

# Polymerization of Melamine and Formaldehyde in Homogeneous Continuous-Flow Stirred-Tank Reactors Using Functional Group Approach: Part A: Conversion of Functional Groups

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## Synopsis

A comprehensive kinetic model using the functional group approach has been proposed for the polymerization of melamine and formaldehyde. The kinetic model is consistent with the basic chemistry of polymerization and involves five rate constants which have been estimated using the experimental data of Tomita. Homogeneous continuous-flow stirred-tank reactors (HCSTRs) have been modelled and the mole balance relations for various functional groups have been written. The performance of HCSTRs is governed by algebraic equations and, for any specified residence time, is found by the method of successive substitution using the Brown's algorithm. The computations show that as long as free formaldehyde is present, the reaction mass would consist predominantly of substituted melamine molecules. However, after formaldehyde is completely reacted, larger oligomers are formed in larger concentrations. On comparison of results with batch reactors, it is found that for the same reaction time HCSTRs yield polymer with higher branching.

## INTRODUCTION

In formalin, formaldehyde can exist either as methylene glycol or as a low molecular weight polymeric molecule. There is a chemical equilibrium between these species and it has been shown that it exists mostly as methylene glycol in the reaction mass. Melamine is a weakly basic material and can react with formaldehyde forming melamine formaldehyde polymer.<sup>1,2</sup>

Industrially melamine formaldehyde polymer is an extremely important material and is mainly used for manufacturing cooking wares. Normally the polymer is prepared in two stages; in the first stage melamine and formaldehyde are reacted to form molding powder which is a low molecular weight polymer. In this stage the predominant reaction is the methylation of melamine, however, there is a small amount of polymer formation. In the second stage, the molding powder is polymerized in molds to give a thermoset polymer.

Commercially, the polymer has been known since 1884, yet the reactions leading to the formation of polymer has been studied only recently. Several works have been reported on the addition of melamine to formaldehyde<sup>3-7</sup> but most of these have been limited to low concentrations of formaldehyde where there has been an addition of methylene glycol to melamine. By keeping low concentrations, the formation of higher oligomers are prevented.

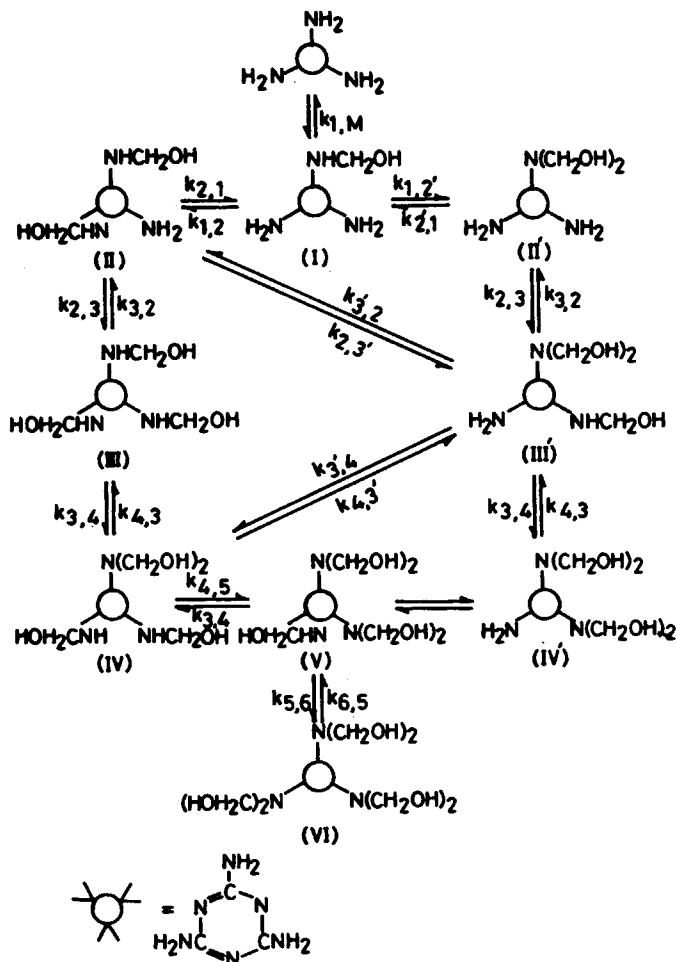


Fig. 1. Kinetic mechanism proposed by Tomita for the polymerization of melamine and formaldehyde.

Melamine has three amino groups and consequently six possible sites for reaction; the various reactions leading to methylation that have been considered in the literature are given in Figure 1.

Okano and Ogata<sup>8,9</sup> have measured the initial reaction rate constants. Further investigation on the kinetics by Gordon et al.<sup>10</sup> have illustrated that quantitative estimate of the products could be made using labelled C-14 formaldehyde. Some deviation from the random behavior 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.,<sup>11</sup> who attempted to match experimental data on the free formaldehyde content with the results obtained from computation.

Tomita<sup>7</sup> has carried out a detailed experimental study of various molecular species distribution of methylol melamines using the reaction mechanism given in Figure 1. This study revealed that the methylation of melamine is a reversible reaction. The mechanism considered in Figure 1 has 10 species and

involves 24 rate constants. Tomita has analyzed the reaction mass using the nuclear magnetic resonance (NMR) spectroscopy and the high speed liquid chromatography. At a given temperature and various melamine to formaldehyde ratios in the feed, he determined the concentrations of various species in Figure 1 as a function of time. Using the kinetic mechanism given in the figure, he evaluated various rate constants from his experimental measurements and has found that these are dependent upon the initial concentration of formaldehyde fed to the batch reactor. In these experiments the reaction conditions were maintained such that only methylation occurs.

In polymerizing melamine with formaldehyde at commercial concentrations there will be formation of higher oligomers even though the concentration of polymer has been shown to be small.<sup>12</sup> The polymerization involving formaldehyde ( $F_1$ ) has been discussed in detail by Drumm and LeBlanc.<sup>2</sup> They state that in solution, formaldehyde remains as methylene glycol and reacts in two stages. On reaction with hydrogen,  $F_1$  leads to methylation and gives a  $CH_2OH$  group which can react once again. A given  $CH_2OH$  group can react with a hydrogen as well as with another  $CH_2OH$  group. In the model that we propose here, we include both these reactions. It may be recognized that these two reactions lead to the formation of higher oligomers. Industrially, polymerization of melamine with formaldehyde is carried out in two stages. In the first stage, melamine is essentially methylolated. In the final stage, the methylolated melamine is polymerized in molds to form a highly crosslinked thermoset polymer. Tomita's kinetic model is valid for the methylation stage only and there is a need to develop a generalized model valid for both the stages.

As the capacity of the plant manufacturing polymer increases, continuous reactors are preferred over batch reactors. Among various possible geometries, the homogeneous continuous-flow stirred-tank reactors (HCSTRs) are preferred industrially. In this paper we present a kinetic model based on functional group approach which accounts for the formation of higher oligomers. The overall mechanism of polymerization is written in terms of reaction of functional groups and the experimental data of Tomita has been curve-fitted by the mole balance relations for batch reactors based on the proposed mechanism. The model proposed in this work involves five rate constants and the experimental data reported by Tomita are described by our model in the entire range, thus justifying the functional groups approach taken in this paper. The rate constants so determined are used to evaluate the performance of HCSTRs and the results have been compared from those obtained from batch reactors. We find that the polymer obtained from HCSTRs is less branched for the same reactor residence time.

### KINETIC MODEL

In the kinetic model shown in Figure 2, species A to J specify the various hydrogen on a melamine ring that can undergo reaction either with formaldehyde or with a  $CH_2OH$  group. If any of these species reacts with a molecule of formaldehyde, it leads to methylation, but if it reacts with another  $CH_2OH$  group, it forms higher oligomers. It is assumed that the reactivity of a given hydrogen is different for a primary and a secondary

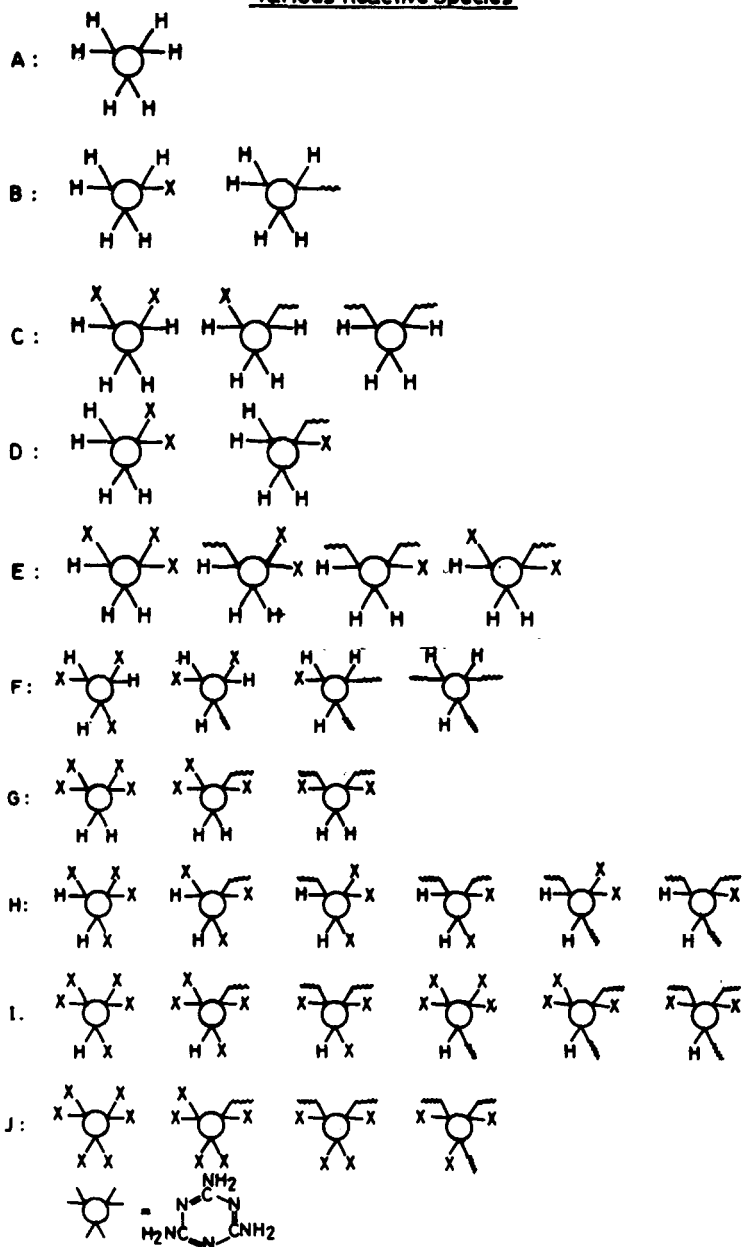
Various Reactive Species

Fig. 2. Various reactive sites used in the kinetic model.

amide hydrogen and the reactivity of a given species is independent of its substituent. In Figure 2, X denotes a  $\text{CH}_2\text{OH}$  bond whereas a  $\sim$  indicates that the melamine ring is part of a polymer chain. Therefore, species B represents two different structures, one with a  $\text{CH}_2\text{OH}$  group and one with a bond. Similarly, species C represents three different structures, and so on.

TABLE I  
Forward Reactions 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. $B + F_1 \xrightarrow{8k_1}$	$C + CH_2OH + H_2O$	$B + CH_2OH \xrightarrow{4k_1} C + Z + H_2O$
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. $C + F_1 \xrightarrow{4k_2}$	$E + CH_2OH + H_2O$	$C + CH_2OH \xrightarrow{2k_2} E + Z + H_2O$
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. $F + F_1 \xrightarrow{6k_2}$	$H + CH_2OH + H_2O$	$F + CH_2OH \xrightarrow{3k_2} H + Z + H_2O$
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. $I + F_1 \xrightarrow{2k_2}$	$J + CH_2OH + H_2O$	$I + CH_2OH \xrightarrow{k_2} J + Z + H_2O$
13.	$CH_2OH + CH_2OH \xrightleftharpoons[k'_4]{k_4} Z + F_1$	

Reaction 13 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.

The kinetic model proposed herein is consistent with the basic chemistry of polymerization. In Table I, the forward reaction of species A to J are given. The list of reactions are clearly divided into two groups: the first one containing reactions of species with formaldehyde while the other containing reactions with a  $CH_2OH$  group. A reacted bond (denoted by Z) can form only when a  $CH_2OH$  group reacts.

To get an idea of higher oligomer formation, we have shown the formation of Z in this class of reactions. Since the reactivity is completely determined by the reactive hydrogen involved, we define the following rate constants:

$k_1$  : forward rate constants between a  $CH_2OH$  and primary amide hydrogen lying on the rings.

$k_2$  : rate constant between a  $CH_2OH$  and a secondary amide group.

$k_4, k'_4$ : rate constants between two  $-CH_2OH$  groups. The reaction leads to formation of Z and a free formaldehyde molecule; this reaction step does not change the nature of the species.

$k_5$  : reverse rate constant involving a bond and a water molecule.

In the reverse reaction there are two possibilities that can exist. In Table II (called model I), which shows the reverse reactions, the reacted sites on

TABLE II  
Reverse Reaction Step in the Polymerization of Melamine with Formaldehyde  
assuming Reacted Sites as Reacted Bonds

Model I		
B + H <sub>2</sub> O	$\xrightarrow{k_5}$	A + CH <sub>2</sub> OH - Z
C + H <sub>2</sub> O	$\xrightarrow{2k_5}$	B + CH <sub>2</sub> OH - Z
D + H <sub>2</sub> O	$\xrightarrow{2k_5}$	B + CH <sub>2</sub> OH - Z
E + H <sub>2</sub> O	$\xrightarrow{2k_5}$	C + CH <sub>2</sub> OH - Z
E + H <sub>2</sub> O	$\xrightarrow{k_5}$	D + CH <sub>2</sub> OH - Z
F + H <sub>2</sub> O	$\xrightarrow{3k_5}$	C + CH <sub>2</sub> OH - Z
G + H <sub>2</sub> O	$\xrightarrow{4k_5}$	E + CH <sub>2</sub> OH - Z
H + H <sub>2</sub> O	$\xrightarrow{2k_5}$	E + CH <sub>2</sub> OH - Z
H + H <sub>2</sub> O	$\xrightarrow{2k_5}$	F + CH <sub>2</sub> OH - Z
I + H <sub>2</sub> O	$\xrightarrow{k_5}$	G + CH <sub>2</sub> OH - Z
I + H <sub>2</sub> O	$\xrightarrow{4k_5}$	H + CH <sub>2</sub> OH - Z
J + H <sub>2</sub> O	$\xrightarrow{6k_5}$	I + CH <sub>2</sub> OH - Z

various species have been assumed to be entirely reacted bonds (denoted by Z) which on reaction with water leads to the formation of a CH<sub>2</sub>OH group. In Table III (called model II), the reacted sites on various species are assumed to be approximately all CH<sub>2</sub>OH groups, which on reaction with water lead to the formation of free formaldehyde.

#### Mole Balance Relations for HCSTRs

A schematic diagram of a HCSTR is shown in Figure 3 in which the feed consists of melamine and formaldehyde at molar ratios  $[A]_0$  and  $[F]_0$ . If the reactor is assumed to be well mixed and operating at the steady state, the concentrations of all species in the exit stream would be the same as those within it. Through various reactions given in Tables I to III, species B to J, CH<sub>2</sub>OH groups, H<sub>2</sub>O and Z are produced and mole balance relations for these can be easily written. As an example, one considers melamine which is the same as species A in Figure 2. This is given by

$$\frac{A - A_0}{\theta} = \mathcal{R}_A \quad (1)$$

where  $\mathcal{R}_A$  is the rate of production of species A written in the dimensionless

TABLE III  
Reverse Reaction Steps in the Polymerization of Melamine with Formaldehyde  
Assuming Reacted Sites as CH<sub>2</sub>OH Groups

Model II		
B + H <sub>2</sub> O	$\xrightarrow{k_5}$	A + F <sub>1</sub> - CH <sub>2</sub> OH
C + H <sub>2</sub> O	$\xrightarrow{2k_5}$	B + F <sub>1</sub> - CH <sub>2</sub> OH
D + H <sub>2</sub> O	$\xrightarrow{2k_5}$	B + F <sub>1</sub> - CH <sub>2</sub> OH
E + H <sub>2</sub> O	$\xrightarrow{2k_5}$	C + F <sub>1</sub> - CH <sub>2</sub> OH
E + H <sub>2</sub> O	$\xrightarrow{k_5}$	D + F <sub>1</sub> - CH <sub>2</sub> OH
F + H <sub>2</sub> O	$\xrightarrow{3k_5}$	C + F <sub>1</sub> - CH <sub>2</sub> OH
G + H <sub>2</sub> O	$\xrightarrow{4k_5}$	E + F <sub>1</sub> - CH <sub>2</sub> OH
H + H <sub>2</sub> O	$\xrightarrow{2k_5}$	E + F <sub>1</sub> - CH <sub>2</sub> OH
H + H <sub>2</sub> O	$\xrightarrow{2k_5}$	F + F <sub>1</sub> - CH <sub>2</sub> OH
I + H <sub>2</sub> O	$\xrightarrow{k_5}$	G + F <sub>1</sub> - CH <sub>2</sub> OH
I + H <sub>2</sub> O	$\xrightarrow{4k_5}$	H + F <sub>1</sub> - CH <sub>2</sub> OH
J + H <sub>2</sub> O	$\xrightarrow{6k_5}$	I + F <sub>1</sub> - CH <sub>2</sub> OH

form. This, along with the rate of production of other species are given in Table IV. In Eq. (1)

$$A = \frac{[A]}{[F_1]_0} \quad (2a)$$

$$A_0 = \frac{[A]_0}{[F_1]_0} \quad (2b)$$

$$\theta = k_1[F_1]_0 V/\dot{Q} \quad (2c)$$

$$r_1 = \frac{k_2}{k_1} \quad (2d)$$

$$r_2 = \frac{k_4}{k_1} \quad (2e)$$

$$r_3 = \frac{k'_4}{k_1} \quad (2f)$$

$$r_4 = \frac{k_5}{k_1} \quad (2g)$$

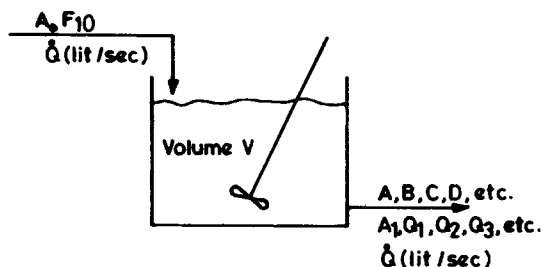


Fig. 3. A schematic diagram of homogeneous continuous flow stirred tank reactors (HCSTRs).

where  $V$  is the volume of the reactor and  $Q$  the feed flow rate. One can make similar mole balance relations for the other species as

$$\frac{B}{\theta} = \mathcal{R}_B \quad (3a)$$

$$\frac{C}{\theta} = \mathcal{R}_C \quad (3b)$$

etc ....

### Comparison of Model I and Model II

As discussed in the kinetic model, the two models (I and II given in Tables II and III) arise due to the ambiguity about the nature of reacted sites on species defined in Figure 2. This would in turn lead to different results for the concentrations of free formaldehyde ( $F_1$ ) and  $\text{CH}_2\text{OH}$  groups in HCSTRs for these two models. It can however be shown that  $(\text{CH}_2\text{OH} + 2F_1)$  is the same for both the models. If Table IV is observed carefully, it is found that the rate of production of any species (A to J) all involve  $(2F_1 + \text{CH}_2\text{OH})$  and not the individual concentrations of  $F_1$  and  $\text{CH}_2\text{OH}$  groups. This implies that the concentrations of various species in the exit stream of the HCSTR is independent of the nature of reacted sites on these species.

### Computation Scheme for the Reactor Performance

There are species A to J, Z,  $\text{H}_2\text{O}$ ,  $F_1$ ,  $\text{CH}_2\text{OH}$  groups in the exit stream of the HCSTRs and therefore in all 14 nonlinear algebraic expressions which must be solved simultaneously. The numerical solution of these is not an easy matter and in the literature, the Newton-Raphson or the Brown's method has been used. Among these, the latter has found more success and in this paper, the Brown's method has been used to determine the performance of the HCSTRs.

The Brown's algorithm of computation generates a Jacobian matrix whose determinant should not be zero. For this reason the solution would never converge if any of these fourteen relations are linearly dependent. Since the



TABLE IV  
Mole Balance Relations for HCSTRs

Model I	
1.	$\frac{A - A_0}{\theta} = -6k_1A(2F_1 + \text{CH}_2\text{OH}) + k_5B.H_2O$
2.	$\frac{B}{\theta} = 6k_1A(2F_1 + \text{CH}_2\text{OH}) - (4k_1 + k_2)B(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(2D + 2C) - K_5B.H_2O$
3.	$\frac{C}{\theta} = 4k_1B(2F_1 + \text{CH}_2\text{OH}) - (2k_1 + 2k_2)C(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(2E + 3F) - k_5H_2O(2C)$
4.	$\frac{D}{\theta} = k_2B(2F_1 + \text{CH}_2\text{OH}) - 4k_1D(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(E) - k_5H_2O(2D)$
5.	$\frac{E}{\theta} = (2k_2C + 4k_1D)(2F_1 + \text{CH}_2\text{OH}) - (2k_1 + k_2)E(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(4G + 2H) - k_5H_2O(3E)$
6.	$\frac{F}{\theta} = (2k_1C(2F_1 + \text{CH}_2\text{OH}) - 3k_2F(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(2H) - k_5H_2O(3F)$
7.	$\frac{G}{\theta} = k_2E(2F_1 + \text{CH}_2\text{OH}) - 2k_1G(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(I) - k_5H_2O(4G)$
8.	$\frac{H}{\theta} = (2k_1E + 3k_2F)(2F_1 + \text{CH}_2\text{OH}) - 2k_2H(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(4k_5I - k_5H_2O(4H)$
9.	$\frac{I}{\theta} = (2k_1G + 2k_2H)(2F_1 + \text{CH}_2\text{OH}) - k_2I(2F_1 + \text{CH}_2\text{OH}) + k_5H_2O(6J) - k_5H_2O(5I)$
10.	$\frac{J}{\theta} = (k_2I)(2F_1 + \text{CH}_2\text{OH}) - k_5H_2O(6J)$
11.	$\frac{F_1 - 1}{\theta} = -2F_1\{6k_1A + (4k_1 + k_2)B + (2k_1 + 2k_2)C + 4k_1D + (2k_1 + k_2)E + 3k_2F + 2k_2G + 2k_2H + k_2I\} + k_4(\text{CH}_2\text{OH})^2 - k_4'ZF_1$
12.	$\frac{\text{CH}_2\text{OH}}{\theta} = +2F_1R_1 - (\text{CH}_2\text{OH})R_1 + k_5H_2O\{B + 2C + 2D + 3E + 3F + 4G + 4H + 5I + 6J\} + 2k_4'ZF - 2k_4(\text{CH}_2\text{OH})^2$
13.	$\frac{Z}{\theta} = (\text{CH}_2\text{OH})R_1 - k_5H_2OR_2 + k_4(\text{CH}_2\text{OH})^2 - k_4'ZF_1$
14.	$\frac{H_2O}{\theta} = (2F_1 + \text{CH}_2\text{OH})R_1 - k_5H_2OR_2$

## Model II

Eqs. (1) to (10) are the same as in case I.

11.	$\frac{F_1 - 1}{\theta} = -2F_1R_1 + k_4(\text{CH}_2\text{OH})^2 - k_4'ZF_1 + k_5H_2OR_2$
12.	$\frac{\text{CH}_2\text{OH}}{\theta} = 2F_1R_1 - \text{CH}_2\text{OH}R_1 + 2k_4'ZF - 2k_4(\text{CH}_2\text{OH})^2$
13.	$\frac{Z}{\theta} = (\text{CH}_2\text{OH})R_1 - k_5H_2OR_2 + k_4(\text{CH}_2\text{OH})^2 - k_4'ZF_1$
14.	$\frac{H_2O}{\theta} = (2F_1 + \text{CH}_2\text{OH})R_1 - k_5H_2OR_2$

where,

$$R_1 = 6k_1A + (4k_1 + k_2)B + (2k_1 + 2k_2)C + 4k_1D + (2k_1 + k_2)E + 3k_2F + 2k_2H + k_2I + 2k_2G$$

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

$$A = \frac{[A]}{[F_1]_0} \quad B = \frac{[B]}{[F_1]_0} \quad C = \frac{[C]}{[F_1]_0} \quad \text{etc.}$$

Residence time of HCSTR,  $\theta_1 = V/\dot{Q}$ .

Dimensionless residence time,  $\theta = k_1[F_1]_0\theta_1$

total species count cannot change due to chemical reaction, one has

$$A_0 = A + B + C + D + E + F + G + H + I + J \quad (4)$$

whatever formaldehyde reacts, it shows up either as  $\text{CH}_2\text{OH}$  group or water. This means that at any time the following stoichiometric relation would be valid

$$2 = 2F_1 + \text{CH}_2\text{OH} + \text{H}_2\text{O} \quad (5)$$

Lastly, it is observed that all the reacted sites would either be  $\text{CH}_2\text{OH}$  group or a Z which would imply that

$$6A_0 - 6A = \text{CH}_2\text{OH} + Z + 5B + 4C + 4D + 3E + 3F + 3G + 2H + I \quad (6)$$

In view of these stoichiometric relations, one must solve only 11 algebraic relations simultaneously and solve the rest of the variables using Eqs. (4) to (6).

Another problem faced in solving these algebraic equations is to provide an initial guess of the eleven variables to be solved. Suppose it is desired to solve the reactor variables at the residence time  $\theta$ . This is divided in small increment  $\Delta\theta$  for the purpose of computation. The initial guess is taken as the same as the conditions existing in the feed stream and the value of  $\Delta\theta$  is adjusted such that there is a convergence. The values of variables at  $\Delta\theta$  serve as the initial guess for the residence time of  $2\Delta\theta$  and in this way, the computations are stepped upto the reactor residence time  $\theta$ . In all our computations reported in this work, the first  $\Delta\theta$  was taken as 0.005, after which  $\Delta\theta$  was assumed to be 0.02. However, when  $\theta$  values reaches 0.5, the  $\Delta\theta$  was changed to 0.1. This set of  $\Delta\theta$  was found to give the convergence.

## RESULTS AND DISCUSSIONS

The kinetic model presented in this work is consistent with the chemistry of polymerization and involves only five rate constants. Tomita has carried out an experimental investigation of the reaction of melamine with formaldehyde in batch reactors. With the rate of production of various species given in Table IV, we have written the mole balance relations for batch reactors. It is found that the reactor performance is described by a set of differential equations which can be easily solved using the fourth-order Runge-Kutta algorithm. We have curve-fitted the limited experimental data of Tomita and our model was found to describe in the entire zone of polymerization as seen in Figure 4. Since the experiments were carried out in the region of low melamine concentrations where the formation of higher oligomers is limited, model II (reactions, given in Table III) was found to be a better representation. It may however be pointed out that as far as the concentrations of reactive species given in Figure 2 are concerned both models give identical results. The discrepancy arises only in determining  $[\text{CH}_2\text{OH}]$  and  $[F_1]$  and model II has been used to find these. The curve fitting of the experimental data shows two important results. The first one is that the rate constants are dependent upon the ratio of formaldehyde to melamine present initially,

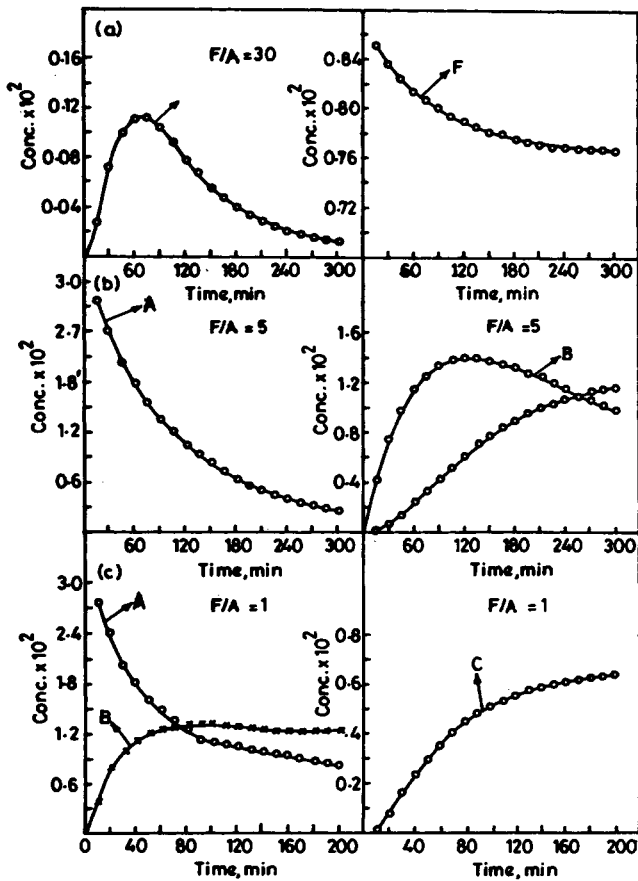


Fig. 4. Use of the kinetic model proposed in this work to fit the experimental data of Tomita. (a)  $[C]$  and  $[F]$  versus time for  $[F_1]/[A] = 30$ ,  $k_1 = 0.0045$ ,  $k_2 = .004$ ,  $k_4 = 0.004$ ,  $k'_4 = 0.3$ ,  $k_5 = 0.005$ . (b)  $[A]$ ,  $[B]$ , and  $[C]$  versus time for  $[F_1]/[A] = 5$ ,  $k_1 = 0.005$ ,  $k_2 = 0.0015$ ,  $k_4 = 0.004$ ,  $k'_4 = 0.3$ ,  $k_5 = 0.01$ . (c)  $[A]$ ,  $[B]$ , and  $[C]$  versus time  $[F_1]/[A] = 0.1$ .  $k_1 = 0.04$ ,  $k_2 = 0.05$ ,  $k_4 = 0.004$ ,  $k'_4 = 0.3$ ,  $k_5 = 1.0$ .

which is consistent with the findings of Tomita. The second one is that a given bond Z can react with both free formaldehyde as well as water. Since the rate constant  $k'_4$  is large (66.67), the polymer chain cannot grow as long as there is free formaldehyde in the reaction mass. This is consistent with the experimental observation that in the first stage of the polymer formation the methylation of melamine is the major reaction.

In the simulation of homogeneous continuous-flow stirred tank reactors (HCSTRs), we have used the rate constants found from the curve fitting of the experimental data of Tomita. These are  $k_1 = 0.0045$ ,  $k_2 = 0.0001$ ,  $k_4 = 0.0004$ ,  $k'_4 = 0.305$ ,  $k_5 = 0.005$  which give

$$r_1 = 0.3, r_2 = 0.089, r_3 = 66.67, r_4 = 1.11 \quad (7)$$

Since these rate constants can in general have different activation energies, in principle the ratios  $r_1$  to  $r_4$  can take on any value as the temperature is

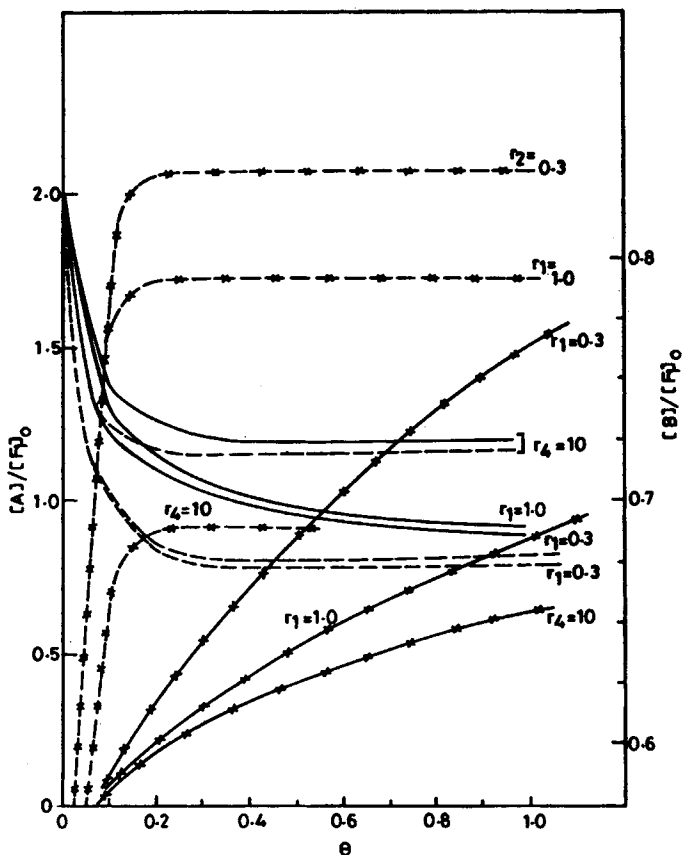


Fig. 5. Effect of  $r_1$  and  $r_4$  on [A] and [B] as a function of the residence time of HCSTRs. Dotted lines give results of batch reactors: Batch (----) A, (-x-) B; HCSTR(—) A, (-x-) B.

increased from a small value. To assess the effect of temperature, in the following study, we have taken a base values of ratios  $r_1$  to  $r_4$  given by Eq. (7) and examined the effect of these upon the progress of polymerization in HCSTRs.

In Figure 5, the effect of  $r_1$  and  $r_4$  have been examined and the concentrations of melamine and reactive species B as a function of the reactor residence time have been plotted. In the figure, results for batch reactors have also been included for comparison. As the residence time of an HCSTR is increased, the concentration of melamine (i.e., species A) begins to fall sharply from its initial value of 2.0, but for large  $\theta$ , these curves approach an asymptotic value as seen in Figure 5. When  $r_1 = 0$ , it means that the secondary amide hydrogens do not react and the functionality of melamine is only 3. As opposed to this, when it is equal to 1, it is implied that the primary and secondary hydrogens react with equal likelihood and melamine exhibits a functionality of six. The experimental value of  $r_1$  is 0.3 and it is varied between 0.3 and 1 in Figure 5 and it is found that this has little effect upon A. The results for batch reactors are shown by dotted lines in this figure and it is found that the conversion of melamine for HCSTRs is always smaller for the same residence

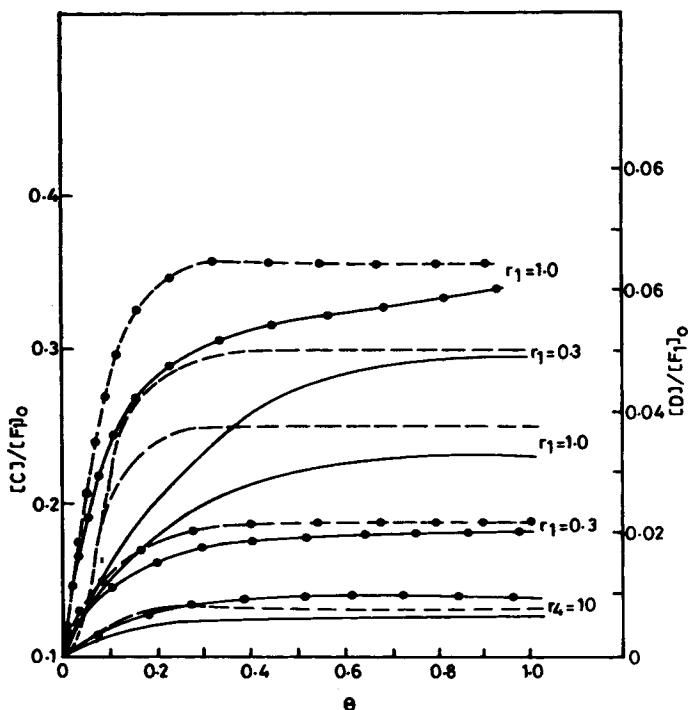


Fig. 6. Effect of  $r_1$  and  $r_4$  on  $[C]$  and  $[D]$  versus  $\theta$ . Dotted lines show results for batch reactors: HCSTR(—) C, (—) D, Batch (----) C, (---) D.

time. The same figure also gives the concentration of species B as a function of residence time  $\theta$ . For HCSTRs, B increases continuously and as  $r_1$  is increased, its preferential formation is found to reduce. As opposed to this, B attains an asymptotic value and is found to form in larger concentrations in batch reactors compared to those for HCSTR. The effect of ratio  $r_4$  upon the polymerization is also examined in this figure and as  $r_4$  increases, the conversion of melamine (species A) reduces and B is formed in smaller concentration. This is because with the increase in  $r_4$ , the reverse reaction of a given bond with water increases, this way limiting the formation B, which would in turn lower the conversion of melamine as seen in Figure 5.

In the sensitivity analysis presented in Figures 6 to 8 we find that the reactivity ratios  $r_2$  and  $r_4$  are very important variables. In Figure 6, the effect of these upon the concentrations of species C and D have been examined. Between Figures 5 and 6, we find that as  $r_2$  is increased, the concentrations of B and C fall, while that of D rises. This is expected if Figure 2 is examined; it occurs because species B and C can react more easily with increase in  $k_2$ , thus leading to their lower concentrations. Figure 6 reveals that as  $r_5$  is increased, the reverse reaction with water becomes more important and this limits the conversion of melamine as well as the formation of other reactive species. In these figures, results for batch reactors are also given and is found that species C and D are always formed in HCSTRs in lower concentrations.

Concentrations of species E and F for HCSTRs have been plotted in Figure 7 and results for batch reactors are indicated by dashed lines. For both these

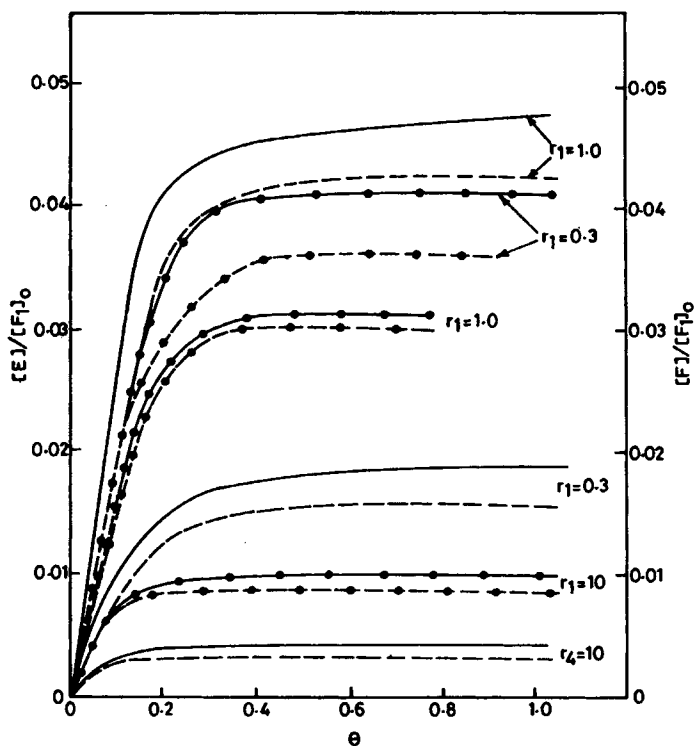


Fig. 7. Effect of  $r_1$  and  $r_4$  on  $[E]$  and  $[F]$  versus  $\theta$ . Dotted lines give results for batch reactors: HCSTR(—) E, (—•—) F; (----) E, (---•---) F.

species, the amount of species F is always less, a result which is of considerable significance. Branching of polymer are indicated through species E to J, which means that the polymer formed in HCSTR is more branched.

The concentration of  $\text{CH}_2\text{OH}$  and free formaldehyde  $F_1$  depends upon whether model I or II is used for the reversed reaction. In case of model I  $[\text{CH}_2\text{OH}]$  is overestimated while for model II,  $[F_1]$  is overestimated. As shown, no matter which model is used, the combination  $2[F_1] + [\text{CH}_2\text{OH}]$  is the same for both. In addition, Tomita had carried out experimental investigation of melamine formaldehyde polymerization using formaldehyde in excess. This would lead to unreacted formaldehyde in the reaction mass which would in turn limit the polymer chain length through reaction 13 of Table I. On curve fitting of the experimental data of Tomita, it was found that model II yielded satisfactory results, and in view of this we have used model II to generate results of Figure 8. The concentration of  $\text{CH}_2\text{OH}$  is found to undergo a maxima before settling on an asymptotic value. Theoretically if one mole of formaldehyde reacts and the polymerization does not progress beyond this stage, one mole of  $\text{CH}_2\text{OH}$  would be formed. If the asymptotic value of  $[\text{CH}_2\text{OH}]$  is less than 1, it is indicated that higher oligomers are formed. In Figure 8, formaldehyde is depleted from the reaction mass independent of  $r_5$ . However for  $r_5$  greater than 10,  $[\text{CH}_2\text{OH}]$  is essentially 1, indicating that only methylation of melamine would occur. Under normal condition, higher

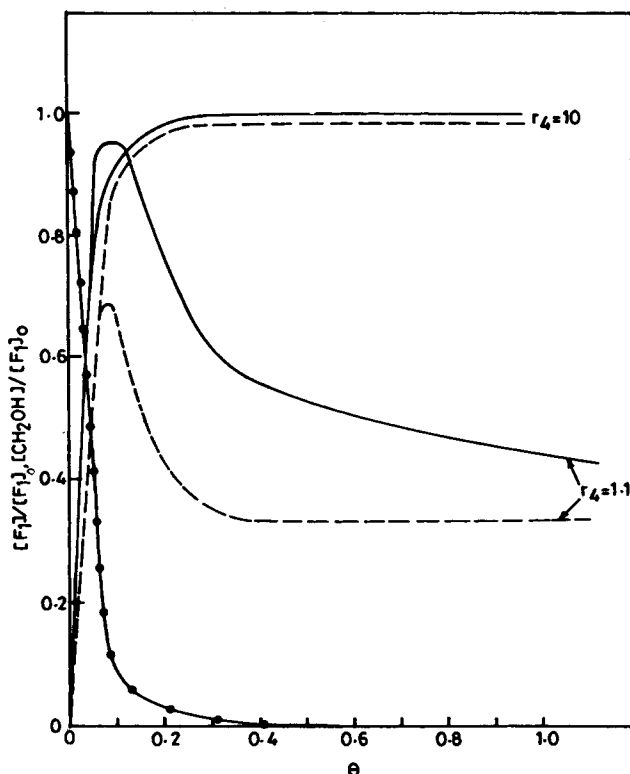


Fig. 8. Effect of  $r_4$  on  $[\text{CH}_2\text{OH}]$  and  $[F_1]$  versus  $\theta$ . Dotted lines give results for batch reactors:  $\text{CH}_2\text{OH}$  (—HCSTR), (-----Batch); (—•—)  $F_1$  in HCSTR.

oligomers would be formed. In a subsequent paper<sup>17</sup> this analysis is extended to find the MWD of the polymer.

### CONCLUSIONS

Melamine formaldehyde polymer is prepared industrially in two stages. In the first stage, melamine and formaldehyde are polymerized in which the methylation of the former is the dominant reaction of polymerization. In the second stage, the product of the first stage is polymerized in molds to give a polymer network. A reversible kinetic scheme has been proposed using functional group approach. The model proposed in this work is consistent with the basic chemistry of polymerization. In this, species A to J have been defined depending upon which of the hydrogen of the amide group is participating in the reaction. Various reactions involving these groups and the mole balance for the batch reactors have been written and these are used in curve fitting the experimental data of Tomita.

As the throughput of the reactor increases, continuous reactors are preferred over batch reactors, and homogeneous continuous-flow stirred-tank reactors is the most popular form of former type. In this paper an HCSTR has been simulated with the rate constants found from the experimental data of Tomita. In the kinetic model proposed in this work, it is shown that a given

chemical bond Z can react with water as well as free formaldehyde. As long as free formaldehyde is present in the reaction mass, methylation of melamine is the dominant reaction. Once free formaldehyde is reacted, higher oligomers are formed which is consistent with the experimental data reported on the polymerization of melamine and formaldehyde. It is further shown that the polymer is more branched compared to that formed in batch reactors. In a subsequent paper<sup>17</sup> the functional group analysis presented herein is extended to determine the MWD of the polymer.

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