

Modeling of Melamine Formaldehyde Polymerization. II. Development of a Simpler Model

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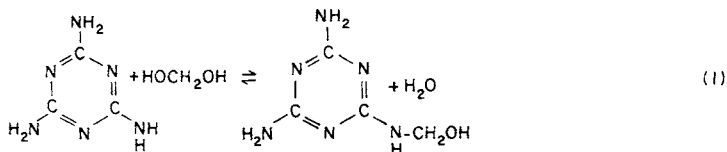
Synopsis

The kinetic modeling of melamine-formaldehyde polymerization presents a relatively formidable mathematical challenge because of the simultaneous presence of several types of deviations from Flory's equal reactivity hypothesis. A molecule of melamine has six reactive amide hydrogens, which can react with the $-\text{CH}_2\text{OH}$ groups of formaldehyde in solution. The reactivity of the secondary hydrogens on the melamine is about 61% of that of the primary hydrogens (induced asymmetry). There is a shielding effect present, i.e., the reactivity of the hydrogens near the outside of a multiringed polymer molecule is higher than that of the hydrogens inside the coiled molecules. Two bound $-\text{CH}_2\text{OH}$ groups on the polymer molecules can self-condense to give methylene linkages, the reactivity depending upon the location of the two groups. And, to confound modeling efforts still further, all these reactions are reversible. An earlier attempt at modeling this system considered the reactions between 36 "basic" species. This model was far too detailed and failed to account for the reverse reactions. In the present study, a simpler model has been proposed which involves fewer "basic" species. An improved model for intramolecular reactions is also developed. Several important characteristics of the polymerization have been obtained as a function of time. Results from this model have been compared with those obtained from the earlier model, and also compared with the short-time experimental results. The present model can be extended to account for the reverse reactions quite easily.

INTRODUCTION

Melamine (2,4,6-triamino-s-triazine) is a weakly basic material that shows reactivity similar to other amides like urea. It can react with formaldehyde to give a mixture of various substituted products, as well as higher oligomeric species. Tollen¹ in 1884 first reported the reaction of formaldehyde with the amide hydrogen, but detailed experimental studies of the chemistry and the kinetics of the reactions involved were reported much later.²⁻⁴

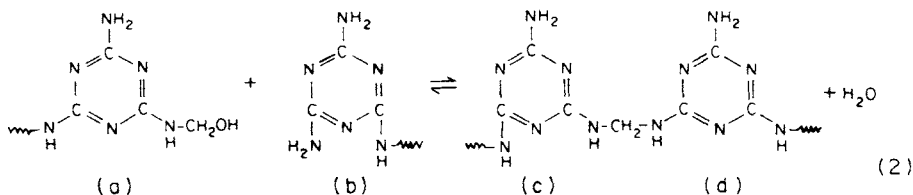
In the reaction between formaldehyde (which exists as HOCH_2OH in water)² and melamine, reactions of the following type occur first:



With time, more of the amide hydrogens (primary as well as secondary) get replaced by CH_2OH groups, and a mixture of mono-, di-, . . . , hexa-

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substituted products are formed. In addition to these reactions, methylene bridges are also formed as shown below by the reaction between $-\text{CH}_2\text{OH}$ and $-\text{H}$ groups, leading to multiring compounds:



In eq. (2), the symbol $-\sim$ represents a methylene linkage to other melamine rings. Substitution of $-\text{H}$ by $-\text{CH}_2\text{OH}$ groups on multiring molecules can occur by their reaction with formaldehyde. Chain extension similar to that represented by eq. (2) can also occur by the condensation of two $-\text{CH}_2\text{OH}$ groups leading to the formation of a methylene linkage and a molecule of HOCH_2OH .

The rate and equilibrium constants associated with the various reactions depicted in eqs. (1) and (2) depend, in general, on the exact location of the reactive groups. For example, the forward rate constant for a primary amide hydrogen on melamine is different from that associated with the secondary amide hydrogen on a monosubstituted compound (referred to as induced asymmetry), and, further, these are different from the reactivity of the primary amide hydrogen on a mono or disubstituted product. In addition, because of molecular shielding, the reactivity of an $-\text{H}$ on a ring which is located near the center or inside of a long-chain multiring polymer molecule [called "internal" rings, as for example, rings c and d in eq. (2)] are lower than those for the $-\text{H}$ on rings lying on the extremities [called "external" rings, as for example, rings a and b in eq. (2)]. The kinetic modeling of this system, therefore, poses a relatively formidable mathematical challenge because of the unequal reactivity of various sites.

Not much experimental work, and far less theoretical work, have been reported on this important polymerization. Okano and Ogata³ measured the initial reaction rates and computed the corresponding rate constants. Gordon et al.⁵ conducted further investigations on the kinetics of this system and illustrated that quantitative estimates of the individual reaction products could be made using C_{14} -labeled formaldehyde. Some deviation from random behavior was noted and parameters were assigned to qualify the rate equations. The validity of these parameters was tested in a computer study by Aldersley et al.,⁶ who tried to match experimental data on the free formaldehyde content with results from computations. Tomita⁷ studied the reaction between melamine and formaldehyde in greater detail. He obtained the more detailed concentrations of the various one-ring molecular species as functions of time, using high speed liquid chromatography and NMR spectroscopy, and estimated the equilibrium and rate constants for the individual reactions. In all these attempts, however, the formation of multiring compounds similar to those depicted in eq. (2) were completely neglected. Even though these compounds are formed in small quantities only (the resins obtained industrially have an average molecular weight of

650–750) their effect on the molecular structure of the final, crosslinked polymer is significant and any modeling exercise must account for their formation.











The first attempt on developing a more comprehensive theoretical model for the polymerization of this complex system was made recently.⁸ In this work, a mathematical framework was developed to analyze the kinetics of melamine–formaldehyde polymerization, accounting for the unequal reactivity of various functional groups. The model presented could predict the number average chain length as well as the average number of branch points per polymer molecule. The approach was similar to that used in our earlier work on the modeling of phenol–formaldehyde polymerization^{9–12} and has been used successfully to treat several other complex step growth polymerizations depicting unequal reactivity of functional groups, as discussed in recent reviews.^{13,14} In this model, 36 “basic entities” or building blocks were proposed, and the progress of the polymerization was studied in terms of the concentrations of these basic entities. This paralleled the study of ARB type step growth polymerizations in terms of functional group concentrations [A] and [B], instead of in terms of the more detailed concentrations of the individual *molecular* species [A-(RBA)_{n-1}-RB]. Even though this detailed model could explain all aspects of unequal reactivity, its extension to account for the reverse reactions present in melamine–formaldehyde polymerization led to insurmountable computational difficulty, and our efforts had to be shelved. However, results obtained from this model were of immense value (in absence of experimental data in the literature on the variation of the degree of polymerization and the degree of branching with time) as a standard for testing the validity of simpler models. Moreover, the predictions from the model matched experimental results on the concentrations of several one-ringed molecular species in the *initial* period.

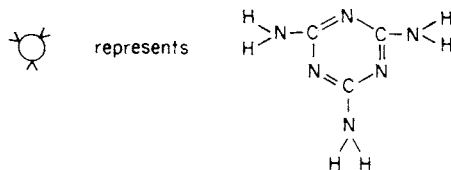
It was suggested that a cruder model with possibly fewer basic entities be developed, based on our experience with the more rigorous model, which could enable us to account for the reverse reactions with reasonable computational effort. This work represents an attempt in that direction. A new model with 13 basic entities only is developed in this paper, somewhat along the lines of work on phenol–formaldehyde polymerization.^{15,16} In this paper, however, the reverse reactions are not accounted for once again, even though this model could be extended to account for them. The focus of attention in this paper, thus, is to develop this new model and test whether the results predicted by it do, in fact, match those by the earlier, more rigorous model. Our work with this new model is continuing, and, in a future publication, we hope to present numerical results which match Tomita's experimental data on the concentrations of the single-ring species over a longer period of time than is possible in the present paper.

Formulation

Table I shows, schematically, the 13 basic entities used in the present model. These have been developed using analogy with our previous work on phenol–formaldehyde polymerization.^{15,16} Here, a dash (—) on a circle

TABLE I
13 Basic Entities Used for Modeling Melamine Formaldehyde Polymerization

A — 	(melamine)	G: — 
B: — 		H: — 
C: — 		I: — 
D: — 		J: — 
E: — 		K: — 
F: HOCH ₂ OH (Formaldehyde in water)		
-CH ₂ OH		
W: Water		



— x represents —CH₂OH or —CH₂—

represents the linkage of a hydrogen atom to the nitrogen on the ring, while —X represents *either* a —CH₂OH group or the presence of a methylene (—CH₂—) linkage to another ring. In the previous model on melamine formaldehyde, the former alone was represented by —X while the latter was represented by the symbol — \sim . Thus, our present model clubs together some of the basic entities of the previous one. The exact equivalence between the two models is given in Table II. It may be mentioned that the concentration of water [W], will not be needed in the present study since the reverse reactions are being neglected. However, this species has been included in Table I for the sake of completeness. A multiring polymer molecule can then be written as a sequence of these basic entities. As an example, in eq. (2), (a), (b), (c), and (d) represent basic entities C, B, C, and C, respectively.

The kinetic scheme (forward reactions only) for the polymerization of melamine formaldehyde in terms of these basic entities is given in Table III. It consists of three sets of reactions: set (a) comprises the substitution of an H on any basic entity, internal or external, by a CH₂OH group by reaction with formaldehyde, set (b) comprises of chain extension when a CH₂OH group on any basic entity reacts with an H on another basic entity (note that the basic entity on which the CH₂OH was located does not change its status on reaction), and set (c) represents the reaction between two CH₂OH groups (this reaction, again, does not change the "status" of either of the two basic entities on which these groups are located—a phenomenon arising because of the clubbing of — \sim and —CH₂OH into a single —X

TABLE II
Exact Equivalence Between Present¹³ and Previous³⁶ Basic Entities

Present	Previous (notation as in Ref. 8)
A	A
B	C, A1
C	D, A2, C1
D	E, A3, C2, D1
E	G, C3
F	B
G	H, C4, D2, G1
H	I, C5, D4, E1, G2, H1
I	J, D3, H2
J	K, D5, E2, H3, I1, J1
K	L, E3, I2, K1
—CH ₂ OH	Not required
W	Required only when reversible reactions are considered

group). The following rate constants characterizing the reactions between *functional groups* are used⁸:

a. k_1 , the forward rate constant for the reaction between a CH₂OH group (either on a substituted ring compound or on formaldehyde) and a primary amide hydrogen lying on an "external" ring. It is assumed that the degree of substitution of the melamine ring does not change the reactivity of the primary amide hydrogens. Such an assumption has been used earlier by Aldersley et al.⁶ and keeps the number of curve-fit parameters low. Values of the individual rate constants as studied by Tomita⁷ also appear to substantiate this approximately.

b. k_2 , the forward rate constant for the reaction between a CH₂OH group and a primary amide hydrogen lying on an "internal"⁸ ring. This can be attributed to some sort of a shielding phenomenon as in the case of phenol formaldehyde.

c. k_3 , the forward rate constant for the reaction between a CH₂OH group and a secondary amide hydrogen lying on an external ring.

d. k_4 , the forward rate constant associated with the reaction between two —CH₂OH groups, leading to the formation of a methylene linkage —N—CH₂—N— between two rings and HOCH₂OH.¹⁷ It is assumed that this reactivity is independent of the units on which the two CH₂OH groups are located.

e. k_5 , the forward rate constant for the reaction between a CH₂OH group and an "internal" secondary amide hydrogen. Usually, k_5 will be quite small compared to k_1 because of severe steric hindrances.

Two reaction schemes are shown in Table III differing only in the associated rate constants. In model 1, the rate constants associated with the individual reactions have been written on the assumption that the group X on species A to J is *always* —CH₂OH while, in model 2, the relevant rate constants are assigned assuming that X is always a methylene linkage —CH₂—. This assumption is necessary because of the clubbing together of the —CH₂OH and —CH₂— groups into X. It is obvious that model 1 will be a better description of data in the early stages of polymerization when most

TABLE III
Kinetic Scheme

Model 1	Model 2 (rate constants only)
(a) Reactions with F (substitution)	
$A + F \xrightarrow{12k_1} B + CH_2OH + W$	$12k_1$
$B + F \xrightarrow{2k_3} E + CH_2OH + W$	$2k_5$
\downarrow $\xrightarrow{8k_1} C + CH_2OH + W$	$8k_1$
$C + F \xrightarrow{4k_1} D + CH_2OH + W$	$4k_2$
\downarrow $\xrightarrow{4k_3} G + CH_2OH + W$	$4k_5$
$D + F \xrightarrow{6k_3} H + CH_2OH + W$	$6k_5$
$E + F \xrightarrow{8k_1} G + CH_2OH + W$	$8k_2$
$G + F \xrightarrow{2k_3} I + CH_2OH + W$	$2k_5$
\downarrow $\xrightarrow{4k_1} H + CH_2OH + W$	$4k_2$
$H + F \xrightarrow{4k_3} J + CH_2OH + W$	$4k_5$
$I + F \xrightarrow{4k_1} J + CH_2OH + W$	$4k_2$
$J + F \xrightarrow{2k_3} K + CH_2OH + W$	$2k_5$
(b) Reactions with $-CH_2OH$ (chain extension)	
$A + CH_2OH \xrightarrow{6k_1} B + W$	$6k_1$
$B + CH_2OH \xrightarrow{k_3} E + W$	k_5
\downarrow $\xrightarrow{4k_1} C + W$	$4k_1$
$C + CH_2OH \xrightarrow{2k_1} D + W$	$2k_2$
\downarrow $\xrightarrow{2k_3} G + W$	$2k_5$
$D + CH_2OH \xrightarrow{3k_3} H + W$	$3k_5$
$E + CH_2OH \xrightarrow{4k_1} G + W$	$4k_2$
$G + CH_2OH \xrightarrow{2k_1} H + W$	$2k_2$
\downarrow $\xrightarrow{k_3} I + W$	k_5
$H + CH_2OH \xrightarrow{2k_3} J + W$	$2k_5$
$I + CH_2OH \xrightarrow{2k_1} J + W$	$2k_2$
$J + CH_2OH \xrightarrow{k_3} K + W$	k_5
(c) Reactions between $-CH_2OH$	
$CH_2OH + CH_2OH \xrightarrow{k_4} F$	k_4

of the X groups are indeed $-\text{CH}_2\text{OH}$ while model 2 will be more appropriate in the later stages of polymerization. In any case, these two models represent the two limiting cases of actual polymerizations, and so are useful theoretical idealizations. It is hoped that there will not be too much difference between the predictions of these two models. It might be emphasized that the assumption of $-\text{X}$ as $-\text{CH}_2\text{OH}$ in model 1 is made for the sole purpose of assigning rate constants, and does not imply that the $-\text{CH}_2\text{OH}$ groups do not react further to give $-\text{CH}_2-$ linkages. The coefficients of the various k_i 's in Table III account for the several possibilities of reaction between the CH_2OH groups and the hydrogens on the basic entities.^{18,19} $-\text{CH}_2\text{OH}$ groups are "formed" in the set of reactions (a) in Table III in the two models (in addition to the formation of basic entities like B, E, C, . . .), because of bookkeeping reasons, similar to the case of phenol-formaldehyde polymerization.¹⁵

Mass balance equations can be easily written using the kinetic scheme of Table III and are given in Table IV. These can be nondimensionalized using the initial concentration $[\text{F}]_0$ of the formaldehyde:

TABLE IV
Mass Balance Equations for the Various Basic Entities^a

$\frac{d[\text{A}]}{dt}$	=	$-6(2[\text{F}] + [\text{CH}_2\text{OH}])k_1[\text{A}]$
$\frac{d[\text{B}]}{dt}$	=	$\{6k_1[\text{A}] - (k_3 \text{ Coef1} + 4k_1)[\text{B}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{C}]}{dt}$	=	$\{4k_1[\text{B}] - 2(k_1 \text{ Coef2} + k_3 \text{ Coef1})[\text{C}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{D}]}{dt}$	=	$\{2k_1 \text{ Coef2}[\text{C}] - 3k_3 \text{ Coef1}[\text{D}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{E}]}{dt}$	=	$\{k_3 \text{ Coef1}[\text{B}] - 4k_1 \text{ Coef2}[\text{E}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{G}]}{dt}$	=	$\{k_3 \text{ Coef1}(2[\text{C}] - [\text{G}]) + 4k_1 \text{ Coef2}[\text{E}] - 2k_1 \text{ Coef2}[\text{G}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{H}]}{dt}$	=	$\{3k_3 \text{ Coef1}[\text{D}] + 2k_1 \text{ Coef2}[\text{G}] - 2k_3 \text{ Coef1}[\text{H}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{I}]}{dt}$	=	$\{k_3 \text{ Coef1}[\text{G}] - 2k_1 \text{ Coef2}[\text{I}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{J}]}{dt}$	=	$\{k_3 \text{ Coef1}(2[\text{H}] - [\text{J}]) + 2k_1 \text{ Coef2}[\text{I}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{K}]}{dt}$	=	$\{k_3 \text{ Coef1}[\text{J}]\} \{2[\text{F}] + [\text{CH}_2\text{OH}]\}$
$\frac{d[\text{F}]}{dt}$	=	$\frac{1}{2}k_4[\text{CH}_2\text{OH}]^2 - 2[\text{F}]\mathcal{R}$
$\frac{d[\text{CH}_2\text{OH}]}{dt}$	=	$-k_4[\text{CH}_2\text{OH}]^2 + \{2[\text{F}] - [\text{CH}_2\text{OH}]\}\mathcal{R}$
$\therefore \frac{d}{dt}$		$\{2[\text{F}] + [\text{CH}_2\text{OH}]\} = -\{2[\text{F}] + [\text{CH}_2\text{OH}]\}\mathcal{R}$
where	\mathcal{R}	$\equiv 6k_1[\text{A}] + (k_3 \text{ Coef1} + 4k_1)[\text{B}] + 2(k_1 \text{ Coef2} + k_3 \text{ Coef1})[\text{C}]$ $+ 3k_3 \text{ Coef1}[\text{D}] + 4k_1 \text{ Coef2}[\text{E}] + (2k_1 \text{ Coef2} + k_3 \text{ Coef1})[\text{G}]$ $+ 2k_3 \text{ Coef1}[\text{H}] + 2k_1 \text{ Coef2}[\text{I}] + k_3 \text{ Coef1}[\text{J}]$

^aCoef1 = 1 (model 1) or k_5/k_3 (model 2); Coef2 = 1 (model 1) or k_2/k_1 (model 2).

$$a = [A]/[F]_0, \quad b = [B]/[F]_0, \quad c = [C]/[F]_0, \dots, \theta = k_1[F]_0 t \quad (3)$$

before integration with appropriate initial conditions, using a Runge-Kutta algorithm.

In order to obtain expressions for the two important molecular characteristics of the product formed, namely, the number-average chain length (defined herein as the number-average number of rings per molecule) and the degree of branching (defined as the average number of branch points in a polymer molecule), we must first obtain an equation to estimate the concentration of "polymer" molecules $[X_p]$ in the system. In this analysis, "polymer" molecules will include not only the multiring species, but also the single-ring ones. Such a definition is quite common in polymer reaction engineering and leads to simpler equations. Figure 1 shows a typical polymer molecule intramolecular reactions. We first obtain an equation for $[X_p]$ neglecting including *branches* as well as *loops*, the latter formed by the formation of loops, since it is easier to do so, and then modify it for loop formation. In the absence of loop formation, it is observed that only the reactions in groups (b) and (c) in Table III lead to chain extension, and the number of polymer molecules in the system decreases by unity everytime any of these reactions occur (this will not be true when intramolecular reactions occur). Thus, we can write

$$\begin{aligned} \left. \frac{-d[X_p]}{dt} \right|_{\text{no loops}} &= \{6k_1[A] + (k_3 \text{Coef1} + 4k_1)[B] \\ &+ 2(k_1 \text{Coef2} + k_3 \text{Coef1})[C] \\ &+ 3k_3(\text{Coef1})[D] + 4k_1(\text{Coef2})[E] \\ &+ (2k_1 \text{Coef2} + k_3 \text{Coef1})[G] \\ &+ 2k_3(\text{Coef1})[H] + 2k_1(\text{Coef2})[I] \\ &+ k_3(\text{Coef1})[J] \} [CH_2OH] \\ &+ \frac{1}{2} k_4 [CH_2OH]^2 \end{aligned} \quad (4)$$

with the initial condition

$$[X_p]_{t=0} = [A]_0 \quad (5)$$

since single-ring compounds, including melamine, are included in our definition of X_p and since we shall consider, in this study, a feed consisting of melamine and formaldehyde only. The terms Coef1 and Coef2 in eq. (4) are defined in Table IV. It may be noted that X_p as defined in this paper differs from the X_p used in Ref. 8.

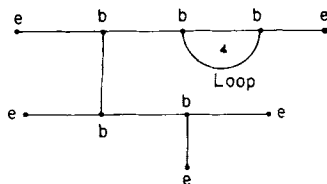


Fig. 1. A typical branched polymer molecule with an intramolecular loop e and b represent end and branch points respectively.

In the presence of intramolecular reactions, one again notices that the reactions in group (a) in Table III are not of interest since they do not lead to chain extension. As far as the reactions in group (b) are concerned, there are two possibilities: A reaction between a $-\text{CH}_2\text{OH}$ and an $-\text{H}$ on a basic entity ϕ_i ($\phi_i \rightarrow \text{A, B, C, D, E, G, H, I, or J}$) could either be intermolecular or intramolecular. In the latter case, the number of polymer molecules in the system does not decrease by unity, as happens in the former case. If \mathcal{F}_{ϕ_i} is the fraction of reactions occurring between the groups $-\text{CH}_2\text{OH}$ and $-\text{H}$ on ϕ_i which are intramolecular, one can write the contribution of *this reaction* to the equation for $[\text{X}_p]$ as

$$\left. \frac{-d[\text{X}_p]}{dt} \right|_{\phi_i, \text{ with loops}} = a_i k_i [\text{CH}_2\text{OH}] [\phi_i] (1 - \mathcal{F}_{\phi_i}) \quad (6)$$

In eq. (6), $a_i k_i$ is the appropriate coefficient in eq. (4), corresponding to this reaction. A very simple expression for \mathcal{F}_{ϕ_i} has been presented in our earlier studies^{8,11} and models the intramolecular reactions in terms of the reactions between "averaged" molecules:

$$\begin{aligned} \mathcal{F}_{\phi_i} = & \left\{ \begin{array}{l} \text{average \# of CH}_2\text{OH in a molecule} \\ \text{average \# of } \phi_i \text{ in a molecule} \end{array} \right\} \times \\ & \left\{ \begin{array}{l} \text{\# of polymer molecules in unit volume} \\ \text{total \# of CH}_2\text{OH in a unit volume} \end{array} \right\} \div \\ & \left\{ \begin{array}{l} \text{total \# of } \phi_i \text{ in a unit volume} \\ \text{total \# of } \phi_i \text{ in a unit volume} \end{array} \right\} \\ = & \frac{\{[\text{CH}_2\text{OH}]N_{\text{av}}/[\text{X}_p]N_{\text{av}}\} \left\{ \frac{[\phi_i]N_{\text{av}}}{[\text{X}_p]N_{\text{av}}} \right\} ([\text{X}_p]N_{\text{av}})}{([\text{CH}_2\text{OH}]N_{\text{av}})([\phi_i]N_{\text{av}})} = \frac{1}{[\text{X}_p]N_{\text{av}}} \quad (7) \end{aligned}$$

where N_{av} is the Avogadro number. Since \mathcal{F}_{ϕ_i} comes out to be independent of $[\phi_i]$ or $[\text{CH}_2\text{OH}]$, it is applicable to all the reactions of group (b) as well as to reaction (c) in Table III. Thus, eq. (4) can be modified for intramolecular reactions quite simply as

$$-\frac{d[\text{X}]_p}{dt} \Big|_{\text{with loops}} = -\left\{ \frac{d[\text{X}]_p}{dt} \Big|_{\text{no loops}} \right\} \left(1 - \frac{1}{[\text{X}]_p N_{av}} \right) \quad (8)$$

The equation for \mathcal{F}_{ϕ_i} in eq. (7) seems dimensionally inconsistent and needs to be corrected. The appropriate correction factor comes from a study of more detailed molecular models for intramolecular reactions,¹⁴ as discussed below.

A simple model for intramolecular reactions has been developed by Jacobson and Stockmayer²⁰ and used quite successfully by Gordon and co-workers.²¹ The rate of reaction between two functional groups on the same polymer molecule, P_n (n monomeric units long), can be written as

$$R_{i,P_n} = k[P_n] \left\{ \frac{1}{i^{3/2}} \left(\frac{3}{2\pi l^2} \right)^{3/2} \frac{1}{N_{av}} \right\} \quad (9)$$

where k is the intrinsic reactivity of the functional groups, l is the backbone-bond length, and i is the number of backbone bonds between the two functional groups. Several approximations are involved in eq. (9)¹⁴ (some of which have been accounted for by more recent studies^{22,23}), but since identical functionalities are obtained if they are taken care of, we need not consider any more detailed model at this stage. The rate of intermolecular reaction for reactive functional groups is given similarly by

$$R_{i,P_n,P_m} = k[P_n][P_m] \quad (10)$$

The corresponding fraction \mathcal{F} of intramolecular reactions in this situation is, thus, approximately,

$$\mathcal{F} = \frac{0.33}{[P_m] N_{av} l^3 i^{3/2}} \quad (11)$$

In our "averaged" model for intramolecular reactions in melamine-formaldehyde polymerization, we can replace $[P_m]$ by $[\text{X}]_p$, and use some mean value (over time as well as over an ensemble of polymer molecules present in the reaction mass), $\bar{i}^{3/2}$, in place of $i^{3/2}$ to give

$$\begin{aligned} \frac{-d[\text{X}]_p}{dt} \Big|_{\text{with loops}} &= \left\{ \frac{-d[\text{X}]_p}{dt} \Big|_{\text{no loops}} \right\} \left(1 - \frac{0.33}{[\text{X}]_p N_{av} l^3 \bar{i}^{3/2}} \right) \\ &\equiv \left\{ \frac{d[\text{X}]_p}{dt} \Big|_{\text{no loops}} \right\} \left(1 - \frac{\mathcal{A}}{[\text{X}]_p} \right) \end{aligned} \quad (12)$$

where \mathcal{A} is a curve-fit parameter having the same units as $[X_p]$ [because of its $1/(N_{av}I^3)$ dependence]. The effects of several of the approximations in the model, e.g., use of random-flight chain statistics in eq. (9), treating \bar{i} as constant with time, etc., are all clubbed together in the empirical parameter \mathcal{A} .

With the equation for $[X_p]$ now established, it is easy to write down expressions for the number-average number of rings per molecule ($\equiv \overline{DP}$) and the degree of branching (DOB) as

$$\overline{DP} = \frac{[A]_0}{[X_p]} \quad (13a)$$

$$\begin{aligned} \text{DOB} &= \frac{\text{concn of branched basic entities}}{[X_p]} \equiv \frac{[X_{br}]}{[X_p]} \\ &= \frac{[D] + [H] + [J] + [K] + ([G] + [I])}{[X_p]} \end{aligned} \quad (13b)$$

Once again, because of the clubbing together of $-\text{CH}_2\text{OH}$ and methylene linkages into X, eq. 13(b) will give the average number of actual (when X is methylene linkage) and potential (when X is $-\text{CH}_2\text{OH}$) branch points per polymer chain.

RESULTS AND DISCUSSION

The equations of the previous section have been integrated numerically using a Runge-Kutta computer package. Two checks were made to confirm the correctness of the program, as well as to ensure that no errors have been made in writing the mass balance equations from the proposed kinetic scheme.

$$\begin{aligned} \text{CHECK1} &\equiv \{[A] + [B] + [C] + [D] + [E] \\ &\quad + [G] + [H] + [I] + [J] + [K]\} / [A]_0 = 1 \end{aligned} \quad (14a)$$

$$\begin{aligned} \text{CHECK2} &\equiv \{[B] + 2[C] + 3[D] + 2[E] + 3[G] + 4[H] + 4[I] \\ &\quad + 5[J] + 6[K] + 2[F] + [\text{CH}_2\text{OH}]\} / (2[F]_0) = 1 \end{aligned} \quad (14b)$$

The first check represents a balance on the total number of rings at any time, and the deviation of CHECK1 from the theoretical value of unity would be indicative of errors. Similarly, CHECK2 represents a balance on the CH_2OH groups on the several species present in the reaction mass. It has been found in our earlier work^{10,11} that such stoichiometric tests are quite sensitive and useful.

Numerical results have been generated using the following *reference* set of parameter values,

$$\begin{aligned}
 k_2/k_1 &= \text{Coef2} = 1 \text{ (model 1) or } 0.35 \text{ (model 2)} \\
 k_3/k_1 &= 0.61 \\
 k_4/k_1 &= 2.5 \\
 k_5/k_1 &\equiv (k_3/k_1) \text{ Coef1} = k_3/k_1 \text{ (model 1) or } 0 \text{ (model 2)} \\
 \mathcal{A} &= 0
 \end{aligned}
 \tag{15}$$

and the following *reference* set of initial conditions,

$$\begin{aligned}
 \alpha_0 &\equiv [\text{A}]_0/[\text{F}]_0 = 0.5 \\
 f_0 &\equiv [\text{F}]_0/[\text{F}]_0 = 1 \\
 x_{p,0} &\equiv [\text{X}_p]_0/[\text{F}]_0 = 0.5
 \end{aligned}
 \tag{16}$$

These values are similar to those used in our previous study and have been obtained from various sources in the literature.⁸ The value of $\Delta\theta$ used was 0.001, and a reduction in its value to 10^{-4} gave identical results. The CPU time on a PRIME 9950 for a single run generating the values of the various quantities of interest up to a value of θ of about 2.0, was about 9 s.

Figures 2–5 show some of the more interesting results obtained for the two models using the reference set of conditions. The dimensionless melamine concentration for the two models considered in the present work are quite close to that predicted by our previous model.⁸ The same is true for the formaldehyde concentration, but *only* for values of θ of about $0 \leq \theta \leq 0.2$. For higher values of θ , it is found that $[\text{F}]/[\text{F}]_0$ obtained from our earlier, more detailed model lies between the values predicted by the present two models, which represent limiting behavior. Since model 2 does not lead to the consumption of too much of formaldehyde ($k_5 = 0$), it is not surprising that $[\text{F}]$ values are higher than predicted by model 1. In any case, since the reverse reactions have been omitted, the predictions of the two models can be of use only for low values of θ , and, under these conditions, the various models give similar results. It may be added that, for low θ , results from model 1 are close to our previous model, as expected. Similar conclusions apparently cannot be made for the behavior of $\overline{\text{DP}}$ as shown in Figure 4. The present two models and the previous one give quite similar results for $0 \leq \theta \leq 0.2$. However, for larger values of θ the results of the previous model do not lie between the two “limiting” models of the present study. A close scrutiny of the various models reveals that, fundamentally, the model for $[\text{X}_p]$ developed in this paper, in the absence of intramolecular reactions, is quite similar to that of the previous one,⁸ even though the two expressions appear to be quite different. Thus, differences between the models are either a consequence of different kinetic schemes or of intramolecular reactions. The fact that $\overline{\text{DP}}$ of the previous model⁸ does not lie between the values from the two present models is indicative of the fact that the intramolecular reactions differ substantially. Since $\mathcal{A} = 0$ for the reference conditions of the present model, Figure 4 attempts to compare

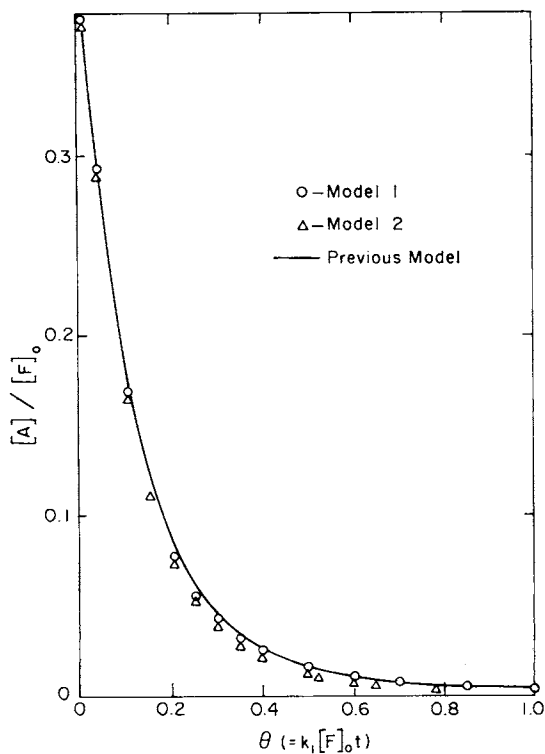


Fig. 2. Melamine concentration as a function of time for models 1 (○) and 2 (△) using the reference set of values given in eqs. (15) and (16); (—) results for our previous model.⁸

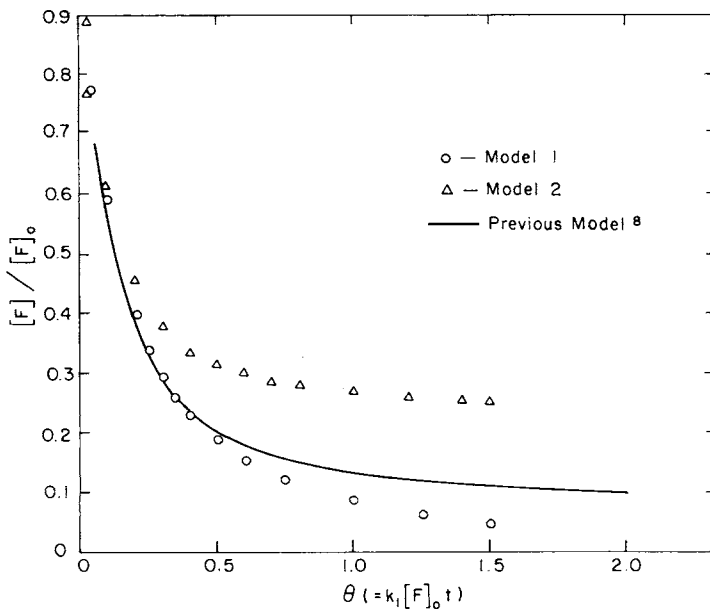


Fig. 3. Formaldehyde concentration as a function of time. Notation same as in Figure 2.

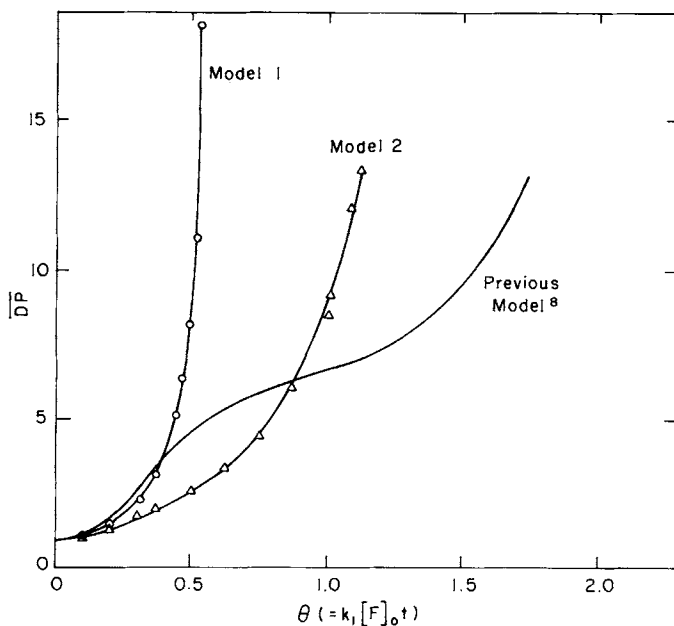


Fig. 4. Number-average number of rings per molecule (\overline{DP}) vs. θ , for the reference conditions.

results of the previous study wherein intramolecular reactions *are* indeed present, to that of the present models wherein they are neglected. It is shown later that \overline{DP} is extremely sensitive to the value of \mathcal{A} and one can get the \overline{DP} of the previous model to lie between the results for models 1 and 2 with an appropriate choice of \mathcal{A} . At larger values of θ , the equations

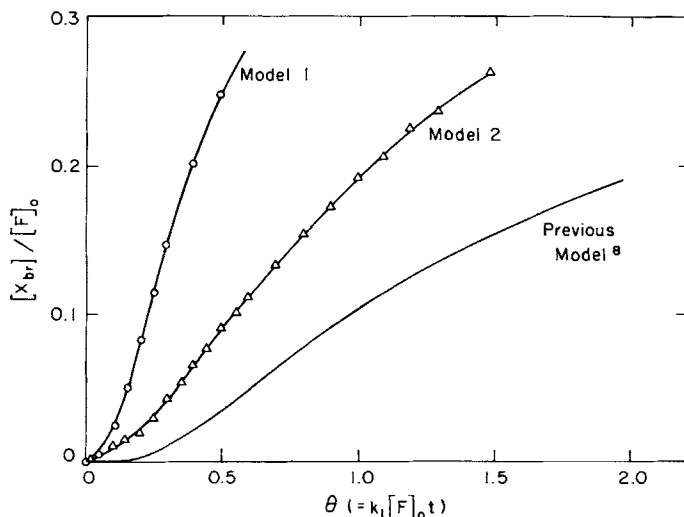
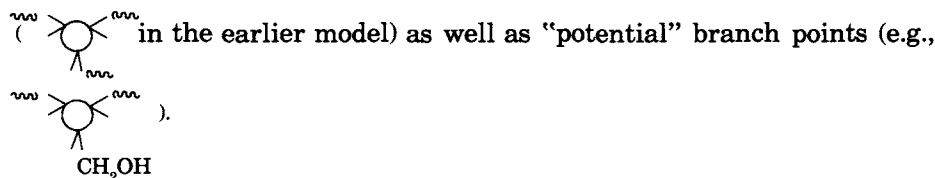


Fig. 5. Concentration of branched basic entities vs. θ for the reference conditions.

become stiff and one must use an extremely low value of $\Delta\theta$ in order to ensure that $[X_p]$ is positive. This approach was not pursued, however, since our interest was limited to low values of θ . Figure 5 also shows that the *concentration* of branch points is much higher in both the models than predicted by our previous model.⁸ This is because in the present study, branch points include both "actual" branches



Parametric sensitivity of the results were now ascertained. It was found in our earlier study⁸ that the most sensitive kinetic parameters were k_5/k_1 and k_2/k_1 . Since both k_5 and k_2 occur only in model 2, parametric sensitivity studies on these were limited to this model. Figures 6 and 7 show some results. The value of Coef1 ($= k_5/k_3$) was varied around the reference value of 0, and two values of this parameter, 0.2 and 0.4, were studied. Similarly, the value of Coef2 ($= k_2/k_1$) was varied around the reference value of 0.35, and two values, 0.7 and 0.2 were studied (keeping Coef1 = 0). It was observed that \overline{DP} was almost unaffected till θ of about 0.4. Even for such a wide variation of parameter values, $[X_{br}]$ was not significantly influenced at low θ . At higher values of θ , however, both \overline{DP} and $[X_{br}]$ showed a significant dependence on the values of these two sensitive parameters, the trends being consistent with intuitive expectations. For example, when Coef1 was larger, both $[X_{br}]$ and \overline{DP} were higher because

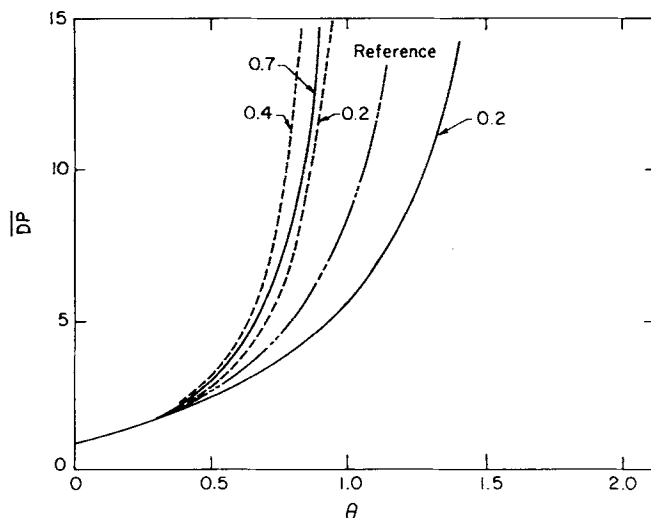


Fig. 6. Effect of varying Coef1 (---) and Coef2 (—) for model 2 on \overline{DP} ; reference run (Coef1 = 0, Coef2 = 0.35) also shown.

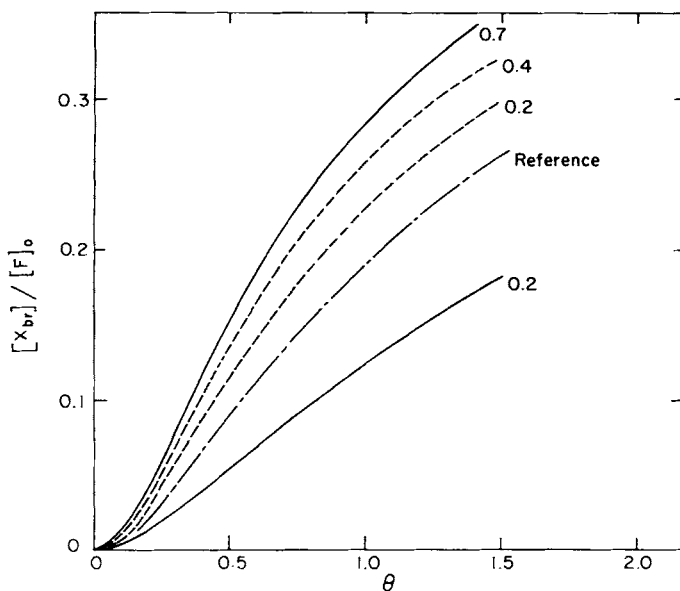


Fig. 7. Effect of varying Coef1 (---) and Coef2 (—) on $[X_{br}]$. Reference run for model 2 also shown.

the substitution and the chain-extension reactions were speeded up. The concentration of unreacted melamine, however, was not significantly influenced by the parameter values, while the value of $[F]/[F]_0$ was only slightly influenced by them, at least till values of θ of about 0.5. The effect of the parameter \mathcal{A} characterizing the intramolecular reactions, is shown in Figure 8 for both models 1 and 2. Increasing \mathcal{A} led to a significant reduction in \overline{DP} for θ beyond about 0.5, but for low θ , where the models are really applicable, the effect was small. It is interesting to observe that the difference (at large θ) between the two models decreased as \mathcal{A} increased.

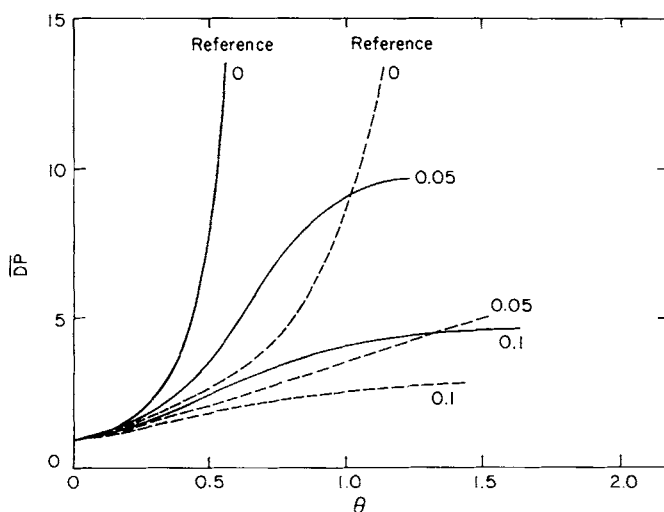


Fig. 8. Effect of \mathcal{A} on \overline{DP} : (—) model 1 and (---) model 2 for values of \mathcal{A} indicated.

Also, the affect of varying \mathcal{A} on $[X_{br}]$ was insignificant even for high values of θ . This means that as the importance of intramolecular reactions increases, the number of polymer molecules in the reaction mass decreases substantially, but the degree of branching (and substitution) remains unaltered.

Figures 9–12 show the affect of varying the initial melamine to formaldehyde ratio $[A]_0/[F]_0$. It is observed that the difference between models 1 and 2 increases as $[A]_0/[F]_0$ is increased, though this is important only at higher values of θ . The opposite effect is observed for the formaldehyde concentration. The value of \overline{DP} , however, is relatively insensitive to the feed composition. Figure 12 shows the degree of branching for the two models, and the affect of the feed composition is small. A comparison of Figures 11 and 12 leads to the conclusion that, at high θ , there is a preponderance of highly branched polymer molecules relative to linear chains, and a gelation type phenomenon occurs. At such values of θ , however, the model is inapplicable because of the importance of reverse reactions which delays this phenomenon.

Figures 13–15 show a comparison of the theoretical results from model 1 (with $[A]_0/[F]_0 = 0.2$, all other parameters same as reference values) with experimental results of Tomita⁷ on the concentrations of some substituted, single-ring compounds. The experiments have been conducted at

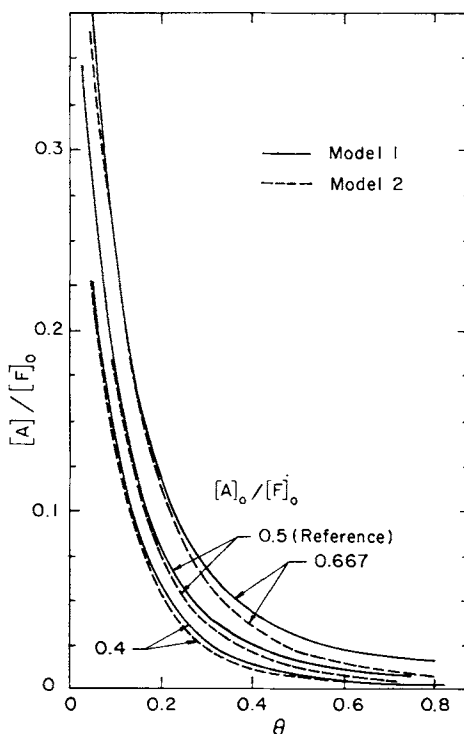


Fig. 9. Effect of feed composition, $[A]_0/[F]_0$ on the melamine concentration: (—) model 1; (---) model 2. Reference values of kinetic parameters used.

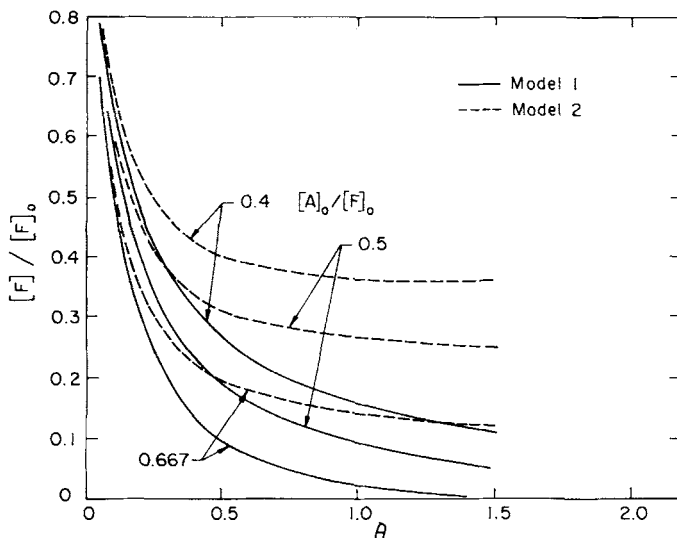


Fig. 10. Effect $[A]_0/[F]_0$ on formaldehyde concentration. Notation same as in Figure 9.

$T = 48^\circ\text{C}$, $\text{pH} = 9$, $[A]_0 = 0.0325$ mol/L, and $[F]_0 = 0.167$ mol/L. The original experimental data have been replotted in terms of θ using a value of k_1 of 0.0067 L/mol min. This choice of k_1 has been made by curve-fitting experimental data on $[A]/[F]_0$ alone vs. θ by theoretical results from model 1, and compares quite well with the value of 0.0073 L/mol min suggested by Tomita. Good agreement is found between experiment and theory for both $[A]/[F]_0$ as well as the monosubstituted melamine concentration (Fig. 13) for values of θ up to about 0.1. It may be mentioned that, as θ increases, reverse reactions start gaining importance and both models 1 and 2 should not be expected to apply. The theoretical results for model 2 for $[A]/[F]_0$

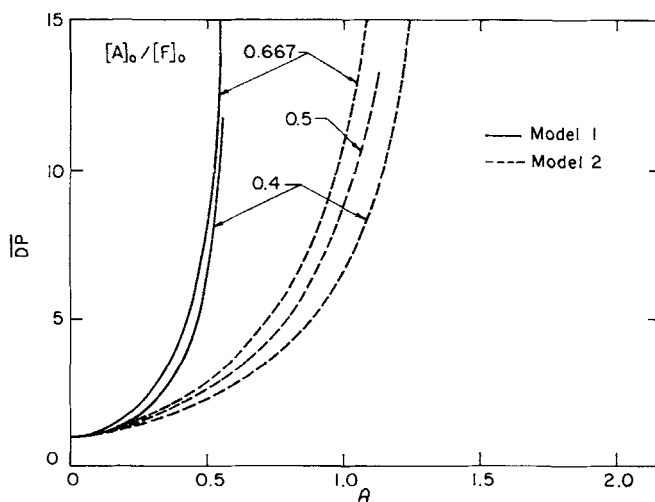


Fig. 11. Effect of $[A]_0/[F]_0$ on the degree of polymerization. Same notation as in Figure 9.

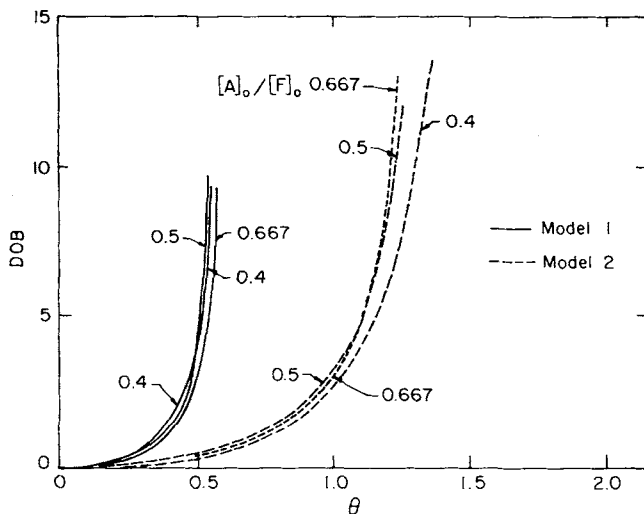


Fig. 12. Effect of feed composition on the degree of branching. Notation same as Figure 9.

are almost identical to those for model 1 under the conditions used. Figure 14 shows a comparison of theoretical results on model 1 with experimental data (using the same k_1) on more highly substituted melamines. It is found that the agreement for the disubstituted melamine is good but only for a lower value of θ (the trend seems to indicate that the reactivity of the primary amide hydrogens on a substituted melamine is different from that on melamine). Figure 14 shows theoretical results from model 2 for $[D]/[F]_0$ vs. θ , and it is observed that the agreement with experiment improves considerably. This is not surprising since model 2 is a better representation of the system as θ increases, than is model 1. Since $[H]/[F]_0$

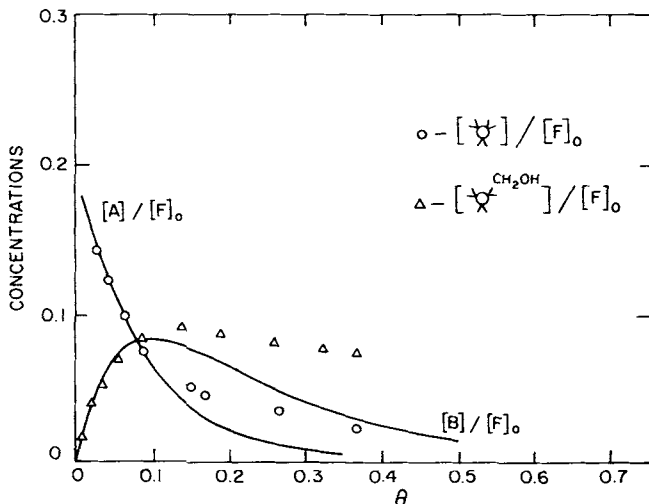


Fig. 13. $[A]/[F]_0$ and $[B]/[F]_0$ vs. θ for model 1 (—). Experimental points are for $[F]_0 = 0.167$ mol/L, $T = 48^\circ\text{C}$, $\text{pH} = 9$, $[A]_0 = 0.0325$ mol/L. k_1 used is 0.0067 L/mol min.

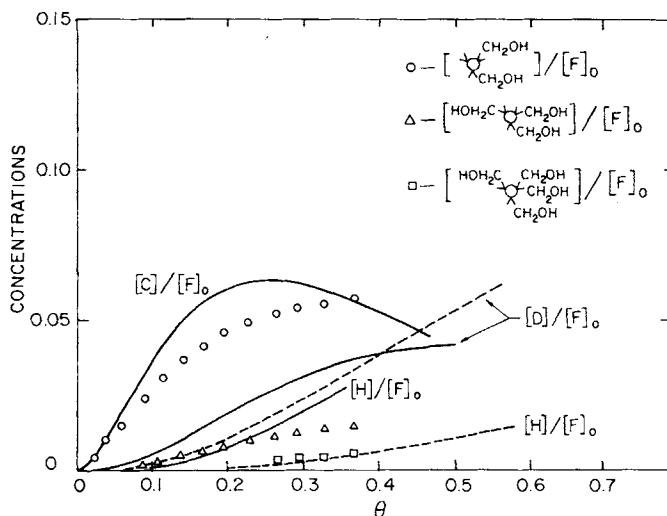


Fig. 14. $[C]/[F]_0$, $[D]/[F]_0$ vs θ for model 1 (—). Experimental data⁷ on corresponding single-ring (substituted melamine) compounds also shown. Conditions same as in Figure 13. (---) $[D]/[F]_0$ vs. θ for model 2 (Coef1 = 0, Coef2 = 0.35) and $[H]/[F]_0$ for model 2 (Coef1 = 0.275, Coef2 = 0.35).

= 0 for all θ when $k_5 = 0$ (reference value), results using model 2 were generated using Coef1 = 0.275, Coef2 = 0.35, $[A]_0/[F]_0 = 0.2$, and it was observed that the experimental results on the tetrasubstituted melamine could be curve-fitted theoretically (see Fig. 14). Figure 15 shows similar results for other substituted melamine products for which experimental results are available. It is found that even though model 1 does explain the trends, quantitative agreement is quite poor, as was found to be the case in our previous paper.⁸ Theoretical results from model 1 using Coef1 = 0.275, Coef2 = 0.35, $[A]_0/[F]_0 = 0.2$ have been used for comparison ($[E]$

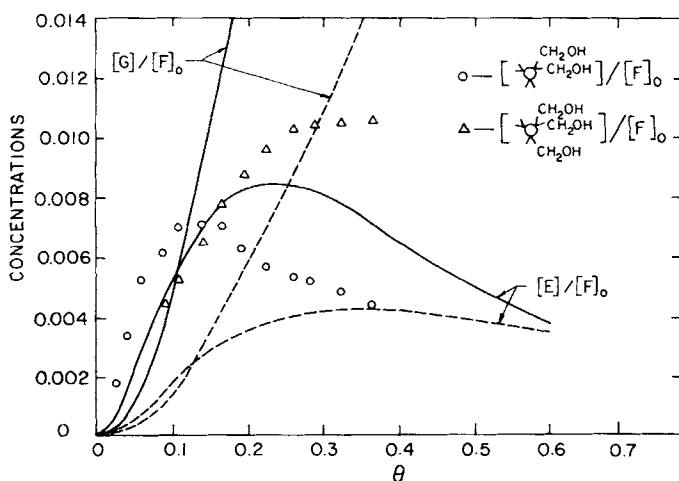



Fig. 15. $[E]/[F]_0$ and $[G]/[F]_0$ vs. θ for model 1 (—). Experimental data on corresponding substituted melamines also shown. Conditions same as in Figure 13. (---) Model 2 results with Coef1 = 0.275, Coef2 = 0.35.

and $[G]$ are 0.0 if $\text{Coef1} = 0$) since this explained results on tetra methylol melamine quite satisfactorily. The agreement is still poor though some improvement could be made if a higher value of Coef1 was chosen (at the cost of worsening the agreement for $[H]$ in Fig. 14). It appears from Figures 13–15 that, for very low θ , experimental results are explained better by model 1, while, as θ increases, model 2 with some finite value of Coef1 appears to be better, and, as θ increases still further, reverse reactions start becoming important. In any case, the limited experimental data that is available can be explained as well by the present models as they can be by the model proposed earlier. The advantage of the present models is that it is quite easy to extend them to account for the reverse reactions.

Since model 2 was found to be better beyond some small value of θ , an attempt was made to switch from model 1 to model 2 at some arbitrarily chosen point where $\overline{DP} = \overline{DP}_{tr}$. This information could be of some use in developing the future models which account for the reverse reactions. Figure 16 shows results on \overline{DP} vs. θ for some typical runs, and it is observed that fine tuning of the parameters \overline{DP}_{tr} , \mathcal{A} and Coef1 can lead to a successful curve-fitting of experimental data. It is interesting to observe that \overline{DP} vs. θ for the conditions corresponding to curve (a) in Figure 16 is quite similar to results obtained from our previous model (shown in Fig. 4). Similar variation of DOB vs. θ with \overline{DP}_{tr} , \mathcal{A} , and Coef1 have also been observed. It must be emphasized that this switchover from models 1 to 2 is justified on purely empirical grounds and that there are some fundamental inconsistencies in doing this (e.g., in model 1, a considerable amount of species E is formed, which is suddenly transformed to

 in model 2, a species which really should not be formed

because of severe steric hindrances).

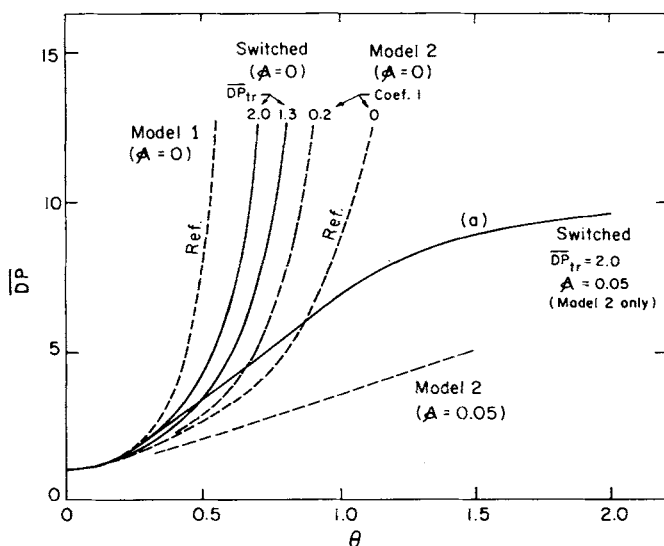
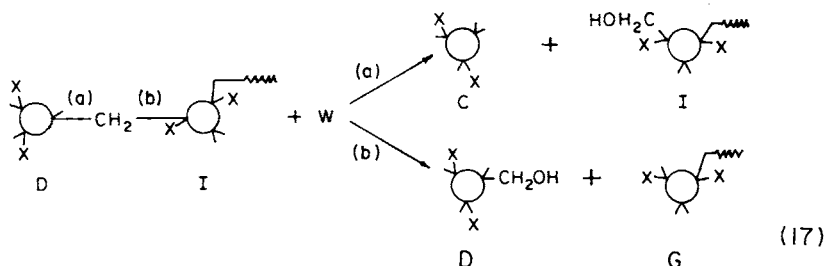


Fig. 16. \overline{DP} vs. θ (solid) with a switch from model 1 ($\text{Coef1} = 1$, $\text{Coef2} = 1$, $\mathcal{A} = 0$) to model 2 (with $\text{Coef1} = 0.2$, $\text{Coef2} = 0.35$, \mathcal{A} specified in plot) at the point where $\overline{DP} = \overline{DP}_{tr}$: (---) results for model 1 and model 2 alone without any switchover (reference values used for parameters not specified).

CONCLUSIONS

Two simplified kinetic models have been developed which explain some initial data on melamine-formaldehyde polymerization. This model is in reasonable agreement with theoretical predictions using our previous, more detailed model, and has the advantage that it can easily account for the reverse reactions present in the polymerization of melamine-formaldehyde. For example, in the reverse reaction of the following type,



the W can attack either of the two bonds (a) and (b) around the methylene linkage, giving two different products as shown. Since both $D + W \rightarrow C + CH_2OH$ and $I + W \rightarrow G + CH_2OH$ exist (reverse) in the set of reactions (b) in Table III, this implies that the kinetic scheme given in this table can easily apply for reversible polymerization provided all the reactions in it are made reversible, and appropriate reverse rate constants are associated with them. The mass balance equations, as well as the equation for $[X_p]$ will have to be rewritten to account for these effects. Work along these lines is in progress, and will be reported in the near future.

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