

Polymerization of Melamine and Formaldehyde in Homogeneous Continuous-Flow Stirred-Tank Reactors Using Functional Group Approach: Part B: Molecular Weight Distribution

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Synopsis

Polymerization of melamine and formaldehyde in homogeneous continuous-flow stirred-tank reactors (HCSTRs) is reversible and leads to formation of branched polymer due to the hexafunctional nature of melamine. The reversed reaction of branched molecules depends upon the chain structure, and herein a simple model is presented to account for this. The functional group analysis of part A of this series has been extended and the molecular weight distribution (MWD) relations for HCSTRs have been solved. The MWD of the polymer is extremely sharp and the molecules are more branched compared to those for batch reactors and can be explained as follows. A given reacted bond can react with water as well as free formaldehyde through the reversed reaction, and the rate constant for the latter step is much larger. Consequently, the chain growth is limited as long as there is free formaldehyde in the reaction mass. Lower conversion of melamine and formaldehyde in HCSTRs is used to explain the behavior observed.

INTRODUCTION

Industrially, the polymerization of melamine and formaldehyde is carried out in two stages. In the first one, the molding powder is formed in which the methylation of melamine is the predominant reaction. In the second stage the molding powder is polymerized in molds to form a polymer network. As a result there is a considerable change in the molecular weight of the polymer.

In part A of this series,¹ a kinetic model based on the functional group approach was proposed that was found to be valid for both stages of the polymer formation. Depending upon the position of the reactive hydrogen, ten reactive species A to J were defined¹ and the polymer formation was written in terms of the reaction of these species. As the capacity of a chemical plant manufacturing the polymer increases, continuous reactors are preferred over batch ones. Among the various existing continuous reactors, homogeneous continuous-flow stirred-tank reactors (HCSTRs) are preferred. In part A, the performance of HCSTRs was computed and results were compared with those for batch reactors.

In HCSTRs, the methylation of melamine continues to be the predominant reaction.¹ However, a substantial amount of higher oligomers are formed and there is a molecular weight distribution of the polymer. Melamine is a hexafunctional monomer and formaldehyde is bifunctional in nature. The latter on reaction first forms a CH_2OH group, which on further reaction leads to the formation of a reacted bond Z. Evidently the polymer formed would in

general be branched. It is of considerable importance to determine the MWD of the polymer, but before this can be done, the reverse reactions of branched molecules must first be written.

In this study, we show that the reverse reaction of branched molecules is dependent upon the chain structure. It is recognized that the functional group species E to J may lead to branching, and based upon this, the average branching is computed. A computer program has been devised that gives the contribution of the reverse reactions of branched molecules. With this knowledge, the mole balance relations for various oligomers formed in HCSTRs have been written after assuming that the reactor is operating at the steady state.

The relations governing the MWD of the melamine-formaldehyde polymer constitute a set of highly nonlinear algebraic equations that must be solved simultaneously. The Brown's method outlined in part A is used to determine the polymer MWD. Various reactor parameters have been systematically varied to determine the region of operation of the HCSTRs that maximizes the formation of polymer.

REVERSE REACTION OF BRANCH MOLECULES^{2,3}

Chemical reaction between reacting polymer molecules Q_m and Q_n can occur only when they undergo collision. The rate of reaction, R , can thus be written in terms of the product of the collision frequency, $\omega_{m,n}$ between Q_m and Q_n and the probability of their reaction $Z_{m,n}$

$$R = \alpha \omega_{m,n} Z_{m,n} \quad (1)$$

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

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

In Figure 1(a), a linear chain with 10 repeat units Q_{10} is shown. If one is interested in the total number of ways a Q_{10} can react with W , δ is the total number of bonds, which means that $\delta = 9$. However, if one is interested in writing the rate of production of Q_5 , the number of sites on Q_{10} must be known, which on reaction with W would give the formation of Q_5 . In general, $\delta_{n \rightarrow m}$ is defined which denotes the number of sites on Q_n which on reaction with W gives the formation of Q_m (where $m < n$). For a linear chain, as can be seen, no matter what the values of n and m are, it is equal to 2, that is

$$\delta_{n \rightarrow m, \text{linear}} = 2; \quad n > m; n, m = 2, 3, \dots \quad (2)$$

For branched molecules, however, the situation is more complex.

In Figure 1(b), a branched Q_{10} is shown with the branching exactly at the middle position. If one wishes to determine the rate of formation of Q_1 , Q_2 , or Q_3 , there are three positions on Q_{10} . However, Q_{10} cannot form Q_4 , Q_5 , and Q_6 at all by the reverse reaction. For the formation of Q_7 , Q_8 , and Q_9 , once

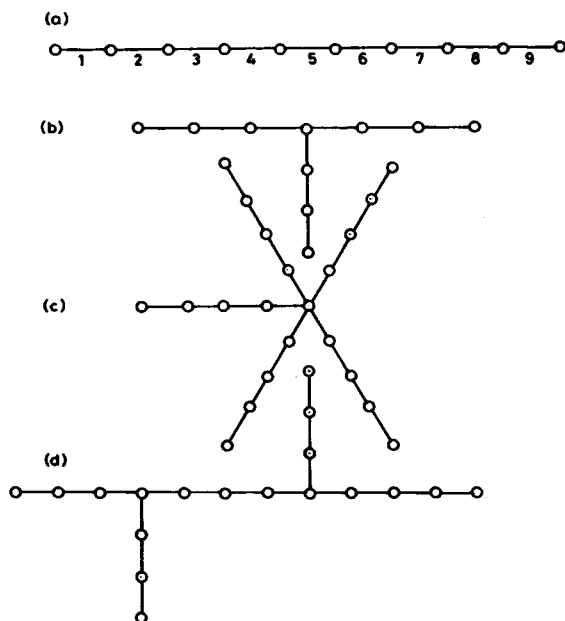


Fig. 1. Possible chain structures of polymer molecules (a) linear Q_{10} , (b) branched Q_{10} , (c) star molecules, (d) chains with branches; spacing equal to branch length.

again there are three sites on Q_{10} . In other words

$$\delta_{10 \rightarrow i} = 3 \quad \text{for } i = 1, 2, 3, 7, 8, 9 \quad (3a)$$

$$= 0 \quad \text{for } i = 4, 5, 6 \quad (3b)$$

It is thus seen that for branched molecules, the reverse reaction is dependent on chain structure. It is possible to derive analytical expressions for $\delta_{n \rightarrow m}$, provided polymer chains have a symmetrical structure. For example, for a star chain shown in Figure 1(c) having b branches with r repeat units per branch

$$\delta_{br \rightarrow (br-i)} = \delta_{br \rightarrow i} = b \quad \text{for } i \leq r \quad (4a)$$

$$\text{otherwise it is equal to } 0 \quad (4b)$$

In Figure 1(d) a polymer chain is shown in which branch spacing is equal to the length of the branch. If b is the number of branches having x repeat units per branch, then its chain length n is given by

$$\begin{aligned} n &= bx + (b - 1)x + 2x + 1 \\ &= (2b + 1)x + 1 \end{aligned} \quad (5)$$

$$\delta_{n \rightarrow i} = \delta_{n \rightarrow (n-i)} = b + 2 \quad \text{if } i \leq x \quad (6a)$$

$$\delta_{n \rightarrow i} = 0 \quad \text{if } mx + 1 \leq i \leq (m + 1)x \quad (6b)$$

$$\delta_{n \rightarrow i} = 2 \quad \text{if } 1 + (m + 1)x \leq i \leq (m + 2)x \quad (6c)$$

For any general branched polymer chain, it is not possible to write an analytical expression for $\delta_{n \rightarrow i}$. However, for a specified chain structure, it is

possible to determine $\delta_{n \rightarrow i}$ either by counting positions manually or by computer. A computer program (whose listing can be had on request) has been prepared which does precisely this if the chain structure is specified. The program scans the branches first if they have any site that gives the formation of Q_i . After finishing this task, it then scans the polymer backbone.

With the computer, the program $\delta_{n \rightarrow i}$ for various values of n, i , and the chain structure has been determined. Even though it can take on any value, $\sum_{i=i}^{n-1} \delta_{n \rightarrow i}$, $\sum_{i=i}^{n-1} i \delta_{n \rightarrow i}$ always obey the following relations

$$\sum_{i=i}^{n-1} \delta_{n \rightarrow i} = 2(n-1) \quad (7a)$$

$$\sum_{i=i}^{n-1} i \delta_{n \rightarrow i} = n(n-1) \quad (7b)$$

In eq. (7a), it is evident that the sum of $\delta_{n \rightarrow i}$ for all values of i must be equal to twice the total number of sites where the reaction can occur. Eq. (7) is useful in determining the moment relations starting from the mole balance relation governing the MWD in HCSTRs.

MODEL FOR THE RATE OF PRODUCTION OF OLIGOMERS^{2,3}

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

The rate of production of species Q_n, R_{Q_n} , can be easily written if it is observed that

1. Q_n is depleted through forward reaction if any of its sites or its bound CH_2OH reacts with any other bound CH_2OH groups.
2. Q_n is formed through forward reaction when sites of A_1 reacts with a bound CH_2OH of Q_{n-1} and is depleted when CH_2OH of Q_n reacts with sites of A_1 .
3. Q_n is formed through forward reaction when either sites or CH_2OH of Q_j ($j \leq n$) reacts with CH_2OH or sites of Q_{n-j} .
4. Q_n is formed through reverse reaction whenever the appropriate site of Q_i ($i > n$) reacts with water on formaldehyde.

With these observations, R_{Q_n} is given by

$$\begin{aligned} R_{Q_n} = & 6k_1[A_1]\{\text{CH}_{Q_{n-1}} - \text{CH}_{Q_n}\} - [\text{CH}_2\text{OH}]R_{Q_n} \\ & - \text{CH}_{Q_n} \sum_{j=1}^{\infty} (R_{Q_j} + k_4 \text{CH}_{Q_j}) \\ & + \sum_{j=1}^{n-1} \left\{ R_{Q_j} \text{CH}_{Q_{n-j}} + \text{CH}_{Q_j} \left(R_{Q_{n-j}} + \frac{1}{2} k_4 \text{CH}_{Q_{n-j}} \right) \right\} \\ & + \{k_5[\text{H}_2\text{O}] + 2k'_4[F_1]\} \sum_{j=n+1}^{\infty} \frac{\delta_{j \rightarrow n} S_{Q_j}}{(j-1)} \\ & - \{k_5[\text{H}_2\text{O}] + 2k'_4[F_1]\} S_{Q_n}; \quad n \geq 2 \end{aligned} \quad (8)$$

where

$$R_{Q_n} = (4k_1 + k_2)B_{Q_n} + (2k_1 + 2k_2)C_{Q_n} + 4k_1D_{Q_n} + (2k_1k_2)E_{Q_n} + 3k_2F_{Q_n} \\ + 2k_1G_{Q_n} + k_2I_{Q_n} \quad (9a)$$

$$S_{Q_n} = B_{Q_n} + 2C_{Q_n} + 2D_{Q_n} + 3E_{Q_n} + 3F_{Q_n} + 4G_{Q_n} + 4H_{Q_n} \\ + 5I_{Q_n} + 6J_{Q_n} \quad (9b)$$

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

The rate of production of A_1 and Q_1 can be written similarly. The main difference arises only in that step 3 does not occur for these molecules. In addition, A_1 is formed in the reverse reaction only when B_Q reacts. The mole balance relations for these species are

$$R_{A_1} = 12k_1[A_1][F_1] - 6k_1[A_1]CH_2OH + k_5[H_2O]B_{Q_1} \\ + 2k_4'[F_1]B_{Q_1} + \sum_{i=2}^{\infty} \delta_{i-1}B_{Q_i}/(i-1) \quad (10)$$

$$R_{Q_1} = -R_{Q_1}[CH_2OH] - CH_{Q_1} \sum_{j=1}^{\infty} (R_{Q_j} + k_4CH_{Q_j}) \\ + 6k_1[A_1](2[F_1] - CH_{Q_1}) + (k_5[H_2O] + 2k_4'[F_1]) \sum_{j=2}^{\infty} \frac{\delta_{j-1}S_{Q_j}}{(j-1)} \\ - (k_5[H_2O] + 2k_4'[F_1])B_{Q_1} \quad (11)$$

MODELLING OF HCSTRS

It is assumed that the reactor is well mixed, which means that the exit concentrations of A_1, Q_1, Q_2 , etc. are the same as those within the reactor. If V is the volume of the reactor and \dot{Q} is the flow rate of the feed, it is possible to mole balance various species on the HCSTRs operating at steady state. Only doing this, one obtains

$$\frac{A_1 - A_0}{\theta} = R_{A_1} \quad (12a)$$

$$\frac{Q_i}{\theta} = R_{Q_i} \quad i = 1, 2, \dots \quad (12b)$$

where

$$\theta = k_1[F_1]_0 V/Q \quad (13a)$$

$$A_1 = \frac{[A_1]}{[F_1]_0} \quad (13b)$$

$$Q_i = \frac{[Q_i]}{[F_1]_0} \quad i = 1, 2, 3, \dots \quad (13c)$$

$$r_1 = \frac{k_2}{k_1} \quad (13d)$$

$$r_2 = \frac{k_4}{k_1} \quad (13e)$$

$$r_3 = \frac{k'_4}{k_1} \quad (13f)$$

$$r_4 = \frac{k_5}{k_1} \quad (13g)$$

The performance of HCSTRs can be solved only when an estimated B_{Q_n} , C_{Q_n} , etc., are available. It is recognized that the total number of sites on Q_n oligomer is given by $n[Q_n]$. If sites B , C , D , etc. are distributed randomly, on an average, it is expected that

$$B_{Q_n} = \frac{[B]}{\sum_{i=1}^{\infty} i[Q_i]} n[Q_n] \quad (14a)$$

$$C_{Q_n} = \frac{[C]}{\sum_{i=1}^{\infty} i[Q_i]} n[Q_n] \quad (14b)$$

etc.

To get $\delta_{i \rightarrow j}$ for $j = 1$ to $(i - 1)$, it is necessary to specify an approximate chain structure. For this, the examination of the structure of the reactive species reveals that species E to J can lead to branching. With the knowledge of the concentrations of the A to J active species it is possible to calculate the branching coefficient, α_1 which is defined as

$$\alpha_1 = \frac{[E] + [F] + [G] + [H] + [I] + [J]}{\sum_{i=1}^{\infty} [Q_i]} \quad (15)$$

In the most general case, the reaction mass would consist of some molecules

with no branch, some with one branch, some with two branches, etc. The branching coefficient α_1 would give a measure of the average number of branches on the polymer molecules and can have a value greater than 1 for melamine formaldehyde polymer.

Intuitively it is expected that the larger the chain length of the polymer molecule, the larger would be the number of branches on it. In the polymerization of melamine, the average chain length of the formed polymer is small and in view of this we approximate the distribution of branches as bimodal. For example, if eq. 15 gives $\alpha_1 = 2.6$, then it is assumed that some molecules (mole fraction x) have two branches per molecule and the rest have three branches, such that

$$2.6 = 2x + 3(1 - x) \quad (16)$$

From this x can be calculated. In most of the computations, it is found that α_1 lies between 0 and 1, which means that on average the reaction mass consists of linear chains and chains with one branch. Lastly, after deciding the number of branches on the polymer chain, the branches are arranged in such a way that it has a structure close to that shown in Figure 1(d). If the number of repeat units does not divide itself into equal branch lengths, the length of branches are increased by one unit at a time until the desired length is obtained. The polymer molecule is then scanned to determine $\delta_{i \rightarrow j}$ for all values of j .

It may be further observed that the mole balance relations given by Eq. (12) for melamine (species A and A_1) in Part A of this publication series¹ are different. This arises because of the assumptions made in establishing the MWD equations in this work. The consistency of Eq. (12) can be checked by determining $\sum_{i=1}^{\infty} i[Q_i] + [A_1]$, which should be time invariant. This can be found to be so if Eq. (12b) is multiplied with n and added for all values of n , and to this equation, Eq. (12a) is added. On doing this, the net formation of $\sum i[Q_i] + [A_1]$ is found to be zero and thus the MWD relations are consistent. The weight fraction distribution W_n of the melamine formaldehyde polymer can be determined using

$$W_1 = \frac{A_1 + Q_1}{A_1 + \sum_{n=1}^{\infty} nQ_n} \quad (15a)$$

$$W_n = \frac{nQ_n}{A_1 + \sum_{n=1}^{\infty} nQ_n} \quad n = 2, 3, \dots \quad (15b)$$

METHOD OF COMPUTATION

In the Brown's algorithm of composition described in Part A, it was pointed out that one should solve only linearly independent variables.¹ It is recognized that by polymerization the total number of repeat units does not change which implies that if it is A_0 in the feed, it should remain unaltered in the

product stream. In other words,

$$A_1 + \sum_{n=1}^{\infty} nQ_n = A_0 \quad (16)$$

In view of this relations, Q_1 , Q_2 , etc. are solved using Brown's algorithm whereas A_1 is determined using Eq. (16).

In view of Eq. (14), the concentrations of species A to J must be known, which implies that MWD relations given in Eq. (12) should be added to the algebraic equations described in Part A. The problem of the initial guess of the MWD is overcome exactly as described in part A. If θ is the residence time of the HCSTR, it is divided into small increments $\Delta\theta$. The MWD is computed for $\Delta\theta$ assuming $Q_n = 0$ for $n = 1$ to ∞ and the value of $\Delta\theta$ is adjusted such that the convergence is attained. This serves as the initial guess for the computation of the MWD for $2\Delta\theta$ and in this way, the computations are stepped up to find results for the HCSTR of residence time θ . Lastly, a certain number of equations, N_{\max} , is solved on computer to determine the MWD. The value of N_{\max} is decided by the concentration of the last species $Q_{N_{\max}}$. In the computation carried out in this work, initially N_{\max} was kept at low value of 5 and it was increased by 5 whenever $Q_{N_{\max}}$ increased above a lower limit of 10^{-4} .

RESULTS AND DISCUSSION

In part A of this series, a kinetic model for the polymerization of melamine and formaldehyde was proposed using a functional group approach. In this, reactive species A to J were defined which specified the position of the reacting hydrogen group on the melamine group. This model was used to curve fit the experimental data of Tomita and was found to fit in the entire range. The kinetic model that has been proposed in this work requires only five rate constants as opposed to 24 in the Tomita's model. After evaluating the rate constants, homogeneous continuous-flow stirred reactors were modelled and in part A of this work, the concentration of reactive species in the product stream were determined. It was shown that as long as free formaldehyde was present in the reaction mass, methylation of melamine was the predominant reaction. However as the formaldehyde is depleted, higher oligomers are formed which is seen from the rapid fall in bound CH_2OH concentration in the reaction mass. In this paper, the analysis of part A has been extended to determine the molecular weight distribution of the melamine formaldehyde polymer.

The MWD of the melamine formaldehyde polymer formed in an HCSTR operating at the steady state has been derived in Eq. (12). These nonlinear algebraic equations have been solved and it was found that the MWD of the polymer is extremely sharp. In normal operating conditions, the concentrations of tetramers and higher oligomers are negligibly small. In Figures 2 to 9, the effect of various reaction parameters on the MWD of the polymer formed in HCSTRs have been examined.

In Figure 2 the weight fractions, w_1 and w_2 , of mono- and dinuclear species, $(A_1 + Q_1)$ and Q_2 , have been examined. At the reactor residence time $\theta = 0$,

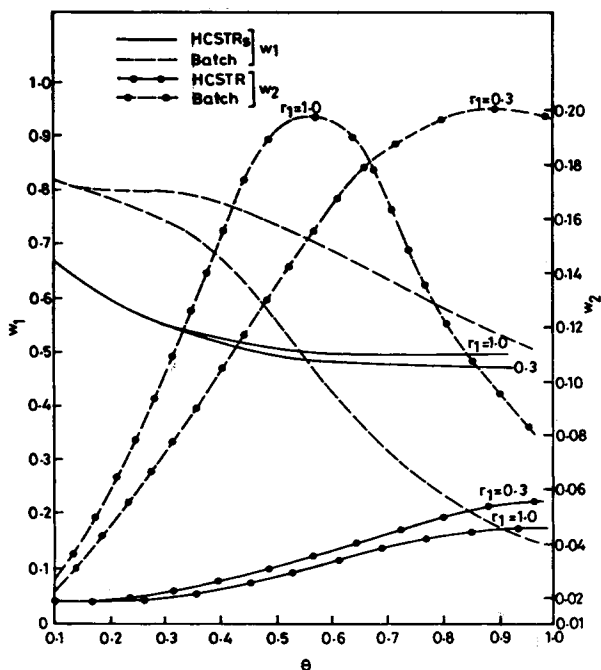


Fig. 2. Effect of r_1 on weight fractions w_1 and w_2 of $(A_1 + Q_1)$ and Q_2 . Results for batch reactors have been shown by dotted lines. $r_2 = 0.089$, $r_3 = 66.7$, $r_4 = 1.11$, $(A_{10}/F_{10}) = 2.0$.

w_1 and w_2 are 1 and 0, respectively, and in this figure results have been shown from $\theta = 0.1$ onward. For HCSTRs, the unequal reactivity of primary and secondary amide hydrogens (measured by ratio r_1) appears to have relatively small effect on w_1 . On the same figure, results for batch reactors have also been shown by dotted lines. As this ratio changes from 0.3 to 1.0, the effective functionality of melamine also increased to the final value of 6. For batch reactors, this seems to have considerable effect while for HCSTRs, the reaction mass consists of predominantly mononuclear species (i.e., A_1 and Q_1) with its substituents as CH_2OH group. On the same figure, w_2 has also been plotted. For batch reactors, Q_2 is formed in considerably larger concentrations. As the reactor residence time is increased, w_2 for batch reactors undergoes a maximum and as r_1 is increased to 1, the maximum shifts to a lower residence time. For HCSTRs, w_2 is considerably smaller in magnitude and for the range of θ studies, it does not have a maximum as was found for batch reactors. In Figure 3 the average chain length, μ_n , of the polymer has been determined from the MWD and it is seen that the polymer is essentially mononuclear species (i.e., A_1 and Q_1), whereas compared to this, the average chain length of the polymer formed in batch reactors is considerably larger. This is because the conversion of melamine in batch reactor is considerably larger and consequently higher oligomers are formed in larger concentrations. As opposed to this, in HCSTRs, the conversion is small and the substitution of melamine occurs preferentially.

In Figures 4 and 5, the effect of variation of the reactivity ratio r_2 has been examined. In Figure 4, w_1 and w_2 have been plotted. As k_4 is increased, the

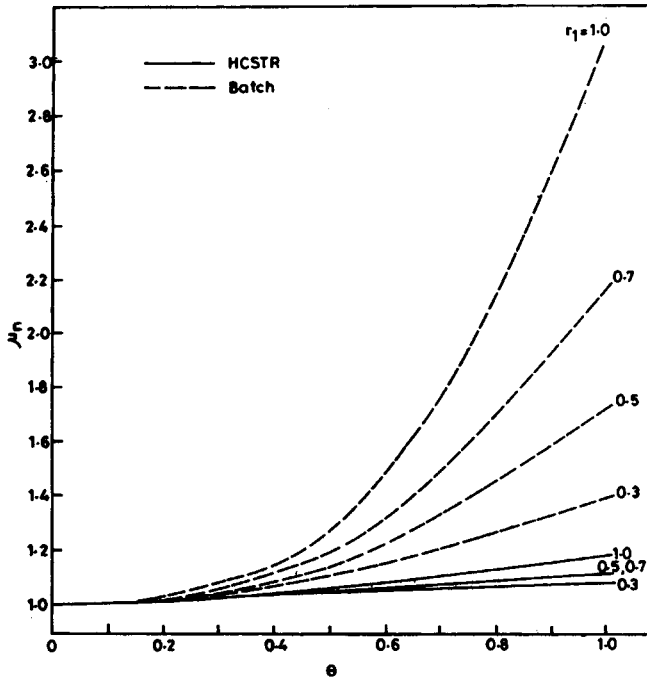


Fig. 3. Effect of r_1 on μ_n and ρ of the polymer formed in HCSTRs. $r_2 = 0.089$, $r_3 = 66.7$, $r_4 = 1.11$ (A_{10}/F_{10}) = 2.0.

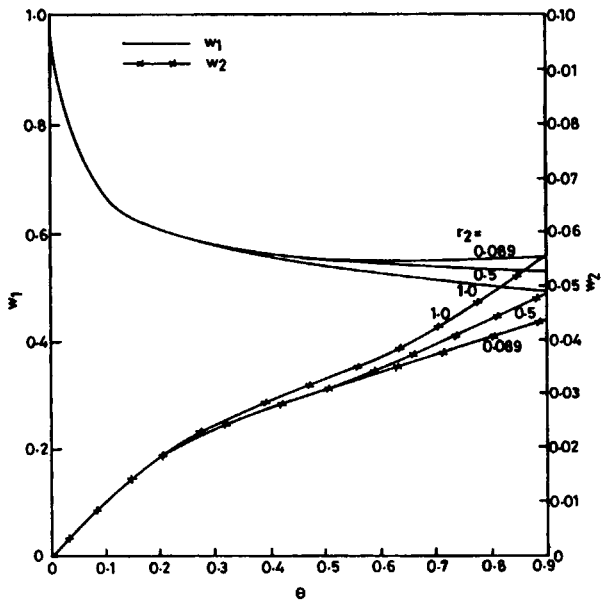


Fig. 4. Effect of r_2 on w_1 and w_2 versus reactor residence time, $r_1 = 0.3$, $r_3 = 66.67$, $r_4 = 1.11$ (A_{10}/F_{10}) = 2.0.

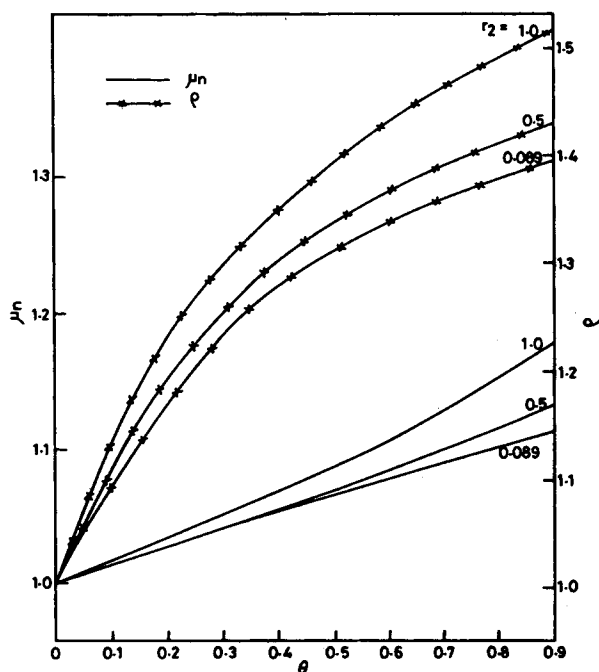


Fig. 5. Effect of r_2 on μ_n and ρ of the polymer. $r_1 = 0.3$, $r_3 = 66.67$, $r_4 = 1.11$, $(A_{10}/F_{10}) = 2.0$.

kinetic mechanism suggests that the reaction between two CH_2OH groups increases. As pointed out in part A, this would lead to formation of higher oligomers, which is precisely found herein. In Figure 5, the number-average chain length μ_n and the polydispersity index ρ of the polymer have been plotted. With the increase in k_4 (or r_2), Q_3 and Q_4 are formed in larger concentrations which is reflected in high μ_n and ρ . In these figures, results obtained from batch reactors have not been shown for comparison. This is because the polymer formed in batch reactors has much higher molecular weight and falls out of the range shown in the graph.

In Figures 6 and 7, the effect of k_5 on the MWD of the polymer formed in HCSTRs is examined. The change in k_5 is obtained by systematically varying r_4 and the asymptotic value of w_1 increases as r_4 is increased. This implies that a larger fraction of the reaction mass is substituted melamine. As r_4 reaches a value of 10, w_2 falls very rapidly and reaches an asymptotic value. In Figures 8 and 9, the effect of melamine formaldehyde ratio (A_1/F), an extremely important variable, on the MWD is examined. When $([A_1]/[F_1]_0)$ is small, there is a lot of unreacted formaldehyde in the reaction mass. It has already been observed that a given reacted bond Z can react with water (with rate constant k_5) as well as with free formaldehyde (with rate constant k'_4). The curve-fitting of the experimental data of Tomita has revealed that k'_4 is very large. This would mean that higher oligomers would tend to depolymerize and this is precisely observed in Figure 7 for w_2 . For $A_{10}/F_{10} = 0.25$, free formaldehyde is in large excess and Q_2 begins to depolymerize for large residence time, θ . This is not found to occur for larger (A_{10}/F_{10}) ratios for which the weight fraction of Q_2 keeps rising for the range of residence time

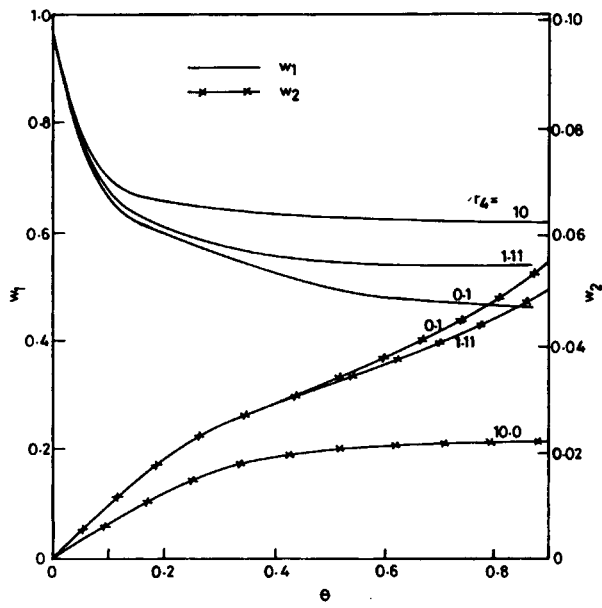


Fig. 6. Effect of r_4 on w_1 and w_2 . $r_1 = 0.3$, $r_2 = 0.089$, $r_3 = 66.67$ ($A_{10}/F_{10}) = 2.0$.

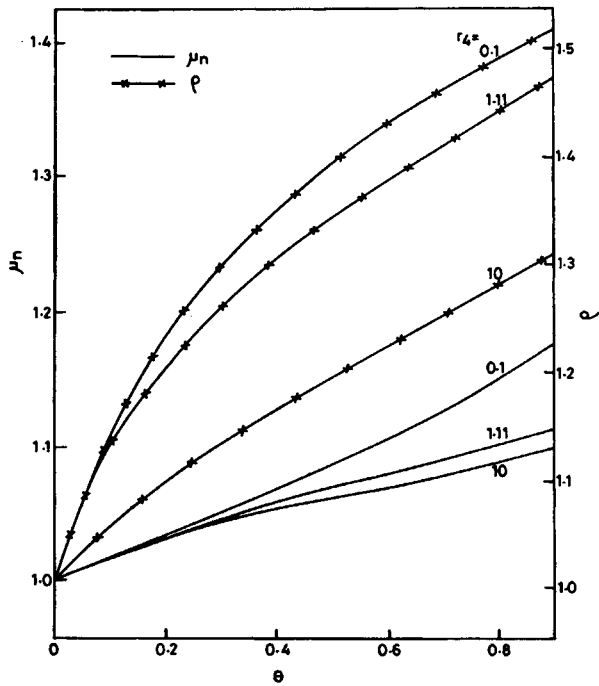


Fig. 7. Effect of r_4 on μ_n and ρ of the polymer $r_1 = 0.3$, $r_2 = 0.089$, $r_3 = 66.67$ ($A_{10}/F_{10}) = 2.0$.

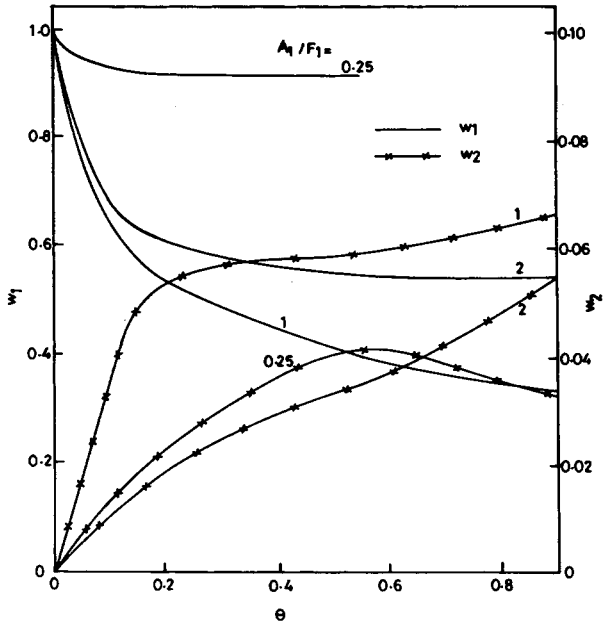


Fig. 8. Effect of melamine to formaldehyde ratio (A_{10}/F_{10}) of feed on w_1 and w_2 . $r_1 = 0.3$, $r_2 = 0.089$, $r_3 = 66.67$, $r_4 = 1.11$.

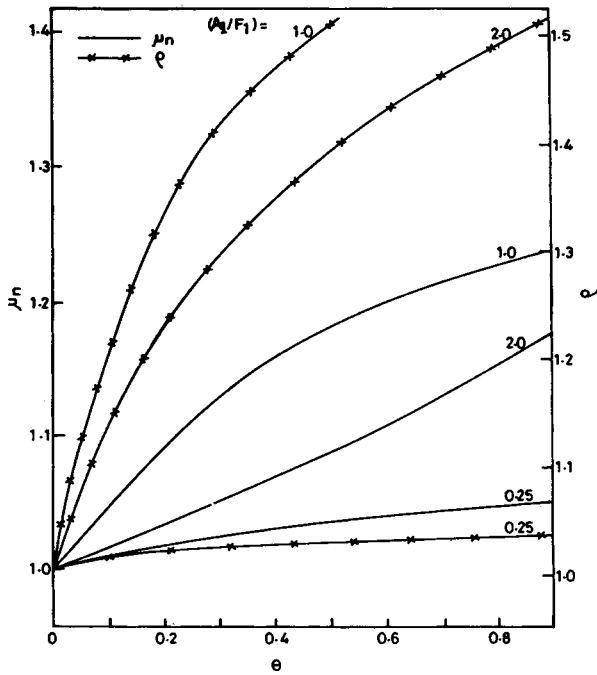


Fig. 9. Effect of (A_{10}/F_{10}) on μ_n and ρ of the polymer $r_1 = 0.3$, $r_2 = 0.089$, $r_3 = 66.67$, $r_4 = 1.11$.

studied. In Figure 9, μ_n and ρ are plotted for various (A_1/F_1) ratios. For $(A_1/F_1) < 1$, there is an unreacted formaldehyde due to which there is preponderance of substituted melamine. As a result, the polydispersity index ρ of the polymer is close to unity. For $(A_{10}/F_{10}) > 1$, there is unreacted melamine due to which the ρ of the polymer is small. However, for (A_{10}/F_{10}) equal to 1, μ_n reaches a large value.

CONCLUSIONS

Melamine is hexafunctional and on polymerization with formaldehyde, branched molecules are formed. In this paper, the reversed reactions of branched molecules have been modelled and applied to the polymerization of melamine and formaldehyde. With the kinetic model proposed in part A, a simple technique has been proposed to determine the molecular weight distribution of melamine formaldehyde polymer formed in HCSTRs. The model involves five rate constants and these have been determined by curve-fitting the experimental data of Tomita. The MWD of the polymer in HCSTRs have been computed and compared with those from batch reactors. The conversion of melamine for the former is considerably lower for the same residence time of the reactor. In addition, the MWD of the polymer formed in HCSTRs is considerably sharper compared to that from the latter.

Various reaction parameters of polymerization in HCSTRs have been identified and a sensitivity analysis has been carried out to determine the region which would yield polymer of high molecular weight. It is shown that a given reacted bond Z can interact with water as well as free formaldehyde F_1 through the reverse reaction. The rate constant for the latter is considerably larger which means that the substituted melamine will be the predominant component of the reaction mass as long as there is free formaldehyde in it. Chain growth of the polymer is found to occur only when most of F_1 is depleted. One of the most important reaction parameter in HCSTRs is the melamine to formaldehyde ratio ($= A_1/F_1$) in the feed and for low ratios, the polydispersity index is close to one indicating negligible formation of higher oligomers.

NOMENCLATURE

A to J:	Functional group species
A_1 :	Melamine molecule (same as species A)
R_{Q_n} :	Rate of formation of Q_n molecule
B_{Q_n}, C_{Q_n} ,	Number of B, C, etc. functional groups on Q_n molecules.
	etc.
R_{Q_n}, S_{Q_n} :	Terms defined in eq. 9.
F_1 :	Free formaldehyde
θ :	dimensionless residence time of HCSTR defined in eq. 13.
r_1 to r_4	dimensionless reactivity ratios defined in eq. 13.
Q_n :	Polymer molecule of chain length n .
$Z_{m,n}$:	Probability of reaction between Q_m and Q_n molecules
V:	Reactor volume
\dot{Q} :	Feed flow rate into the reactor

W_n :	Weight fraction of Q_n in the reaction mass defined in eq. 15.
$[A]_0, [F_1]_0$:	Concentration of melamine and formaldehyde in the feed
$\omega_{m, n}$:	Collision frequency between Q_m and Q_n molecules
α_1 :	Branching coefficient defined in eq. 15
$\delta_{n \rightarrow i}$:	Number of sites on Q_n that would give $Q_i (i < n)$ on the reverse reaction.
μ_n :	Average chain length of the polymer.
ρ :	Polydispersity index of the polymer.

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