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# Modeling and Experimental Investigation of Melamine–Formaldehyde Polymerization

**Anil Kumar* and Vimal Katiyar**

*Department of Chemical Engineering, Indian Institute of Technology, Kanpur-208016, India*

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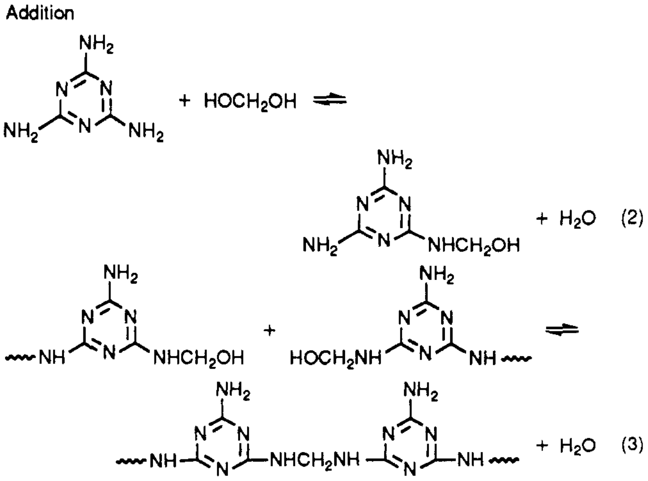
ABSTRACT: Polymerization of melamine with formaldehyde has been studied at high temperatures and molar ratios of monomers similar to those used in industry. Melamine dissolves in formaldehyde slowly and ionizes in the reaction mass to some extent. The polymer formation is a complex process of polymerization of the un-ionized molecules of melamine. Using the functional group approach, we have modeled the batch polymerization and determined the rate constants through curve-fitting. We find that the rate constants are a function of temperature only, and the kinetic model proposed in our work describes the polymerization in the entire region.

## Introduction

Polymers of melamine (2,4,6-triamino-*s*-triazine) and formaldehyde form an important class of amino resins and have a large industrial application. Melamine molding compound is the hardest commercial plastic and is used mainly for molded dinnerware because of its outstanding hardness and water stain resistance.[1-4] It is also used as protective coating because of its high chemical resistance and is preferred for applications involving outdoor exposures. In recent applications it has also been used as automobile top coats and in textile finishes. In the latter it provides wash and wear properties to cellulosic fibers, enhances wash durability, and gives flame-retardant finishes. The resin has also been applied as an adhesive in plywood industries in place of urea–formaldehyde polymer due to its higher strength, durability, and chemical resistance. In the polymerization of melamine with formaldehyde, formalin (37% by weight of formaldehyde in water) is mixed with melamine. In the aqueous state formaldehyde combines with water to give methylene glycol[5] as

$$HCHO + H_2O \rightarrow HOCH_2OH \qquad (1)$$

The reaction of methylene glycol with melamine has been described by Okano and Ogata[6] in the following two steps. In the first one melamine adds on a molecule of $HOCH_2OH$. This is an addition reaction, and it takes place for all pHs. The second step is a condensation reaction, which involves the linking of melamine with the product of reaction 2 to form either a dimer or a polymer chain (multiring compound). The product of eq 2 can also self-condense to provide a dimer and a polymer chain. This is referred to as methylene bridge formation and can schematically be represented as



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* To whom correspondence should be addressed.

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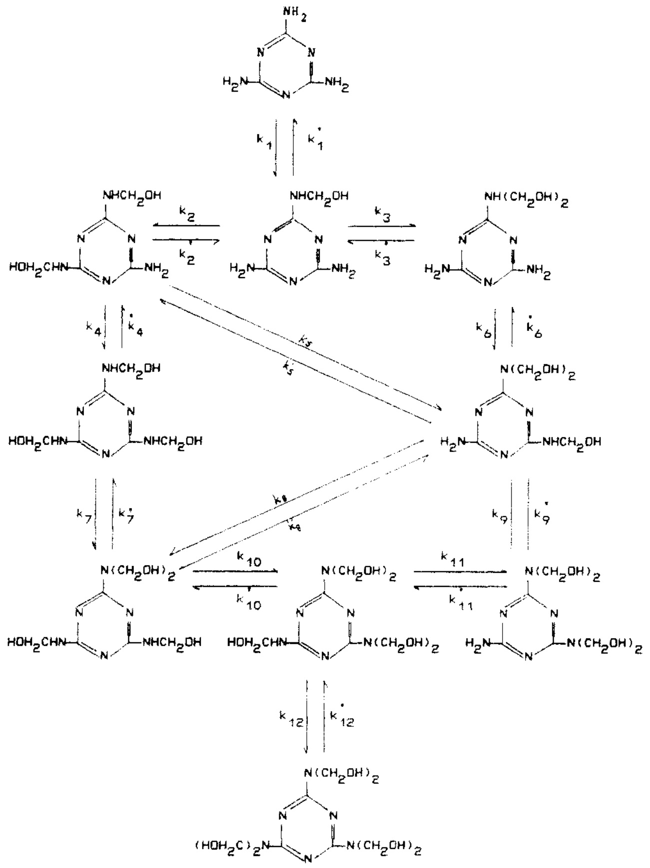

**Figure 1.** Reaction scheme proposed by Gordon and Tomita.

Above, we have shown polymerization to occur mainly by methylene bridge formation. Through $^{13}C$ NMR spectroscopy[7,8] it has been shown that polymerization could also occur through dimethylene ether linkage ($-NCH_2OCH_2N-$). In this work, we have modeled the polymerization, and in doing this we have assumed its contribution to the overall process is small.

Gordon et al.[9] have studied this reaction in the temperature range 25–55 °C. They have investigated the addition stage of the reaction and have proposed the scheme shown in Figure 1. In addition, in this model the methylolation as well as the demethylolation rate constants have been assumed to be the same in all steps, which means that, in the scheme of Figure 1, $k_1$, $k_2$, $k_3$, etc., are equal and $k'_1$, $k'_2$, etc., are also equal.

Tomita[10] has carried out studies on the addition reaction by limiting his studies to low-temperature polymerization only. He has followed the same reaction scheme as proposed by Gordon et al. but has proposed different rate constants for the methylolation and demethylolation steps. This implies that 24 rate constants are required to describe the total reaction kinetics. Tomita has measured the concentrations of the intermediate species and evaluated some of the rate constants through a suitable curve fit technique.

In commercial practice the melamine–formaldehyde resin is made by a batch process in two steps.[1-4] In the first step formaldehyde and melamine are charged to a kettle, the pH is adjusted to 9–9.5, and the reaction mass is heated. At very high pH the formaldehyde may undergo several side reactions including a Cannizarro reaction to form formic acid and methanol. In addition, it may also react with oxygen to form formic acid as follows:

$$2HCHO + H_2O \rightarrow CH_2OH + HCOOH \qquad (4)$$

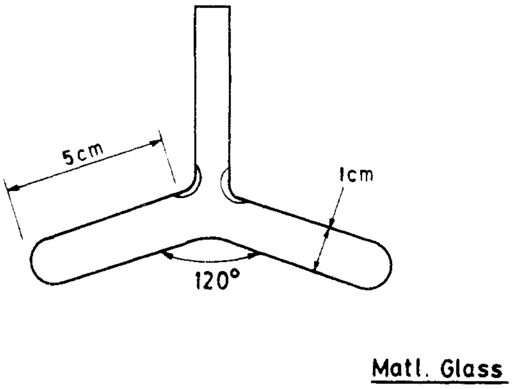

**Figure 2.** Dimensions of the special reactor used in this study.

$$2HCHO + O_2 \rightarrow HCOOH \qquad (5)$$

The presence of HCOOH can catalyze the condensation reaction to such an extent that a premature gelation may occur. To prevent this, the pH of the solution is never exceeded beyond 9.5 even though a high pH leads to a higher rate of polymerization. The reaction temperature can be safely kept at around 80 °C at this pH level, and oxidation is minimized by excluding air from the reactor. Under these reaction conditions a syrup consisting of the melamine–formaldehyde resin is formed that could be used as an adhesive or a laminating resin. It is also an intermediate for the manufacture of cross-linked materials where it is mixed with suitable polymers like acrylic copolymers.[11,12] This condenses to form a hard material that is used in various coatings and textile finishes.

In this paper, we have experimentally studied the polymerization of melamine with formaldehyde at conditions around those used commercially. At these temperature and pH conditions, polymerization occurs through a combination of addition as well as the condensation steps. We have proposed a comprehensive kinetic model for the polymerization of melamine and formaldehyde by using a functional group approach and developed the mole balance relations for the functional groups.[13-16] Through detailed computer simulation, we have determined the set of rate constants that fits the experimental data in the entire range. We show that melamine dissolves in the reaction mass slowly and ionizes in the reaction mass to some extent. The polymer formation is a complex process of polymerization of the un-ionized molecules of melamine. We have modeled this and determined the rate constants experimentally by carrying out polymerization at reaction conditions close to those used industrially.

## Experimental Procedure

The analytical reagent-grade formalin supplied to us was acidic, having a pH of 3.25. It was first neutralized, and then a fixed volume of it was reacted with sodium sulfite. The resulting solution was immediately titrated against standard hydrochloric acid to get the exact concentration of formaldehyde in formalin. Solutions of formaldehyde of various strengths were prepared thereafter and the pHs of the solutions adjusted by addition of 0.5 N NaOH or HCl as per experimental conditions required. The pH was measured by a digital pH meter with an accuracy of ±0.1.

The reaction vessel was designed as a Y-shaped glass tube as shown in Figure 2. Its dimensions have been chosen such that sufficient sample was available for the formaldehyde analysis, with minimum vapor space. A precalculated amount of powder melamine was charged to one arm of the glass reactor. The quantity was based on the amount required to give a desired molar ratio of formaldehyde to melamine for each 8 mL of formaldehyde of known concentration. Formaldehyde was carefully added to the other arm by a hypodermic syringe to prevent contact with melamine. The mouth of the Y tube was later glass sealed. It was then held on the shaft of the stirrer, which was also used to stir the constant-temperature water bath. The shaft of the stirrer was purposely held at an angle of 50° with vertical, so that the reactants melamine and formaldehyde are thoroughly mixed during the polymerization. Sufficient time was allowed for the reactants to reach the bath temperature. The motor was then switched on, keeping the rpm in the vicinity of 60 to allow proper mixing of the reactants.

In the sulfite method the formaldehyde solution (or the reaction mixture) is mixed with an excess of 0.1 N sodium sulfite solution. The produced sodium hydroxide is immediately titrated with standard HCl solution. The number of moles of sodium hydroxide present in the solution is the measure of the number of moles of formaldehyde. The indicator used for this process is thymolphthalein.

When the analysis for the reaction mixture is carried out, the titration should be done as fast as possible because the alkali, which is present originally to maintain the pH of the reaction mixture or produced by the reaction of sulfite, accelerates the decomposition of methylolmelamine into melamine and formaldehyde and thus the titer value of HCl may increase. At the end of a required polymerization time the tube is taken out and broken in cold sodium sulfite solution. The resulting solution is immediately titrated against HCl to get the free formaldehyde content. The cold sulfite solution prevents the reaction from continuing while the titration is carried out. Kinetic data have thus been obtained for varying temperatures, pH, and molar ratio. These are summarized in Table I.

## Theoretical Development

Earlier work of Tomita modeled the polymerization of formaldehyde with melamine, and their model has been shown in Figure 1. In his model, he has ignored the formation of higher ring species. In order to explain the formation of larger ring compounds (eq 3), in this paper, we have adopted the functional group approach of modeling the polymerization.

In our earlier work,[13] we had modeled the polymerization of melamine with formaldehyde by defining 10 reactive species as shown in Figure 3 and had successfully fitted the experimental data of Tomita. Here species A represents a melamine molecule, species B a monosubstituted methylolmelamine, species C and D disubstituted methylolmelamines, species E a trisubstituted methylolmelamine, and so on. In this figure X denotes a $CH_2OH$ group and a 〰 indicates that the species is a part of the polymer chain. Thus each species specify the various hydrogen on a melamine ring, which can react either with formaldehyde or with a $CH_2OH$ group. If these species react with a $CH_2OH$ group, a methylene bridge is formed and leads to the growth of a chain. The polymerization consists of the following reactions: (i) Melamine undergoes an addition reaction to give methylolmelamine groups, (ii) condensation of methylolmelamines and melamine to form the methylene bridge, and (iii) condensation of two methylolmelamines to give a methylene bond and formaldehyde, with the latter reacting again by the first mode. In the following it is shown that all these can be represented by reaction of species A–J.

From the chemistry of polymerization of melamine, the reactivity of hydrogen is known to be different for primary and secondary amide positions, and reactivity of a particular species is independent of its substituents. Hence, the following rate constants have been defined:

| | |
|---|---|
| $k_1$ | reaction between a $CH_2OH$ group and a primary |
| $k_2$ | reaction between a $CH_2OH$ group and a secondary amide group |
| $k_4$ | reaction between two $CH_2OH$ groups giving a methylene linkage (or Z) and a free formaldehyde molecule (this 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 |

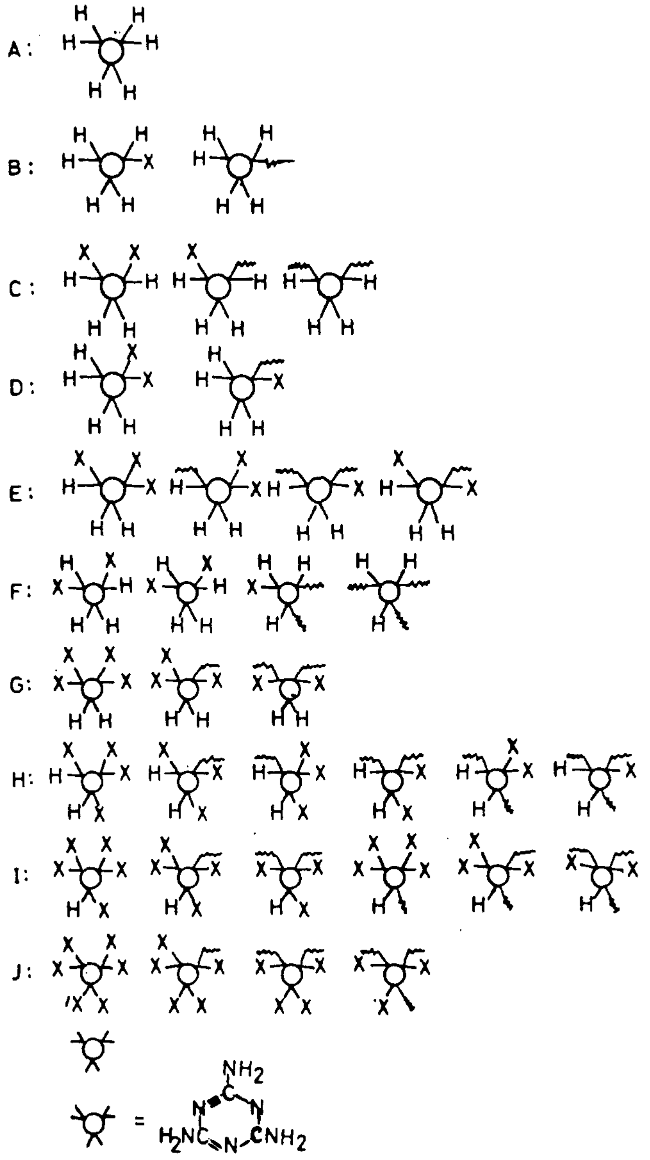

**Figure 3.** Various reactive functional groups needed for the modeling of melamine–formaldehyde polymerization.

In the reverse reaction two possibilities exist. The various bonds of the reactive sites can be assumed to be predominantly reacted bonds, Z, which on reaction with water lead to the formation of a $CH_2OH$ group. This has been called model I. As opposed to this, in model II, the bonds can be assumed to be essentially all $CH_2OH$ groups, which on reaction with water leads to the formation of free formaldehyde. On the basis of the above descriptions, the reaction mechanisms in terms of species A–J are shown below and the mole balance for various species in a batch reactor are given in Table II. In writing these equations, the rate constants of the species are assumed to be independent of the nature of the bond on the reacting species. This is because the individual concentrations of

**Table I**
**Kinetic Data Using Melamine in the Powder Form**

| time, min | mole ratio $F_1$:A | pH | temp, °C | formaldehyde concn, mol/L |
|---|---|---|---|---|
| 0 | 30:1 | 9.5 | 48 | 0.873 |
| 10 | | | | 0.865 |
| 20 | | | | 0.860 |
| 30 | | | | 0.858 |
| 40 | | | | 0.845 |
| 60 | | | | 0.838 |
| 80 | | | | 0.830 |
| 90 | | | | 0.820 |
| 110 | | | | 0.818 |
| 120 | | | | 0.818 |
| 0 | 2:1 | 9.5 | 50 | 0.529 |
| 10 | | | | 0.475 |
| 20 | | | | 0.440 |
| 30 | | | | 0.398 |
| 40 | | | | 0.396 |
| 60 | | | | 0.375 |
| 80 | | | | 0.370 |
| 90 | | | | 0.362 |
| 110 | | | | 0.358 |
| 120 | | | | 0.358 |
| 0 | 2:1 | 9.5 | 67 | 0.615 |
| 10 | | | | 0.505 |
| 20 | | | | 0.401 |
| 30 | | | | 0.361 |
| 40 | | | | 0.331 |
| 60 | | | | 0.315 |
| 80 | | | | 0.308 |
| 90 | | | | 0.296 |
| 110 | | | | 0.281 |
| 120 | | | | 0.280 |
| 0 | 15:1 | 9.5 | 75 | 0.636 |
| 10 | | | | 0.610 |
| 20 | | | | 0.575 |
| 30 | | | | 0.562 |
| 40 | | | | 0.550 |
| 60 | | | | 0.535 |
| 80 | | | | 0.525 |
| 90 | | | | 0.520 |
| 110 | | | | 0.512 |
| 120 | | | | 0.513 |
| 0 | 2:1 | 9.5 | 81 | 0.533 |
| 10 | | | | 0.370 |
| 20 | | | | 0.291 |
| 30 | | | | 0.251 |
| 40 | | | | 0.228 |
| 60 | | | | 0.215 |
| 80 | | | | 0.206 |
| 90 | | | | 0.198 |
| 110 | | | | 0.190 |
| 120 | | | | 0.188 |
| 0 | 1:1 | 9.5 | 81 | 0.5330 |
| 10 | | | | 0.2050 |
| 20 | | | | 0.1150 |
| 30 | | | | 0.1050 |
| 40 | | | | 0.0920 |
| 60 | | | | 0.0770 |
| 80 | | | | 0.0725 |
| 90 | | | | 0.0721 |
| 110 | | | | 0.0718 |
| 120 | | | | 0.0715 |
| 0 | 3:1 | 9.5 | 81 | 0.533 |
| 10 | | | | 0.415 |
| 20 | | | | 0.330 |
| 30 | | | | 0.291 |
| 40 | | | | 0.270 |
| 60 | | | | 0.252 |
| 80 | | | | 0.236 |
| 90 | | | | 0.231 |
| 110 | | | | 0.230 |
| 120 | | | | 0.230 |

formaldehyde ($F_1$) and $CH_2OH$ occur nowhere; instead a collective term ($2[F_1] + [CH_2OH]$) appears. Forward reaction steps in the polymerization of melamine with formaldehyde are as follows:

$$A + F_1 \xrightarrow{12k_1} B + CH_2OH + H_2O \tag{6a}$$

$$B + F_1 \xrightarrow{8k_1} C + CH_2OH + H_2O \tag{6b}$$

$$B + F_1 \xrightarrow{2k_1} D + CH_2OH + H_2O \tag{6c}$$

$$C + F_1 \xrightarrow{4k_1} F + CH_2OH + H_2O \tag{6d}$$

$$C + F_1 \xrightarrow{4k_2} E + CH_2OH + H_2O \tag{6e}$$

$$D + F_1 \xrightarrow{8k_1} E + CH_2OH + H_2O \tag{6f}$$

$$E + F_1 \xrightarrow{4k_1} H + CH_2OH + H_2O \tag{6g}$$

$$E + F_1 \xrightarrow{2k_2} G + CH_2OH + H_2O \tag{6h}$$

$$F + F_1 \xrightarrow{6k_2} H + CH_2OH + H_2O \tag{6i}$$

$$G + F_1 \xrightarrow{4k_1} I + CH_2OH + H_2O \tag{6j}$$

$$H + F_1 \xrightarrow{4k_2} I + CH_2OH + H_2O \tag{6k}$$

$$I + F_1 \xrightarrow{2k_2} J + CH_2OH + H_2O \tag{6l}$$

$$A + CH_2OH \xrightarrow{6k_1} B + Z + H_2O \tag{7a}$$

$$B + CH_2OH \xrightarrow{4k_1} C + Z + H_2O \tag{7b}$$

$$B + CH_2OH \xrightarrow{k_1} D + Z + H_2O \tag{7c}$$

$$C + CH_2OH \xrightarrow{2k_1} F + Z + H_2O \tag{7d}$$

$$C + CH_2OH \xrightarrow{2k_2} E + Z + H_2O \tag{7e}$$

$$D + CH_2OH \xrightarrow{4k_1} E + Z + H_2O \tag{7f}$$

$$E + CH_2OH \xrightarrow{2k_1} H + Z + H_2O \tag{7g}$$

$$E + CH_2OH \xrightarrow{k_2} G + Z + H_2O \tag{7h}$$

$$F + CH_2OH \xrightarrow{3k_2} H + Z + H_2O \tag{7i}$$

$$G + CH_2OH \xrightarrow{2k_1} I + Z + H_2O \tag{7j}$$

$$H + CH_2OH \xrightarrow{2k_2} I + Z + H_2O \tag{7k}$$

$$I + CH_2OH \xrightarrow{k_2} J + Z + H_2O \tag{7l}$$

Another important reaction is the reaction between two $CH_2OH$s.

$$CH_2OH + CH_2OH \underset{k'_4}{\overset{k_4}{\rightleftharpoons}} Z + F \tag{8}$$

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

The reverse reaction steps are written assuming Z as reacted bonds. We call this as model I, and it is represented as

Model I

$$B + H_2O \xrightarrow{k_5} A + CH_2OH - Z \tag{9a}$$

$$C + H_2O \xrightarrow{2k_5} B + CH_2OH - Z \tag{9b}$$

$$D + H_2O \xrightarrow{2k_5} B + CH_2OH - Z \tag{9c}$$

$$E + H_2O \xrightarrow{2k_5} C + CH_2OH - Z \tag{9d}$$

$$E + H_2O \xrightarrow{k_5} D + CH_2OH - Z \tag{9e}$$

$$F + H_2O \xrightarrow{3k_5} C + CH_2OH - Z \tag{9f}$$

$$G + H_2O \xrightarrow{4k_5} E + CH_2OH - Z \tag{9g}$$

$$H + H_2O \xrightarrow{2k_5} E + CH_2OH - Z \tag{9h}$$

$$H + H_2O \xrightarrow{2k_5} F + CH_2OH - Z \tag{9i}$$

$$I + H_2O \xrightarrow{k_5} G + CH_2OH - Z \tag{9j}$$

$$I + H_2O \xrightarrow{4k_5} H + CH_2OH - Z \tag{9k}$$

$$J + H_2O \xrightarrow{6k_5} I + CH_2OH - Z \tag{9l}$$

In model II, the reverse reaction steps are written assuming reacted sites as $CH_2OH$ groups.

Model II

$$B + H_2O \xrightarrow{k_5} A + F_1 - CH_2OH \tag{10a}$$

$$C + H_2O \xrightarrow{2k_5} B + F_1 - CH_2OH \tag{10b}$$

$$D + H_2O \xrightarrow{2k_5} B + F_1 - CH_2OH \tag{10c}$$

$$E + H_2O \xrightarrow{2k_5} C + F_1 - CH_2OH \tag{10d}$$

$$E + H_2O \xrightarrow{k_5} D + F_1 - CH_2OH \tag{10e}$$

$$F + H_2O \xrightarrow{3k_5} C + F_1 - CH_2OH \tag{10f}$$

$$G + H_2O \xrightarrow{4k_5} E + F_1 - CH_2OH \tag{10g}$$

$$H + H_2O \xrightarrow{2k_5} E + F_1 - CH_2OH \tag{10h}$$

$$H + H_2O \xrightarrow{2k_5} F + F_1 - CH_2OH \tag{10i}$$

$$I + H_2O \xrightarrow{k_5} G + F_1 - CH_2OH \tag{10j}$$

$$I + H_2O \xrightarrow{4k_5} H + F_1 - CH_2OH \tag{10k}$$

$$J + H_2O \xrightarrow{6k_5} I + F_1 - CH_2OH \tag{10l}$$

It is possible to make mole balance for each of these species, and these are given in Table II.

## Results and Discussion

The low-temperature polymerization of melamine with formaldehyde at high dilutions has been carried out in detail by Tomita. We first dissolved melamine in water and then mixed the solution with formaldehyde to get the desired formaldehyde to melamine ratio ($F_1/A$ ratio) in order to compare our data with those of Tomita. We carried out polymerization of melamine in the aqueous phase at a formaldehyde to melamine ratio ($F_1/A$) of 30:1, a pH 9, and a temperature 48 °C. The results have been plotted in Figure 4. We find that our experimental results are extremely close to those of Tomita, and our data points, if at all, appear to be shifted a little upward. Tomita has not discussed the reaction vessel employed for the polymerization in his paper, and perhaps the results of Figure 4 can be explained through a minor loss of formaldehyde by evaporation in his setup. In the same figure we have plotted the experimental results when melamine powder (instead of using an aqueous solution) is added to the formaldehyde, its pH being adjusted through a pH meter to the exact value of 9.0. When the polymerization is done under this condition, we find that the conversion of formaldehyde is smaller compared to conditions when polymerization is carried out in "aqueous phase". This can be explained as follows. We have observed that solid melamine at this temperature takes about 20 min to dissolve. As soon as solid melamine is added to formaldehyde, in addition to the slow dissolution, polymerization also starts. Due to this heterogeneity, the concentration of the dissolved melamine is smaller in the reaction mass, which in turn gives lower conversion of formaldehyde as seen in Figure 4.

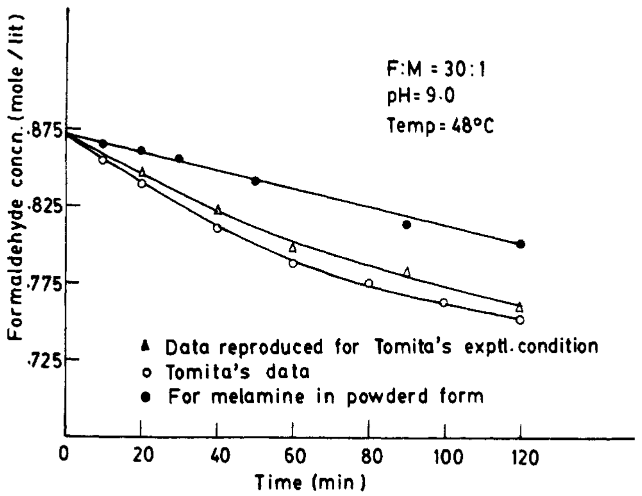

**Figure 4.** Effect of slow dissolution of melamine upon the course of polymerization.

Industrially melamine powder and formaldehyde are charged to the reactor in one shot. We observe that, at higher temperatures, dissolution rate is higher and the condition of heterogeneity (Figure 4) always exists within the reactor until all of the melamine is dissolved. In order to simulate the industrially prevalent conditions, we have carried out polymerization at low values of formaldehyde to melamine ratios (1:1, 2:1, 3:1). In Figure 5 we have systematically varied the temperature of polymerization and determined the formaldehyde concentrations as a function of reaction time. It is observed that at a given temperature for short intervals of polymerization the fall in the concentration of formaldehyde is sharp; however, for large times it attains an equilibrium value. As the temperature is increased the equilibrium concentration and the initial rate of fall of formaldehyde concentration both increase as seen in Figure 6. It may be remembered that all polymerization reactions are exothermic in nature. This would mean that as the reaction temperature is increased the equilibrium concentration of formaldehyde should increase, which is contrary to the observations made in Figure 5. This suggests that the overall polymerization must be a complex reaction. In addition to the temperature, the $F_1/A$ ratio is known to be a very important parameter. In Figure 6 we have varied the $F_1/A$

**Table II**
**Mole Balance Relations for Species in a Batch Reactor for Model I**

1. $d[A]/dt = -6k_1[A](2[F_1] + [CH_2OH]) + k_5[B][H_2O]$
2. $d[B]/dt = 6k_1[A](2(F_1] + [CH_2OH]) - (4k_1 + k_2)[B](2[F_1] + [CH_2OH]) + k_5[H_2O](2[D] + 2[C]) - k_5[B][H_2O]$
3. $d[C]/dt = 4k_1[B](2[F_1] + [CH_2OH]) - 2(k_1 + k_2)[C](2[F_1] + [CH_2OH]) + k_5[H_2O](2[E] + 3[F]) - k_5[H_2O]2[C]$
4. $d[D]/dt = k_2[B](2[F_1] + [CH_2OH]) - 4k_1[D](2[F_1] + [CH_2OH]) + k_5[H_2O][E] - k_5[H_2O]2[D]$
5. $d[E]/dt = 2k_2[C] + 4k_2[D](2[F_1] + [CH_2OH]) - (2k_1 + k_2) \times [E](2[F_1] + [CH_2OH]) + k_5[H_2O](4[G] + 2[H]) - k_5[H_2O](3[E])$
6. $d[F]/dt = 2k_1[C](2[F_1] + [CH_2OH]) - 3k_2(2[F_1] + [CH_2OH])[F] + k_5[H_2O](2[H]) - k_5[H_2O](3[F])$
7. $d[G]/dt = k_2[E](2[F_1] + [CH_2OH]) - 2k_1[G](2[F_1] + [CH_2OH]) + k_5[H_2O][I] - k_5[H_2O](4[G])$
8. $d[H]/dt = (2k_1[E] + 3k_2[F])(2[F_1] + [CH_2OH]) - 2k_2[H](2[F_1] + [CH_2OH]) + k_5[H_2O](4[G])$
9. $d[I]/dt = (2k_1[G] + 2k_2[H])(2[F_1] + [CH_2OH]) - k_2[I](2[F_1] + [CH_2OH]) + k_5[H_2O](4[I]) - k_5[H_2O](4[H])$
10. $d[J]/dt = k_2[I](2[F_1] + [CH_2OH]) - k_5[H_2O](6[J])$
11. $d[F_1]/dt = -2[F_1]R_1 + k_4[CH_2OH]^2 - k_4'[Z][F_1]$
12. $d[CH_2OH]/dt = 2[F_1]R_1 - [CH_2OH]R_1 + k_5[H_2O]R_2$
13. $d[Z]/dt = [CH_2OH]R_2 - k_5[H_2O]R + k_4[CH_2OH]^2 - k_4'[Z][F_1]$
14. $d[H_2O]/dt = (2[F_1] + [CH_2OH])R_1 - k_5[H_2O]R_2$

$R_1 = 6k_1[A] + (4k_1 + k_2)[B] + (2k_1 + 2k_2)[C] + 4k_1[C] + (2k_1 + k_2)[E] + 3k_2[F] + 2k_1[G] + 2k_2[H] + k_2[I]$

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

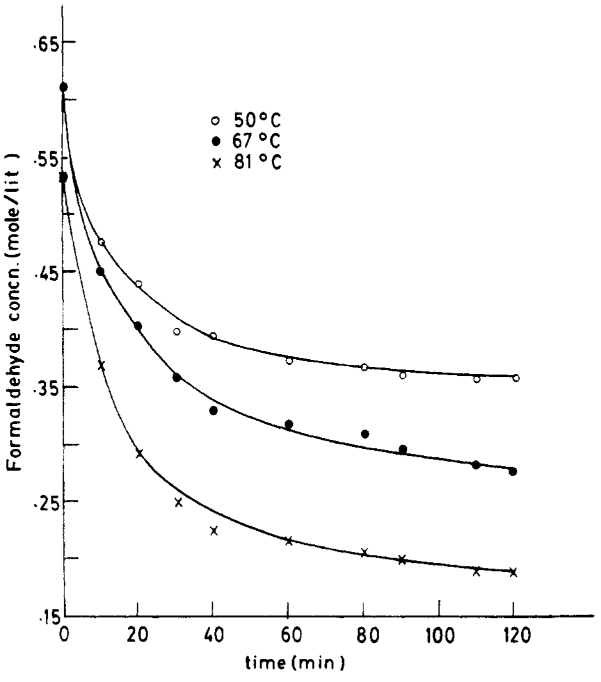

**Figure 5.** Effect of temperature upon formaldehyde concentration versus reaction time $F_1/A = 2/1$ and pH 9.5.

ratio from 1:1 to 3:1, keeping the temperature at 81 °C, and we find that, as the formaldehyde to melamine ratio is increased, the equilibrium value of formaldehyde concentration also increases. Gordon et al. have reported the pH of the reaction mass as one of the most important variables in Figure 7. We have varied the pH from 3.25 to 9.5, and we find that the equilibrium concentration of formaldehyde is little affected by the wide variation of pH.

After having examined the formaldehyde polymerization experimentally, we have proposed a kinetic model as given in eq 7 and 8. It is known that melamine ionizes in the solution to some extent, in which its amine group dissociates according to the following equation.

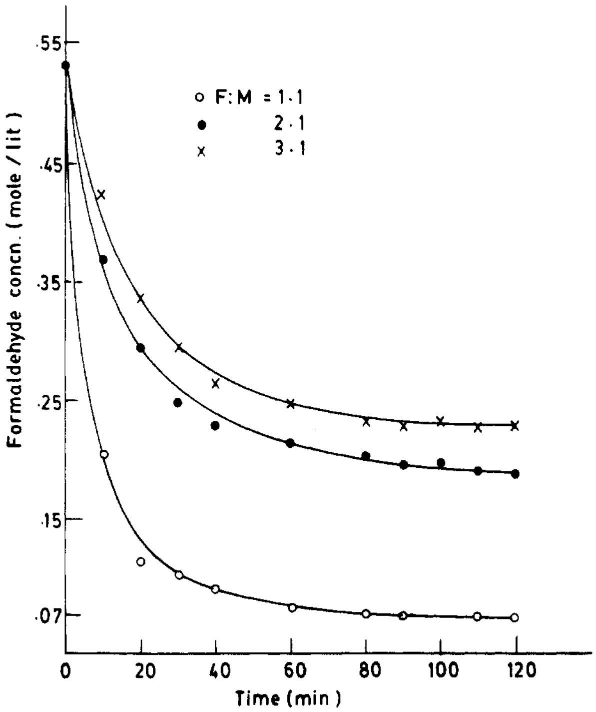

**Figure 6.** Effect of $F_1/A$ ratio upon formaldehyde concentration versus reaction time at 81 °C and pH 9.5.

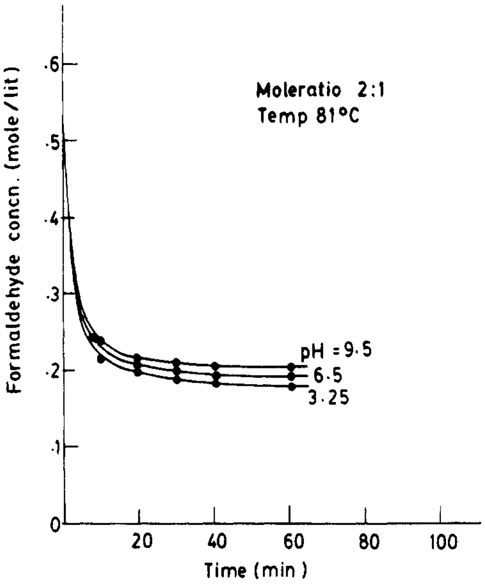

**Figure 7.** Effect of pH upon formaldehyde concentration versus reaction time at $F_1/A = 2/1$ and 81 °C.

$$-NH_2 + H_2O \rightleftharpoons -NH_2OH^- + H^+ \quad (11)$$

If the total melamine concentration in solution is [A], then the concentration of un-ionized melamine, $[A]_{un}$, can be written in terms of [A] as

$$[A]_{un} = k_s[A] \quad (12)$$

where $k_s$ is the apparent dissociation constant of melamine. It is expected that $k_s$ is a function of temperature as well as the F/M ratio. Equations 6a and 7a can now be modified to

$$A + F_1 \xrightarrow{2k_{11}} B + CH_2OH + H_2O \quad (6a')$$

$$A + CH_2OH \xrightarrow{k_{11}} B + Z + H_2O \qquad (7a)$$

where

$$k_{11} = k_s k_1 \qquad (13)$$

and the mole balance equations for model I as given in Table II for formaldehyde, melamine, and species B modify to

1. $d[A]/dt = -6k_{11}[A](2[F_1] + [CH_2OH]) + k_5[B][H_2O]$
2. $d[B]/dt = 6k_{11}[A](2[F_1] + [CH_2OH]) - (4k_{11} + k_2)[B](2[F_1] + [CH_2OH]) + k_5[H_2O](2[C] + [D]) - k_5[B][H_2O]$
11. $d[F_1]/dt = -2[F_1]R_{11} + k_4[CH_2OH]^2 - k'_4[Z][F_1]$
12. $d[CH_2OH]/dt = 2[F_1]R_{11} - [CH_2OH]R_{11} + k_5[H_2O]R_2$
13. $d[Z]/dt = [CH_2OH]R_{11} - k_5[H_2O]R_2 + k_4[CH_2OH]^2 - k'_4[Z][F_1]$
14. $d[H_2O]/dt = (2[F_1] + [CH_2OH])R_{11} - k_5[H_2O]R_2$

where

$$R_{11} = 6k_{11}[A] + (4k_1 + k_2)[B] + (2k_1 + 2k_2)[C] + 4k_1[D] + (2k_1 + k_2)[E] + 3k_2[F] + 2k_1[G] + 2k_2[H] + k_2[I]$$

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

and solved for the concentration of formaldehyde numerically by using the Runge–Kutta technique. The following checks are made in the computer program at every iteration of computation.

check 1 $[A] + [B] + [C] + [D] + [E] + [F] + [G] + [H] + [I] + [J] = [A]_0$

check 2 $2[F_1] + [CH_2OH] + [H_2O] = 2[F_1]_0$

The first check represents a balance on the total number of rings at any time, and the deviation from it is indicative of numerical instability of computation. Similarly, check 2 represents a balance for $F_1$ groups. We have varied $k_{11}$, $k_1$, and $k_2$ to match the initial rate of polymerization whereas we changed $k_4$, $k'_4$, and $k_5$ to match the equilibrium level of formaldehyde concentrations. The results of our simulation are shown in Figures 5–7 and are seen to describe the entire range of polymerization very well. The set of rate constants giving the fit are given in Table III.

It is interesting to observe that all rate constants are independent of the $F_1/A$ ratio. It may be recalled that, in kinetic theory, the rate constants must be a function of temperature alone, which is indeed what we find in our kinetic model. We have carried out reactions for five temperatures, viz., 48, 50, 67, 75, and 81 °C, and we have prepared the Arrhenius plot in Figures 8 and 9. The activation energies are shown in Table IIIC.

**Table III**

A. Rate Constants at Different Temperatures

| temp, °C | $k_1$, L/mol·min | $k_2$, L/mol·min | $k_4$, L/mol·min | $k_4'$, L/mol·min | $k_5$, L/mol·min |
|---|---|---|---|---|---|
| 48 | 0.0059 | 0.0275 | 0.093 | 0.075 | 0.00098 |
| 50 | 0.0064 | 0.030 | 0.100 | 0.080 | 0.000985 |
| 67 | 0.0139 | 0.098 | 0.18 | 0.174 | 0.001073 |
| 75 | 0.0198 | 0.171 | 0.230 | 0.239 | 0.00110 |
| 81 | 0.0235 | 0.230 | 0.28 | 0.305 | 0.01150 |

B. Values of $k_{11}$ at Different Temperatures and Mole Ratios

| $F_1$:A | temp, °C | $k_{11}$ |
|---|---|---|
| 30:1 | 48 | 0.0030 |
| 2:1 | 50 | 0.00627 |
| 2:1 | 67 | 0.0107 |
| 15:1 | 75 | 0.0095 |
| 3:1 | 81 | 0.0156 |
| 2:1 | 81 | 0.0175 |
| 1:1 | 81 | 0.0201 |

C. Activation Energies

$E_1$ = 8665 cal/g·mol
$E_2$ = 14076 cal/g·mol
$E_4$ = 7290 cal/g·mol
$E_4'$ = 9260 cal/g·mol
$E_5$ = 1200 cal/g·mol

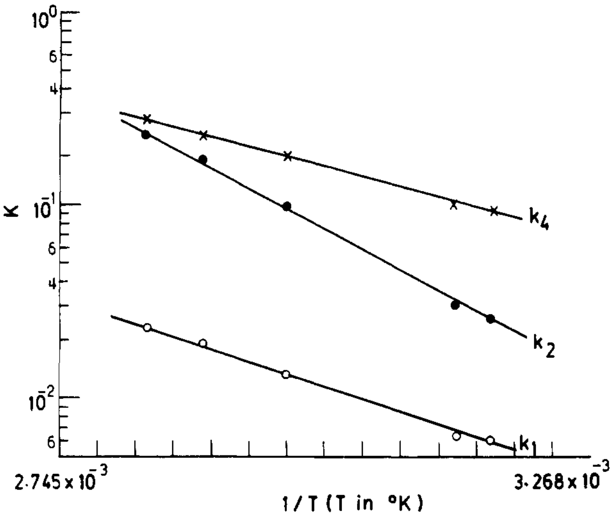

Figure 8. Arrhenius plots for rate constants $k_1$, $k_2$, and $k_4$.

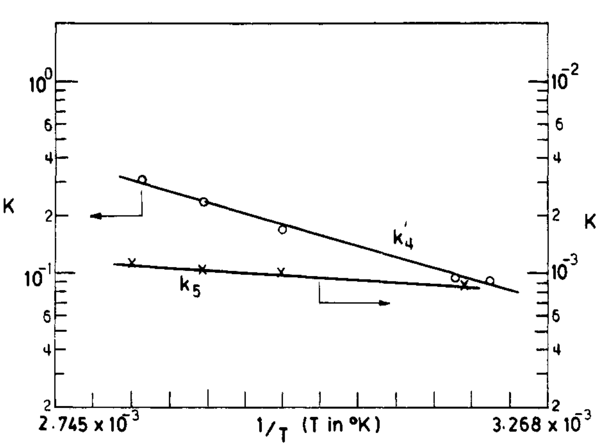

Figure 9. Arrhenius plots for $k'_4$ and $k_5$.

## Conclusions

We have studied the polymerization of melamine with formaldehyde at conditions existing in an industrial reactor. The polymerization was carried out in a special Y-shaped reactor, and the conversion of formaldehyde was measured as a function of temperature. The reaction temperature, the formaldehyde to melamine ratio ($F_1/A$), and the pH were systematically varied, and their effect on the course of the reaction was followed by the formaldehyde conversion. It was found that melamine dissolves in the reaction mass slowly and plays some role in determining the ultimate course of polymerization. In addition, melamine partially ionizes in the reaction mass, and experimental results suggest that it is the un-ionized species that participates in the polymerization.

We have proposed a kinetic model using that functional group approach to model the polymerization. In order to include the formation of a multiring polymer, we have used 10 species (A-J), and in order to take care of the inequality of reactive sites, we have used five rate constants. Subsequently, we have accounted for the ionization of melamine and solved the mole balance equations numerically. We have varied the rate constants to fit the experimental data and in this way evaluated all the rate constants of the model. It was found that these rate constants were a function of temperature alone, which is consistent with the basic kinetic theory.

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**Registry No.** Formaldehyde, 50-00-0; melamine, 108-78-1.

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# Living Carbocationic Polymerization of *p*-Halostyrenes. 1. Living Poly(*p*-chlorostyrene)[†,‡]

**J. P. Kennedy* and Joseph Kurian**

*Department of Polymer Science, The University of Akron, Akron, Ohio 44325*

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ABSTRACT: The living carbocationic polymerization of *p*-chlorostyrene (pClSt) has been achieved by the use of the 2-chloro-2,4,4-trimethylpentane (TMPCl)/TiCl$_4$ initiating system in the presence of dimethylacetamide (DMA) as electron donor and 2,6-di-*tert*-butylpyridine (D*t*BP) as proton trap in CH$_3$Cl/methylcyclohexane (MCHx) solvent mixtures at -80 °C under conventional laboratory conditions. The living nature of the polymerization was demonstrated by linear $\bar{M}_n$ versus $W_p$ (g of poly(*p*-chlorostyrene) (PpClSt) formed) plots passing through the origin and horizontal $N$ (number of moles of PpClSt formed) versus $W_p$ plots. The $\overline{DP}_n$ obeys [pClSt]/[TMPCl], and the molecular weight distributions (MWD) are narrow, $\bar{M}_w/\bar{M}_n$ = 1.3-1.9. pClSt polymerization by the cumyl methyl ether (CumOMe)/BCl$_3$ initiating system in CH$_3$Cl solvent has also been studied. The effects of the nature of the solvent and solvent composition on rates, $\bar{M}_n$s, and MWDs have been investigated. Functionality analysis by chloride-selective electrode, FTIR spectroscopy, and blocking experiments with tetrahydrofuran (THF) demonstrate that end groups of PpClSts are most likely secondary benzylic chlorines and that indanyl end groups are absent. The number-average end functionality ($\bar{F}_n$) was determined to be close to unity.

## 1. Introduction

Living polymerization is one of the simplest and most effective means to control the molecular weight (MW), MWD, and end functionality of polymers. In view of recent significant advances in living carbocationic polymerization of vinyl ethers[1] and olefins,[2,3] it appeared of interest to investigate that possibility of synthesizing well-defined PpClSt by this new technique.

The cationic polymerization of pClSt has been the subject of previous investigations;[4a] however, studies have not been carried out with respect to end groups, MWs, and MWD control. The polymerization of pClSt by the 1,4-bis(2-chloropropyl)benzene/BCl$_3$ binifer system has recently been investigated in our laboratories.[4b] While the cationic polymerization of pClSt is somewhat slower than that of other styrene derivatives,[5] we theorized that intramolecular alkylation leading to terminal indanyl structures will not occur on account of the highly deactivated ring. Indanyl structure formation is one of the most difficult to control side reactions in the cationic polymerization of styrenes.[4a] Anionic living polymerization methods cannot be employed for the homo- and copolymerization of pClSt because of the propensity of numerous side reactions.[6] Similarly, free radical

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[†] Paper 34 in the series "Living Carbocationic Polymerization".

[‡] Parts of this paper were presented at the American Chemical Society Meeting, Boston, 1990.

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