

Molecular weight distributions in novolac-type phenol-formaldehyde polymerization

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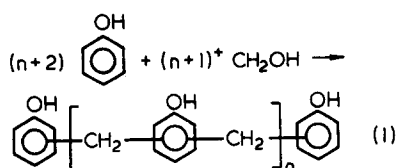
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To model the reversible novolac polymerization, five reactive species A to E have been defined. Molecules having bound CH_2OH (Q_n) are distinguished from those without it (P_n) and it is assumed that molecules of Q_n do not have more than one bound CH_2OH group. A kinetic model has been written and, based upon it, balance equations for molecules of novolac polymer in batch reactors have been derived. Based upon our earlier studies, the phenomenon of molecular shielding has been neglected. As a result, the reactivities of the *ortho* and *para* positions of phenol which are available in the literature could be used. The kinetic model for the molecular weight distribution (*MWD*) of reversible novolac polymer formation thus involves only one parameter. The study of the *MWD* of novolac polymer reveals two very important design variables: the phenol-formaldehyde ratio, $[\text{P}]_0/[\text{F}]_0$, in the feed and the vacuum applied on the reactor. As the $[\text{P}]_0/[\text{F}]_0$ ratio is increased, the breadth of the distribution is found to increase and it undergoes a maximum at $[\text{P}]_0/[\text{F}]_0 \approx 1.4$ for the set of rate constants chosen. At this ratio, the chain length average molecular weight is also found to be the largest. Industrially, the $[\text{P}]_0/[\text{F}]_0$ ratio used in producing novolac polymer is 1.67 and it is usually desired that the polymer be linear with minimal branching. On application of vacuum, for a given time of polymerization, the chain length molecular weight is found to increase when the results are compared with those of batch reactors. The breadth of the distribution is also found to reduce thus giving a lower polydispersity index of the polymer formed.

Keywords Novolac; reactor modelling; condensation polymerization; polymerization with formaldehyde

INTRODUCTION

The polymerization of phenol with formaldehyde leads to the formation of either novolac or resole polymers depending upon whether it is base- or acid-catalysed. For the formation of novolac polymer, the usual catalyst is sulphuric acid and the phenol to formaldehyde ratio $[\text{P}]_0/[\text{F}]_0$ in the feed is about 1.67^{1,2}. The polymer consists of essentially linear chains and the reaction can be represented schematically by:



where



indicates that the $-\text{CH}_2-$ linkage between the phenolic rings is at either the *ortho* or *para* positions of the phenol rings.

Phenol can undergo reaction at both the *ortho* and the

para positions and thus has a functionality of 3. Formaldehyde, on the other hand, exists in water as methylene glycol ($\text{OH}-\text{CH}_2-\text{OH}$) and has a functionality of 2. The *ortho* and *para* positions of phenol have been shown to have different reactivities³. In addition all the reactive sites on polymer chains other than those on the ends, called internal sites, have lower reactivities compared to the corresponding sites at the chain ends (called external sites)². The lower reactivity of the internal sites has been explained to be due to some kind of molecular shielding.

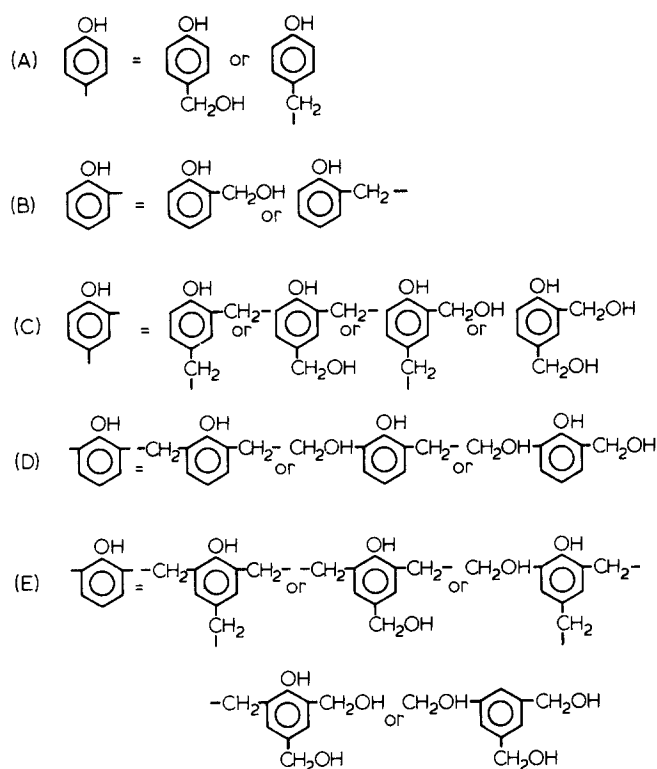
In order to describe novolac formation kinetically, one way is to enumerate all the chain structures and the various routes by which they are formed². This procedure runs into difficulty for molecular structures having more than three phenol rings. To overcome this difficulty, we defined the following reactive sites in our earlier work⁴⁻⁷:

- (a) external *ortho* site, o_{ET} ;
- (b) internal *ortho* site, o_i ;
- (c) external *para* site, p_e ; and
- (d) internal *para* site, p_i .

These were assumed to be distributed over polymer molecules of chain lengths 2 and beyond. Formaldehyde, on the other hand, reacts in two stages, first giving a bound CH_2OH group which on further reaction with these sites gives a reacted $-\text{CH}_2-$ bond. In view of this, at any given time there are phenol, formaldehyde and bound

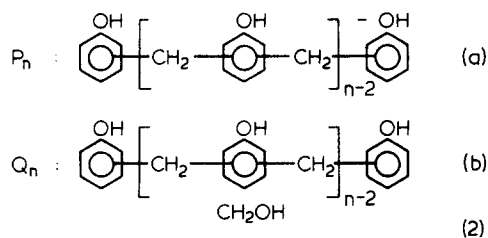
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Table 1 The structure of various species used for the modelling of reversible novolac formation

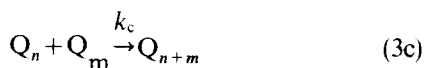


CH_2OH in addition to reactive sites o_{CT} , o_i , p_e and p_i present in the reaction mass. A reaction mechanism was proposed for the irreversible polymerization of phenol and formaldehyde accounting for the fact that these sites react with different rate constants.

In order to obtain the molecular weight distribution (*MWD*) of the polymer, the molecules having a bound CH_2OH (denoted as Q_n) groups were distinguished from these without bound CH_2OH (denoted as P_n). Since the concentration of bound CH_2OH groups in the reaction mass was shown to be small, it was assumed that Q_n does not have more than one bound CH_2OH and molecules P_n and Q_n can then be represented as:



In terms of P_n and Q_n , the growth of polymer chains for irreversible polymerization can then be represented as:



Drumm and LeBlanc² and Frontini *et al.*⁸ considered reactions (3a) and (3b) only and assumed that the rate constants for P_n and Q_n were proportional to the number of reactive sites on these molecules. They derived expressions for the *MWD*. Borrajo *et al.*⁹ have used equations derived by Macosco and Miller¹⁰ to predict the performance of a novolac reactor by assigning the average functionality of phenol as 2.31. In our earlier work⁴⁻⁷, we incorporated reaction (3c) into the kinetic scheme and obtained a more rigorous expression for the *MWD* in terms of the reactions of the various sites o_{CT} , o_i , p_e and p_i .

The modelling of reversible novolac formation cannot be done by simply extending the approach adopted for irreversible polymerizations. The difficulty arises because of the fact that one must know the precise linkages of the reacted $-\text{CH}_2-$ bonds as well as those of the bound CH_2OH groups. An effort in this direction was made⁷ and it was found that it became necessary to define 29 species in the reaction mass which is an impracticably high number for modelling the *MWD* of the polymer. While modelling irreversible resole formation¹¹⁻¹³, we used 19 reactive species. It was noted in a recent review¹⁴ that this particular model is a more detailed version of the kinetic model for novolac formation and the results for the latter can be derived by neglecting the set of reactions that occur only in resole formation. An attempt was also made to extend the kinetic model for resoles to describe the reversible novolac formation, but it ran into difficulty because the reverse reaction for some of the species cannot be written using this approach.

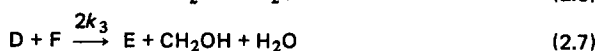
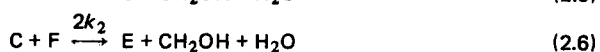
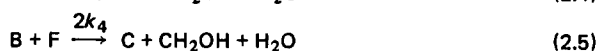
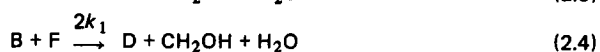
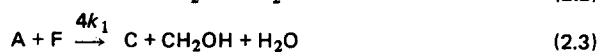
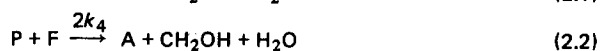
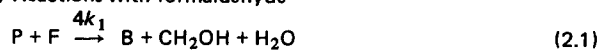
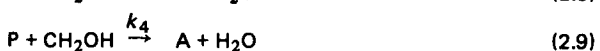
In this paper, we have proposed five species A to E, given in Table 1 where a dash on the phenyl rings denotes a linkage either to a $-\text{CH}_2-$ bond or a bound CH_2OH group¹⁵. It is possible to describe reversible novolac polymerization in terms of these species. The corresponding forward and reverse reactions are given in Table 2. It is found that the reactions can be written in two possible ways, called models I and II. It is shown in this paper that both these models yield the same concentrations of species A to E and results differ only in predicting the concentrations of formaldehyde and bound CH_2OH groups. Therefore if the purpose is to follow the formation of polymer, both these models are equivalent. Using the concentrations of these species, a kinetic model has been proposed to obtain the molecular weight distribution of the polymer.

Our earlier work on the *MWD* in the irreversible polymerization of novolac has shown that the phenomenon of molecular shielding has little effect on the weight distribution of the polymer under a wide range of rate constants. This means that one can make the approximation that the internal and external *ortho* sites have the same reactivity. Similarly the internal and external *para* sites react with the same rate constant. Using the experimental values of the rate constants for the *ortho* and *para* positions of phenol³ and treating the reverse rate constant as a parameter, the molecular weight distribution of the novolac polymer has been calculated for isothermal batch reactors. As the $[\text{P}]_0/[\text{F}]_0$ ratio in the feed is reduced, it may be expected that the assumption of one CH_2OH group per polymer chain might break down. Our calculations show that for $[\text{P}]_0/[\text{F}]_0 \geq 1$, the total concentration of CH_2OH remains very small. This would mean that if there are any chains at all with more than one CH_2OH group, they are present in negligible concentration, thus justifying our assumption.

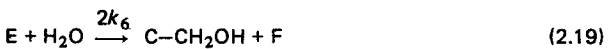
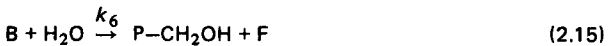
Table 2 Various reactions involving species A to E of Table 1 in reversible novolac formation, models I and II

Forward reactions of models I and II

(a) Reactions with formaldehyde


(b) Reactions with CH₂OH


Reverse reactions of model I



Reverse reactions of model II


 k_1 = reactivity of o_T sites

 k_2 = reactivity of o_i sites

 k_3 = reactivity of p_i sites

 k_4 = reactivity of p_e sites

 k_5 = reactivity of *para* linkage in the reverse reaction

 k_6 = reactivity of *ortho* linkage in the reverse reaction

P = phenol

F = formaldehyde HO-CH₂-OH

It may be recalled that phenol has a functionality of 3 and formaldehyde a functionality of 2, which means that for the formation of linear chains, one should use a $[P]_0/[F]_0$ ratio of unity in the feed. From this study the ratio of phenol and formaldehyde concentrations $[P]_0/[F]_0$ in the feed and the vacuum applied on the reaction mass emerge as the two very important design variables. For $[P]_0/[F]_0 \approx 1.4$, the average chain length of the novolac polymer is found to be the highest for the set of rate constants assumed in this calculation. Interestingly enough, the $[P]_0/[F]_0$ used in the industrial production of novolacs is 1.67. The kinetic model for the novolac formation presented in this paper is thus expected to be useful to industry for the purposes of processing.

KINETIC MODEL

To be able to describe the reversible polymerization of phenol and formaldehyde, five 'species' have been defined. These are given in Table 1⁵. The dash on these species represents a linkage either to a CH₂OH group or a -CH₂- bond. The various forward reactions that lead to the formation and depletion of these species are given in Table 2.

The overall reactivity of a given reaction in Table 2 has been assumed to be completely determined by the site involved. For example, in reactions (2.1) and (2.2) of Table 2, phenol (P) has two *ortho* and one *para* positions. In addition, formaldehyde has two functional groups. Therefore the overall reactivity of reaction (2.1) is $4k_1$ and that of reaction (2.2) is $2k_4$. In these reactions, in addition to the formation of species B and A, a bound CH₂OH group is formed which is shown on their right-hand sides for the purpose of book-keeping.

While writing the reverse reactions, on reaction of water with the linkages of species A to E, a CH₂OH would be formed when the linkage is a -CH₂- bond and formaldehyde (F) is formed if it is a bound CH₂OH group. Consequently models I and II have been proposed in Table 2. These give asymptotic behaviours because, in actual polymerization, there are -CH₂- bonds as well as bound CH₂OH groups which are interacting with water through the reverse reactions.

Using the kinetic models of Table 2, the balance equations for various species have been derived in Table 3, for both these models. As observed from this table, the balance equations for species A to E and H₂O are identical for models I and II and differ only in formaldehyde and CH₂OH. Thus, the concentrations of A to E for models I and II depend implicitly on [F] and [CH₂OH] only. With the help of equations (3.7)–(3.10) of Table 3

$$\frac{d}{dt}([CH_2OH] + 2[F])$$

can be determined for both models and this is found to yield identical expressions. Thus, it can be concluded that both models yield identical results for [A] to [E] versus time. Later we show that the molecular weight distribution of the novolac polymer is completely determined by the concentrations of these species in the reaction mass. This would imply that, if the aim of the study is to predict the properties of the polymer formed, either of the two models could be used equivalently.

Table 3 Rates of formation for species A to E in batch reactors

 Rates of formation for species A to E and H₂O valid for both models I and II

$$\frac{d[A]}{dt} = k_4[P](2[F] + [CH_2OH]) - 2k_1[A](2[F] + [CH_2OH]) - k_5[A][H_2O] + k_6[C][H_2O] \quad (3.1)$$

$$\frac{d[B]}{dt} = 2k_1(2[F] + [CH_2OH])[P] - 2k_1[B]([CH_2OH] + 2[F]) - k_4[B](2[F] + [CH_2OH]) - k_6[B][H_2O] + k_5[C][H_2O] + k_6[D][H_2O] \quad (3.2)$$

$$\frac{d[C]}{dt} = 2k_1[A](2[F] + [CH_2OH]) + k_4[B](2[F] + [CH_2OH]) - k_2[C](2[F] + [CH_2OH]) - k_5[C][H_2O] - k_6[C][H_2O] + 2k_6[E][H_2O] \quad (3.3)$$

$$\frac{d[D]}{dt} = k_1[B](2[F] + [CH_2OH]) - k_3[D](2[F] + [CH_2OH]) - 2k_6[D][H_2O] + k_5[E][H_2O] \quad (3.4)$$

$$\frac{d[E]}{dt} = k_2[C](2[F] + [CH_2OH]) + k_3[D](2[F] + [CH_2OH]) - 2k_6[E][H_2O] - k_5[E][H_2O] \quad (3.5)$$

$$\frac{d[H_2O]}{dt} = 2k[A](2[F] + [CH_2OH]) + (k_1 + k_4)[B](2[F] + [CH_2OH]) + k_2[C](2[F] + [CH_2OH]) + k_3[D](2[F] + [CH_2OH]) + (2k_1 + k_4)[P](2[F] + [CH_2OH]) - k_5[H_2O]([A] + [C] + [E]) - k_6[H_2O]([B] + [C] + 2[D] + 2[E]) \quad (3.6)$$

 Rates of formation for [F] and [CH₂OH] for model I

$$\frac{d[F]}{dt} = -2[F]\{2k_1[A] + (k_1 + k_4)[B] + k_2[C] + k_3[D] + (2k_1 + k_4)[P]\} + k_5[H_2O]([A] + [C] + [E]) + k_6[H_2O]([B] + [C] + 2[D] + 2[E]) \quad (3.7)$$

$$\frac{d[CH_2OH]}{dt} = +2[F]\{2k_1[A] + (k_1 + k_4)[B] + k_2[C] + k_3[D] + (2k_1 + k_4)[P]\} - [CH_2OH]\{2k_1[A] + (k_1 + k_4)[B] + k_2[C] + k_3[D] + (2k_1 + k_4)[P]\} - k_5[H_2O]([A] + [C] + [E]) - k_6[H_2O]([B] + [C] + 2[D] + 2[E])$$

 Rates of formation for [F] and [CH₂OH] for model II

$$\frac{d[F]}{dt} = -2[F]\{2k_1[A] + (k_1 + k_4)[B] + k_2[C] + k_3[D] + (2k_1 + k_4)[P]\} \quad (3.9)$$

$$\frac{d[CH_2OH]}{dt} = 2[F]\{2k_1[A] + (k_1 + k_4)[B] + k_2[C] + k_3[D] + (2k_1 + k_4)[P]\} - [CH_2OH]\{2k_1[A] + (k_1 + k_4)[B] + k_2[C] + k_3[D] + (2k_1 + k_4)[P]\} + k_5[H_2O]([A] + [C] + [E]) + k_5[H_2O]([B] + [C] + 2[D] + 2[E]) \quad (3.10)$$

Table 3 (continued)

Dimensionless variables

$$\begin{aligned} R_1 &= k_2/k_1 & Y_A &= [A]/[F]_0 \\ R_2 &= k_3/k_1 & Y_B &= [B]/[F]_0 \\ R_3 &= k_4/k_1 & Y_P &= [P]/[F]_0 \\ R_4 &= k_5/k_1 & Y_C &= [C]/[F]_0 \\ R_5 &= k_6/k_1 & Y_D &= [D]/[F]_0 \\ x &= k_1[F]_0 t & Y_E &= [E]/[F]_0 \end{aligned}$$

To establish expressions for the molecular distribution of the polymer, as usual, molecules Q_n having a bound CH_2OH group are distinguished from those (P_n) without CH_2OH . Further, it is assumed that molecules Q_n do not have more than *one* bound CH_2OH group. This is also justified from our earlier work on the modelling of irreversible novolac formation, namely that the concentration of CH_2OH in the reaction mass remains small for all times⁴⁻⁷.

After time t of polymerization has elapsed, we focus our attention on all the molecules of Q_n (where n represents its chain length) and count the reactive sites A to E on them. Let these be A_{Q_n} , B_{Q_n} , C_{Q_n} , D_{Q_n} and E_{Q_n} . Similarly on P_n molecules, the number of these sites are assumed to be A_{P_n} , B_{P_n} , C_{P_n} , D_{P_n} and E_{P_n} . Evidently

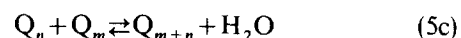
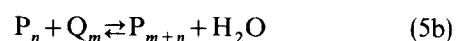
$$C_{Q_i} = D_{Q_i} = E_{Q_i} = 0 \quad (4a)$$

$$C_{P_2} = D_{P_2} = E_{P_2} = 0 \quad (4b)$$

$$E_{Q_2} = 0 \quad (4c)$$

$$E_{P_2} = 0 \quad (4d)$$

The various reactions between P_n and Q_n that occur in reversible novolac formation can be represented schematically as:



A molecule of Q_n is formed when:

- P_n reacts with formaldehyde;
- CH_2OH of Q_i ($i \leq n-1$) reacts with the various sites of the species of Q_{n-i} through the forward reaction;
- bonds of P_m ($m \geq n+1$) interact with water to give Q_n through the reverse reaction; and
- bonds of Q_m ($m \geq n+1$) interact with water to give Q_n through the reverse reaction.

On the other hand, Q_n is depleted when:

- the CH_2OH of Q_n reacts with any of the active species of P_i through the forward reaction;
- the CH_2OH of Q_n reacts with any site of Q_i through the forward reaction;
- any of the sites of Q_n reacts with CH_2OH of any Q_i through the forward reaction; and
- any of the species of Q_n reacts with H_2O by the reverse reaction.

With this in mind, the equation for the rates of formation of species Q_n ($n \geq 3$) is given by:

$$\begin{aligned} \frac{d[Q_n]}{dt} = & H_{P_n}(2[F]) + \sum_{i=1}^{n-2} [Q_i]H_{Q_{n-i}} + [Q_{n-i}]H_{Q_n} \\ & - [Q_n] \sum_{i=3}^{\infty} H_{P_i} - [Q_n]H_{P_2} - (2k_1 + k_4)[P][Q_n] \\ & - [Q_n] \sum_{i=2}^{\infty} H_{Q_i} - [Q_n]H_{Q_1} - H_{Q_n} \sum_{i=1}^{\infty} [Q_i] - R_{Q_n}[H_2O] \\ & + \sum_{m=n+1}^{\infty} \frac{R_{P_m}}{m-1} [H_2O] + 2 \sum_{m=n+1}^{\infty} \frac{R_{Q_m}}{m-1} [H_2O] \end{aligned} \quad (6)$$

Similar balance equations for the rate of formation of species P_n can be written and they are

for $n \geq 3$, where

$$H_{P_2} = 2k_1 A_{P_2} + (k_1 + k_4) B_{P_2} \quad (7a)$$

$$H_{P_n} = 2k_1 A_{P_n} + (k_1 + k_4) B_{P_n} + k_2 C_{P_n} + k_3 D_{P_n} \quad n \geq 3 \quad (7b)$$

$$H_{Q_1} = 2k_1 A_{Q_1} + (k_1 + k_4) B_{Q_1} \quad (7c)$$

$$H_{Q_n} = 2k_1 A_{Q_n} + (k_1 + k_4) B_{Q_n} + k_2 C_{Q_n} + k_3 D_{Q_n} \quad n \geq 2 \quad (7d)$$

$$R_{P_2} = k_5 A_{P_2} + k_6 B_{P_2} \quad (7e)$$

$$R_{P_n} = k_5(A_{P_n} + C_{P_n}) + k_6(B_{P_n} + C_{P_n} + 2D_{P_n}) \quad (7f)$$

$$R_{P_n} = k_5(A_{P_n} + C_{P_n} + E_{P_n}) + k_6(B_{P_n} + C_{P_n} + 2D_{P_n} + E_{P_n}) \quad n \geq 4 \quad (7g)$$

$$R_{Q_1} = k_5 A_{Q_1} + k_6 B_{Q_1} \quad (7h)$$

$$R_{Q_2} = k_5(A_{Q_2} + C_{Q_2}) + k_6(B_{Q_2} + C_{Q_2} + 2D_{Q_2}) \quad (7i)$$

$$R_{Q_n} = k_5(A_{Q_n} + C_{Q_n} + E_{Q_n}) + k_6(B_{Q_n} + C_{Q_n} + 2D_{Q_n} + 2E_{Q_n}) \quad n \geq 3 \quad (7j)$$

In equation (6), R_{P_n} and R_{Q_n} give the total rate of depletion of P_n and Q_n by the reverse reaction and when it is divided by the number of bonds (i.e. $m-1$) on P_n and Q_n , the average rate of reaction with water per bond is obtained.

Equation (6) does not hold for Q_1 and Q_2 and the corresponding equations for the rates of formation for these are:

$$\begin{aligned} \frac{d[Q_1]}{dt} = & 2(2k_1 + k_4)[P][F] - (2k_1 + k_4)[P][Q_1] \\ & - [Q_1] \sum_{i=2}^{\infty} H_{P_i} - [Q_1] \sum_{i=1}^{\infty} H_{Q_i} - H_{Q_1} \sum_{i=1}^{\infty} [Q_i] \\ & - R_{Q_1}[H_2O] + \sum_{m=2}^{\infty} \frac{R_{P_m}}{m-1} [H_2O] \\ & + 2 \sum_{m=2}^{\infty} \frac{R_{Q_m}}{m-1} [H_2O] \end{aligned} \quad (8)$$

$$\frac{d[Q_2]}{dt} = H_{P_2}(2[F]) + H_{Q_1}[Q_1] - [Q_2] \sum_{i=2}^{\infty} H_{P_i}$$

$$\begin{aligned} \frac{d[P]}{dt} = & -(2k_1 + k_4)[P] \sum_{i=1}^{\infty} [Q_i] - 2(2k_1 + k_4)[P][F] \\ & + R_{Q_1}[H_2O] + \sum_{i=1}^{\infty} \frac{R_{P_i}}{i-1} [H_2O] \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{d[P_2]}{dt} = & (2k_1 + k_4)[P][Q_1] - 2H_{P_2}[F] - H_{P_2} \sum_{i=1}^{\infty} [Q_i] \\ & - R_{P_2}[H_2O] + \sum_{i=3}^{\infty} \frac{H_{P_i}}{i-1} [H_2O] \end{aligned} \quad (11)$$

and

$$\begin{aligned} \frac{d[P_n]}{dt} = & \sum_{i=1}^{n-2} [Q_i]H_{P_{n-i}} + (2k_1 + k_4)[P][Q_{n-1}] - 2H_{P_n}[F] \\ & - H_{P_n} \sum_{i=1}^{\infty} [Q_i] - R_{P_n}[H_2O] + \sum_{i=n+1}^{\infty} \frac{R_{P_i}}{i-1} [H_2O] \end{aligned} \quad (12)$$

for $n \geq 3$.

Above P_1 is the same as phenol and its mass balance is given in equation (10). Equations (5)–(12) can be solved provided an estimate of A_{Q_n} to E_{Q_n} and A_{P_n} to E_{P_n} can be made, for which the following approximations are used:

$$A_{Q_n} = \frac{[A]}{\sum_{i=1}^{\infty} [Q_i] + \sum_{i=2}^{\infty} [P_i]} [Q_n] \quad (13a)$$

$$B_{Q_n} = \frac{[B]}{\sum_{i=1}^{\infty} [Q_i] + \sum_{i=2}^{\infty} [P_i]} [Q_n] \quad (13b)$$

$$C_{Q_n} = \frac{[C]}{\sum_{i=2}^{\infty} [Q_i] + \sum_{i=3}^{\infty} [P_i]} [Q_n] \quad (13c)$$

$$D_{Q_n} = \frac{[D]}{\sum_{i=2}^{\infty} [Q_i] + \sum_{i=4}^{\infty} [P_i]} [Q_n] \quad (13d)$$

$$E_{Q_n} = \frac{[E]}{\sum_{i=2}^{\infty} [Q_i] + \sum_{i=4}^{\infty} [P_i]} [Q_n] \quad (13e)$$

Similar relations would hold for A_{P_n} to E_{P_n} . In these equations, [A] to [E] are the bulk concentrations of species A to E in the reaction mass. The approximation made in equations (13) amounts to stating that the fraction of active species on all the Q_n molecules is equal to the fraction of these in the bulk. We have made a similar

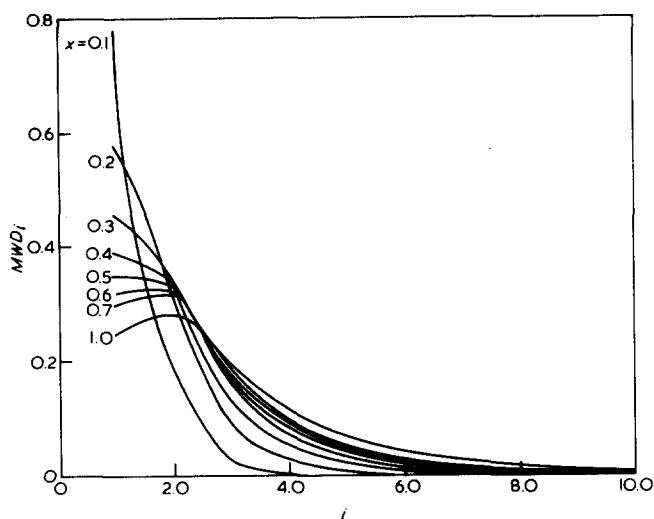


Figure 1 The weight fraction distribution of the novolac polymer as a function of dimensionless time, x . $R_1 = 1$, $R_2 = R_3 = 2.4$, $R_4 = 0.24$, $R_5 = 0.1$, $[P]_0/[F]_0 = 1.67$

approximation in our earlier work of modelling the MWD in irreversible novolac formation⁵⁻⁷ and such assumptions are quite commonly made in deriving solution properties and the excluded volume effect¹⁶.

NUMERICAL CALCULATION OF MWDs

Equations (6)–(12) involve six rate constants, k_1 to k_6 . In our earlier work, the effect of molecular shielding on the conversion and MWD was found to be very small. If it is neglected, one has:

$$k_1 = k_2 \quad (14a)$$

$$k_3 = k_4 \quad (14b)$$

In addition, it can be assumed that the reactivities of the *ortho* and *para* linkages in the reverse reactions differ by the same ratio as they do in the forward reaction, which means

$$\frac{k_5}{k_6} = \left(\frac{k_4}{k_1} \right) \quad (15)$$

where k_4 and k_1 are the reactivities of *ortho* and *para* positions in phenol, which are available experimentally³. If it is used, the kinetic model presented in this work involves only one parameter, i.e. k_6 .

The effect of the variation of R_5 ($=k_6/k_1$), ratio of phenol and formaldehyde, $[P]_0/[F]_0$, in the feed and the vacuum applied on the MWD of the polymer formed has been studied by integrating equations (6)–(12) using the fourth-order Runge-Kutta method. The incremental dimensionless time, Δx ($=k_1[F]_0\Delta t$), was chosen to be 10^{-3} and the numerical stability of the solution was checked by the results obtained for $\Delta x = 10^{-4}$ and 10^{-5} . They were found to match identically. Our earlier experience^{12,13,17,18} has shown that the ring count, RC, defined by:

$$RC = \sum_{n=1}^{\infty} n[Q_n] + \sum_{n=2}^{\infty} n[P_n] + [P] \quad (16)$$

is the most sensitive parameter and can serve as an indicator of truncation errors and any inconsistency in a large set of equations. We have calculated the RC for every increment of time and found it to be a constant. This should be so because RC measures the number of phenyl rings in the reaction mass, which must be constant if the set of equations giving the MWD are consistent.

RESULTS AND DISCUSSION

Equations (6)–(12) have been solved and the distributions of P_n and Q_n have been combined as follows:

$$MWD_i = \frac{i[P_i + i[Q_i]]}{\sum_{i=1}^{\infty} (i[P_i] + i[Q_i])} \quad (17)$$

This is done because the molecules of P_i and Q_i are never separated in practice. In Figure 1, the weight fraction distribution has been plotted for different times. As polymerization progresses, the distribution becomes broader and for x beyond 0.4 it begins to undergo a maximum. It is significant that oligomers having 7 or 8 repeat units are present in finite concentrations in the reaction mass.

The chain length and weight average molecular weights of P alone, μ_{NP} and μ_{WP} , Q alone, μ_{NQ} and μ_{WQ} , and their combination, μ_{NT} and μ_{WT} , have been plotted as a function of x in Figure 2. As expected, μ_{NT} always lies between μ_{NP} and μ_{NQ} and μ_{WT} between μ_{WP} and μ_{WQ} . Since the μ_{NT} and μ_{WT} curves are closer to those for μ_{NP} and μ_{WP} , it signifies that the molecules of Q_i are considerably smaller in number. This would in turn mean that the concentration of bound CH_2OH ($\sum_{i=1}^{\infty} [Q_i]$) in the reaction mass is small. It may be recalled that this was one of the important assumptions made in formulating this kinetic model. In Figure 3, the polydispersity index, ρ_P , ρ_Q and ρ_T of P_i , Q_i and their combination has been plotted. The index ρ_P for the distribution of P_i is considerably lower than that for the distribution of Q_i because of the preponderance of unreacted phenol (i.e. P_1). The ρ_T for the combined distribution rises to a high value of 1.5 within the dimensionless time $x = 1$ and the curve is still found to be rising, even though the increase in chain length and weight

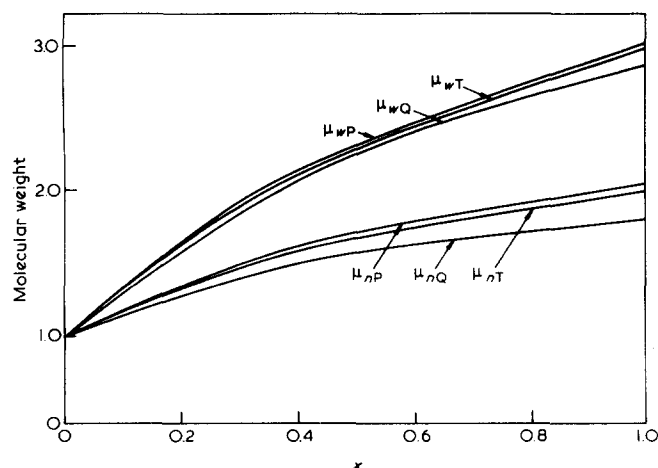


Figure 2 The chain length, μ_{NP} , μ_{NQ} and μ_{NT} , and weight average, μ_{WP} , μ_{WQ} and μ_{WT} , molecular weights of P_n and Q_n and their combination as a function of time, x . $R_1 = 1$, $R_2 = R_3 = 2.4$, $R_4 = 0.24$, $R_5 = 0.1$, $[P]_0/[F]_0 = 1.67$

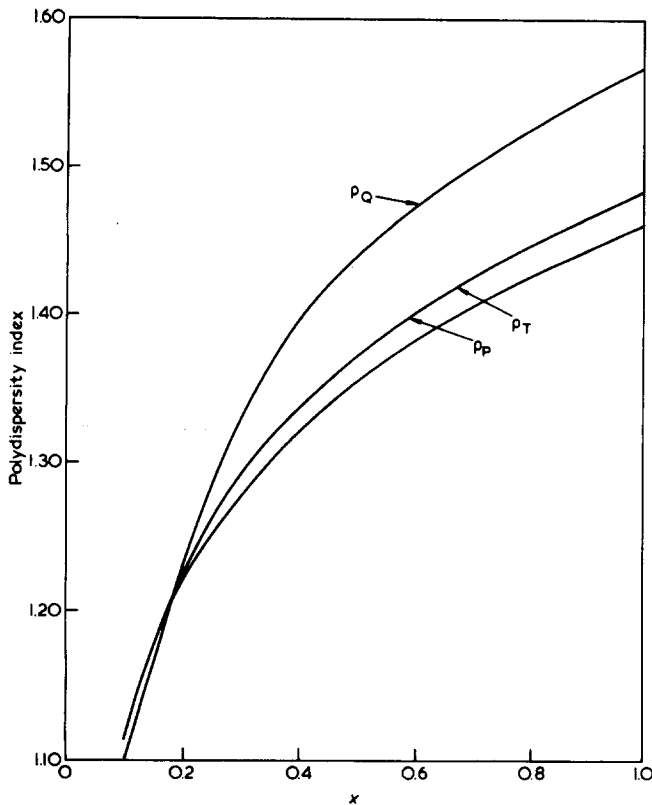


Figure 3 The polydispersity indices ρ_P , ρ_Q and ρ_T of the distribution of P_n , Q_n and their combination versus x . $R_1 = 1$, $R_2 = R_3 = 2.4$, $R_4 = 0.24$, $R_5 = 0.1$, $[P]_0/[F]_0 = 1.67$

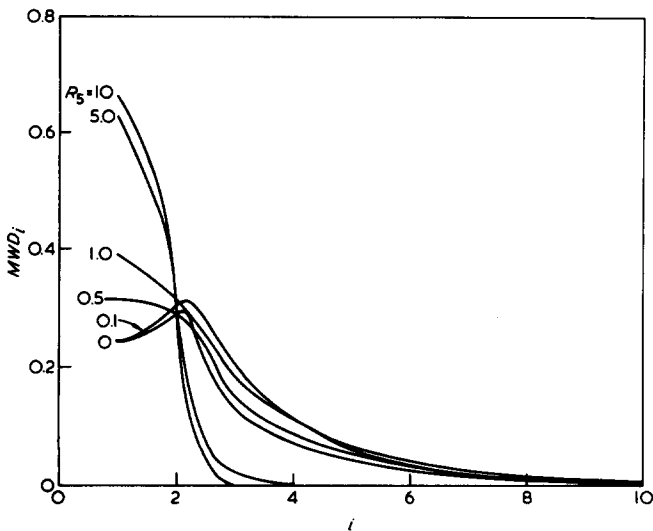


Figure 4 The effect of R_5 on the MWD of the novolac polymer. $R_1 = 1$, $R_2 = R_3 = 2.4$, $R_4 = 2.4R_5$, $[P]_0/[F]_0 = 1.67$

averages μ_{NT} and μ_{WT} in Figure 2 appears to be small. The effect of the variation of $R_5 (=k_6/k_1)$ on the MWD has been examined in Figure 4. Results for $x=1.0$ have been plotted for various values of R_5 . The value $R_5=0$ corresponds to the results of irreversible novolac formation and the MWD is found to be the broadest, undergoing a maximum. As R_5 increases, this maximum slowly disappears and the MWD becomes sharper. This is expected because, with the increase in R_5 , the conversion reached for a given time of polymerization becomes

smaller and molecules of higher chain lengths are formed in smaller proportion.

In Figure 5, the ratio of phenol to formaldehyde, $[P]_0/[F]_0$, in the feed has been varied and the MWD of the polymer examined at the dimensionless time of polymerization, $x=1.0$. Results derived for very low $[P]_0/[F]_0$ ratio (less than 0.5) through this model are not strictly correct because the assumption of having only one bound CH_2OH group per chain is expected to break down. Results derived show that the MWD becomes broader and broader as $[P]_0/[F]_0$ is increased from a very low value of 0.2 up to 1.4. The breadth of the distribution, however, is found to reduce as the $[P]_0/[F]_0$ ratio is increased beyond 1.4. The effect of this ratio is more clearly shown in Figure 6 in which the chain length

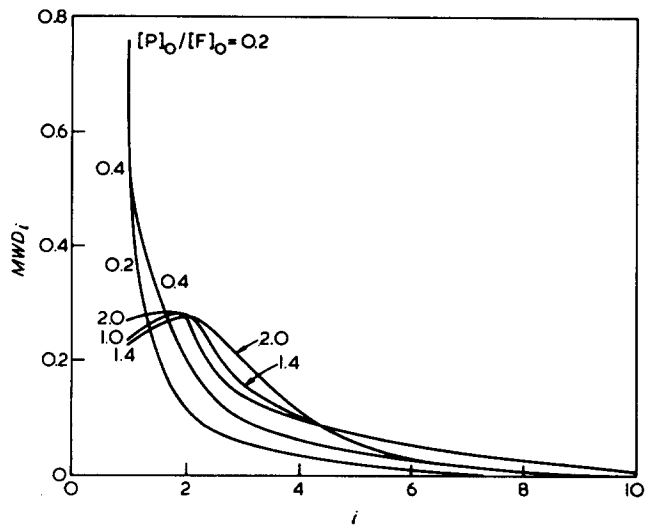


Figure 5 The effect of $[P]_0/[F]_0$ on the MWD of the novolac polymer. $R_1 = 1$, $R_2 = R_3 = 2.4$, $R_4 = 0.24$, $R_5 = 0.1$

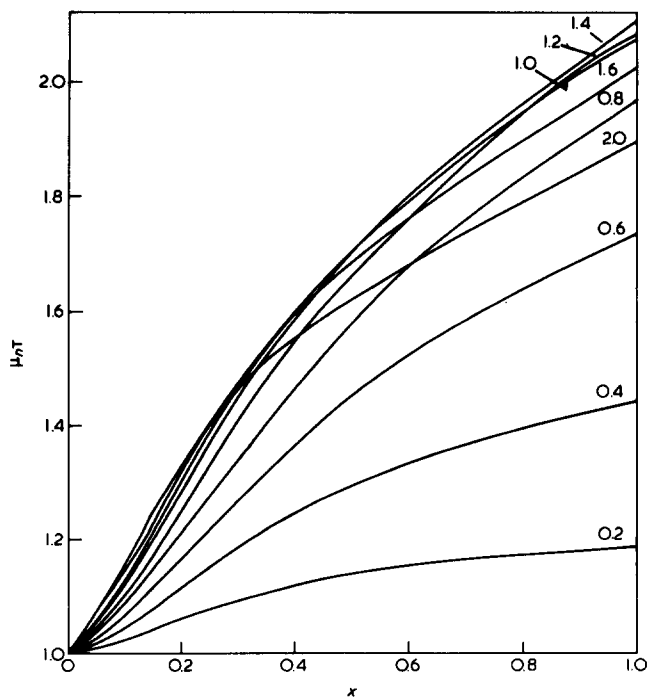


Figure 6 The effect of $[P]_0/[F]_0$ on the chain length molecular weight of novolac polymer versus x

average molecular weight versus the time of polymerization has been plotted. As $[P]_0/[F]_0$ is increased, at the ratio of 1.4, μ_{NT} undergoes a maximum. It is interesting to note that, industrially, the phenol-formaldehyde ratio used in the feed is 1.67, which is supposed to maximize the formation of linear chains. Indeed, our kinetic model predicts such an optimal feed ratio for the set of rate constants chosen.

If a vacuum is applied to the reaction mass, the condensation product is removed and, in reversible polymerization, the overall reaction is expected to move in the forward direction. When vacuum is applied, the interface concentration of water quickly attains the value governed by the thermodynamic equilibrium relation existing at the vacuum level applied. The concentration profile existing in the reaction mass can in general be solved using suitable transport equations^{19,20}. However, when the diffusional resistance is small, it is generally not necessary to solve the diffusion equation and the reaction mass as a whole could be assumed to be at the uniform concentration existing at the interface. In phenol-formaldehyde polymerization, in the initial region, therefore, one could assume the existence of a uniform concentration governed by the vapour-liquid equilibrium existing at the vacuum applied. Thus to study the effect of vacuum, in Figure 7 the water concentration in the reaction mass has been varied and the *MWD* of the polymer plotted at two values of x . The *MWD* so obtained has also been compared with those for batch reactors where the water is not removed. The advantages of the application of vacuum are evident: the maximum in the *MWD* curves shift to the right and distribution becomes sharper. The reduction of the vacuum level from $[H_2O]=0.1$ to $[H_2O]=0.01$, however, does not appear to have much advantage.

CONCLUSIONS

Five reactive species A to E have been defined to model the reversible novolac formation. These species differ from each other in terms of their linkages, where these linkages could either be to a $-CH_2-$ bond or a bound CH_2OH group. Two kinetic models have been proposed which serve as two asymptotes to the actual description of the process of polymerization and both have been shown rigorously to yield the same concentrations of these reactive species. After ascertaining this, the polymer molecules have been classified as those having bound CH_2OH groups (Q_n) and those without (P_n). It is assumed that $[CH_2OH]$ in the reaction mass is low to the extent that Q_n has only one group per molecule. This assumption was not only found to be valid for the modelling of irreversible novolac formation studied earlier, but was also justified from the results derived from the present model.

Based upon the concentrations of reactive species A to E in the reaction mass, a kinetic model has been proposed from which expressions for $d[P_n]/dt$ and $d[Q_n]/dt$ in batch reactors have been written. These balance equations involve six rate constants. Our earlier studies have shown that the phenomenon of molecular shielding can be neglected, which means that the terms accounting for the forward reactions only involve two rate constants (k_1 and k_4) of the *ortho* and *para* positions of phenol, and these are experimentally available. If, in the reverse reaction, the reactivities of the *ortho* and *para* linkages differ by the

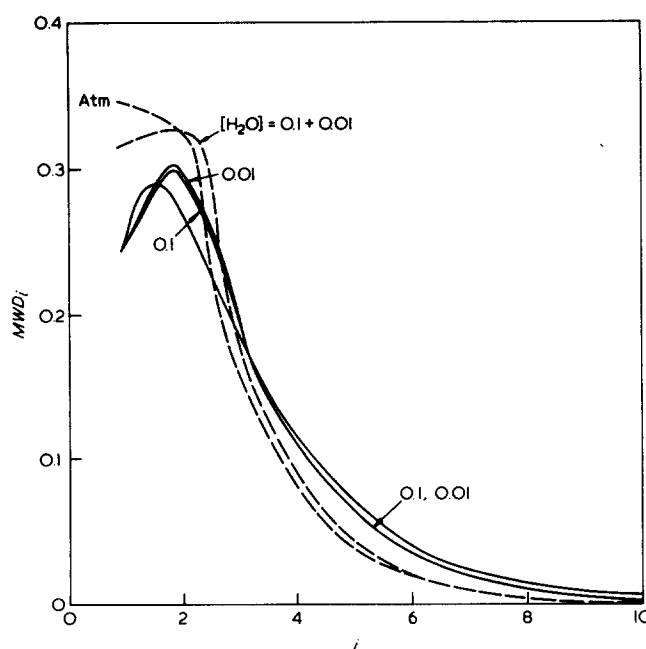


Figure 7 The effect of vacuum measured by $[H_2O]_0$ level on the *MWD* of the polymer. $R_1 = 1$, $R_2 = R_3 = 2.4$, $R_4 = 0.24$, $R_5 = 0.1$, $[P]_0/[F]_0 = 1.67$

same ratio as in the forward reaction of these sites, the balance equations derived in this work reduce to those involving only one parameter.

The study of the molecular weight distribution of reversible novolac formation reveals two very important design variables: the ratio of phenol and formaldehyde, $[P]_0/[F]_0$, in the feed and the application of vacuum on the reaction mass. As the $[P]_0/[F]_0$ ratio is increased from a very low value, the *MWD* of the polymer formed becomes broader, undergoing a maximum at $[P]_0/[F]_0 \approx 1.4$ for the set of rate constants used in the computation. This is so because at this feed ratio, the formation of linear chains is maximized. The chain length average is also the largest at this $[P]_0/[F]_0$ value. It may be recalled that in novolac formation it is desired to maximize the formation of linear chains, and industrial reactors manufacturing novolacs are operated at $[P]_0/[F]_0 \approx 1.67$.

To examine the effect of vacuum applied on the reaction mass, the mass transfer resistance has been neglected and the reaction mass has been assumed to be at a uniform concentration of water given by the vapour-liquid equilibrium existing at the vacuum applied. Treating the water level in the reaction mass as a parameter, the effect of vacuum on the *MWD* of the polymer has been examined. As the level of H_2O is reduced, the *MWD* is found to become sharper, a result of great commercial value where it is desired to reduce the polydispersity index of the polymer.

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