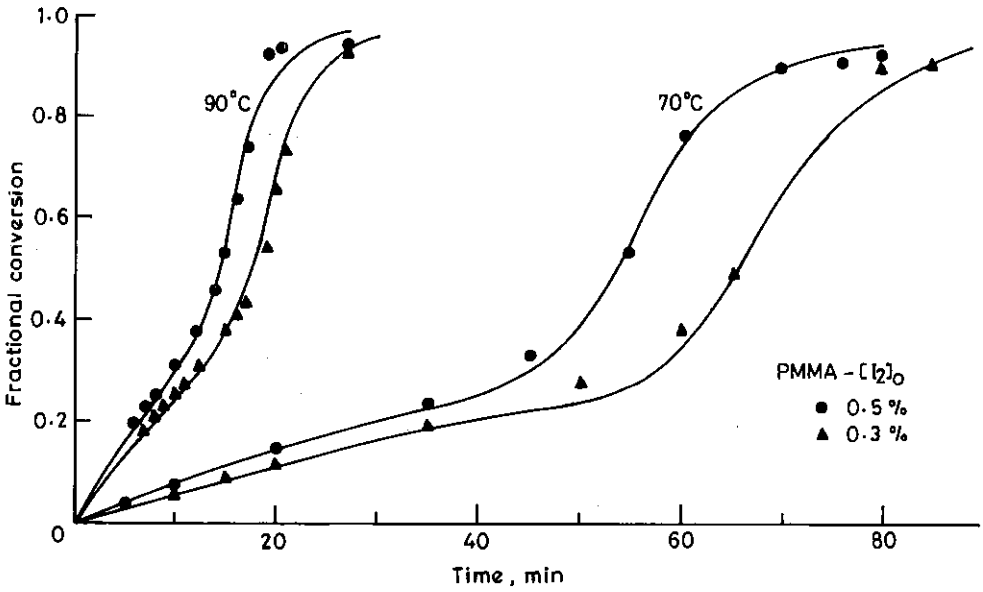

Figure 15 Experimental and predicted values of conversion versus time of polymerization for methyl methacrylate $[I_2]_0$ for (●) 0.5% and (▲) 0.3%. (Reprinted from Ref. 82, with permission of John Wiley and Sons, New York.)

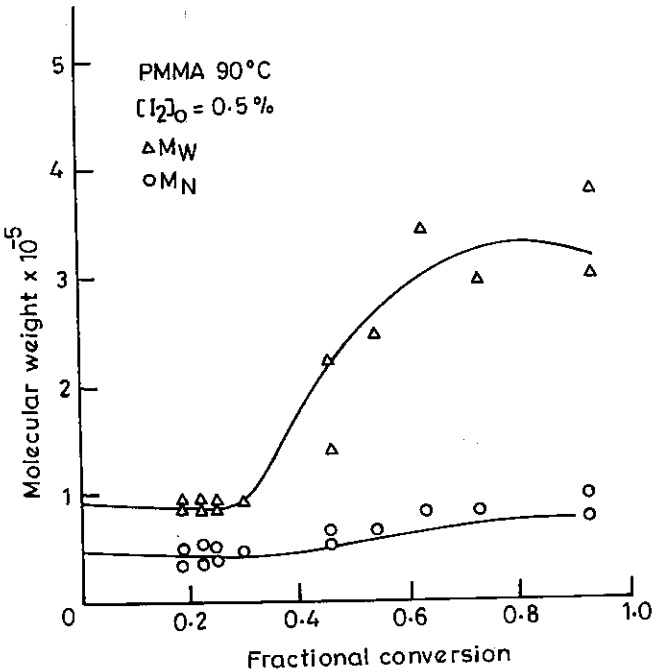

Figure 16 Experimental and predicted values of molecular weight versus fractional conversion for methyl methacrylate with initiator concentration 0.5%. (Reprinted from Ref. 82, with permission of John Wiley and Sons, New York.)

Temperature Effects in Radical Polymerization

In the initial stages (i.e., before the gel effect sets in) the temperature dependence of various rate constants can be expressed through the Arrhenius law:

$$k_I = k_{I0}e^{-E_I/RT}$$
$$k_p = k_{p0}e^{-E_p/RT}$$
$$k_t = k_{t0}e^{-E_t/RT}$$

In this representation, E_I, E_p, and E_t are activation energies of the initiation, propagation, and termination steps respectively and are tabulated extensively in polymer handbooks [76]. The temperature dependence of r_p and μ_n can be derived as

$$r_p = \frac{k_{p0}k_{I0}^{1/2}}{k_{t0}^{1/2}} \exp\left(-\frac{E_p - E_t/2 + E_I/2}{RT}\right)\{f[\mathrm{I_2}]^{1/2}[\mathrm{M}]\}$$

$$\mu_n = \frac{k_{p0}}{2k_{I0}^{1/2}f^{1/2}k_{t0}^{1/2}} \frac{[\mathrm{M}]}{[\mathrm{I_2}]^{1/2}} \exp\left(-\frac{E_p - E_I/2 - E_t/2}{RT}\right)$$

The activation energies are such that the overall polymerization for thermally dissociating initiator is exothermic, i.e., $(E_p - E_t/2 + E_p/2)$ is positive and rate increases with temperature. As opposed to this, $\{E_p - E_I/2 - E_t/2\}$ is normally negative for such cases and μ_n decreases with increasing temperature.

After the gel point sets in, the temperature dependence of k_p and k_t can be modeled by

$$k_p = k_{p0} \exp\left\{-E\left(\frac{1}{V_F} - \frac{1}{V_{Fc1}}\right)\right\}$$

$$k_t = k_{t0}\left(\frac{\mu_{wc}}{\mu_w}\right)^{1.75} \exp\left\{-A\left(\frac{1}{V_F} - \frac{1}{V_{Fc2}}\right)\right\}$$

where A and B are constants, whereas V_F is free volume fraction defined as

$$V_F = \{0.025 + \alpha_P(T - T_{gP})\}\frac{V_P}{V_T} + \{0.025 + \alpha_M(T - T_{gM})\}\frac{V_M}{V_T}$$
$$+ \{0.025 + \alpha_S(T - T_{gS})\}\frac{V_S}{V_T}$$

In these equations, subscripts P, M, and S denote polymer, monomer, and s respectively. T is the polymerization temperature, T_g is the glass transition temp and α_g is the thermal expansion coefficient for the glassy state. V_{Fc2} is determined point where the gel point starts and is given by

$$K_c = \mu_\omega^{0.5} \exp\left(\frac{A}{V_{Fc2}}\right)$$

V_{Fc1} is determined by the point where the propagation rate constant becomes di controlled. V_T is the specific volume of the reaction mass.

REVERSIBLE RADICAL POLYMERIZATION

All polymerization reactions are reversible and have an equilibrium for a given ture at which point the Gibbs free energy is zero. In the preceding section, reaction steps were assumed to be irreversible in radical polymerization, which serve as good approximation only for low temperatures. Let us first consider the dy dynamic equilibrium for addition polymerization before presenting the kinetic made for reversible addition polymerization.

It is assumed that the formation of the polymer can be represented by

$$n\mathrm{M} \rightleftharpoons \mathrm{M}_n$$

which states that n monomer molecules combine to form a polymer molecule of length n. The change in the Gibbs free energy ΔG for this process is defined by

$$\Delta G = \frac{1}{n}G_{\text{polymer}} - G_{\text{monomer}}$$
$$= \left(\frac{1}{n}H_{\text{polymer}} - H_{\text{monomer}}\right) - T\left(\frac{1}{n}S_{\text{polymer}} - S_{\text{monomer}}\right)$$
$$\triangleq \Delta H_p - T\Delta S_p$$

where H and S represent enthalpy and entropy and ΔH_p and ΔS_p are the change enthalpy and entropy of polymerization per monomer unit, respectively.

Almost all addition polymerizations are exothermic. Moreover, polymerization is process of joining monomer molecules by covalent bonds, something equivalent to

After the gel point sets in, the temperature dependence of k_p and k_t can be represented by

$$k_p = k_{p0} \exp\left\{-E\left(\frac{1}{V_F} - \frac{1}{V_{Fc1}}\right)\right\}$$

$$k_t = k_{t0}\left(\frac{\mu_{wc}}{\mu_w}\right)^{1.75} \exp\left\{-A\left(\frac{1}{V_F} - \frac{1}{V_{Fc2}}\right)\right\}$$

where A and B are constants, whereas V_F is free volume fraction defined as

$$V_F = \{0.025 + \alpha_P(T - T_{gP})\}\frac{V_P}{V_T} + \{0.025 + \alpha_M(T - T_{gM})\}\frac{V_M}{V_T} + \{0.025 + \alpha_S(T - T_{gS})\}\frac{V_S}{V_T}$$

In these equations, subscripts P, M, and S denote polymer, monomer, and solvent, respectively. T is the polymerization temperature, T_g is the glass transition temperature, and α_g is the thermal expansion coefficient for the glassy state. V_{Fc2} is determined by the point where the gel point starts and is given by

$$K_c = \mu_\omega^{0.5} \exp\left(\frac{A}{V_{Fc2}}\right)$$

V_{Fc1} is determined by the point where the propagation rate constant becomes diffusion controlled. V_T is the specific volume of the reaction mass.

REVERSIBLE RADICAL POLYMERIZATION

All polymerization reactions are reversible and have an equilibrium for a given temperature at which point the Gibbs free energy is zero. In the preceding section, various reaction steps were assumed to be irreversible in radical polymerization, which would serve as good approximation only for low temperatures. Let us first consider the thermodynamic equilibrium for addition polymerization before presenting the kinetic model made for reversible addition polymerization.

It is assumed that the formation of the polymer can be represented by

$$n\mathrm{M} \rightleftharpoons \mathrm{M}_n \tag{116}$$

which states that n monomer molecules combine to form a polymer molecule of chain length n. The change in the Gibbs free energy ΔG for this process is defined by

$$\begin{aligned}\Delta G &= \frac{1}{n} G_{\text{polymer}} - G_{\text{monomer}} \\ &= \left(\frac{1}{n} H_{\text{polymer}} - H_{\text{monomer}}\right) - T\left(\frac{1}{n} S_{\text{polymer}} - S_{\text{monomer}}\right) \\ &\triangleq \Delta H_p - T\Delta S_p \end{aligned} \tag{117}$$

where H and S represent enthalpy and entropy and ΔH_p and ΔS_p are the changes in enthalpy and entropy of polymerization per monomer unit, respectively.

Almost all addition polymerizations are exothermic. Moreover, polymerization is the process of joining monomer molecules by covalent bonds, something equivalent to the

stringing of beads into a necklace, the final state being more ordered and consequently having a lower entropy. Thus ΔS_p is always negative and is normally a large negative number, which cannot be neglected. Equation 117 therefore suggests that there is a ceiling temperature T_c at which the addition polymerization is at equilibrium (or $\Delta G = 0$), i.e.,

$$T_c = \frac{\Delta H_p}{\Delta S_p} \tag{118}$$

For a given monomer concentration [M], ΔS in this equation is equal to

$$\Delta S_p = \Delta S_p^0 + R \ln [\mathrm{M}] \tag{119}$$

where ΔS_p^0 is the entropy change when the polymerization is carried out at standard state and is independent of [M]. The standard state of a liquid monomer is defined to be that at which monomer concentration is one molar at the temperature and pressure of the polymerization. If $[\mathrm{M}]_e$ is the monomer concentration at equilibrium, then

$$\ln [\mathrm{M}]_e = \frac{\Delta H_p^0}{RT} - \frac{\Delta S_p^0}{R} \tag{120}$$

where ΔH_p is the same as ΔH_p^0 by definition. As an example, for styrene being polymerized at 60°C, ΔH_p^0 is 16,700 cal mol^{-1} and ΔS^0 25 cal mol-K^{-1}. $[\mathrm{M}]_e$ for styrene at 60°C is given by

$$[\mathrm{M}]_e = \exp\left\{-\frac{16{,}700}{1.987(273 + 60)} + \frac{25}{1.987}\right\} = 3.7 \times 10^{-6} \text{ mol L}^{-1} \tag{121}$$

It is thus seen that at 60°C, polymerization would go to complete conversion. Polystyrene has a ceiling temperature of 670 K and as the polymerization temperature approaches this value, various reaction steps would become reversible and the analysis of the preceding section must be modified as follows.

In the irreversible mechanism of radical polymerization given in Table 7, the propagation step has considerably lower activation energies. Consequently, this step would become reversible first and the polymerization then can be represented as follows.

Initiation:

$$\mathrm{I}_2 \xrightarrow{k_1} 2\mathrm{I} \tag{122a}$$

$$\mathrm{M} + \mathrm{I} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{P}_1 \tag{122b}$$

Propagation:

$$\mathrm{P}_n + \mathrm{M} \underset{k_p'}{\overset{k_p}{\rightleftharpoons}} \mathrm{P}_{n+1} \tag{123}$$

Termination:

$$\mathrm{P}_n + \mathrm{P}_m \xrightarrow{k_{td}} \mathrm{M}_n + \mathrm{M}_m, \qquad n \geq 1 \tag{124a}$$

$$\mathrm{P}_n + \mathrm{P}_m \xrightarrow{k_{tc}} \mathrm{M}_{n+m} \qquad n \geq 1 \tag{124b}$$

$$\mathrm{P}_n + \mathrm{S} \xrightarrow{k_{tr,S}} \mathrm{P}_1 + \mathrm{M}_n$$

$$\mathrm{P}_n + \mathrm{M} \xrightarrow{k_{tr,M}} \mathrm{P}_1 + \mathrm{M}_n$$

Reactions in Eq. 124c and
molecule or any transfer age
approximation is assumed t

$$\frac{d[\mathrm{P}_1]}{dt} = k_1[\mathrm{M}][\mathrm{I}] - k_1[$$

$$+ k_{tr,S}[\mathrm{S}] \sum_{n=2}^{\infty} [$$

$$\frac{d[\mathrm{P}_2]}{dt} = k_p[\mathrm{M}]\{[\mathrm{P}_1] - [$$

$$- \{k_t[\mathrm{P}] + k_{tr,M}$$

$$\frac{d[\mathrm{P}_n]}{dt} = k_p[\mathrm{M}]\{[\mathrm{P}_{n-1}] -$$

$$- \{k_t[\mathrm{P}] + k_{tr,M}$$

where

$$k_t = k_{tc} + k_{td}$$

and

$$[\mathrm{P}] = \sum_{i=1}^{\infty} [\mathrm{P}_i]$$

On adding all relations from

$$\frac{d\Sigma_{n=2}^{\infty}[\mathrm{P}_n]}{dt} = 0 = k_p[\mathrm{M}][$$

$$- \{k_t[\mathrm{P}] +$$

or

$$\sum_{n=2}^{\infty} [\mathrm{P}_n] = \frac{k_p[\mathrm{M}}{k_t[\mathrm{P}] + k_{tr,M}[\mathrm{M}}$$

$$- \frac{}{k_t[\mathrm{P}] + k_{tr,M}}$$

$$P_n + S \xrightarrow{k_{tr,S}} P_1 + M_n \qquad n \geq 2 \tag{124c}$$

$$P_n + M \xrightarrow{k_{tr,M}} P_1 + M_n \qquad n \geq 2 \tag{124d}$$

Reactions in Eq. 124c and d are transfer reactions, which can occur to a monomer molecule or any transfer agent that may be present in the reaction mass. If the steady-state approximation is assumed to hold, the mole balance for P_n is given by

$$\frac{d[P_1]}{dt} = k_1[M][I] - k_1[P_1] - k_p[M][P_1] + k_p'[P_2] + k_{tr,M}[M]\sum_{n=2}^{\infty}[P_n] + k_{tr,S}[S]\sum_{n=2}^{\infty}[P_n] - (k_{tc} + k_{td})[P_1][P] = 0$$

$$\frac{d[P_2]}{dt} = k_p[M]\{[P_1] - [P_2]\} + k_p'\{[P_3] - [P_2]\} - \{k_t[P] + k_{tr,M}[M] + k_{tr,S}[S]\}[P_2] = 0$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\frac{d[P_n]}{dt} = k_p[M]\{[P_{n-1}] - [P_n]\} + k_p'\{[P_{n+1}] - [P_n]\} - \{k_t[P] + k_{tr,M}[M] + k_{tr,S}[S]\}[P_n] = 0 \tag{125}$$

$$\vdots \qquad \vdots \qquad \vdots$$

where

$$k_t = k_{tc} + k_{td} \tag{126a}$$

and

$$[P] = \sum_{i=1}^{\infty}[P_i] \tag{126b}$$

On adding all relations from P_2 on, one gets

$$\frac{d\Sigma_{n=2}^{\infty}[P_n]}{dt} = 0 = k_p[M][P_1] - k_p'[P_2] - \{k_t[P] + k_{tr,}M[M] + k_{tr,S}[S]\}\sum_{n=2}^{\infty}[P_n] \tag{127}$$

or

$$\sum_{n=2}^{\infty}[P_n] = \frac{k_p[M]}{k_t[P] + k_{tr,M}[M] + k_{tr,S}[S]}[P_1] - \frac{k_p'}{k_t[P] + k_{tr,M}[M] + k_{tr,S}[S]}[P_2] \tag{128}$$

Substituting this in the balance for P_1, one has

$$\frac{d[P_1]}{dt} = k_1[M][I] - k_1'[P_1] + k_{tr,S}[S][P] + k_{tr,M}[M][P] + k_p'[P_2] \tag{129}$$

Balance for [I] combined with the steady-state hypothesis yields

$$\frac{d[I]}{dt} = 0 - 2fk_1[I_2] + k_1'[P_1] - k_1[M][I] = 0 \tag{130}$$

On adding all balance relations, one obtains [P] as

$$\frac{d[P]}{dt} = 0 = k_1[M][I] - k_t[P_1] - k_t[P]^2 \tag{131}$$

If we substitute

$$\alpha = k_p u[M] \tag{132a}$$
$$\beta = k_p' \tag{132b}$$
$$\gamma = k_p[M] + k_p' + k_{tr,M}[M] + k_{tr,S}[S] + k_t[P] \tag{132c}$$
$$\theta = {}_{tr,M}[M] + k_{tr,S}[S] + k_t[P] \tag{132d}$$

Eq. 125 reduces to the set of algebraic equations given in Eq. A1 in the appendix. Then in terms of P_1, P_n can be determined as

$$[P_n] = [P_1](\alpha x_\infty)^{n-1} \tag{133}$$

But

$$[P] = \sum_{n=1}^{\infty} [P_n] = [P_1]\{1 + \alpha x_\infty + (\alpha x_\infty) + \cdots\} = \frac{[P_1]}{(1 - \alpha x_\infty)}$$

or

$$[P_1] = (1 - \alpha x_\infty)[P] \tag{134}$$

Equation 133 therefore reduces to

$$[P_n] = [P](1 - \alpha x_\infty)(\alpha x_\infty)^{n-1} \tag{135}$$

The mole balance of inactive polymer M_n is given by

$$\frac{d[M_n]}{dt} = \{k_{tr,M}[M] + k_{tr,S}[S] + k_{td}[P]\}[P_n] + \frac{k_{tc}}{2}\sum_{r=1}^{n-1}[P_r][P_{n-r}] \tag{136}$$

One defines the following kth moment of M_n distributions as

$$\lambda_k = \sum_{1}^{\infty} n^k[M_n] \tag{137}$$

and the moment generation relations for λ_0, λ_1, and λ_2 can be easily derived as

$$\frac{d\lambda_0}{dt} = \{k_{tr,S}[S] + k_{tr,M}[M] + k_{td}[P]\}(1 - \alpha x_\infty)[P]\frac{\alpha x_\infty}{1 - \alpha x_\infty} + \frac{1}{2}k_{tc}[P]^2 \tag{138a}$$

$$\frac{d\lambda_1}{dt} = \{k_{tr,S}[S] + k_{tr,M}[$$

$$\frac{d\lambda_2}{dt} = \{k_{tr,S}[S] + k_{tr,M}[$$

$$+ k_{tc}[P_1]^2 \qquad \frac{}{(1$$

Equations 138 reveal that
polymerization are a functi
constant. Irreversible polym
comparison with Eqs. 138, it
to that seen in these equatic
defined as

$$\alpha^* = \frac{k_p[}{k_p[M] + k_{tr,}S[S] +}$$

It can be shown that as $k_p' \rightarrow$
most general form of the resu

CONCLUSIONS

Polymerization can in general
chapter it is observed that pol
ible. In any reasonable modeli

Step growth polymerizatio
chains, whereas for that of n
polymer is either branched o
bifunctional monomers has be
tion, the MWD equations can
ically. The reversible polymer
after the reaction of branched n
the number of sites on a P_r mo
been denoted by $\delta_{r\rightarrow n}$ and it is
tional polymerization involves
there is a computer program tha
Numerical solution of the MV
formed is higher than that of th

Chain growth polymerizatio
nism, and the discussion is focu
shown that radical polymerizati
nation. If the polymerization is
essentially irreversible and can b
are separated by a gel point. Be
diffusion controlled and there is
high rate of polymerization with
the polymer. The overall polym
librium but by the occurrence of

$$\frac{d\lambda_1}{dt} = \{k_{tr,S}[S] + k_{tr,M}[M] + k_{td}[P]\}[P_1]\frac{(\alpha x_\infty)(2 - \alpha x_\infty)}{(1 - \alpha x_\infty)^2} + \frac{k_{tc}[P_1]^2}{(1 - \alpha x_\infty)^3} \tag{138b}$$

$$\frac{d\lambda_2}{dt} = \{k_{tr,S}[S] + k_{tr,M}[M] + k_{td}[P]\}[P_1]\frac{4(\alpha x_\infty) - 3(\alpha x_\infty)^2 + (\alpha x_\infty)^3}{(1 - \alpha x_\infty)^3} + k_{tc}[P_1]^2 \quad \frac{2 + \alpha x_\infty}{(1 - \alpha x_\infty)^4} \tag{138c}$$

Equations 138 reveal that the moments of the polymer formed by reversible radical polymerization are a function of a term (αx_∞) in which x_∞ involves the reverse rate constant. Irreversible polymerization has been completely analyzed in the literature. On comparison with Eqs. 138, it is found that irreversible polymerization has a form identical to that seen in these equations if (αx_∞) is replaced by probability of propagation, α^*, defined as

$$\alpha^* = \frac{k_p[M]}{k_p[M] + k_{tr,S}[S] + k_{tr,M}[M] + k_t[P]} \tag{139}$$

It can be shown that as $k_p' \to 0$, (αx_∞) reduces to α^* and in this regard Eqs. 138 give the most general form of the result.

CONCLUSIONS

Polymerization can in general be classified as step growth and chain growth type. In this chapter it is observed that polymer formation, like any other reaction in nature, is reversible. In any reasonable modeling, this must be taken into account.

Step growth polymerization of bifunctional monomers leads to the formation of linear chains, whereas for that of monomers having functionality more than 2, the resultant polymer is either branched or network. The reversible step growth polymerization of bifunctional monomers has been modeled and it is shown that under a certain transformation, the MWD equations can be decoupled and are considerably easier to solve numerically. The reversible polymerization of multifunctional monomers can be modeled only after the reaction of branched molecules is written. In order to do that, one needs to know the number of sites on a P_r molecule whcih would give P_n $(n < r)$ on cleavage. This has been denoted by $\delta_{r\to n}$ and it is shown that the MWD equations for reversible multifunctional polymerization involves this factor. $\delta_{r\to n}$ is dependent on the chain structure, and there is a computer program that gives the value for specified chain length and structure. Numerical solution of the MWD shows that the polydispersity index of the polymer formed is higher than that of the polymer formed through irreversible mechanism.

Chain growth polymerization can occur through an ionic as well as a radical mechanism, and the discussion is focused on the latter in view of its industrial importance. It is shown that radical polymerization involves three steps: initiation, propagation, and termination. If the polymerization is carried out at low temperatures, the polymerization is essentially irreversible and can be roughly divided into initial and advanced stages which are separated by a gel point. Beyond the gel point the termination rate constants become diffusion controlled and there is a considerable drop in magnitude, which gives a very high rate of polymerization with a corresponding increase in the average chain length of the polymer. The overall polymerization at low temperatures is not limited by the equilibrium but by the occurrence of a glass state of the reaction mass. To control molecular

weight in radical polymerization, one is forced to use high temperatures to suppress the formation of the undesirable glassy state, but some of the reaction steps then become reversible. A kinetic scheme for radical polymerization has been discussed and analyzed for the average chain length and the polydispersity index of polymerization.

APPENDIX: ANALYTICAL SOLUTION OF ALGEBRAIC EQUATIONS INVOLVED IN ADDITION POLYMERIZATION

Let us consider the following infinite set of algebraic equations which must be solved for p_n for all n:

$$\frac{p_2}{\theta} = \frac{p_{20}}{\theta} + \alpha(p_1 - p_2) + \beta(p_3 - p_2)$$

$$\frac{p_3}{\theta} = \frac{p_{30}}{\theta} + \alpha(p_2 - p_3) + \beta(p_4 - p_3)$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$\frac{p_n}{\theta} = \frac{p_{n0}}{\theta} + (P_{n-1} - P_n) + (p_{n+1} - p_n) \tag{A1}$$

where p_{i0} (for $i = 1,2,3, \ldots$), α, θ, and β are constants.

In order to solve for p_n for all n, it is assumed that p_{N_1+1} is known precisely, where N_1 is any integer greater than 2. Equation A1 yields p_{N_1} as

$$p_{N_1} = x_{N_1}P_{N_1-1} + y_{N_1}P_{N_1} + \frac{1}{\theta}Z_{N_1N_1}P_{N_10} \tag{A2}$$

where

$$x_{N_1} = \frac{1}{\gamma} \tag{A3a}$$

$$y_{N_1} = \frac{1}{\gamma} \tag{A3b}$$

$$Z_{N_1N_1} = \frac{1}{\gamma} \tag{A3c}$$

$$\gamma = \left(\alpha + \beta + \frac{1}{\theta}\right) \tag{A3d}$$

The expression for p_{N_1-1} involves p_{N_1}, which can be eliminated using Eq. A2. This way p_{N_1-1} can be written in terms of p_{N_1-2} and p_{N_1+1}. Proceeding in this way, it is possible to derive for any n ($< N_1$)

$$p_n = \alpha x_n p_{n-1} + \beta y_n p_{N_1+1} + \frac{1}{\theta}\sum_{i=n}^{N_1} Z_{in}p_{i0} \tag{A4}$$

where

$$x_n = \frac{1}{\gamma - \alpha\beta x_{n+1}} \tag{A5a}$$

$$y_n = \frac{\beta y_{n+1}}{\gamma - \alpha\beta x_{n+1}} =$$

$$Z_{in} = \begin{cases} x_n \\ \dfrac{\gamma}{\beta}\, y_{N_1+n-i} \\ y_n \end{cases}$$

Proceeding this way, it is p

We next examine the pr

Eq. A5a can be written in t

$$\lim_{N_1 \to \infty,\ n \ll N_1} x_n \triangleq x_\infty = \frac{}{\gamma -}$$

As $N_1 \to \infty$, x_n for $n \ll N_1$ a

gives

$$x_\infty = \frac{1}{\gamma - \dfrac{1}{\gamma_1 - x_\infty}}$$

where

$$\gamma_1 = \frac{\gamma}{\alpha\beta}$$

Equation A7 can be solved f

$$x_\infty = \frac{\gamma - \sqrt{\gamma^2 - 4\alpha\beta}}{2\alpha\beta}$$

where the lower root serves a

To study the properties of

first recognized that no matte

unity:

$$\beta x_\infty = \beta\frac{\gamma}{2\alpha\beta}\left\{1 - \sqrt{1 -}\right.$$

$$= \left(\frac{\gamma}{2\alpha}\right)\left\{\frac{1}{2}\,\frac{2\alpha}{\gamma}\,\frac{2\beta}{\gamma} +\right.$$

i.e., since α/γ and β/γ both a

recalled from Eq. A5 that $y_n =$

$x_n = x_\infty$ is a good approximati

$$y_{n-i} = y_n^*(\beta x_\infty)^i, \qquad i = 1,$$

Since $(\beta x_\infty) < 1$, y_n can be m

large. Furthermore, as $N_1 \to \infty$

$$y_n = \frac{\beta y_{n+1}}{\gamma - \alpha\beta x_{n+1}} = \frac{1}{\beta}\prod_{i=n}^{N_1}(\beta x_i), \qquad 2 \le n \le N \tag{A5b}$$

$$Z_{in} = \begin{cases} x_n & \text{for } i = n \\ \dfrac{\gamma}{\beta}\, y_{N_1+n-i} & \text{for } n+1 \le i \le N_1 - 1 \\ y_n & \text{for } i = N_1 \end{cases} \tag{A5c}$$

Proceeding this way, it is possible to determine p_1 in terms of p_{N_1+1}.

We next examine the properties of the solution as N_1 approaches ∞. The value of x_n in Eq. A5a can be written in the form of an infinite successive fraction as

$$\lim_{\substack{N_1 \to \infty \\ n \ll N_1}} x_n \triangleq x_\infty = \cfrac{1}{\gamma - \cfrac{\alpha\beta}{\gamma - \cfrac{\alpha\beta}{\gamma - \cfrac{\alpha\beta}{\gamma - \cdots}}}} \tag{A6}$$

As $N_1 \to \infty$, x_n for $n \ll N_1$ approaches an asymptotic value independent of n, and Eq. A6 gives

$$x_\infty = \cfrac{1}{\gamma - \cfrac{1}{\gamma_1 - x_\infty}} \tag{A7}$$

where

$$\gamma_1 = \frac{\gamma}{\alpha\beta} \tag{A8}$$

Equation A7 can be solved for x_∞ as

$$x_\infty = \frac{\gamma - \sqrt{\gamma^2 - 4\alpha\beta}}{2\alpha\beta} \tag{A9}$$

where the lower root serves as a physically relevant quantity.

To study the properties of the infinite continued fraction formed by y_n in Eq. A5, it is first recognized that no matter what the values of α, β, and θ, βx_∞ is always less than unity:

$$\begin{aligned} \beta x_\infty &= \beta\frac{\gamma}{2\alpha\beta}\left\{1 - \sqrt{1 - \frac{2\alpha}{\gamma}\frac{2\beta}{\gamma}}\right\} \\ &= \left(\frac{\gamma}{2\alpha}\right)\left\{\frac{1}{2}\frac{2\alpha}{\gamma}\frac{2\beta}{\gamma} + 0\left(\frac{\alpha^2}{\gamma_2}\frac{\beta^2}{\gamma_2}\right)\right\} = \frac{\beta}{\gamma} + 0\left(\frac{\alpha^2}{\gamma^2}\frac{\beta^2}{\gamma^2}\right) \end{aligned} \tag{A10}$$

i.e., since α/γ and β/γ both are less than unity, (βx_∞) is always less than unity. If it is recalled from Eq. A5 that $y_n = y_{n+1}(\beta x_\infty)$ and if we denote by y_n^* the value of n at which $x_n = x_\infty$ is a good approximation, then y_{n-1}, y_{n-2}, etc., can be written as

$$y_{n-i} = y_n^*(\beta x_\infty)^i, \qquad i = 1,2, \ldots, n-1 \tag{A11}$$

Since $(\beta x_\infty) < 1$, y_n can be made sufficiently close to zero by choosing N_1 sufficiently large. Furthermore, as $N_1 \to \infty$ and $n \ll N_1$, the following are also true:

$$Z_n \to x_\infty \tag{A12a}$$

$$Z_{N_1 n} \to 0 \tag{A12b}$$

or more generally

$$Z_{in} \to x_\infty(\beta x_\infty)^{i-n}, \qquad \text{for } n \leq i \tag{A13}$$

As $N_1 \to \infty$, p_n in Eq. A1 is given by

$$p_n = \frac{x}{\theta} \sum_{i=n}^{\infty} (\beta x_\infty)^{i-n} p_{i0} + (\alpha x_\infty) p_{n-1} \tag{A14}$$

and this gives p_n for all n in Eq. A1 as follows. Using this, p_2 is written in terms of p_1, which is substituted in the relation of p_1, and p_n is determined by successively evaluating p_2, p_3, etc.

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