# Modelling of intramolecular reactions in the step-growth polymerization of multifunctional monomers

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A general kinetic model for the polymerization of multifunctional monomers $RY_f$ valid up to the gel point has been presented, which accounts for the intramolecular reactions. In this model, various molecular species have been distinguished on the basis of the total number of intramolecular bonds existing on them. Various reactions leading to formation and depletion of a molecular species of given degree of polymerization are identified and the differential mole balance equations for these have been written down. The intramolecular rate constant has been assumed to be that proposed by Platé and Noah (based on their Monte Carlo studies of intramolecular reactions) and the various mole balances have been solved numerically. Numerical computations confirm that, as the gel point is approached, larger polymer chains are formed and these have a higher tendency to react intramolecularly. However, even at high conversions, the average number of rings per polymer chain remains small, which is consistent with experimentally observed results.

**(Keywords: step-growth polymerization; multifunctional monomers; intramolecular reactions; batch reactors; cyclic polymerization; gelation)**

## INTRODUCTION

There are several industrially important systems (e.g. polyesters from adipic acid or phthalic anhydride and glycerol or pentaerythritol (alkyd resins); curing of epoxy prepolymers with diamines; curing of phenol formaldehyde polymers with hexamethylene tetramine; etc.) that involve the use of compounds with functionalities larger than 2. In these polymerizations, branched molecules are formed at low conversions of functional groups. At some definite conversion, some of these branched molecules are found to convert into an infinite network structure of macroscopic dimensions, called a gel. This phenomenon occurs long before the functional groups are completely consumed, and the point at which it 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 up through it.

The study of nonlinear step-growth polymerizations is more complex than the linear case, and several alternative approaches have been taken by different workers in this area to model the process. Flory[1-3] and Stockmayer[4-7] have approached the problem by determining the probabilities of finding various branched molecular structures in the reaction mass. Thereafter, they have 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. Gordon and coworkers[8-15] have used the theory of stochastic branching processes, also called cascade theory, with vectorial probability generating functions. The molecular weight averages can be directly determined using this approach without first determining the molecular weight distribution, but the technique is conceptually very complex and is tedious to apply to systems of practical importance. These techniques, however, are easier to use than the earlier theories of Flory and Stockmayer, particularly for more complex polymerization systems. The rate theory proposed by Stanford and Stepto[16-19] considers the subsets of states of monomer units but adopts the traditional statistical approach of Flory. One defines the existence probabilities of molecular species rather than those of structural units in terms of functional groups. Given the existence probabilities of molecular species in terms of the extent of reaction, the rate theory evaluates the rates at which the species interconvert as functions of the extent of reaction. Intramolecular reaction has been introduced as a perturbation to the resulting set of independent differential equations with the sum of existence probabilities normalized to unity. The technique proposed by Macosko, Miller and coworkers[20-24] is of more recent origin, is easier conceptually as well as mathematically, and yields results that are identical to those obtained using the method of Gordon and coworkers. The kinetic approach has also been used recently[25-32] to predict chain length distributions and the onset of gelation, both for batch reactors[25,27,28] as well as for homogeneous continuous-flow stirred tank reactors (HCSTRs)[29-32]. The kinetic approach is particularly well suited for modelling nonlinear polymerizations in HCSTRs. In fact, probabilistic techniques have not yet been applied for this purpose. For batch reactors, the kinetic and probabilistic methods give identical results for most cases. Statistically speaking, however, these approaches are not equivalent because, in the kinetic

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approach, the integrity of the existing structures and information on the formation history is preserved; whereas, in the approach of Gordon and coworkers, where the *final* assembly of molecules is generated from building blocks, it is not. In fact, Mikes and Dusek[32] have shown, using a Monte Carlo method to simulate these systems in batch reactors that, even though in most cases these two techniques give virtually the same results, there are *some* special cases where they differ.

The experimental verification of the critical conversion for the onset of gelation in nonlinear polymerizations has been a subject of intensive research activity[25,33-40]. Recently, Stafford[25] has compiled the available information and has compared the results with theoretical predictions. It has been found that, even though in some systems the onset of gelation corresponds to the theoretically predicted conditions when $\bar{M}_w \to \infty$, results on several other systems are better explained if the critical point is defined *empirically* as that where $\bar{M}_n \to \infty$. However, this is theoretically the wrong basis for the gel point[41].

The deviation of experimental results from theoretical predictions in the pre-gel region has been attributed to the presence of intramolecular reactions[1,31,39]. Experimental results on an $R_1A_3+R_2B_2$ system[42] (poly(oxypropylene triol) + hexamethylene diisocyanate in bulk and in benzene at 70°C) and many other systems[43-48] reveal that the average number of ring structures per molecule increases with conversion but remains small all the way up to the gel point. The ultimate value of this quantity at the gel point, however, depends upon the chain flexibilities, molar masses and functionalities of the reactants[39]. Any meaningful modelling exercise must, therefore, account for intramolecular reactions. In fact, Stepto and coworkers[43,44] find that the properties of the network material formed can be markedly affected by these reactions.

Several attempts have been made to study the effect of intramolecular reactions theoretically, and these have been reviewed recently by Stepto[41]. Most of these studies[12,14,49] use the cascade theory. Experimental confirmation of these theoretical results, both for the gel point as well as for the variation of the average number of ring structures per molecule with conversion in the pre-gel region, is still to be made[41,43]. The kinetic approach has also been extended to account for intramolecular reactions in nonlinear polymerization[50]. Initial results of Temple[50] on $R_1A_3+R_2B_2$ systems, which were limited to very low conversion due to the complexity of the equations, reveal that the cascade theory underestimates the effect of intramolecular reactions, a discrepancy that has also been referred to by Mikes and Dusek[32] using Monte Carlo generation of polymer chains on the computer.

Two approaches have been taken in the literature to model the rate constants for intramolecular reactions[41]. In one approach, the rate of reaction $\mathscr{R}_{i,P_n}$, between two given functional groups located $i$ monomeric units apart in a molecule $P_n$, is written as[41,51,52]

$$\mathscr{R}_{i,P_n}=k[P_n]\left\{\frac{1}{i^{3/2}}\left(\frac{3}{2\pi \nu l^2}\right)^{3/2}\frac{1}{N_A}\right\}\equiv\frac{k[P_n]}{i^{3/2}}a \qquad (1)$$

where $k$ is the intrinsic reactivity of functional groups (and is the same as that used for intermolecular reactions) and $l$ is the backbone bond length. In equation (1) $\nu$ is the number of backbone bonds per monomeric unit (so that $\nu i$ is approximately the number of backbone bonds between the reacting functional groups) and $N_A$ is the Avogadro number.

In the second approach[53,54] the rate of removal of species $C_{n,j}$ by cyclization is written as $k[C_{n,j}]\bar{Z}_{n,j}$ and chains with intramolecular cycles are generated on a computer using the Monte Carlo technique to obtain $\bar{Z}_{n,j}$. Here $\bar{Z}_{n,j}$ is the probability that a molecule of chain length $n$ undergoes cyclization by intramolecular reaction of two functional groups separated by $j$ repeat units. There are several simplifying assumptions in deriving equation (1) that are overcome in this analysis. It was found that the results of this second approach could be fitted *empirically* by the following equation:

$$\bar{Z}_{n,j}=a(n)j+b(n) \qquad (2)$$

up to a certain value of $j$, where $a$ and $b$ are constants depending on $n$.

In this paper, an alternative and more rigorous method to account for the intramolecular reactions in $R_1A_f$ polymerization has been proposed. In this, one defines $A_n$, $B_n$, $C_n$, ... such that $A_n$ represents a molecule with $n$ $R_1A_f$ units without any rings due to intramolecular reactions and $B_n$, $C_n$, etc., represent molecules with $n$ $R_1A_f$ units, but having one, two, etc., rings respectively (irrespective of where they are placed) caused by intramolecular reactions. Mole balance equations can then be written for each of these species, keeping in mind that $A_n$ can cyclize (intramolecularly) to give $B_n$, it can react with $B_m$ (intramolecularly) to give $B_{m+n}$, in addition to reacting (intermolecularly) with $A_m$ to give $A_{n+m}$. Similarly, the various $B_n$, $C_n$, etc., can cyclize (intramolecularly) to give $C_n$, $D_n$, etc., or react (intermolecularly) with $C_m$ to give molecules with a higher number of rings. The rate constants for intramolecular reaction have been chosen according to equation (2) and the mole balance equations written for various species in the reaction mass. The analysis presented in this paper can be easily extended to the polymerization of a mixture of monomers. Lastly the theory presented in this work does not account for the detailed molecular structure of chains, like for example the various isomers of the chain and the degree of branching. It is assumed that the reactivity of a given functional group is independent of the chain structure (i.e. degree of branching and isomer). In fact, in the framework of equal reactivity of functional groups, this assumption can always be made, even though the theory does not yield information on branching and isomers. Also cyclization is known to be affected by chain flexibility and is indirectly accounted for by the parameters $a$ and $b$ in $\bar{Z}_{n,j}$.

## KINETIC MODEL

In order to model the intramolecular reactions in step-growth polymerization of $RA_f$ monomers (with functional group A reacting with A), one defines the following molecular species:

$A_n$ = polymer chains with $n$ $RA_f$ units ($n=1, 2, 3, \ldots$) having no intramolecular bonds (3a)

$B_n$ = polymer chains with $n$ $RA_f$ units ($n \geqslant n_B$) having one intramolecular bond (3b)

$C_n$ = polymer chains with $n$ $RA_f$ units ($n \geqslant n_C$) having two intramolecular bonds (3c)
$D_n$ = polymer chains with $n$ $RA_f$ units ($n \geqslant n_D$) having three intramolecular bonds (3d)
$P_n$ = polymer chains with $n$ $RA_f$ units ($n \geqslant n_P$) having $p$ intramolecular bonds (3e)

Here it is assumed that the maximum number of cyclic bonds in the reaction mass is $p$. It may be recognized that intramolecular bond formation occurs only when two functional groups of the same polymer chain come close to one another and react. Evidently, chain flexibility plays a major role in this and there is a minimum chain length below which there can be no cyclization. For similar reasons, there is a minimum chain length of polymer in which two rings could be accommodated, and so on. In equations (3), $n_B, n_C, n_D \ldots n_P$ are such limits below which 1, 2, 3 ... $p$ rings respectively cannot be formed on the chain.

An attempt is now made to enumerate all possible reactions in terms of these molecular species. Whenever $A_n$ reacts with any *other* molecular species, there is an increase in chain length but there is no increase in the number of rings. Assuming all reactions as irreversible, one can write the reactions for the various species as:

$$A_m \xrightarrow{k_0, \bar{Z}_{m,0}} B_m \qquad m \geqslant n_B \tag{4a}$$

$$A_m + A_n \xrightarrow{k} A_{m+n} \qquad m, n \geqslant 1 \tag{4b}$$

$$A_m + B_n \xrightarrow{k} B_{m+n} \qquad m \geqslant 1, n \geqslant n_B \tag{4c}$$

$$A_m + C_n \xrightarrow{k} C_{m+n} \qquad m \geqslant 1, n \geqslant n_C \tag{4d}$$

$$\vdots$$

$$B_m \xrightarrow{k_0, \bar{Z}_{m,1}} C_m \qquad m \geqslant n_C \tag{5a}$$

$$B_m + C_n \xrightarrow{k} D_{m+n} \qquad m \geqslant n_B, n \geqslant n_C \tag{5b}$$

$$B_m + D_n \xrightarrow{k} E_{m+n} \qquad m \geqslant n_B, n \geqslant n_D \tag{5c}$$

where $k_0$ and $k$ are the rate constants for the intra- and intermolecular reactions and $\bar{Z}_{n,j}$ is the average number of reactive contacts in a molecule of chain length $n$ in the conformation between two functional groups situated $j$ intramolecular bonds apart. $\bar{Z}_{n,j}$ cannot be evaluated analytically because of the change in the chain statistics of the polymer molecule with the occurrence of every intramolecular bond. Based on Monte Carlo simulation, Platé and Noah have suggested equation (2) for $\bar{Z}_{n,j}$. In the kinetic model presented in equations (5), $j$ can take any value ranging from a minimum value (which largely depends upon the chain flexibility) to a maximum value. If this minimum value is approximated as 1 independent of the number of intramolecular bonds on the chain, $\bar{Z}_{n,j}$ can be averaged over all possible values of $j$. If $n$ is assumed to be large, such that the summation can be replaced by an integral, the average value of $\bar{Z}_{n,j}$, namely $\bar{Z}_n$, is given by

$$\bar{Z}_n = \tfrac{1}{2}g(n)(n+1) + h(n) \tag{6}$$

We have already stated that the maximum number of rings does not exceed $p$, which means that $P_n$ reacts with $A_m$ only and does not undergo any intramolecular reaction, i.e.

$$P_m + A_n \xrightarrow{k} P_{m+n} \qquad m \geqslant n_P \tag{7}$$

This is done for book-keeping purposes to ensure that all the reacting species are properly accounted for. Computations have shown that the average number of intramolecular bonds is usually not very large[40] and $p$ in practice can be chosen such that equation (7) does not introduce any significant error.

Using the reaction mechanism written in equations (4) to (7), it is possible to write down the mole balance equations for various species as follows. It is observed that two functional groups must react to form either an intra- or intermolecular linkage, which means that $A_n$, $B_n$, $C_n$, ... and $P_n$ must have $(nf-2n+2)$, $(nf-2n)$, $(nf-2n-2)$, ... and $(nf-2n+2-2p)$ unreacted functional groups respectively. For chain lengths $n \geqslant n_P$, the various mole balance equations can now be given.

For $n \geqslant n_P$:

$$\begin{aligned}\frac{d[A_n]}{dt} = {} & k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}] \\ & -2k(an+1)[A_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty} ai[B_i]\right. \\ & \left. + \sum_{i=n_C}^{\infty}(ai-1)[C_i] + \ldots + \sum_{i=n_P}^{\infty}(ai-p+1)[P_i]\right) \\ & -2k_0\bar{Z}_n[A_n]\end{aligned} \tag{8a}$$

$$\begin{aligned}\frac{d[B_n]}{dt} = {} & 2k_0\bar{Z}_n[A_n] - 2k_0\bar{Z}_n[B_n] \\ & +2k\sum_{r=1}^{n-n_B}(ar+1)a(n-r)[A_r][B_{n-r}] \\ & -2kan[B_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty} ai[B_i]\right. \\ & \left. + \sum_{i=n_C}^{\infty}(ai-1)[C_i] + \ldots + \sum_{i=n_O}^{\infty}(ai-o+1)[O_i]\right)\end{aligned} \tag{8b}$$

$$\begin{aligned}\frac{d[P_n]}{dt} = {} & 2k_0\bar{Z}_n[O_n] + 2k\sum_{r=1}^{n-n_P}(ar+1)\{a(n-r)-p+1\}[A_r][P_{n-r}] \\ & +2k\sum_{r=n_B}^{n-n_C} ar\{a(m-r)-o+1\}[B_r][O_{n-r}] + \ldots \\ & -2k(an-p+1)[P_n]\sum_{i=1}^{\infty}(ai+1)[A_i]\end{aligned} \tag{8c}$$

where

$$a = (f-2)/2 \tag{8d}$$

It has already been noted that there is a minimum chain length below which there is no cyclization. The following special condition arises when these minimum limits ($n_B$, $n_C$, $n_D$, etc.) are different. It has earlier been observed that the presence of cyclic rings changes the chain statistics, making it stiffer with increasing number of cyclic rings. It is therefore expected in general that $n_P > n_O > n_N > n_M > \ldots$. If there is a molecule $M_n$ whose chain length lies between $n_N$ and $n_M$, it cannot cyclize to form $N_n$. In the following equation, this special condition has been accounted for and the corresponding mole balance relations for $n_P > n > n_O$ can be given.

For $n_O < n < n_P$:

$$\frac{d[A_n]}{dt} = k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}] - 2k_0\bar{Z}_n[A_n] - 2k(an+1)[A_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i] + \ldots + \sum_{i=n_P}^{\infty}(ai-p+1)[P_i]\right) \quad (9a)$$

$$\frac{d[B_n]}{dt} = 2k_0\bar{Z}_n[A_n] + 2k\sum_{r=1}^{n-n_B}(ar+1)a(n-r)[A_r][B_{n-r}] - 2k\bar{Z}_n[B_n] - 2kan[B_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i] + \ldots\right) \quad (9b)$$

$$\frac{d[O_n]}{dt} = 2k_0\bar{Z}_n[N_n] - 2k_0\bar{Z}_n[O_n] + 2k\sum_{r=1}^{n-n_O}(ar+1)\{a(n-r)-o+1\}[A_r][O_{n-r}] + \ldots - 2k(an-o+1)[O_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i]\right) \quad (9c)$$

The following mole balance relations are obtained similarly.

For $n_N < n < n_O$:

$\vdots$ $\vdots$

For $n_B < n < n_C$:

$$\frac{d[A_n]}{dt} = k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}] - 2k_0\bar{Z}_n[A_n] - 2k(an+1)[A_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i] + \ldots + \sum_{i=n_P}^{\infty}(ai-p+1)[P_i]\right) \quad (10a)$$

$$\frac{d[B_n]}{dt} = 2k_0\bar{Z}_n[A_n] + 2k\sum_{r=1}^{n-n_B}(ar+1)a(n-r)[A_r][B_{n-r}] - 2k_0\bar{Z}_n[B_n] - 2kan[B_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i] + \ldots + \sum_{i=n_O}^{\infty}(ai-o+1)[O_i]\right) \quad (10b)$$

For $1 < n < n_B$:

$$\frac{d[A_1]}{dt} = 2k(a+1)[A_1]\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i] + \ldots + \sum_{i=n_P}^{\infty}(ai-p+1)[P_i] \quad (11a)$$

$$\frac{d[A_n]}{dt} = k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}] - 2(an+1)[A_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i] + \sum_{i=n_B}^{\infty}ai[B_i] + \ldots + \sum_{i=n_P}^{\infty}(ai-p+1)[P_i]\right) \quad (11b)$$

## METHOD OF COMPUTATION

The solution of equations (8) to (11) cannot be found analytically and in this work we have presented numerical results computed on a DEC 1090 computer using the Runge–Kutta algorithm of fourth order. It has already been pointed out earlier[39–42] that the average number of rings per molecule is small even near the gel point. In view of this, it is assumed that the maximum number of cyclic rings on polymer chains does not exceed 2, which implies that there are only species $A_n$, $B_n$ and $C_n$ in the reaction mass. It is also assumed that because of steric hindrance:

$$n_B = n_C = 4 \quad (12)$$

It may be recognized that the formation of $C_n$ through the combination of $B_m$ plus $B_m$ cannot occur for $n < 8$, which means that the terms accounting for this in equations (8) to (11) must be modified accordingly. The correct equations governing the molecular weight distribution are given in *Table 1*. The values of $\bar{Z}_n$ have been determined by empirically curve-fitting the Monte Carlo results of Platé and Noah[53] and are summarized in *Table 2*.

The mole balance equations of *Table 1* have been nondimensionalized using

$$a_n = [A_n]/[A_1]_0 \quad (13a)$$

$$b_n = [B_n]/[A_1]_0 \quad (13b)$$

$$c_n = [C_n]/[A_1]_0 \quad (13c)$$

$$k_{d0} = k_0/k \qquad n \geqslant 4 \quad (13d)$$

and

$$x = k[A_1]_0 t \quad (13e)$$

where $[A_1]_0$ is the concentration of the (pure) monomer $RA_f$ fed to the batch reactor. The nondimensional differential equations have been solved with incremental time, $x$, as 0.001 to obtain numerically stable solutions. We have calculated the total count of repeat units, $RC$, as

$$RC=\sum_{n=1}^{N_a} na_n+\sum_{n=4}^{N_b} nb_n+\sum_{n=4}^{N_c} nc_n \tag{14}$$

where $N_a$, $N_b$ and $N_c$ are the number of equations for species $A_n$, $B_n$ and $C_n$ respectively that have been solved for obtaining the *MWD*. Theoretically these should be infinity, but for purposes of computation, they are taken large enough such that the truncation error $(1-RC)$ is kept minimal. In the computer program, $N_a$, $N_b$ and $N_c$ are increased whenever either $aN_a$, $bN_b$ or $cN_c$ increase beyond $10^{-8}$ in magnitude.

As an example, the *MWD* equations of *Table 1* have been solved for hexafunctional monomers with increasing $N_a$, $N_b$ and $N_c$ as described above. The value of $N_a$ is found to increase very rapidly and values of $N_a$, $N_b$ and $N_c$ as a function of the conversion $p_A$ of functional groups are given in *Table 3*. For the polymerization of hexafunctional monomer without cyclization, gelation would occur theoretically at 20% conversion ($p_A=0.20$) and by the time we reach the value of $p_A$ of about 0.19 we are solving a set of about 1000 differential equations. By then, the computation time increases very rapidly and at present to reach the gel point using this kinetic approach appears to be a very difficult task. Numerical results presented in this paper go up to about 18% conversion of functional groups in the polymerization of hexafunctional monomers.

**Table 1** Mole balance equations for various species in batch reactors for the case when $p=2$ and $n_B=n_C=4$

(a) For $n\leqslant 3$

$$\frac{d[A_1]}{dt}=-2k(a+1)[A_1]\left(\sum(ai+1)[A_i]+\sum ai[B_i]+\sum(ai-1)[C_i]\right)$$

$$\frac{d[A_n]}{dt}=k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}]$$
$$-2k(an+1)[A_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i]+\sum ai[B_i]+\sum(ai-1)[C_i]\right)$$
$$n\geqslant 2$$

(b) For $4\leqslant n\leqslant 7$

$$\frac{d[A_n]}{dt}=k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}]-2k_0\bar{Z}_n[A_n]$$
$$-2k(an+1)[A_n]\left(\sum(ai+1)[A_i]+\sum ai[B_i]+\sum(ai-1)[C_i]\right)$$

$$\frac{d[B_n]}{dt}=2k_0\bar{Z}_{n,0}[A_n]+2k\sum_{r=1}^{n-4}[A_r][B_{n-r}](ar+1)a(n-r)-2k_0\bar{Z}_{n,1}[B_n]$$
$$-2kan[B_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i]+\sum_{i=4}^{\infty}ai[B_i]\right)$$

$$\frac{d[C_n]}{dt}=2k_0\bar{Z}_n[B_n]+2k\sum_{r=1}^{n-4}(ar+1)\{a(n-r)-1\}[A_r][C_n]$$
$$-2k(an-1)[C_n]\sum(ai+1)[A_i]$$

(c) For $n\geqslant 8$

$$\frac{d[A_n]}{dt}=k\sum_{r=1}^{n-1}(ar+1)\{a(n-r)+1\}[A_r][A_{n-r}]$$
$$-2k(an+1)[A_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i]+\sum_{i=4}^{\infty}ai[B_i]+\sum_{i=4}^{\infty}(ai-1)[C_i]\right)$$
$$-2k_0\bar{Z}_n[A_n]$$

$$\frac{d[B_n]}{dt}=2k_0\bar{Z}_n[A_n]-2k_0\bar{Z}_n[B_n]+2k\sum_{r=1}^{n-4}a(ar+1)(n-r)[A_r][B_{n-r}]$$
$$-2kan[B_n]\left(\sum_{i=1}^{\infty}(ai+1)[A_i]+\sum_{i=4}^{\infty}ai[B_i]\right)$$

$$\frac{d[C_n]}{dt}=2k_0\bar{Z}_n[B_n]+k\sum_{r=4}^{n-4}a^2r(n-r)[B_r][B_{n-r}]$$
$$+2k\sum_{r=1}^{n-4}(ar+1)\{a(n-r)-1\}[A_r][C_{n-r}]$$
$$-2k(an-1)[C_n]\sum_{j=1}^{\infty}(aj+1)[A_j]$$

**Table 2** Values of $a$ and $b$ for various ranges in equation (6)

| Range of $n$ | $g(n)$ | $h(n)$ |
|---|---|---|
| 0–30 | 5 | 0.75 |
| 31–50 | 8 | 1.50 |
| 51–100 | 21 | 1.68 |
| 101–150 | 40 | 2.07 |

## RESULTS AND DISCUSSION

To check the stability of our computations, we set $k_{d0}$ equal to zero and compared our numerical results with the analytical solution[25]:

$$\frac{[A_n]}{[A_1]_0}=\frac{\{n(f-1)\}!}{n!\{n(f-2)+2\}!}fp_A^{n-1}(1-p_A)^{n(f-2)+2} \tag{15}$$

The above equation is valid for the case when there is no cyclization. Complete agreement was found between the analytical solution and our numerically integrated results with $k_{d0}=0$. For our computations, $\bar{Z}_n$ have been found from curve fitting the results of Platé and Noah and are given in *Table 2*. Computations were also made assuming that up to four ring species exist, which means that the reaction mass consisted of species $A_n$, $B_n$, $C_n$ and $D_n$ only. It was found that the dimensionless concentrations of species $D_n$ always remains less than $10^{-8}$ and in view of this the equations given in *Table 1* were found to be appropriate for describing the intramolecular reactions in the step-growth polymerization of hexafunctional monomers.

Using the computational scheme suggested in this paper, results have been obtained for the molecular

**Table 3** Values of $N_a$, $N_b$ and $N_c$ in equation (14) for $k_{d0}=0.1$ and $f=6$

| Reaction time, $x$ | $p_A$ | $N_a$ | $N_b$ | $N_c$ | $RC$ |
|---|---|---|---|---|---|
| 0.001 | 0.003 | 100 | 10 | 10 | 1.000000 |
| 0.020 | 0.057 | 100 | 30 | 10 | 1.000000 |
| 0.040 | 0.107 | 100 | 30 | 10 | 0.999998 |
| 0.050 | 0.130 | 100 | 50 | 30 | 0.999993 |
| 0.060 | 0.153 | 175 | 90 | 30 | 0.99945 |
| 0.065 | 0.163 | 250 | 130 | 50 | 0.999809 |
| 0.069 | 0.172 | 325 | 170 | 50 | 0.999515 |
| 0.071 | 0.176 | 325 | 190 | 50 | 0.9992879 |
| 0.073 | 0.181 | 400 | 210 | 50 | 0.9987988 |
| 0.076 | 0.188 | 475 | 270 | 70 | 0.9971317 |
| 0.078 | 0.193 | 550 | 310 | 70 | 0.9948202 |

weight distribution of the polymer below the critical conversion. In *Figures 1*, *2* and *3*, the weight fraction distributions of $A_n$, $B_n$ and $C_n$ have been plotted for various values of cyclization parameters. The distribution of $A_n$ in *Figure 1* is found to be little affected up to as high a value of $k_{d0}$ as 0.1 and can be described by equation (15) to a large extent. By changing the functionality $f$, the nature of this conclusion does not change. This is consistent with the observation[25,55–60] made by various experimental studies, which find that the effect of the cyclization reaction is considerably enhanced on the overall distribution only as the gel point is approached.

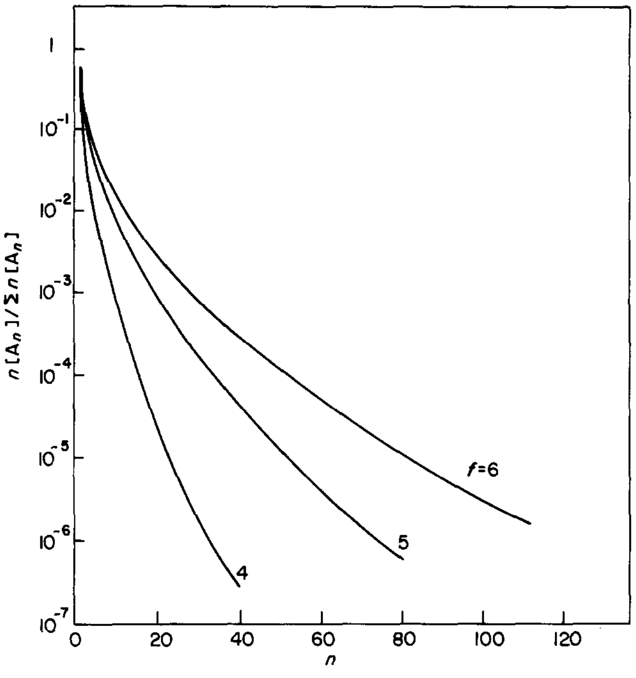

**Figure 1** Weight fraction distribution of species $A_n$ at $x=0.069$ for various values of $f$ (p=0.077)

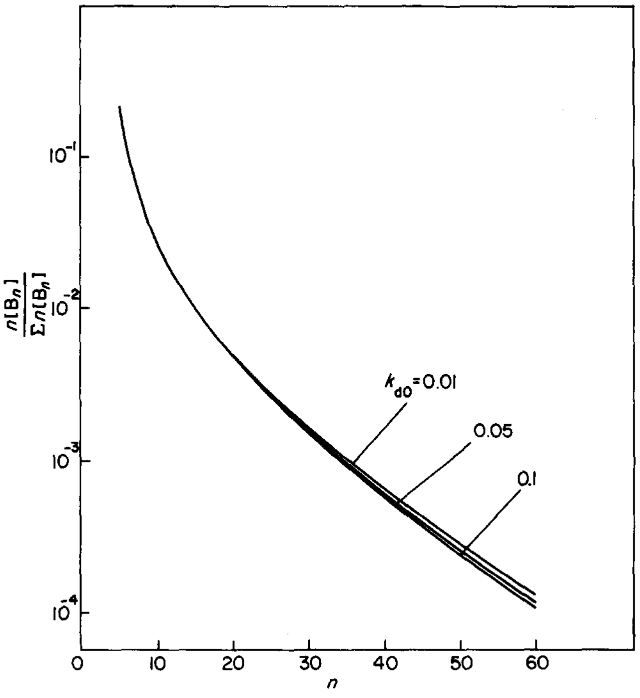

**Figure 2** Weight fraction distribution of species $B_n$ at $x=0.069$ for $f=6$ for various values of $k_d$ ($p=0.077$)

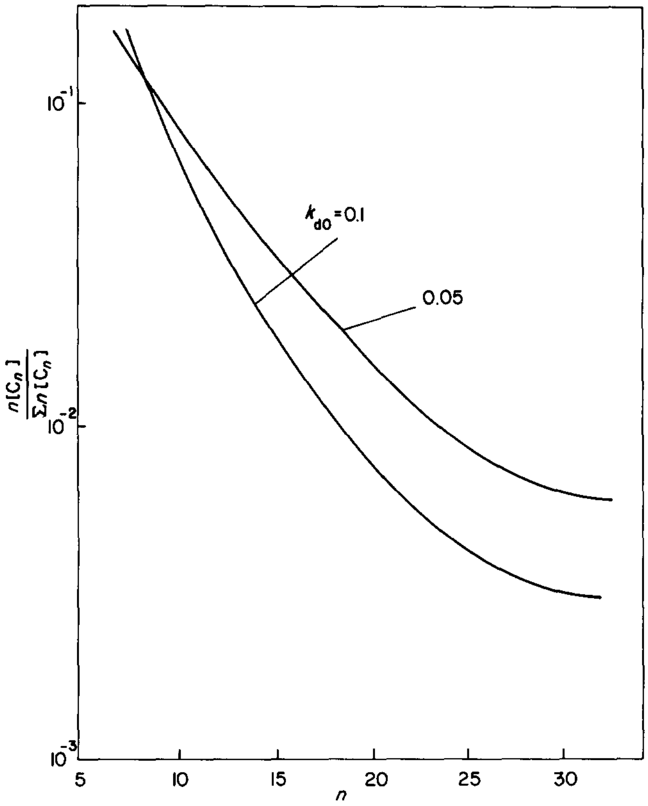

**Figure 3** Weight fraction distribution of species $C_n$ at $x=0.069$ for $f=6$ for various values of $k_d$ ($p=0.077$)

The weight fraction distribution of species B and C are shown in *Figures 2* and *3*. The total amounts of these species formed are small and the distributions of these are found to decrease monotonically with $n$. These curves broaden in width as $k_{d0}$ is increased. In the range of values of $k_{d0}$ from 0.005 to 0.01, it is negligibly affected whereas for values of $k_{d0}$ beyond 0.01, the *MWD* begins to broaden as seen in *Figures 2* and *3*. It may be emphasized here that there is an artificiality inherent in the balance equations of *Table 1*, in which species C has been assumed not to react either with itself or with species B. This assumption is justified only when the concentration of species C is negligibly small. Near the gel point, where the cyclic oligomers are formed in larger concentrations, the equations of *Table 1* would predict that species A and B would all convert to species C, which neither reacts nor grows in size. This would imply that, at the gel point, the average molecular weight of the polymer is finite, which is evidently not correct. It is therefore important that as the gel point is approached, in addition to increasing the total number of equations (as done in *Table 3*), one must also simultaneously increase the types of species to be able to obtain the correct numerical solution. However, up to about 18% conversion, computations have shown that defining species having up to a maximum of two intramolecular bonds is sufficient because the assumption of small concentration of species C in the reaction mass is very well satisfied.

From the *MWD* thus calculated, the average chain length $\mu_n$ and the polydispersity index $\rho$ of species A, B and C have been calculated and plotted in *Figures 4* to *6*. As the gel point is approached, $\mu_n$ as well as $\rho$ for all these species begin to increase rapidly and the value of the latter is not limited to 2, as expected in the polymerization of

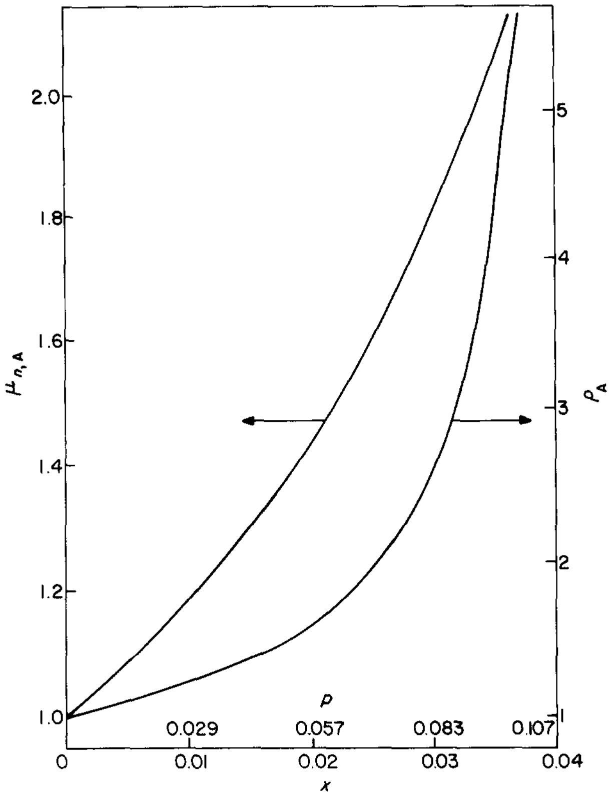

**Figure 4** Average chain length and polydispersity index of species $A_n$ *versus* $x$ for $f=6$

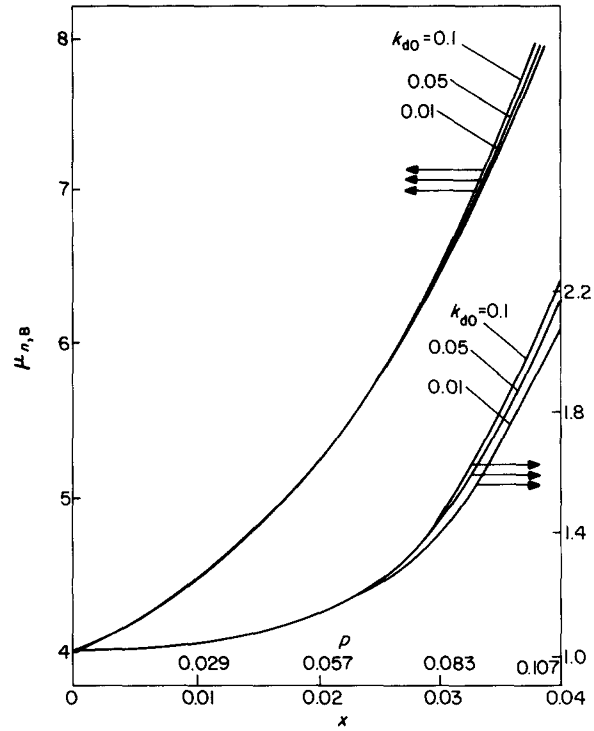

**Figure 5** Average chain length and polydispersity index of species $B_n$ *versus* $x$ for $f=6$

bifunctional monomers. The average chain length of species A remains of the order of 2 whereas those of species B and C are of the order of 10 even though the total moles of cyclic polymer formed is very small (*Figure 7*). *Figure 8* shows the average number of cyclic rings in the reaction mass, which is found to grow as polymerization progresses. This indicates that molecules of species with large chain lengths have a greater tendency to react intramolecularly to form B and C. It is thus expected that, as the gel point is approached, molecules of very large chain length are formed and these would have several intramolecular bonds with considerably high probability. As has been pointed out above, to carry out the computation above about 18% conversion of functional

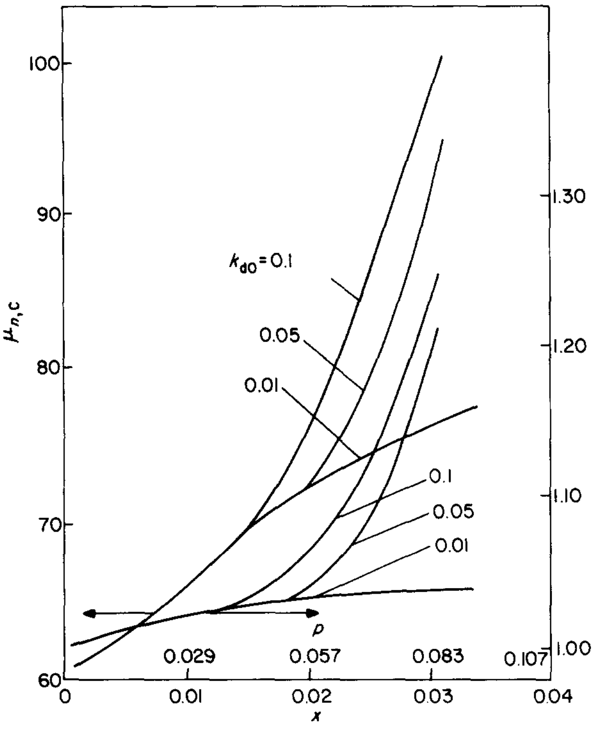

**Figure 6** Average chain length and polydispersity index of species $C_n$ versus $x$ for $f=6$

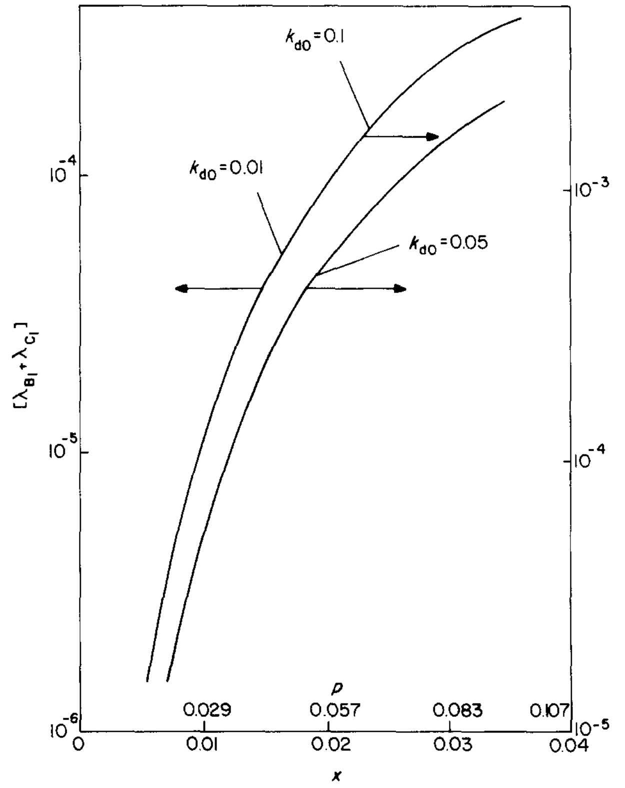

**Figure 7** Total weight of cyclic oligomers in the reaction mass for various values of $k_{d0}$ *versus* $x$

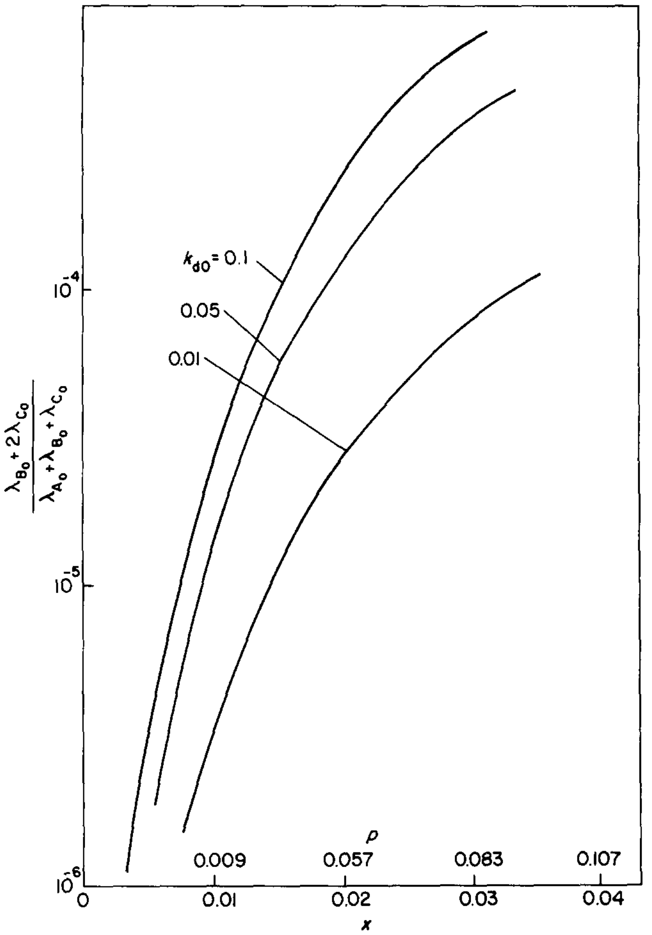

**Figure 8** Average number of rings per molecule *versus* $x$ of polymerization for various values of $k_{d0}$

groups with only three species (A, B and C) is not meaningful, but one can deduce what should be happening near the gel point. As the gel point is approached, larger polymer chains are formed, which have a greater tendency to react intramolecularly and, in the limit, reaction by this mechanism would dominate, no matter how $k_{d0}$ is taken.

The mathematical formulation presented in this paper is completely general and is valid for any functionality all the way up to the gel point provided a sufficient number of species are defined. If it is indeed done for the above problem, one can obtain meaningful results even beyond 18%, but to solve it numerically is a difficult proposition. One of the approaches that can be taken to get to the gel point is to reduce the *MWD* equations into moment equations for the various species. On doing this, it is found that the equations governing the zeroth moments involve the first moments, those for the first moments involve the second moments, and so on. There is a need to develop a moment closure approximation to break this hierarchy of equations. The numerical computations presented in this work are necessary in order to check the applicability of the moment closure approximations. Thus, the present computations not only give quantitative results for the effect of cyclization on the *MWD* of the polymer formed in the pre-gel region, but what is more important, provide a framework against which computationally easier equations for the moments can be checked. The latter method can then be used to go to higher conversions and so get the effect of cyclization on the critical conversion.

## CONCLUSIONS

A general kinetic model accounting for the intramolecular reactions in step-growth polymerization of multifunctional monomers has been presented. The model is valid for any functionality. These equations have been rewritten for the specific case of hexafunctional monomers and results have been derived to demonstrate the feasibility of numerical computation.

In the step-growth polymerization of hexafunctional $RA_f$ monomers for conversions below about 18%, it is found that assuming a maximum of two intramolecular bonds per molecule is sufficient to describe the cyclization reaction very well. This sufficiency was justified by comparing the results with those found from the case when the reaction mass was assumed to consist of higher ring species. In this case, when a maximum of two ring species are assumed to exist, species in the reaction mass can have zero ($A_n$), one ($B_n$) and two ($C_n$) intramolecular bonds. Mole balance equations for each of these species are written out and are solved numerically. Computed results indicate that large molecules have a higher tendency to react intramolecularly. Near the gel point, very large polymer molecules are formed (i.e. $\bar{M}_w \rightarrow \infty$) in which case it is expected to react more favourably by an intramolecular mechanism than by an intermolecular one.

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