

# Modeling of Polymerization of Urea and Formaldehyde Using Functional Group Approach

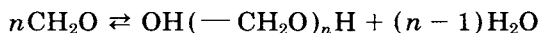
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## Synopsis

The urea formaldehyde polymerization has been modeled using the functional group approach, which accounts for the formation of higher oligomers. The kinetic model involves four molecular species and three rate constants, as opposed to six as proposed in earlier studies. The experimental data of Price et al. have been curve fitted using our model, which is found to describe them very well in the entire range of temperature and urea formaldehyde ratio. Based on the activation energies, it has been argued that the reverse reaction step must involve the condensation product, water.

## INTRODUCTION

The polymerization of urea and formaldehyde is normally carried out by mixing water solution of formaldehyde (formalin) and urea and subjecting it to high temperature.<sup>1,2</sup> Formaldehyde is highly reactive, and when it is present in large concentration it polymerizes into white powder called polyformaldehyde as follows<sup>4-6</sup>



where  $n$  is usually of the order of 10. Under alkaline conditions polyformaldehyde depolymerizes into formaldehyde, which exists mostly as methylene glycol<sup>5-9</sup> in aqueous solution.

Formaldehyde can polymerize with phenol, cresol, urea, and melamine, and depending upon the reaction conditions, it can either form a linear polymer or a network.<sup>10-14</sup> In this study, we have analyzed the formation of urea formaldehyde polymer. The proposed kinetic model accounts for the addition as well as the condensation reactions and is completely general. This involves only three rate constants, as opposed to six used in earlier studies.

The urea-formaldehyde resin is mainly used as an adhesive in plywood and particle board industries.<sup>1,10</sup> The resin is prepared as prepolymer in the first stage. This is subsequently mixed with suitable hardener and catalyst and applied on sheets to be jointed. There is a gelation of the polymer leading to the formation of a network in the second stage.

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There have been several studies reported on the formation of prepolymer of urea and formaldehyde.<sup>15-32</sup> Urea ( $\text{NH}_2\text{—CO—NH}_2$  denoted by U) has four reactive hydrogens, and each of them has a different reactivity. Three of its hydrogens are highly reactive compared to the fourth one.<sup>15-21</sup> On reaction of urea with formaldehyde (existing as methylene glycol,  $\text{OH—CH}_2\text{—OH}$ , in water) there is a formation of  $\text{U—CH}_2\text{OH}$ .<sup>23-32</sup> This is called the addition step and a methylol bond is formed. If urea is in excess in the acidic medium,  $\text{U—CH}_2\text{OH}$  reacts with another U preferentially to give diurea methyl ether,  $\text{U—CH}_2\text{—O—CH}_2\text{U}$  or methyl diurea  $\text{U—CH}_2\text{—U}$ . In addition to this, low molecular weight polymer is also formed, and this is sometimes called the polycondensation step. As the pH increases, methylene linkages reduce, and the primary products are methylols and ethers, and the chain length of the polymer is limited to a small value.

The gelation of resins occurs at low pH, and the process can be induced by any method that lowers the pH of the reaction mass. Due to the difficulty of instrumental analysis, the progress in the studies of gelation has been relatively slow. The gelation has been followed using X-ray, differential thermal analysis, infrared spectroscopy, thermal gravimetric analysis, and nuclear magnetic resonance.<sup>23,24,33,34</sup> Mayer<sup>1</sup> has discussed at great length the effect of pH, various additives, and their concentrations upon the gelation time.

Most of the analysis of the urea-formaldehyde system has been limited to the first stage. Price et al.<sup>31</sup> have assumed the absence of the polycondensation step and only two of the sites of urea participate in the first stage as follows:



In this, U and F represent a urea and a formaldehyde molecule whereas  $\text{UF}_1$  and  $\text{UF}_2$  are two of their substitution products. Price et al.<sup>31</sup> have experimentally measured the free formaldehyde in the reaction mass. They observed that the kinetic model of eq. (1) fits the experimental results for low temperature only. For high temperatures they proposed the following additional reaction:



The urea-formaldehyde polymer has been analyzed by Katuscak et al.,<sup>29</sup> who clearly show that it contains higher oligomers. They have studied several samples and characterized them with a molecular weight distribution, average molecular weight, and polydispersity index.

In this study, we have used the functional group approach in which we follow the polymerization by defining four reactive species. Based on the chemistry of polymer formation, we have rewritten the mechanism involving these species. In addition, eqs. (1) and (2) seem to indicate that the reversed step is unimolecular, and there is a bond scission that may not occur at moderate tem-

peratures. In view of this, we have considered an additional kinetic model in which water was assumed to participate in the reverse step of polymerization. Using both these kinetic schemes, we have shown in this study that it was possible to describe the experimental data of Price et al.<sup>31</sup> in the complete range.

**KINETIC MODEL FOR THE FORMATION OF UREA-FORMALDEHYDE POLYMER**

Since formaldehyde exists in the aqueous medium as methylene glycol, OH—CH<sub>2</sub>—OH, it shows a functionality of two. In urea there are four hydrogens that can undergo reaction with the hydroxyl group of methylene glycol. In view of this, the first methylene glycol molecule can react at four positions of a urea with equal likelihood, thus urea exhibiting a functionality of four. We have attempted to model the polymerization by using functional group approach. In this we identify species in terms of which the formed polymer can be represented. In Figure 1, we have defined four species, A, B, C, and D. At a given

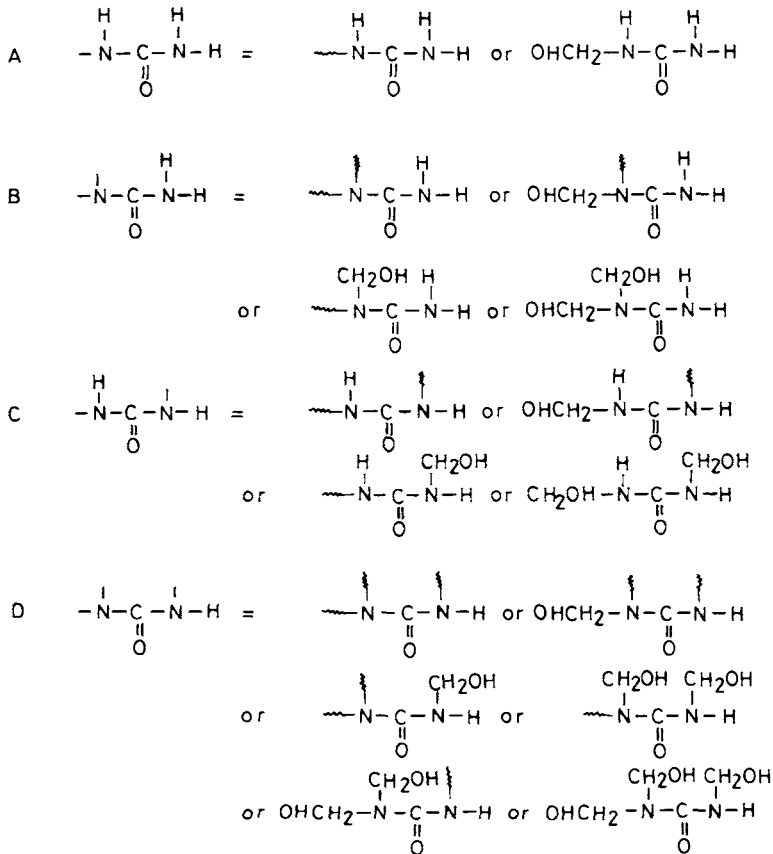
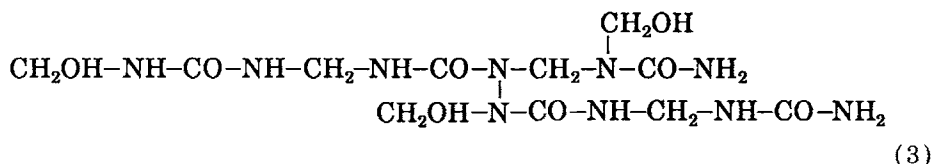


Fig. 1. Reactive species used for modeling reversible urea-formaldehyde polymerization.

time within the reactor, we have unreacted  $\text{CH}_2\text{OH}$  groups on the polymer molecule formed during reaction as well as the reacted  $\text{CH}_2$  bond. The latter formed whenever two repeat units react, which also leads to formation of higher oligomers. In defining these species, no distinction has been made whether the linkages at these reacted sites are a reacted  $-\text{CH}_2-$  bond or a  $-\text{CH}_2\text{OH}$  group.

Species A to D can be used to represent any polymer molecule. For example,



can be represented by



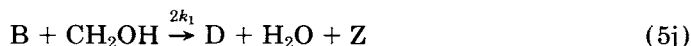
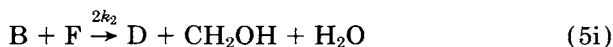
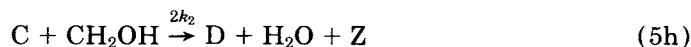
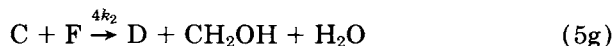
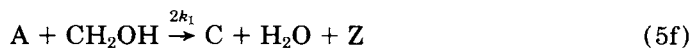
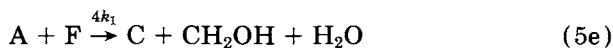
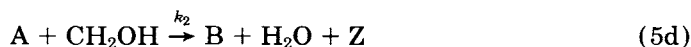
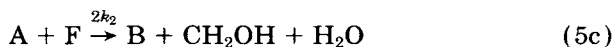
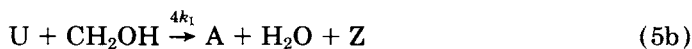
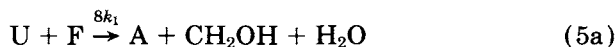
Instead of attempting to find out the concentration of different isomers in a polymer, an effort is made here to determine the conversion of urea and formaldehyde in the reaction mass as a function of time. When polymerization is carried out for some time starting with a feed consisting of urea and formaldehyde, polymers of various lengths and structures are formed. One plausible description of the progress of reaction would be to follow the concentration of species A to D in the reaction mass. The overall polymerization represented by reaction of functional groups can be written in terms of the following rate constants:

$k_1$  = rate constant for the reaction of primary hydrogen of urea with the OH groups.

$k_2$  = rate constant for the secondary or tertiary hydrogen of urea with the OH group.

$k_3$  = rate constant for the reverse reaction occurring between a reacted  $-\text{CH}_2-$  bond (denoted by Z) and water molecule.

Experimental work of de Jong<sup>12</sup> have shown that the reactivity of various hydrogens on urea is dependent upon the number of sites already reacted. Also at moderate reaction conditions, there is little evidence of finding reacted tetra-substituted urea, whether it is part of a polymer chain or it is a freely existing molecule. Based on this chemistry of polymerization of urea and formaldehyde, the forward reaction can be written in terms of species A to D. Since there is no formation of tetrasubstituted urea, polymerization can be represented by

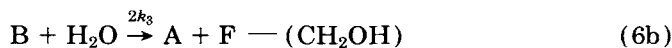
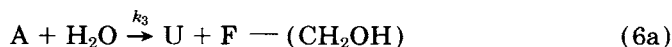


In writing these reactions it has been assumed that the overall reactivity of a given reaction is completely governed by the site involved. Therefore when urea consisting of four hydrogens reacts with formaldehyde (or methylene glycol) having two —OH groups, it forms species A as in eq. (5a), and the overall reactivity is  $8k_1$ . Lastly, species D does not have any reactive site left, therefore it is assumed not to react anymore.

Since in species A to D, the —CH<sub>2</sub>— bond and the CH<sub>2</sub>OH linkage have not been distinguished, it is not possible to write the mechanism of the reverse reaction exactly. In view of this, two extreme possibilities have been proposed.<sup>4,34</sup> In the first one (model I) the various linkage of species A to D have all been assumed to be mainly CH<sub>2</sub>OH groups. As opposed to this, in the second one (model II) the linkage of species A to D have all been assumed to be mainly reacted —CH<sub>2</sub>— bonds. It is assumed that model I would be a better representation of the situation in the initial phases of polymerization whereas model II would give a better description in the final stages of polymerization. For these two models the mechanism of polymerization is given next.

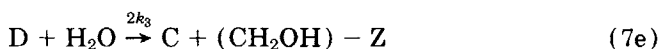
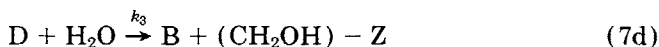
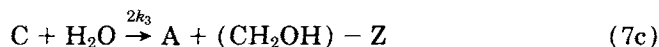
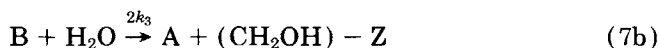
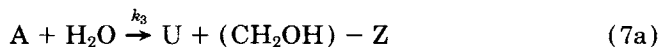
### Reverse Reaction for Model I

All linkage are assumed to be reacted —CH<sub>2</sub>OH groups.



**Reverse Reaction for Model II**

All linkage are assumed to be  $-\text{CH}_2-$ .



The mole balance relation for various species in batch reactors can now be easily written for both these mechanisms. It may be observed that the mole balances for species A to D and water are identical for both these models, and these are considered next.

**Model I and II**

$$\frac{d[\text{A}]}{dt} = (2[\text{F}] + [\text{CH}_2\text{OH}]) \times \{4k_1[\text{U}] - k_2[\text{A}] - 2k_1[\text{A}]\} + k_3[\text{H}_2\text{O}]\{2[\text{B}] + 2[\text{C}] - [\text{A}]\} \quad (8)$$

$$\frac{d[\text{B}]}{dt} = (2[\text{F}] + [\text{CH}_2\text{OH}])\{k_2[\text{A}] - 2k_1[\text{B}]\} + k_3[\text{H}_2\text{O}]( [\text{D}] - 2[\text{B}] ) \quad (9)$$

$$\frac{d[\text{C}]}{dt} = (2[\text{F}] + [\text{CH}_2\text{OH}])\{2k_1[\text{A}] - 2k_2[\text{C}]\} + 2k_3[\text{H}_2\text{O}]( [\text{D}] - [\text{C}] ) \quad (10)$$

$$\frac{d[\text{D}]}{dt} = (2[\text{F}] + [\text{CH}_2\text{OH}])\{2k_1[\text{B}] + 2k_2[\text{C}]\} - 3k_3[\text{H}_2\text{O}][\text{D}] \quad (11)$$

$$\frac{d[\text{U}]}{dt} = k_3[\text{H}_2\text{O}][\text{A}] - (2[\text{F}] + [\text{CH}_2\text{OH}])4k_1[\text{U}] \quad (12)$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = (2[\text{F}] + [\text{CH}_2\text{OH}])\{2k_1(2[\text{U}] + [\text{A}] + [\text{B}]) + k_2([\text{A}] + 2[\text{C}])\} - k_3[\text{H}_2\text{O}]\{[\text{A}] + 2[\text{B}] + 2[\text{C}] + 3[\text{D}]\} \quad (13)$$

**Model I**

$$\frac{d[\text{F}]}{dt} = -2[\text{F}]\{2k_1(2[\text{U}] + [\text{A}] + [\text{B}]) + k_2([\text{A}] + 2[\text{C}])\} + k_3[\text{H}_2\text{O}]( [\text{A}] + 2[\text{B}] + 2[\text{C}] + 3[\text{D}] ) \quad (14)$$

$$\frac{d[\text{CH}_2\text{OH}]}{dt} = (2[\text{F}] - [\text{CH}_2\text{OH}])\{2k_1(2[\text{U}] + [\text{A}] + [\text{B}]) + k_2([\text{A}] + 2[\text{C}])\} - k_3[\text{H}_2\text{O}]( [\text{A}] + 2[\text{B}] + 2[\text{C}] + 3[\text{D}] ) \quad (15)$$

$$\frac{d[\text{Z}]}{dt} = [\text{CH}_2\text{OH}]\{2k_1(2[\text{U}] + [\text{A}] + [\text{B}]) + k_2([\text{A}] + 2[\text{C}])\} \quad (16)$$

Model II

$$\frac{d[F]}{dt} = -[F]\{2k_1(2[U] + [A] + [B]) + k_2([A] + 2[C])\} \quad (17)$$

$$\begin{aligned} \frac{d[CH_2OH]}{dt} = & (2[F] - [CH_2OH])\{2k_1(2[U] + [A] + [B]) \\ & + k_2([A] + 2[C])\} + k_3[H_2O]\{[A] + 2[B] + 2[C] + 3[D]\} \quad (18) \end{aligned}$$

$$\begin{aligned} \frac{d[Z]}{dt} = & [CH_2OH]\{2k_1(2[U] + [A] + [B]) + k_2([A] + 2[C])\} \\ & - k_3[H_2O]\{[A] + 2[B] + 2[C] + 3[D]\} \quad (19) \end{aligned}$$

RESULTS AND DISCUSSION

Price et al.<sup>31</sup> have carried out polymerization of urea and formalin (37% formaldehyde in water by weight) in a special shaped sealed reactor. A careful examination of the experimental data reported in ref. 31 reveals that the concentrations of free formaldehyde in the reaction mass falls very rapidly for short times. However, for large times, depending upon the temperature of the reaction mass, it attains an equilibrium. In the kinetic model proposed in this work, there are two equilibrium constants,  $K_1$  and  $K_2$  defined as

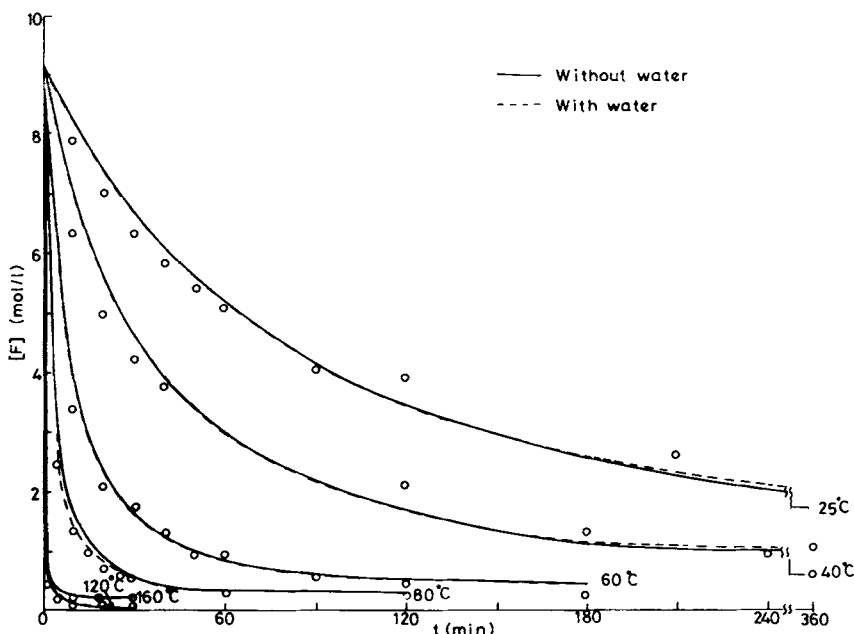


Fig. 2. Experimental data of Price et al.<sup>31</sup> for U/F = 1 : 1.33 curve fitted by the kinetic model of this article.

$$K_1 = k_1/k_3 \quad (20a)$$

$$K_2 = k_2/k_3 \quad (20b)$$

This clearly means that the initial fall in  $F$  is largely affected by the choice of  $k_1$  and  $k_2$  while for large times asymptotic level of  $F$  is controlled by  $K_1$  and  $K_2$ . With this background, we simulated eqs. (8)–(16) for model I on a computer. We first kept  $k_2 = k_3 = 0$  and determined  $k_1$ , which would give the same initial fall as observed experimentally, and determined  $k_2$  and  $k_3$  from the asymptotic levels of free formaldehyde in the reaction mass. The final simulation for  $U : F$  ratio as 1 : 1.33 and 1 : 2.2 are shown in Figures 2 and 3, and on the same plots the experimental results of Price et al.<sup>31</sup> have been shown. It is found that for the  $U : F$  ratio of 1 : 2.20 and a temperature of 100°C, the initial rate of fall and the equilibrium value are lower than that for 160°C. This is found to have the opposite trend from that seen in the rest of the data. Even for these, it is possible to find the set of rate constants to fit the data in the entire range. It is thus seen that the kinetic model proposed in this work describes the experimental data very well.

We have already observed that de Jong et al.<sup>12</sup> and Price et al.<sup>31</sup> assumed that the reversed reaction was unimolecular. Assuming the breakage of bonds to occur this way, we modified the mechanism in eqs. (6) and (7) and the mole balance relations in eqs. (8)–(16). These were similarly simulated on computer, and it was possible to determine the rate constants similarly. We have summarized rate constants in Table I for comparison, while we have shown results

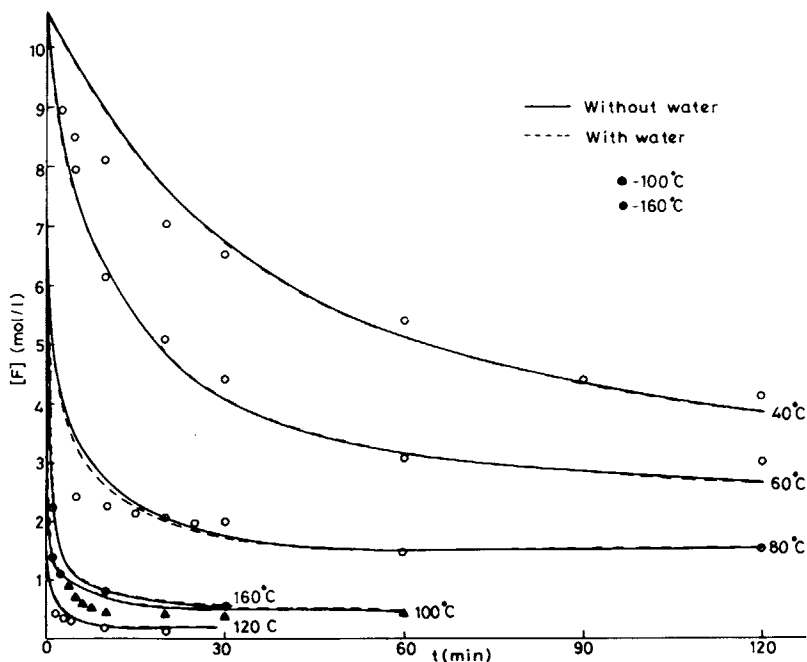


Fig. 3. Experimental data of Price et al.<sup>31</sup> for  $U/F = 1 : 2.2$  curve fitted by this kinetic model.



TABLE I  
Rate Constants Needed to Fit the Experimental Data of Price et al.<sup>31</sup>

(a) Kinetic Model Assuming the Reverse Step as Unimolecular						
Rate Constant Temperature (°C)	$k_1$ for U/F = 1/1.33	$k_2$ for U/F = 1/2.2	$k_2$ for U/F = 1/1.33	$k_2$ for U/F = 1/2.22	$k_3$ for U/F = 1/1.33	$k_3$ for U/F = 1/2.22
25	$3.5 \times 10^{-6}$	—	$1.75 \times 10^{-7}$	—	$5.0 \times 10^{-7}$	—
40	$8.5 \times 10^{-6}$	$8.5 \times 10^{-6}$	$4.25 \times 10^{-7}$	$4.25 \times 10^{-7}$	$8.3 \times 10^{-7}$	$8.3 \times 10^{-7}$
60	$3.5 \times 10^{-5}$	$3.0 \times 10^{-5}$	$1.75 \times 10^{-6}$	$1.5 \times 10^{-6}$	$1.25 \times 10^{-6}$	$1.25 \times 10^{-6}$
80	$1.0 \times 10^{-4}$	$2.0 \times 10^{-4}$	$8.0 \times 10^{-6}$	$3.0 \times 10^{-6}$	$4.0 \times 10^{-6}$	$8.0 \times 10^{-6}$
100	—	$4.0 \times 10^{-5}$	—	$4.0 \times 10^{-5}$	—	$9.0 \times 10^{-6}$
120	$2.3 \times 10^{-3}$	$4.0 \times 10^{-2}$	$3.0 \times 10^{-5}$	$4.0 \times 10^{-4}$	$8.0 \times 10^{-6}$	$5.0 \times 10^{-7}$
160	$2.9 \times 10^{-3}$	$4.0 \times 10^{-3}$	$4.0 \times 10^{-6}$	$5.5 \times 10^{-6}$	$1.25 \times 10^{-5}$	$1.0 \times 10^{-5}$

(b) Kinetic Model Assuming the Reverse Step Involving Water						
Rate Constant Temperature (°C)	$k_1^a$	$k_1^b$	$k_2^a$	$k_2^b$	$k_3^a$	$k_3^b$
25	$3.5 \times 10^{-6}$	—	$1.75 \times 10^{-7}$	—	$7.0 \times 10^{-6}$	—
40	$8.5 \times 10^{-6}$	$8.5 \times 10^{-6}$	$4.25 \times 10^{-7}$	$4.25 \times 10^{-7}$	$8.0 \times 10^{-8}$	$8.0 \times 10^{-8}$
60	$3.5 \times 10^{-5}$	$3.0 \times 10^{-5}$	$1.75 \times 10^{-6}$	$1.0 \times 10^{-6}$	$9.0 \times 10^{-8}$	$9.0 \times 10^{-8}$
80	$1.0 \times 10^{-4}$	$2.0 \times 10^{-6}$	$3.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	$1.0 \times 10^{-7}$	$2.0 \times 10^{-7}$
100	—	$4.0 \times 10^{-3}$	—	$4.0 \times 10^{-5}$	—	$9.0 \times 10^{-7}$
120	$2.3 \times 10^{-3}$	$4.0 \times 10^{-3}$	$3.0 \times 10^{-5}$	$4.0 \times 10^{-4}$	$2.0 \times 10^{-7}$	$5.0 \times 10^{-8}$
160	$2.6 \times 10^{-3}$	$4.0 \times 10^{-3}$	$4.0 \times 10^{-5}$	$4.0 \times 10^{-5}$	$3.0 \times 10^{-7}$	$3.0 \times 10^{-7}$

<sup>a</sup> Indicates that rate constants are for U/F = 1/1.33.

<sup>b</sup> Indicates that rate constants are for U/F = 1/2.2.

by dotted lines on Figures 2 and 3. It is seen that the two simulations almost overlap for all cases, indicating a relative insensitivity of these models to the concentration of water in the reaction mass. This is found because in formalin there is already a large amount of water present and its concentration changes only by a small amount due to polymerization. We have prepared Arrhenius plots for these in Figure 4, and we find that the choice of inclusion of water in the reverse step has an effect only on  $k_{i0}$  ( $i = 1, 2, 3$ ) while activation energies are affected only negligibly.

Price et al.<sup>31</sup> have presented experimental data for two different U : F ratios. We have curve-fitted experimental data for both these sets, and results have been plotted in Figures 4 and 5. In Figure 4 we assume that water affects the depropagation reaction, while in generating Figure 5, we assume that it does not. In both these figures, the filled legends have been used for U : F as 1 : 2.20. We have already observed that for 100 and 120°C and U : F ratio as 1 : 2.2, the experimental data have different trends from those observed for the rest of the data. Consequently, the rate constants needed to fit these are higher than those for 160°C as the reaction temperature. If these are ignored, it is possible to draw a decent single straight line for  $k_1$ ,  $k_2$ , and  $k_3$  as seen, which is independent of the U/F ratio. These figures give rate constants that are temperature dependent only, in contrast to that found in earlier kinetic models

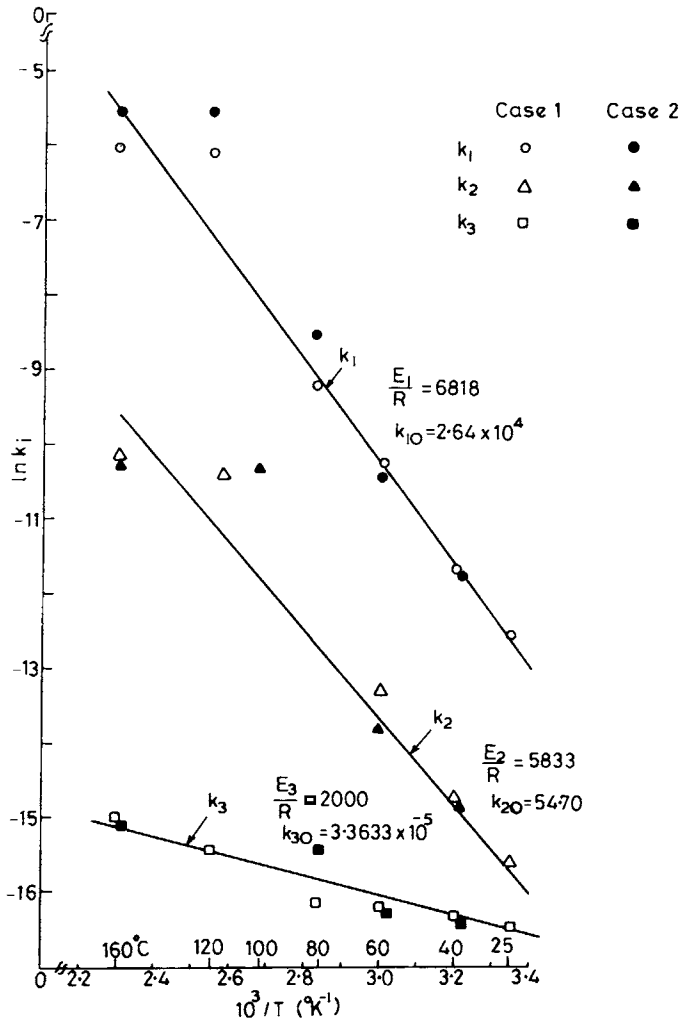


Fig. 4. Arrhenius plots of rate constants  $k_1$  to  $k_3$  assuming water having no effect on the reverse step.

proposed in the literature. Comparison of Figures 4 and 5 shows smaller scatter of data in the latter. It is very difficult to conclude from the limited data of Price et al.<sup>31</sup> as to whether the condensation product, water, participates in the reverse reaction. The activation energy of rate constant  $k_3$  is found to be small compared to the degradation reaction, which suggests that water must be playing some role in the reverse reaction.

With the rate constants so found, we have simulated the urea-formaldehyde polymerization in batch reactors. Figures 6 and 7 give some results; the former gives the unreacted urea in the reaction mass as a function of time at different temperatures. The unreacted urea decreases rapidly in the initial region, ultimately leveling at the equilibrium value. With increasing reaction temperature, it is found that the rate of fall in the initial region increases while the equilibrium

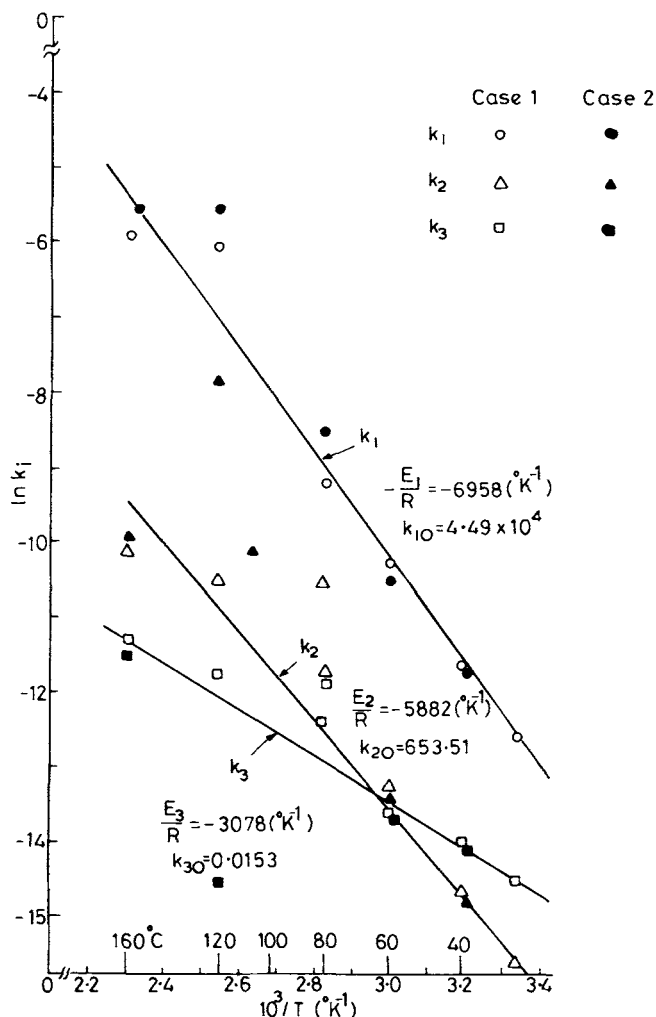


Fig. 5. Arrhenius plots of rate constants  $k_1$  to  $k_3$  assuming bimolecular reaction between water and reacted bonds.

value falls. In Figure 7, we have plotted the concentration of species A as a function of time with temperature. The behavior observed is similar to those of intermediate species in a set of consecutive reactions. At a given temperature, the concentration of species A first rises, and after passing through a maximum, it falls to the equilibrium value. As the temperature is increased, the peak height falls, and its position shifts to smaller times as seen.

Earlier studies of de Jong and de Jong<sup>12</sup> were carried out at low temperatures, and the kinetic model proposed by them completely neglected the formation of higher oligomers. Assuming monosubstitution of formaldehyde on urea, they evaluated the rate constants. Price et al.<sup>31</sup> have performed their experiments at much higher temperatures when the formation of higher oligomers cannot be ignored. In fact in their kinetic model, they have relaxed the earlier as-

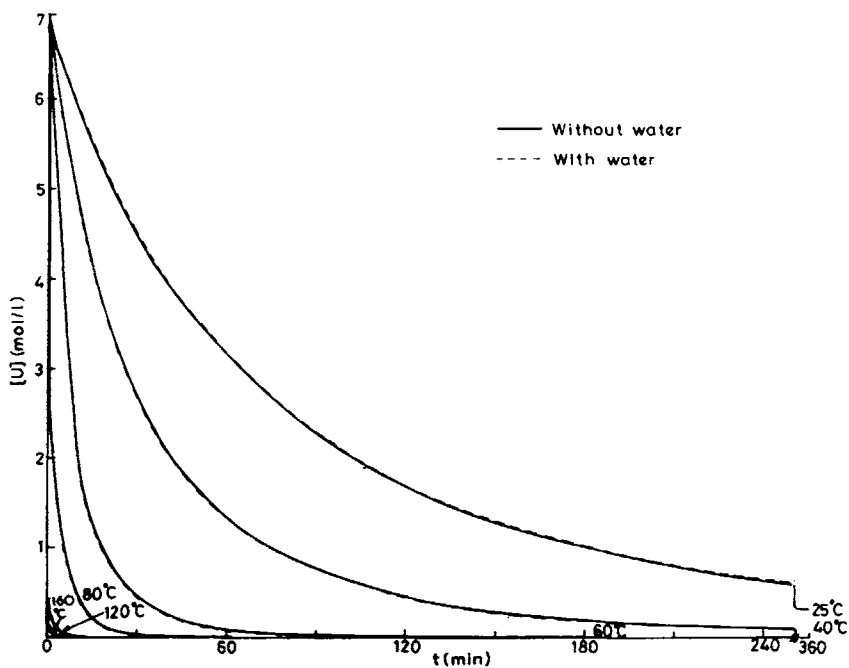


Fig. 6. Concentration of unreacted urea versus reaction time.

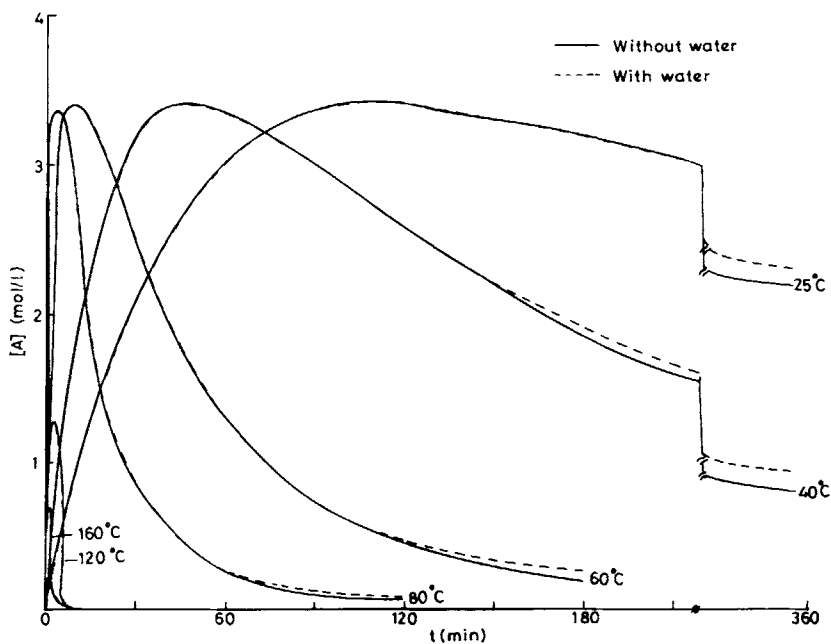


Fig. 7. Concentration of species A versus reaction time.

sumption of monosubstitution and included reactions given in eq. (2). They observe the insufficiency of their kinetic model in fitting the experimental data at high temperatures. The kinetic model proposed in this work involves fewer rate constants (only three as opposed to six) and accounts for the formation of higher oligomers. Polymerization of urea-formaldehyde has been reviewed by Meyer,<sup>1</sup> and he observed that it was possible to divide the polymer formation into two stages for low temperatures only. In the first stage, according to Meyer, addition is the predominant reaction, even though small amount of condensation reaction also occurs. As opposed to this, in the second stage most of the chain growth occurs through the condensation mechanism. Industrially, the polymer formed in the first stage is available as a syrup. Katuscak et al.<sup>29</sup> have subjected this to GPC studies and shown that it has a polydispersity index more than unity, thus indicating the formation of higher oligomers. The kinetic model proposed in this work serves as a basis for determining the MWD of the polymer formed using the kinetic approach.

### CONCLUSIONS

A kinetic model for reversible urea-formaldehyde polymerization based upon functional group analysis has been proposed. This accounts for the formation of higher oligomer and is found to be extremely suitable for the correlation of experimental data at high temperatures. The model proposed in this work involves only three rate constants, as opposed to other models reported in literature that use at least six rate constants.

The kinetic model proposed in this work has been computer simulated and experimental data of Price et al.<sup>31</sup> have been curve fitted using rate constants as the parameters. It is found that the model fits in the entire range and the rate constants, so determined, can be represented by a suitable Arrhenius relation. In the earlier kinetic models of de Jong<sup>12</sup> and Price et al.,<sup>31</sup> the reverse reaction was shown to be a unimolecular reaction. It was argued in this article that this way of representation is similar to chain degradation and therefore should have high activation energy. We have also examined a kinetic model in which the reverse step was assumed to be a bimolecular reaction involving the condensation product. On comparison of experimental data of Price et al.<sup>31</sup> with computed results, one finds that it is not possible to distinguish them from each other. This is due to the fact that polymerization has been carried out with formalin, which already has large amount of water. However, it was felt that the activation energy of rate constant  $k_3$  is small, and hence water must have some role to play, and a second-order kinetic for the reverse step is a better representation.

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