Molecular weight distribution in the polymerization of melamine and formaldehyde using a functional group approach

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The reversible polymerization of melamine with formaldehyde has been described by the reaction of ten species. The proposed kinetic model involves only six rate constants and fits the experimental data of Tomita. To determine the molecular weight distribution (*MWD*) of the melamine polymer, the reversible reactions of branched molecules are described. It is shown that the reverse reaction depends upon the chain structure (i.e. the location and length of the branches). A rigorous technique has been given and a flow chart of a computer program is described which gives the rate of formation of a chain from a larger branched chain through reverse reaction. Using the technique proposed here, the *MWD* of the melamine polymer is calculated. Finally a sensitivity analysis has been used to determine the range of conditions that would lead to formation of higher oligomers.

(Keywords: step growth polymerization; melamine; formaldehyde; reversible polymerization; branch polymers; reverse reaction modelling; molecular weight distribution)

INTRODUCTION

Formaldehyde is a gas at room temperature and is commercially available as formalin, which is a 37% solution in water. In formalin, formaldehyde can exist either as methylene glycol or as low molecular weight polymeric molecules and the equilibrium between these molecular species can be represented by[1,2]:

$$CH_2O + H_2O \underset{K_2}{\overset{K_1}{\rightleftharpoons}} HO\text{–}CH_2OH \qquad (1a)$$

$$n\,HOCH_2\text{–}OH \rightleftharpoons HO(CH_2O)_nH + (n-1)H_2O \qquad (1b)$$

$$OH\text{–}CH_2OH + OH(CH_2O)_nH \overset{K_3}{\rightleftharpoons} OH(CH_2O\text{–})_{n+1}H + H_2O \qquad (1c)$$

Melamine (2,4,6-triamino-5-triazine) is a weakly basic material. It can react with formaldehyde and leads to the formation of a melamine–formaldehyde polymer. The latter is used commercially mostly in making kitchenware. The polymer has been known since 1884, but studies of the reactions leading to polymer formation were carried out only recently. Several investigations have been reported on the addition of melamine to formaldehyde[3–7]. Most of these studies have been limited to low concentrations of melamine where there is only the addition of methylene glycol to a melamine molecule. By keeping the concentration low, the formation of higher oligomers is prevented. Melamine has three amino groups and hence there are six possible reactions with the addition of methylene glycol. The various reactions leading to the methylolation of melamine that have been considered are shown in *Figure 1*.

Okano and others[8,9] have measured the initial reaction rate constants. Gordon *et al.*[10] have conducted further investigations into the kinetics of the system and have illustrated that a quantitative estimate of the products could be made using ^{14}C-labelled formaldehyde. Some deviation from random behaviour was noted and parameters were assigned to quantify the rate constants. The validity of these parameters was tested in a computer study by Aldersley *et al.*[11] who tried to match experimental data on the free formaldehyde content with results from computation.

Tomita[7] has carried out a detailed experimental study of the molecular species distribution of a methylol melamines using the reaction mechanism given in *Figure 1*. This study revealed that the methylolation of melamine is a reversible reaction. The mechanism considered in *Figure 1* has 10 species and involves 24 rate constants. Tomita has analysed the reaction mass using n.m.r. spectroscopy and high-speed liquid chromatography. For one temperature and various melamine-to-formaldehyde ratios, he has determined the concentrations of various species in *Figure 1* as a function of time. Using a kinetic model in which only methylolation occurs, he has determined rate constants from his experimental measurements and has found that these are dependent upon the initial concentration of formaldehyde fed to the batch reactor.

For commercial polymerizations where melamine is present in the feed at higher concentrations, the analysis of Tomita is of little significance for the following reasons. In polymerizing melamine with formaldehyde at commercial concentrations, there will be formation of higher oligomers even though it is small in normal conditions of experimentation. The polymerization

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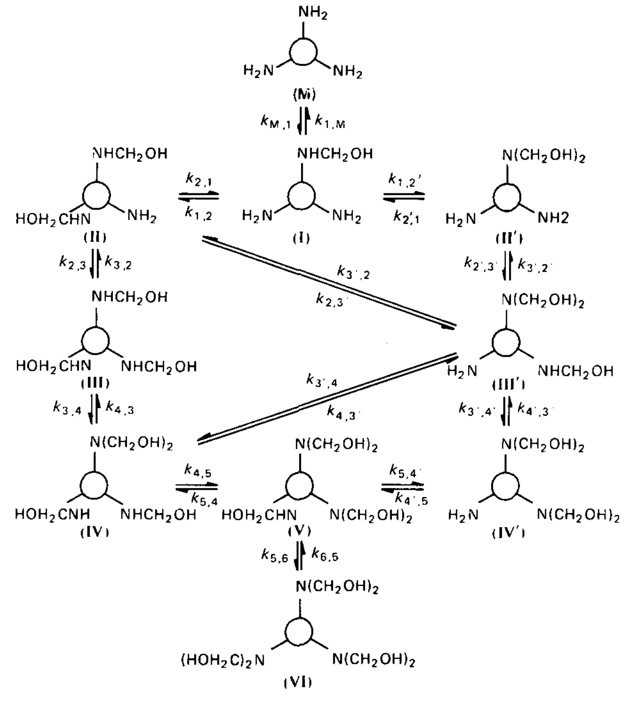
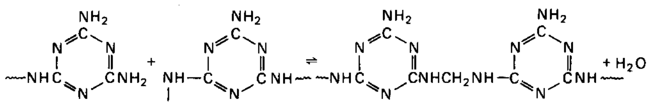


Figure 1 Kinetic mechanism by Tomita for the polymerization of melamine and formaldehyde

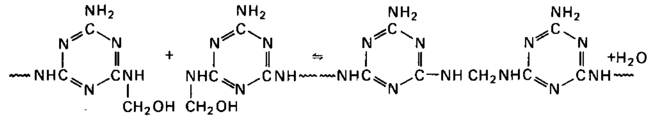
involving formaldehyde has been discussed in detail by Drum and LeBlanc[2]. They state that, in solution, it remains as methylene glycol and reacts in two stages. On reaction with hydrogen, it leads to methylolation and gives a CH_2OH group which can react once again. A given CH_2OH group can react with another hydrogen as well as with another CH_2OH group and in our kinetic model both these reactions have been accounted for:

(a) Reaction of bound CH_2OH group with H



(2)

(b) Reaction of bound CH_2OH group with another bound CH_2OH group



(3)

It may be appreciated that these two reactions lead to the formation of higher oligomers[12]. Industrially, polymerization of melamine is carried out in two stages. In the first stage, melamine is essentially methylolated, whereas in the second stage, the polymer so formed is further polymerized in moulds to form a highly crosslinked thermoset polymer. Tomita's kinetic model is valid for the first stage only and there is a need to develop a generalized kinetic model for both the stages[13].

In this paper, we have considered the formation of higher oligomers of melamine–formaldehyde polymer. In order to do so, we have first described the reversible polymerization using a functional group approach. The various rate constants involved in this model have been evaluated using the experimental data of Tomita.

Since melamine is hexafunctional in nature, the polymer formed in any reactor would be in general branched in structure. In this paper we have shown that the reverse reaction of branched molecules in general would depend upon the chain topology. An algorithm has been developed which gives the reverse reaction of branched chains. Using this algorithm we have established the mole balance relations for various oligomers in the melamine–formaldehyde polymerization. We have solved for the molecular weight distribution (*MWD*) numerically and the approach taken here is similar to our earlier work on novolac formation[14–18].

THE FUNCTIONAL GROUP APPROACH TO DESCRIBING MELAMINE–FORMALDEHYDE POLYMERIZATION

In the kinetic model shown in *Figure 2*, species A to J specify the various hydrogens on a melamine ring which can undergo reaction either with formaldehyde or with CH_2OH groups. The reactions could be of the types shown in equations (2) and (3). It is assumed that the reactivity of a given hydrogen is different for a primary and secondary amide hydrogen and the reactivity of a given species is independent of its substituents. In *Figure 2*, X denotes a CH_2OH group and a ~ indicates that the species is part of a polymer chain. Species A represents a melamine molecule, species B represents two different structures, C three different structures as shown in *Figure 2*.

In *Table 1*, the forward reactions are written. When species react with formaldehyde, a CH_2OH group is formed, whereas when they react with a CH_2OH, there is formation of a reacted bond (represented by Z). Since the reactivity is completely determined by the reactive hydrogen, we define the following rate constants:

k_1 reaction between a CH_2OH and a primary amide hydrogen on the ring;
k_2 reaction between a CH_2OH and a secondary amide group;
k_4 reaction between two $-CH_2OH$ groups, giving a methylene linkage $-N-CH_2-N-$ (or Z) and a free formaldehyde molecule (this reaction step does not change the nature of the functional group);
k_4' reaction involving a bond and a methylene glycol molecule;
k_5 reverse reaction involving a bond and a water molecule.

In the reverse reaction there are two possibilities that exist. In *Table 2*, while writing the reverse reactions, the various bonds of the reactive sites have been assumed to be predominantly reacted bonds Z, which on reaction with water leads to the formation of a CH_2OH group. This has been called model I in *Table 2*. As opposed to this in *Table 3* (called model II) bonds are assumed to be essentially all CH_2OH groups, which on reaction with water leads to the formation of free formaldehyde (denoted by F_1). Based on this kinetic model the mole balance relations for various species in a batch reactor can be easily written and are given in *Table 4*. On careful

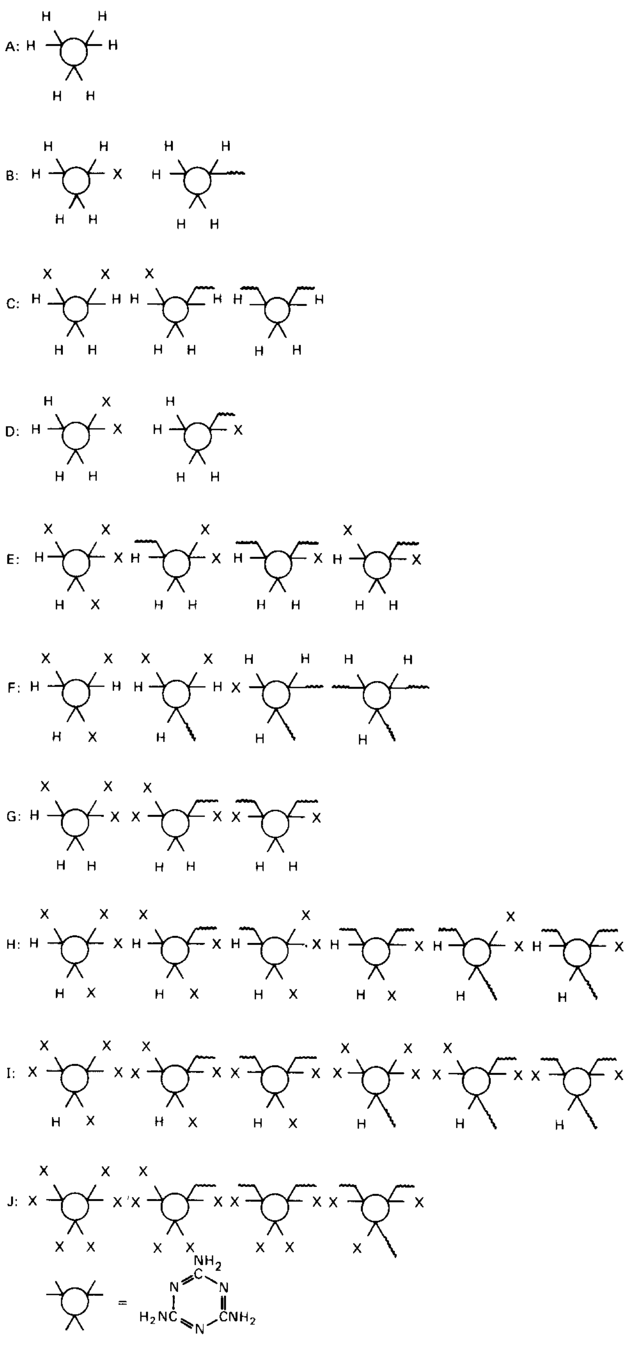


Figure 2 Various reactive species

Table 1 Forward reaction steps in the polymerization of melamine with formaldehyde

1.	$A+F_1\xrightarrow{12k_1}B+CH_2OH+H_2O$	$A+CH_2OH\xrightarrow{6k_1}B+Z+H_2O$
2.	$B+F_1 8k_1\rightarrow C+CH_2OH+H_2O$	$B+CH_2OH\xrightarrow{4k_1}C+Z+H_2O$
3.	$B+F_1\xrightarrow{2k_2}D+CH_2OH+H_2O$	$B+CH_2OH\xrightarrow{k_2}D+Z+H_2O$
4.	$C+F_1\xrightarrow{4k_1}F+CH_2OH+H_2O$	$C+CH_2OH\xrightarrow{2k_1}F+Z+H_2O$
5.	$C+F_1\xrightarrow{4k_3}E+CH_2OH+H_2O$	$C+CH_2OH\xrightarrow{2k_2}E+Z+H_2O$
6.	$D+F_1\xrightarrow{8k_1}E+CH_2OH+H_2O$	$D+CH_2OH\xrightarrow{4k_1}E+Z+H_2O$
7.	$E+F_1\xrightarrow{4k_1}H+CH_2OH+H_2O$	$E+CH_2OH\xrightarrow{2k_1}H+Z+H_2O$
8.	$E+F_1\xrightarrow{2k_2}G+CH_2OH+H_2O$	$E+CH_2OH\xrightarrow{k_2}G+Z+H_2O$
9.	$F+F_1\xrightarrow{6k_1}E+CH_2OH+H_2O$	$F+CH_2OH\xrightarrow{3k_2}H+Z+H_2O$
10.	$G+F_1\xrightarrow{4k_1}I+CH_2OH+H_2O$	$G+CH_2OH\xrightarrow{2k_1}I+Z+H_2O$
11.	$H+F_1\xrightarrow{4k_2}I+CH_2OH+H_2O$	$H+CH_2OH\xrightarrow{2k_2}I+Z+H_2O$
12.	$I+F_1\xrightarrow{2k_2}J+CH_2OH+H_2O$	$I+CH_2OH\xrightarrow{k_2}J+Z+H_2O$

Factor of 2 because of two –OH groups on formaldehyde

$$CH_2OH+CH_2OH\underset{k'_4}{\overset{k_4}{\rightleftharpoons}}Z+F_1$$

This reaction does not change the nature of the species. In the reverse reaction also, the nature of species does not change. Only the concentration of Z is required

Table 2 Reverse reaction steps in the polymerization of melamine with formaldehyde assuming Z as reacted bonds (model I)

$$B+H_2O\xrightarrow{k_5}A+CH_2OH-Z$$
$$C+H_2O\xrightarrow{2k_5}B+CH_2OH-Z$$
$$D+H_2O\xrightarrow{2k_5}B+CH_2OH-Z$$
$$E+H_2O\xrightarrow{2k_5}C+CH_2OH-Z$$
$$E+H_2O\xrightarrow{k_5}D+CH_2OH-Z$$
$$F+H_2O\xrightarrow{3k_5}C+CH_2OH-Z$$
$$G+H_2O\xrightarrow{4k_5}E+CH_2OH-Z$$
$$H+H_2O\xrightarrow{2k_5}E+CH_2OH-Z$$
$$H+H_2O\xrightarrow{2k_5}F+CH_2OH-Z$$
$$I+H_2O\xrightarrow{k_5}C+CH_2OH-Z$$
$$I+H_2O\xrightarrow{4k_5}I+CH_2OH-Z$$
$$J+H_2O\xrightarrow{6k_5}I+CH_2OH-Z$$

Table 3 Reverse reaction steps in the polymerization of melamine with formaldehyde (model II)

$$B+H_2O\xrightarrow{k_5}A+F_1$$
$$C+H_2O\xrightarrow{2k_5}B+F_1$$
$$D+H_2O\xrightarrow{2k_5}B+F_1$$
$$E+H_2O\xrightarrow{2k_5}C+F_1$$
$$E+H_2O\xrightarrow{k_5}D+F_1$$
$$F+H_2O\xrightarrow{3k_5}C+F_1$$
$$G+H_2O\xrightarrow{4k_5}E+F_1$$
$$H+H_2O\xrightarrow{2k_5}E+F_1$$
$$H+H_2O\xrightarrow{2k_5}F+F_1$$
$$I+H_2O\xrightarrow{k_5}G+F_1$$
$$I+H_2O\xrightarrow{4k_5}H+F_1$$
$$J+H_2O\xrightarrow{6k_5}I+F_1$$

examination of *Table 4*, it is found that the concentration of various species is independent of the nature of bonds on the reactive species. This is because in all these equations, a term ($[CH_2OH]+2[F_1]$) appears instead of individual concentrations $[CH_2OH]$ and $[F_1]$. It is thus seen that if one is interested in determining the concentration of the species, one can do so accurately without actually specifying the nature of bonds on the reactive species in *Figure 2.*

Reverse reaction of branch molecules

Chemical reaction between reacting polymer molecules P_m and P_n can occur only when they undergo collision. 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

Table 4 Mole balance relations for batch reactors

(a) Model I

1. $$\frac{d[A]}{dx}=-6A[2F_1+CH_2OH]+m_4B[H_2O]$$
2. $$\frac{d[B]}{dx}=6A[2F_1+CH_2OH]-(4+m_1)B[2F+CH_2OH]+m_4[H_2O](2D+2C)-m_4B[H_2O]$$
3. $$\frac{d[C]}{dx}=4B[2F_1+CH_2OH]-(2+2m_1)C[2F_1+CH_2OH]+m_4[H_2O](2E+3F)-m_4[H_2O](2C)$$
4. $$\frac{d[D]}{dx}=m_1B[2F_1+CH_2OH]-4D[2F_1+CH_2OH]+m_4[H_2O](E)-m_4[H_2O](2D)$$
5. $$\frac{d[E]}{dx}=(2m_1C+4m_1D)[2F_1+CH_2OH]-(2+m_1)E[2F_1+CH_2OH]+m_4[H_2O](4G+2H)-m_4[H_2O](3E)$$
6. $$\frac{d[F]}{dx}=2C[2F_1+CH_2OH]-3m_1F[2F_1+CH_2OH]+m_4[H_2O](2H)-m_4[H_2O](3F)$$
7. $$\frac{d[G]}{dx}=m_1E[2F_1+CH_2OH]-2m_1G[2F_1+CH_2OH]+m_4[H_2O](I)-m_4[H_2O](4G)$$
8. $$\frac{d[H]}{dx}=(2E+3m_1F)[2F_1+CH_2OH]-2m_1H[2F_1+CH_2OH]+m_4[H_2O](4kI)-m_4[H_2O](4H)$$
9. $$\frac{d[I]}{dx}=(2m_1G+2m_1H)[2F_1+CH_2OH]-m_1I[2F_1+CH_2OH]+m_4[H_2O](6J)-m_4[H_2O](5I)$$
10. $$\frac{d[J]}{dx}=m_1I[2F_1+CH_2OH]-m_4[H_2O](6J)$$
11. $$\frac{d[F_1]}{dx}=-2[F_1]R_1+m_2[CH_2OH^2-m_3[Z][F_1]$$
12. $$\frac{d[CH_2OH]}{dx}=2[F_1]R_1-[CH_2OH]R_1+m_4[H_2O]R_2$$
13. $$\frac{d[Z]}{dx}=[CH_2OH]R_1-m_4[H_2O]R_2+m_2[CH_2OH]^2-m_3[Z][F_1]$$
14. $$\frac{d[H_2O]}{dx}=[2F_1+CH_2OH]R_1-m_4[H_2O]R_2$$

(b) Model II

Equations (1) to (10) are the same as in model I

11. $$\frac{d[F_1]}{dx}=-2[F_1]R_1+m_2[CH_2OH]^2-m_3[Z][F_1]+m_4[H_2O]R_2$$
12. $$\frac{d[CH_2OH]}{dx}=2[F_1]R_1-[CH_2OH]R_1+2m_3[Z][F_1]-2m_4[CH_2OH]^2$$
13. $$\frac{d[Z]}{dx}=[CH_2OH]R_1-m_4[H_2O]R_2+m_2[CH_2OH]^2-m_3[Z][F_1]$$
14. $$\frac{d[H_2O]}{dx}=[2F_1+CH_2OH]R_1-m_4[H_2O]R_2$$

Where

$$R_1=6A+(4+m_1)B+(2+2m_1)C+4D+(2+m_1)E+3m_1F+2m_1G\ 2m_1H+m_1I$$

$$R_2=B+2C+2D+3E+3F+4G+4H+5I+6I$$

$$A=\frac{[A]}{[A]_0}\quad B=\frac{[B]}{[A]_0}\quad C=\frac{[C]}{[A]_0}\quad \text{etc.}$$

t = time of reaction, x = dimensionless time

$$x=k_1[A]_0t$$

$$m_1=\frac{k_2}{k_1}\quad m_2=\frac{k_4}{k_1}\quad m_3=\frac{k'_4}{k_1}\quad m_4=\frac{k_5}{k_1}$$

and the probability of the reaction $Z_{m,n}$. Therefore

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

where α is a constant of proportionality. If the probability of reaction of functional groups is assumed to be independent of chain length (say it is β), then the probability of reaction of P_m and P_n is equal to $\delta\beta$, where δ is the number of ways these two molecules can react.

The reverse step in a step-growth polymerization involves the reaction of condensation product W with polymer molecules P_n. Once again, if the probability of reaction of W with a given bond is independent of chain length of the polymer molecule (say β), the probability of reaction of W with P_n is $\delta\beta$, where δ is equal to the number of sites on P_n where W can react.

In *Figure 3a*, a linear chain with 10 repeat units, P_{10}, has been shown and its bonds have been numbered. If we are interested in total number of ways a P_{10} can react with W, δ is nothing but the total number of bonds, which means that $\delta=9$ for P_{10}. However, if we are writing the mole balance for P_5, we also need to know the number of sites on P_{10} which on reaction with W would give the formation of P_5. In general, we define $\delta_{n\to m}$ which denotes the number of sites on P_n which on reaction with W gives the formation of P_m (where $m<n$). For a linear chain, it can be seen that, no matter what the values of n and m, δ is equal to 2, i.e.

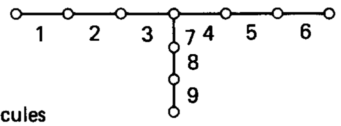
$$\delta_{n\to m}=2 \qquad n>m;\ n,m=2,3,\ldots \tag{5}$$

For branched molecules, however, the situation is more complex, as shown below.

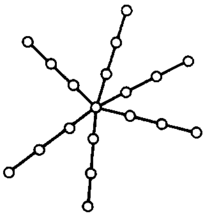
In *Figure 3b*, a branched P_{10} is shown with the

a Linear P_{10}

b Branched P_{10}



c Star molecules



d Chains with branches—spacing equal to branch length

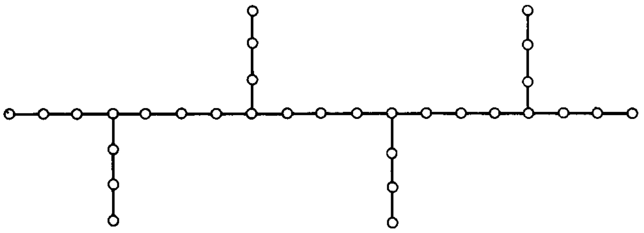


Figure 3 Possible chain structures of polymer molecules

branching exactly at the middle position. If we are interested in the formation of P_1, P_2 or P_3, there are three positions on P_{10}. However P_{10} cannot form P_4, P_5 and P_6 at all by the reverse reaction. For the formation of P_7, P_8 and P_9, once again there are three sites on P_{10}. In other words

$$\delta_{10\to i}=\begin{cases}3 & \text{for } i=1,2,3,7,8.9 \quad (6a)\\ 0 & \text{for } i=4,5,6 \quad (6b)\end{cases}$$

It is thus seen that, for branched molecules, the reverse reaction is dependent on chain structure. It is possible to derive analytical expressions for $\delta_{n\to m}$, provided polymer chains have a symmetrical structure. For example, for a star chain shown in *Figure 3c*, having b branches with r repeat units per branch:

$$\delta_{br\to(br-i)}=\delta_{br\to i}=\begin{cases}b & \text{for } i\leqslant r \quad (7a)\\ 0 & \text{otherwise} \quad (7b)\end{cases}$$

In *Figure 3d* a polymer chain is shown in which branch spacing is equal to the length of the branch. If b is the number of branches, having x repeat units per branch, then its chain length n is given by

$$\begin{aligned} n&=bx+(b-1)x+2x+1\\ &=(2b+1)x+1 \end{aligned} \tag{8}$$

and in this case

$$\delta_{n\to i}=\delta_{n\to(n-i)}=b+2 \qquad \text{if } i\leqslant x \tag{9a}$$

$$\delta_{n\to i}=\begin{cases}0 & \text{if } mx+1\leqslant i\leqslant(m+1)x \quad (9b)\\ 2 & \text{if } 1+(m+1)x\leqslant i\leqslant(m+2)x \quad (9c)\end{cases}$$

For any general branched polymer chain, it is not possible to write an analytical expression for $\delta_{n\to i}$. However, for a specified chain structure, it is possible to determine $\delta_{n\to i}$ either by counting positions manually or by computer. We have devised a computer program (whose listing can be had on request) which does precisely this if the chain structure is specified. The program scans the branches first to see if they have any site that gives the formation of P_i. After finishing this task, it then scans the polymer backbone.

Using the computer program mentioned above, we have found that for various values of n and the chain structure $\delta_{n\to i}$ can take on any value, yet $\sum_{i=1}^{n-1}\delta_{n\to i}$ and $\sum_{i=1}^{n-1}i\delta_{n\to i}$ always obey the following relations:

$$\sum_{i=1}^{n-1}\delta_{n\to i}=2(n-1) \tag{10a}$$

$$\sum_{i=1}^{n-1}i\delta_{n\to i}=n(n-1) \tag{10b}$$

Relation (10a) is evident in that the sum of $\delta_{n\to i}$ for all values of i must be equal to twice the total number of sites where the reaction can occur. Equations (10) are useful in determining the moment relations starting from the mole balance equations of the molecular weight distribution.

Mole balance relation of oligomers

For the *MWD* of the polymer we define A_1 as the melamine and Q_1, Q_2,... as the molecular species of chain lengths 1, 2, etc. A_1 and Q_1 have been distinguished here in that the latter has undergone reaction with formaldehyde.

Mole balance for species Q_n can be easily written if it is observed that:

(1) Q_n is depleted through forward reaction if any of its sites or its bound CH_2OH reacts with any other bound CH_2OH groups;

(2) Q_n is formed through forward reaction when sites of A_1 react with a bound CH_2OH of Q_{n-1} and is depleted when CH_2OH of Q_n reacts with sites of A_1;

(3) Q_n is formed through forward reaction when either sites of CH_2OH of Q_j $(j<n)$ reacts with CH_2OH or sites of Q_{n-j};

(4) Q_n is formed through reverse reaction whenever the appropriate site of Q_i $(i>n)$ reacts with water or formaldehyde.

With these observations, one can easily write the mole balance of Q_n as

$$\begin{aligned} \frac{d[Q_n]}{dt}&=6k_1[A_1](CH_{Q_{n-1}}-CH_{Q_n})-[CH_2OH]R_{Q_n}\\ &-CH_{Q_n}\sum_{j=1}^{\infty}(R_{Q_j}+k_4CH_{Q_j})+\sum_{j=1}^{n-1}R_{Q_j}\{CH_{Q_{n-j}}\\ &+CH_{Q_j}(R_{Q_{n-j}}+\tfrac{1}{2}k_4CH_{Q_{n-j}})\}+(k_5[H_2O]\\ &+2k_4'[F_1]\sum_{j=n+1}^{\infty}\frac{\delta_{j\to n}S_{Q_j}}{(j-1)}\\ &-(k_5[H_2O]+2k_4'[F_1])S_{Q_n} \qquad n\geqslant 2 \end{aligned} \tag{11}$$

where

$$\begin{aligned} R_{Q_n}&=(4k_1+k_2)B_{Q_n}+(2k_1+2k_2)C_{Q_n}+4k_1D_{Q_n}\\ &+(2k_1+k_2)E_{Q_n}+3k_2F_{Q_n}+2k_1G_{Q_n}+k_2I_{Q_n} \end{aligned} \tag{12a}$$

$$\begin{aligned} S_{Q_n}&=B_{Q_n}+2C_{Q_n}+2D_{Q_n}+3E_{Q_n}+3F_{Q_n}+4G_{Q_n}+4H_{Q_n}+5I_{Q_n}\\ &+6J_{Q_n} \end{aligned} \tag{12b}$$

Above B_{Q_n}, C_{Q_n}, etc., refer to B, C, etc., species and CH_{Q_n} are CH_2OH groups on Q_n molecules. In this counting process we do not distinguish Q_n with different chain topologies. S_{Q_n} represents the total number of sites on Q_n where the reverse reaction can occur. If all sites are assumed to occur with equal likelihood, the reaction of any given site must be proportional to $S_Q/(i-1)$.

We define species A_1 which is the same as melamine and Q_1 as a unimolecular species which has CH_2OH groups on it. Evidently A_1 and Q_1 are different but their mole balances can be written similarly. The main difference arises only in that step (3) does not occur for these molecules. In addition, A_1 is formed in the reverse reaction only when B_{Q_1} reacts. The mole balance relations for these species are

$$\frac{d[A_1]}{dt} = -12k_1[A_1][F_1] - 6k_1[A_1][CH_2OH]$$

$$+k_5[H_2O]B_{Q_1} + 2k_4'[F_1]B_{Q_1} + \sum_{i=2}^{\infty} \delta_{i\to 1} B_{Q_i}/(i-1) \quad (13)$$

$$\frac{d[Q_1]}{dt} = -R_{Q_1}[CH_2OH] - CH_{Q_1}\sum_{j=1}^{\infty}(R_{Q_j} + k_4 CH_{Q_j})$$

$$+6k_1[A_1](2[F_1] - CH_{Q_1}) + (k_5[H_2O] + 2k_4'[F_1])$$

$$\sum_{j=2}^{\infty} \frac{\delta_{j\to 1} S_{Q_j}}{(j-1)} - (k_5[H_2O] + 2k_4'[F_1])B_{Q_1} \quad (14)$$

To solve the *MWD* equations, estimates of A_{Q_n} to J_{Q_n} are needed. We assume that the fraction of active species on all Q_n is equal to the fraction of these in the bulk. We have made this kind of approximation in our earlier work and this leads to

$$B_{Q_n} = \frac{[B]}{\sum_{i=1}^{\infty}[Q_i]}[Q_n] \quad (15a)$$

$$C_{Q_n} = \frac{[C]}{\sum_{i=1}^{\infty}[Q_i]}[Q_n] \quad (15b)$$

etc.

To get $\delta_{i\to j}$ for $j=1$ to $(i-1)$, we have to specify an approximate chain structure. For this, the examination of *Figure 2* reveals that species E to J *can* lead to branching. With the knowledge of the concentrations of the active species A to J, we can calculate the branching coefficient α_1, which we define as

$$\alpha_1 = \frac{[E]+[F]+[G]+[H]+[I]+[J]}{\sum_{i=1}^{\infty}[Q_i]} \quad (16)$$

In the most general case, the reaction mass would consist of some molecules with no branches, some with one branch, some with two branches, etc. The branching coefficient α_1 would give a measure of the average number of branches on the polymer molecules.

Intuitively it is expected that the larger the chain length of the polymer molecule, the larger would be the number of branches on it. In the polymerization of melamine, the average chain length of the polymer formed is small and in view of this we approximate the distribution of branches as bimodal in nature. For example if equation (16) gives $\alpha_1 = 2.6$, then we have assumed that some molecules (mole fraction x) have two branches per molecule and the rest have three branches, such that

$$2.6 = 2x + 3(1-x) \quad (17)$$

and from this we can calculate x. In most of the computations, we find that α_1 lies between 0 and 1, which means that on average the reaction mass consists of linear chains and chains with one branch. Lastly, after deciding the number of branches on the polymer chain, we arrange the branches in such a way that it has a structure close to that shown in *Figure 3d*. If the number of repeat units does not divide itself into equal branch lengths, we increase the length of branches by one unit at a time till we obtain the desired chain lengths. We scan the polymer molecule rigorously to determine $\delta_{i\to j}$ for all values of j.

It may be further observed that the mole balance relations for melamine (species A and A_1) given in *Tables 2–4* and that given in equation (13) are different. This arises because of the assumptions made in establishing the *MWD* equations in this work. The consistency of equations (11) to (15) can be checked by determining $\sum_{i=1}^{\infty}(i[Q_i]+[A_1])$, which should be time invariant. This can be found to be so if equation (11) is multiplied by n and summed for all values of n and then adding equations (13) and (14) to the resulting equation. On doing this, the rate of formation of $\sum_{i=1}^{\infty}(i[Q_i]+[A_1])$ is found to be zero and thus the *MWD* relations are consistent. Lastly, the *MWD* equations can be nondimensionalized using the following variables:

$$A = \frac{[A]}{[A]_0} \quad B = \frac{[B]}{[A]_0} \quad C = \frac{[C]}{[A]_0} \quad \text{etc.} \quad (18a)$$

$$A_1 = \frac{[A_1]}{[A]_0} \quad Q_i = \frac{[Q_i]}{[A]_0} \quad i = 1,2\ldots \quad (18b)$$

$$x = k_1[A]_0 t \quad (18c)$$

The weight fraction distribution has been computed as follows:

$$W_1 = \frac{[A_1]+[Q_1]}{\sum_{i=1}^{\infty} i[Q_i] + A_1} \quad (19a)$$

$$W_i = \frac{i[Q_i]}{\sum_{i=1}^{\infty} i[Q_i] + A_1} \quad i = 2,3,4,\ldots \quad (19b)$$

RESULTS AND DISCUSSION

On examination of the mole balance relations of active species A to J given in *Table 4*, it is seen that concentrations of F_1 and CH_2OH do not occur individually, but they appear as $[2F_1 + CH_2OH]$. It may be observed that $[2F_1 + CH_2OH]$ represents the total concentration of reactive OH groups in the reaction and as far as the concentrations of species A to J are concerned, it is the same for models I and II. However, concentrations of species F_1, CH_2OH, H_2O, Z and H_2O are going to be different for the two models.

Tomita has reported experimental data on the melamine and formaldehyde polymerization. In analysing his experimental data, he assumes that only single molecular species are formed and has proposed the kinetic mechanism given in *Figure 1*. This model involves 24 rate constants in contrast to the kinetic model we have proposed which involves only five rate constangts. In addition to this, the kinetic model given in *Tables 1* to *3* is consistent with the chemistry of polymerization and

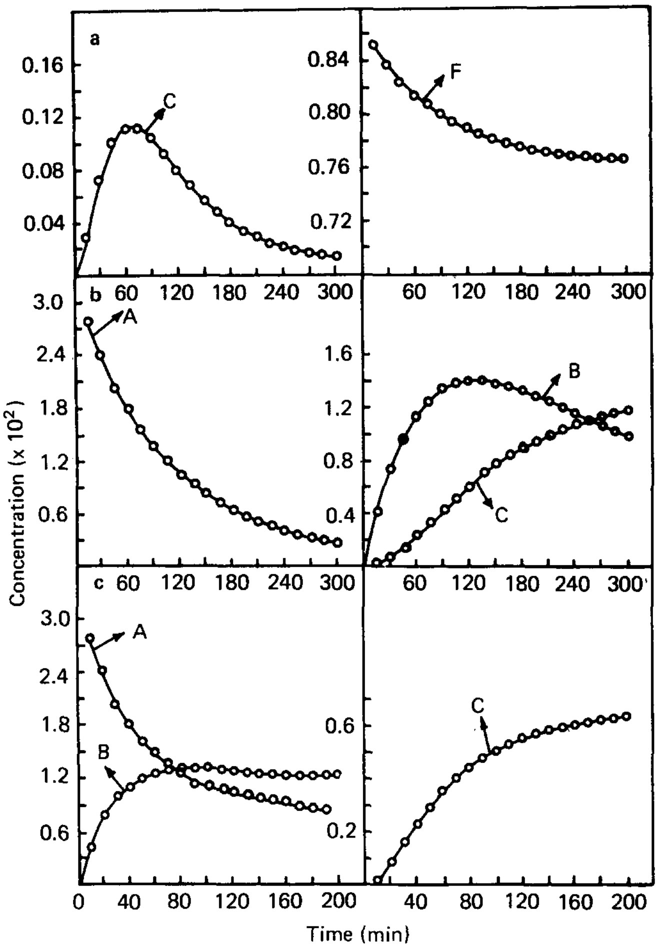


Figure 4 Fitting of experimental data of Tomita using the kinetic model proposed in this work. (a) Concentrations of species C and F *versus* time for $[F_1]_0/[A]_0=30$; $k_1=0.0045$, $k_2=0.004$, $k_4=0.004$, $k'_4=0.3$, $k_5=0.005$. (b) Concentrations of species A, B and C *versus* time for $[F_1]_0/[A]_0=5$; $k_1=0.005$, $k_2=0.0015$, $k_4=0.004$, $k'_4=0.3$, $k_5=0.01$. (c) Concentrations of species A, B and C *versus* time for $[F_1]_0/[A]_0=1$; $k_1=0.004$, $k_2=0.005$, $k_4=0.004$, $k'_4=0.3$, $k_5=0.1$

allows the formation of higher oligomers. We have varied the rate constants k_1, k_2, k_4, k'_4 and k_5 to fit the experimental data of Tomita and the results are shown in *Figure 4*. It is seen that our kinetic model describes the experimental data of Tomita completely.

To obtain the molecular weight distribution, equations (11) to (19) have been solved numerically using the Runge–Kutta method of fourth order. For the study of the molecular weight distribution of melamine polymer, we have chosen the following base values of the rate constants:

$$k_1=0.0045 \quad k_2=0.001 \quad k_4=0.0040 \quad k'_4=0.3 \quad k_5=0.005 \tag{20}$$

We have varied each of these rate constants systematically and have examined the effect of these on the molecular weight distribution of the melamine polymer. Lastly, it is pointed out that the differential equations (11) to (19) are 'stiff' numerically, which means that the dimensionless time increment, Δx, must be chosen carefully to obtain a stable solution. We define a ring count RC as

$$RC=A_1+\sum_{i=1}^{\infty} iQ_i \tag{21}$$

which should remain unchanged with time of polymerization. Theoretically, one should solve an infinitely large number of equations in the set (11) to get the *MWD* of the polymer. However, we chose an arbitrary upper limit on n, namely N_c, such that the ring count RC remains time invariant. The computer program starts from a low value of N_c (say 10) but as the time of polymerization increases, it keeps incrementing N_c in such a way that RC remains within a maximum allowable error (in our computations, it is 1%).

The *MWD* of the polymer computed in this way has been found by changing one of the rate constants in equation (20) at a time. In all cases, we have found that the formation of Q_4 and beyond occur in negligibly small quantities. In *Figures 5* and *6*, we have varied k_2. This particular rate constant gives the effect of unequal reactivity in the formation of melamine polymer and *Figure 5* gives the weight fraction of one-ring species in the reaction mass. When k_2 is zero, melamine has effectively three sites where polymerization can occur. As opposed to this, when $k_2=k_1$, it has six equivalent sites for reaction. Since chances of reaction increase with increasing availability of sites, the concentrations of Q_1 and A_1 are found to reduce as k_2 increases from a low value, as seen in *Figure 5*. In *Figure 6*, the weight fraction of dimer has been plotted as a function of time for various values of k_2. It may be observed that Q_2 is formed from the reactions involving Q_1, and A_1 and can form higher homologues. This would imply that W_2 must undergo a maximum which is precisely what is being observed in *Figure 6*. This figure reveals that Q_2 is formed in sufficiently high quantity and, as k_2 is increased, a maximum in W_2 occurs for smaller times and the curve becomes less broad. This behaviour can be explained as

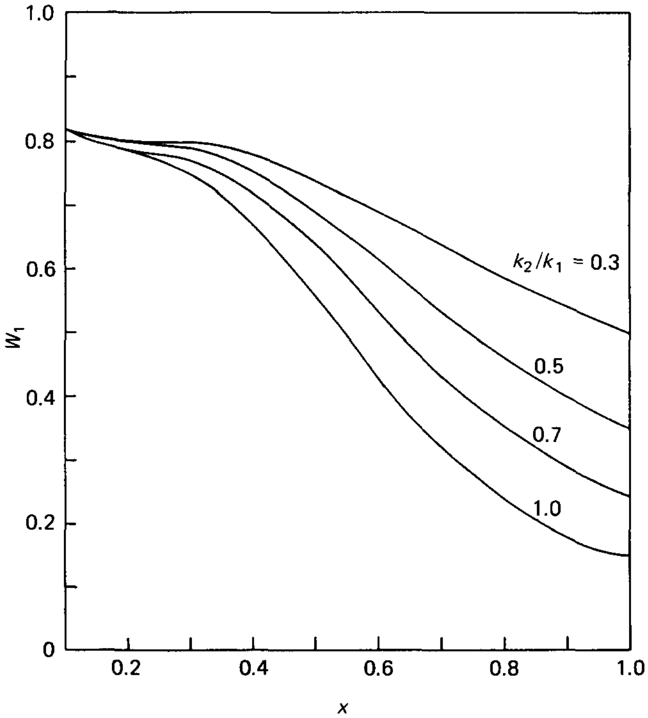


Figure 5 Effect of unequal reactivity (i.e. k_2) on the weight fraction of one ring species in the reaction mass for $[F_1]/[A]=5$

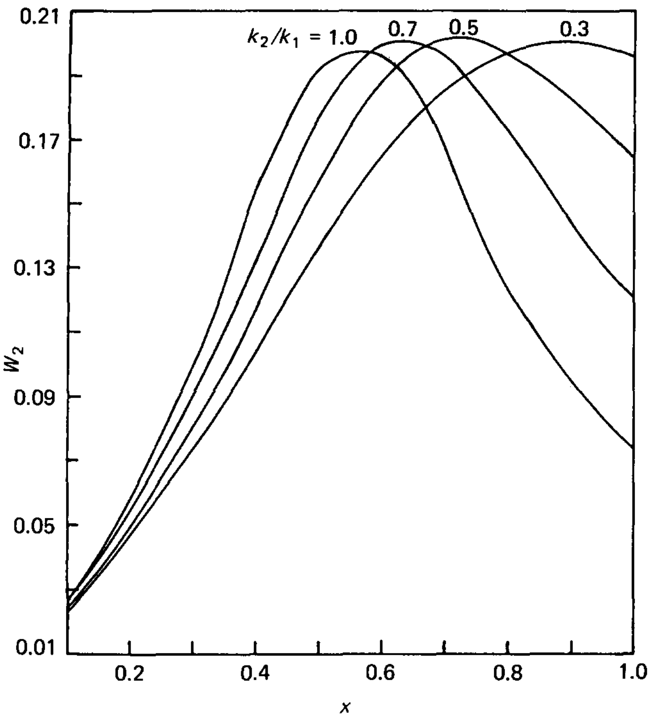


Figure 6 Effect of unequal reactivity on the weight fraction of dimer in the reaction mass for $[F_1]/[A]=5.0$

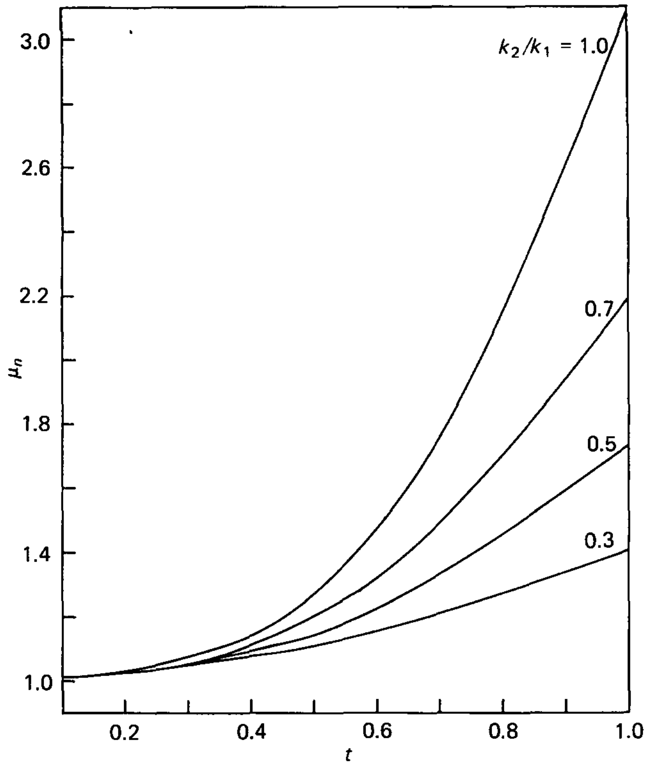


Figure 7 Effect of k_2 on average chain length μ_n of the melamine polymer for $[F_1]/[A]=5$

follows. With an increase in k_2, more secondary sites are available for reaction, which implies that Q_2 reacts to form higher oligomers with more ease. This in turn reduces the time where the maxima occurs and the breadth of the distribution. In *Figures 7* and *8*, the average chain length μ_n and the polydispersity index ρ have been calculated from the *MWD* for various values of k_2. In *Figure 7*, μ_n is found to increase with increase in k_2 and μ_n as high as 3 is found for $k_2=k_1$. The results in *Figure 8* for ρ are found to be more interesting in the following way. For polymer formed from bifunctional monomers in batch reactors, ρ is limited to a maximum value of 2. In the case of melamine polymers, there is no such limitation due to the branching of the molecules. In addition, in this case, there is an unequal reactivity of various reactive sites and chain growth occurs through two distinct reactions: (a) reaction of CH_2OH groups with H groups and (b) reaction of two CH_2OH groups.

As pointed out above, there are two distinct reactions by which chain growth can occur. In *Figures 9* to *12*, the effects of these on μ_n and ρ *versus* time of polymerization have been examined. When k_5 and k'_4 are small, overall polymerization is pushed more in the forward direction and polymer of higher chain lengths is produced, as seen in *Figures 9* and *10*. In the mechanism given here, a given reacted bond Z can break through reaction with either free formaldehyde F_1 or water. As k'_4 *and* k_5 are increased, polymerization favours the formation of smaller molecules with less branching. As a consequence μ_n as well should fall. In *Figure 9*, for $k_5=3k_1$, the reaction mass is essentially Q_1 and A_1. Polymerization is found to be less sensitive to variation of k'_4 in *Figure 10* even though μ_n falls as expected. *Figures 11* and *12* give the polydispersity index ρ *versus* x. Lastly the comparison of *Figures 5* to *12* shows that the polymerization is far from equilibrium for the range of x studied.

CONCLUSIONS

Ten reactive species A to J have been defined in which a reacted bond and CH_2OH have not been distinguished. Two kinetic models I and II have been proposed in which

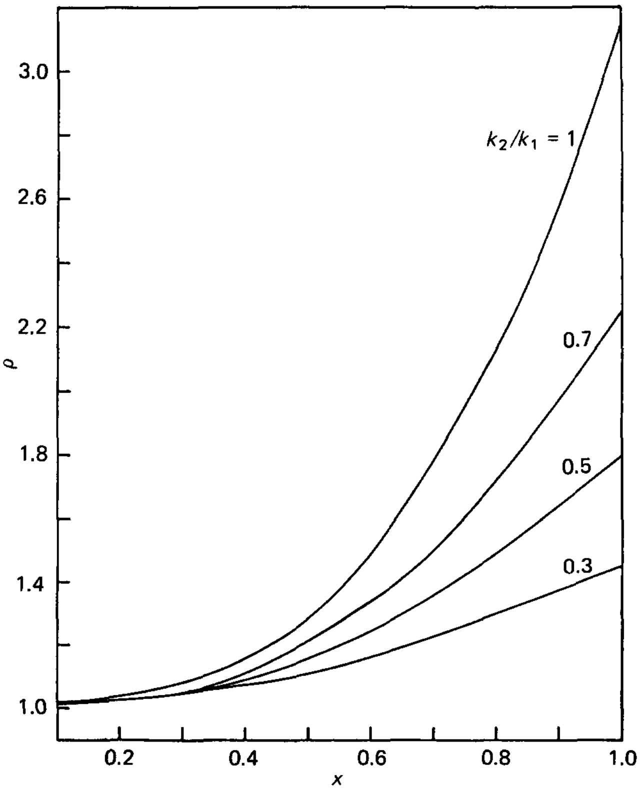


Figure 8 Effect of k_2 on the polydispersity index ρ of the melamine polymer for $[F_1]/[A]=5$

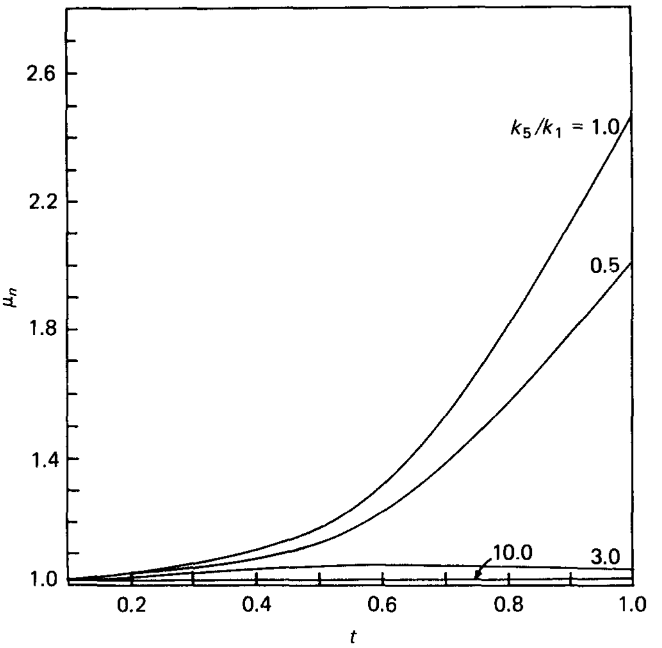


Figure 9 Effect of k_5 on μ_n *versus* x for $[F_1]/[A]=5$

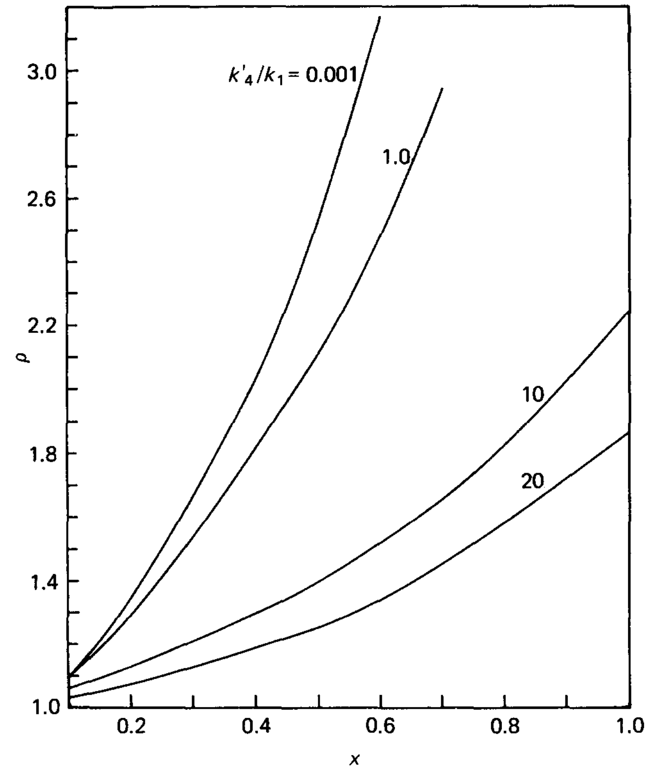


Figure 10 Effect of k'_4 on μ_n *versus* x for $[F_1]/[A]=5$

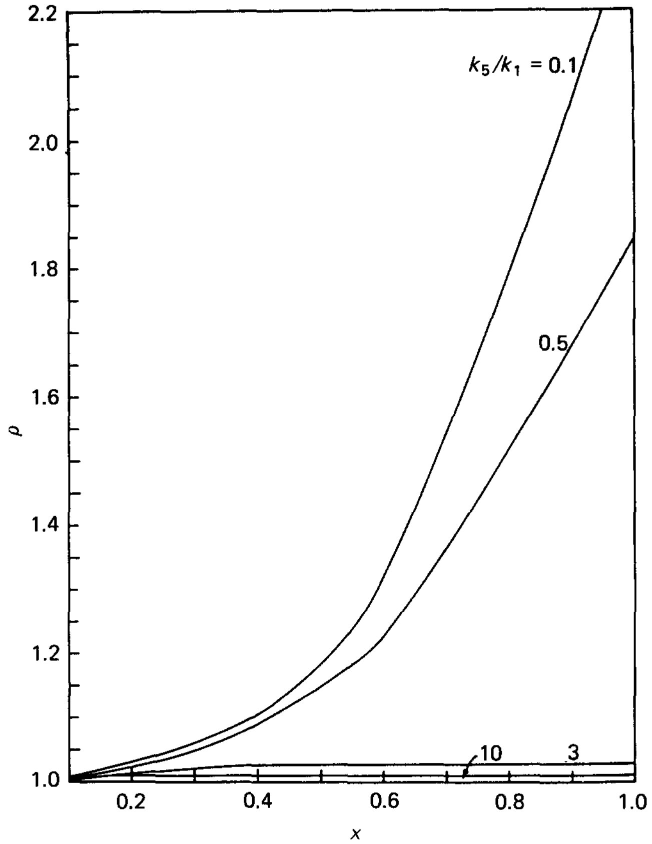


Figure 11 Effect of k_5 on ρ *versus* x for $[F_1]/[A]=5$

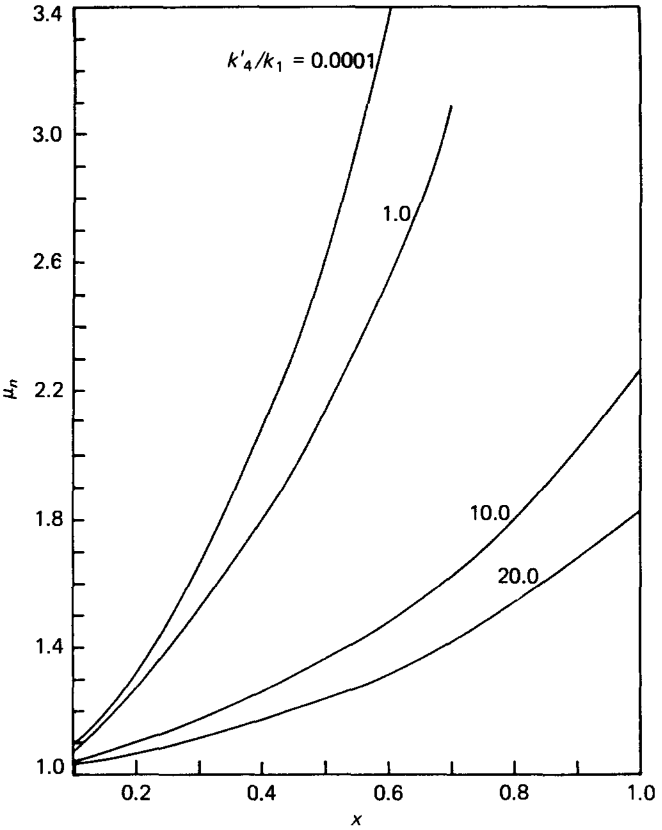


Figure 12 Effect of k'_4 on ρ *versus* x for $[F_1]/[A]=5$

reverse reactions are written assuming that reacted sites are entirely bonds or entirely CH_2OH groups. It is subsequently shown that if the purpose is to find out the conversion of functional groups, models I and II both give identical results. Both these kinetic models involve five rate constants which have been evaluated by curve fitting the experimental data of Tomita.

The formation of melamine polymer is reversible and, in addition to this, due to the hexafunctional nature of melamine, the polymer formed is branched in structure. We have shown in this work that the reverse reaction of branched molecules is strongly dependent upon the chain structure. For common symmetrical molecules, analytical expressions for reverse reactions have been derived. However, for a general structure, a computer program has been suggested which scans first the branches and then the backbone of the chain and generates a parameter $\delta_{i\to n}$ $(n < i)$. The reverse reaction can then be written in terms of $\delta_{i\to n}$.

To determine the *MWD* of the polymer, the concentrations of various reactive species A to J are first determined. It is subsequently recoginized that species E to J lead to branching. Since the reaction mass does not contain molecules of very large chain lengths, it is assumed that the branching of molecules at a given time is bimodally distributed. The mole balance relations for batch reactors have been written and numerically solved. It is seen that the *MWD* of the polymer is very sharp and the concentration of Q_4 oligomers and beyond is negligibly small; dimer Q_2, however, is formed in significant concentration. Since melamine is a hexafunctional monomer and there is more than one distinct chemical reaction leading to the formation of polymer, the polydispersity index ρ is not limited to a value of 2.

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