Molecular weight distributions in novolac type phenol–formaldehyde polymerizations

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In the acid-catalysed condensation polymerization of phenol and formaldehyde, the *ortho* and *para* positions of the phenol ring are known to exhibit different reactivities[1,2]. Along with this on polymer molecules, the internal sites have lower reactivity due to molecular shielding. To model the novolac formation, five reactive sites have been proposed[3] and their reactivities are assumed to be completely determined by the site involved To find the molecular weight distribution (*MWD*) of the polymer from this information, a given polymer chain has been assumed to consist of these sites in the same relative ratio as in the reaction mass. A mass balance, on polymer molecules of given size, has been made and solved numerically as a function of time The sensitivity analysis has been carried out to show that the *MWD* is little affected by the variation of reactivities of the internal sites. The reactivity of *para* external positions and the ratio of phenol and formaldehyde, however, play a major role in determining the *MWD*

Keywords Polymerization; catalysis; phenol, formaldehyde; condensation; molecular weight distribution; novolac

INTRODUCTION

There are several classes of polycondensation reactions which do not obey an equal reactivity hypothesis[1–3] and novolac formation from the acid catalysed polymerization of phenol and formaldehyde is one of them. Formaldehyde in water exists as methylene glycol (OH–CH$_2$–OH) and has a functionality of two. Phenol has three reactive sites, two *ortho* and one *para*, where it can undergo polymerization. Experimental studies have shown that the *ortho* and *para* positions have different reactivities[4–7]. The study of gelation reveals that phenol has a functionality slightly less than three and the molecular growth is found to occur mainly by the reaction of end groups. Drumm and Le Blanc explain this phenomena through molecular shielding and they assign a lower reactivity to internal reactive sites.

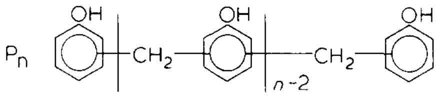
When the equal reactivity hypothesis does not hold, the expression for reaction rate cannot be written in terms of reaction between functional groups. As a consequence, differential equations governing the concentration of a polymer molecule of a given chain length for batch reactors must be solved numerically. Our previous studies[8–14] have shown that the term accounting for the unequal reactivity, greatly affects conversion, polydispersity index and molecular weight distribution (*MWD*).

Even though novolac formation is one of the oldest reactions, there have been very few attempts at theoretical modelling of this system[1–3]. Based upon experimental evidence, in our previous work[3], five kinds of reactive sites were proposed and the conversion of each of these was calculated for batch reactors as a function of time.

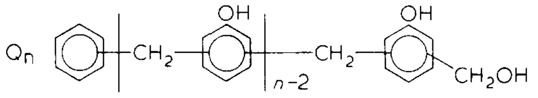
In this paper, from the knowledge of conversion, the distribution of these sites on polymer molecules of given chain length have been modelled and the molecular weight distribution in the novolac formation has been derived in terms of basic kinetic parameters. This is a three parameter model and sensitivity analysis has been carried out to establish the effect of various parameters upon the molecular weight distribution.

KINETIC MODEL

In the reaction mass, the polymer chains are assumed to consist of all those molecules which have chain lengths equal to or greater than 2. There are two kinds of molecular species



(1a)



(1b)

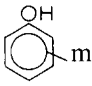
where the symbol  means that the bond formation has occurred either at the *para* or the *ortho* position. The P_n and Q_n differ from each other only by a substituted -CH$_2$OH. It is assumed that there is only one bound CH$_2$OH per chain which can be anywhere on the chain. These polymer molecules contain external *ortho* (O_{eT}) and *para* positions (p_e) which are present at the chain ends and internal *ortho* and *para* positions (O_i and p_i) situated within the chain. All these positions have been shown to differ in their reactivities. Also, the examination of chain ends reveals that the following two molecular structures give rise to external *ortho* position, O_{eT}

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Table 1 Reactions of O_e, O_e', p_i, O_i and p_e

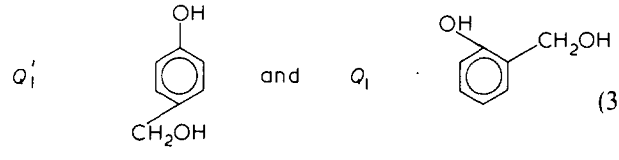
(1) With formaldehyde	
$O_e' + F \xrightarrow{2k_1} (-CH_2OH) + O_i - O_e'$	(a)
$O_e + F \xrightarrow{2k_1} (-CH_2OH) + p_i - p_e$	(b)
$O_i + F \xrightarrow{2k_2} (-CH_2OH)$	(c)
$p_i + F \xrightarrow{2k_3} (-CH_2OH)$	(d)
$p_e + F \xrightarrow{2k_4} (-CH_2OH) + O_i - O_e$	(e)
(2) With bound formaldehyde $(-CH_2OH)$	
$O_e' + (-CH_2OH) \xrightarrow{k_1} O_i - O_e'$	(f)
$O_e + (-CH_2OH) \xrightarrow{k_1} p_i - p_e$	(g)
$O_i + (-CH_2OH) \xrightarrow{k_2}$ Consumption	(h)
$p_i + (-CH_2OH) \xrightarrow{k_3}$ Consumption	(i)
$p_e + (-CH_2OH) \xrightarrow{k_4} O_i - O_e$	(j)

(2)

These are distinguished and denoted as O_e' and O_e.

At a given time in the reaction mass, there can be free formaldehyde molecules and bound CH_2OH groups and the reactive sites can interact with both these. The different reactions have been summarized in *Table 1* and these have been written to satisfy the site balance. As an example, reaction (a) in *Table 1* stands for the fact that on reaction of O_e', a bound $-CH_2OH$ at that site is formed. The adjoining site, O_e', is assumed to be not available for further reaction which becomes O_i on reaction of CH_2OH. This fact has been represented by writing $-O_e'$ and $+O_i$ in the right hand side. The reactivity of a given reaction is assumed to be completely determined by the reactive sites involved. In reactions (a) to (e) in *Table 1*, the rate constants have been multiplied by a factor of 2 because in formaldehyde molecules, there are 2 (OH) groups where the reaction can occur with equal likelihood.

The schematic reactions shown in *Table 1* do not include those involving phenol. When phenol reacts with formaldehyde, the following two species are formed



(3)

Reactions of Q_1 and Q'^1 are also not included in *Table 1* and these have been listed in *Table 2*. In reaction (a) in *Table 2*, there are two positions on phenol (P) and two positions on F and therefore the reactivity has been shown to be $4k_1$ and so on. A mass balance on these species for batch reactors are

$$\frac{d[O_e']}{dt} = -2k_1[O_e']\{Q_1] + 2[F] + [CH_2OH]\} + [Q_i']\{2k_1[O_e] + 2k_2[O_i] + 2k_3[p_i] + 2k_4[p_e] + 4(k_1+k_4)[P]\} + \{[Q_1] + [CH_2OH]\}2k_4[P] \tag{4}$$

$$\frac{d[O_e]}{dt} = [Q_1]\{k_1[O_e'] + k_2[O_i] + k_3[p_i] + (4k_1+k_4)[P]\} - [Q_1']\{k_1[O_e] + k_4[p_e] - 2k_1[P]\} - 2[F]\{k_1[O_e] + k_4[p_e]\} - [CH_2OH]\{k_4[p_e] - 2k_1[P] + k_1[O_e]\} \tag{5}$$

$$\frac{d[O_i]}{dt} = [Q_1]\{k_1[O_e'] - k_2[O_i] + k_4[p_e]\} + [Q_1']\{k_1[O_e'] - k_2[O_i] + k_4[p_e]\} + 2[F]\{k_1[O_e'] - k_2[O_i] + k_4[p_e]\} + [CH_2OH]\{[O_e']k_1 - k_2[O_i] + k_4[p_e]\} \tag{6}$$

$$\frac{d[p_i]}{dt} = k_1[O_e]\{[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\} - k_3[p_i]\{[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\} \tag{7}$$

$$\frac{d[p_e]}{dt} = [Q_1]\{k_1[O_e'] + k_2[O_i] + (4k_1+k_4)[P] + k_3[p_i]\} + [Q_1']\{2k_1[P] - k_1[O_e] - k_4[p_e]\} - 2[F]\{k_1[O_e] + k_4[p_e]\} + [CH_2OH]\{2k_1[P] - k_4[p_e]\} \tag{8}$$

$$\frac{d[Q_1]}{dt} = 4k_1[F][P] - (2k_1+k_4)[Q_1][P] - [Q_1]\{k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - 2(k_1+k_4)[Q_1]^2 (3k_1+k_4)[Q_1][Q_1'] - (k_1+k_4)[Q_1][CH_2OH] \tag{9}$$

Table 2 Reactions of P, Q_1 and Q_1'

(a) Reactions of P with F and $(-CH_2OH)$	
$P + F \xrightarrow{4k_1} Q_1$	(a)
$P + F \xrightarrow{2k_4} Q_1'$	(b)
$P + (-CH_2OH) \xrightarrow{2k_1} p_e + O_e$	(c)
$p + (-CH_2OH) \xrightarrow{k_4} 2O_e'$	(d)
(b) Reactions of p with Q_1 and Q_1'	
$p + Q_1' \xrightarrow{2k_1} p_e + 2O_e' + O_e$	(e)
$p + Q_1' \xrightarrow{k_4} 4O_e'$	(f)
$p + Q_1 \xrightarrow{2k_1} 2p_e + 2O_e$	(g)
$p + Q_1 \xrightarrow{k_4} O_e + p_e + 2O_e'$	(h)
(c) Reactions of Q_1 and Q_1' with reactive sites	
$O_e' + Q_1' \xrightarrow{k_1} O_i + 2O_e' - O_e'$	(i)
$O_e' + Q_1 \xrightarrow{k_1} p_e + O_e + O_i - O_e'$	(j)
$O_e + Q_1 \xrightarrow{k_1} p_e + O_e + p_l - p_e$	(k)
$O_e + Q_1' \xrightarrow{k_1} 2O_e' + p_i - p_e$	(l)
$p_i + Q_1 \xrightarrow{k_3} 2O_e' + p_e$	(m)
$p_i + Q_1' \xrightarrow{k_3} 2O_e'$	(n)
$O_i + Q_1' \xrightarrow{k_2} 2O_e'$	(q)
$O_i + Q_1 \xrightarrow{k_2} O_e + p_e$	(r)
$p_e + Q_1 \xrightarrow{k_4} O_i + O_e + p_e - O_e$	(s)
$p_e + Q_1' \xrightarrow{k_4} O_i + 2O_e' - O_e$	(t)

$$\frac{d[Q_1']}{dt} = 2k_4[P][F] - 2k_1 + k_4)[Q_1'][P] - [Q_1']\{k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - 4k_1[Q_1']^2 - (3k_1 + k_4)[Q_1][Q_1'] - 2k_1[Q_1'][\mathrm{CH_2OH}] \qquad (10)$$

$$\frac{d[F]}{dt} = -2[F]\{(2k_1 + k_4)[P] + k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} \qquad (11)$$

$$\frac{d[P]}{dt} = -(2k_1 + k_4)[P]\{[Q_1] + [Q_1'] + 2[F] + [\mathrm{CH_2OH}]\} \qquad (12)$$

MODELLING OF MOLECULAR WEIGHT DISTRIBUTION (*MWD*)

Previous studies[3] have shown that the concentration of bound CH_2OH in the reaction mass is small. In view of this, it is assumed that a polymer molecule in the reaction mass either has one bound CH_2OH or has none at all. In view of this, the growth of polymer molecules can be represented by following reactions:

$$P_n + F \rightarrow Q_n \qquad (13a)$$

$$Q_n + P_m \rightarrow P_{n+m} \quad n,m = 2,3, \ldots \qquad (13b)$$

and

$$Q_n + Q_m \rightarrow Q_{n+m} \quad n,m = 2,3, \ldots \qquad (13c)$$

The reaction between Q_n and Q_m can occur in two ways: (a) reactive sites on Q_n react with ($-CH_2OH$) on Q_m; and (b) reactive sites on Q_m react with ($-CH_2OH$) on Q_n.

If O_{eQ_n}, O'_{eQ_n}, O_{iQ_n}, p_{iQ_n} and p_{eQ_n} are the total number of sites on all Q_n in the reaction mass and O_{eQ_m}, O'_{eQ_m}, O_{iQ_m}, p_{iQ_m}, and p_{eQ_m} on all Q_m in the system, the reaction rate, r_{mn} between Q_n and Q_m can be written as

$$r_{mn} = (k_1 O_{eQ_n} + k_1 O'_{eQ_n} + k_2 O_{iQ_n} + k_3 p_{iQ_n} + k_4 p_{eQ_n})[Q_m] + (k_1 O_{eQ_m} + k_1 O'_{eQ_m} + k_2 O_{iQ_m} + k_3 p_{iQ_m} + k_4 p_{eQ_m})[Q_n] \quad m,n = 3,4 \qquad (14)$$

This equation must be modified when either m or n are equal to 2. This is because polymer molecules of chain length 2 do not have internal sites and the above equation is modified to

$$r_{m2} = (k_1 O_{eQ_m} + k_1 O'_{eQ_m} + k_2 O_{iQ_m} + k_3 p_{iQ_m} + k_4 p_{eQ_m})[Q_2] + (k_1 O_{eQ_2} + k_1 O'_{eQ_2} + k_4 p_{eQ_2})[Q_m] \quad m = 3,4 \qquad (15)$$

In the reaction between Q_n and P_m, the bound CH_2OH of Q_n alone can react with reactive sites of P_m. Thus, the corresponding rate of reaction, r'_{mn}, can be written as

$$r'_{mn} = (k_1 O_{eP_m} + k_1 O_{eP_m} + k_2 O_{iP_m} + k_3 p_{iP_m} + k_4 p_{eP_m})[Q_n] \quad n = 2,3,\ldots;\ m = 3,4,\ldots \qquad (16)$$

When $m = 2$, the above equation must be modified to

$$r'_{2n} = (k_1 O_{eP_2} + k_1 O'_{eP_2} + k_4 p_{eP_2})[Q_n] \quad n = 2,3,\ldots \qquad (17)$$

The fraction of different sites on Q_n is assumed to be the same, on average, as that of the overall average of these in the reaction mass. In other words, for O_{eQ_n},

$O_{eQ_n} \simeq [Q_n]$ (overall fraction of O_e sites on all polymer molecules)

$$= [Q_n] \frac{[O_e]}{\sum_2^{\prime}[P_n] + \sum_2^{\prime}[Q_n]} \qquad (18)$$

Similarly for other reactive sites, one has

$$O'_{eQ_n} = \frac{[O_e'][Q_n]}{SUM} \qquad (19a)$$

$$O_{iQ_n} = \frac{[O_i][Q_n]}{SUM} \qquad (19b)$$

$$p_{iQ_n} = \frac{[p_i][Q_n]}{SUM} \qquad (19c)$$

$$p_{eQ_n} = \frac{[p_e][Q_n]}{SUM} \qquad (19d)$$

where

$$SUM = \left(\sum_2^{\prime}[P_n] + \sum_2^{\prime}[Q_n]\right) \qquad (20)$$

In terms of these, equations (14)–(17) can easily be written as

$$r_{mn} = \frac{2CN}{SUM}[Q_m][Q_n] \qquad (21a)$$

$$r_{m2} = \frac{CN}{SUM}[Q_m][Q_2] + \frac{CM}{SUM}[Q_m][Q_2] \qquad (21b)$$

$$r'_{mn} = \frac{CN}{SUM}[P_m][Q_n] \qquad (21c)$$

$$r'_{2n} = \frac{CM}{SUM}[P_2][Q_m] \qquad (21d)$$

where

$$CN = k_1[O_e] + k_1[O_e'] + k_2[O_i] + k_3[p_i] + k_4[p_e] \qquad (22a)$$

and

$$CM = k_1[O_e] + k_1[O_e'] + k_4[p_e] \qquad (22b)$$

The mass balance of molecular species P_n and Q_n can be carried out as follows. For Q_n, it is noted that it is formed when P_n reacts with formaldehyde and Q_m reacts with Q_{n-m} where m could have any value between 1 and $(n-1)$. Similarly Q_n is reduced, when it reacts with phenol or P_n and Q_m where $m = 2,3,\ldots$ Therefore the balance for batch reactor gives

$$\begin{aligned}\frac{\mathrm{d}[Q_n]}{\mathrm{d}r} = &-(2k_1+k_4)[P][Q_n] - \Big\{CN[Q_n] + \\ &\frac{CN}{SUM}[Q_n]\left(\sum_{m=2}^{\infty}[Q_m]+[Q_1]+[Q'_1]\right)+(2k_1[Q'_1]+ \\ &k_1[Q_1]+k_4[Q'_1])[Q_n]\Big\}+\frac{2CN}{SUM}[F][P_n]+ \\ &\frac{CN}{SUM}\sum_{i=2}^{n-3}[Q_i][Q_{n-i}]+\frac{CN}{SUM}[Q_2][Q_{n-2}]+ \\ &\frac{CN}{SUM}[Q_1][Q_{n-1}]+(k_1+k_4)[Q_1][Q_{n-1}]+ \\ &\frac{CN}{SUM}[Q_{n-1}][Q'_1]+2k_1[Q'_1][Q_{n-1}] \\ &\qquad n\geqslant 4 \end{aligned}\tag{23}$$

and the balances for Q_2 and Q_3 are given by:

$$\begin{aligned}\frac{\mathrm{d}[Q_2]}{\mathrm{d}t} = &(k_1+k_4)[Q_1]^2+3(k_1+k_4)[Q_1][Q'_1]+2k_1[Q_1]^2+ \\ &\frac{2CM}{SUM}[P_2][F]-(2k_1+k_4)[Q_2][P]-CN[Q_2]- \\ &\frac{CM}{SUM}[Q_2]\left(\sum_2^{\infty}[Q_m]+[Q_1]+[Q'_1]\right) \\ &-Q_2(2k_1[Q'_1]+k_1[Q_1]+k_4[Q_1])\end{aligned}\tag{24}$$

and

$$\begin{aligned}\frac{\mathrm{d}[Q_3]}{\mathrm{d}t} = &-(2k_1+k_4)[Q_3][P]-CN[Q_3]- \\ &\frac{CN}{SUM}[Q_3]\left(\sum_2^{\infty}[Q_m]+[Q_1]+(Q'_1]\right)+ \\ &\frac{2CN}{SUM}[P_3][F]+(k_1+k_4)[Q_1][Q_2]+ \\ &2k_1[Q'_1][Q_2]+\frac{CM}{SUM}[Q_2]([Q_1]+[Q'_1])- \\ &(2k_1[Q'_1+k_1[Q_1]+k_4[Q_1])[Q_3]\end{aligned}\tag{25}$$

On summation of equations (24)–(26), one obtains:

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{CH_2OH}]}{\mathrm{d}t} \equiv \frac{\mathrm{d}\sum[Q_n]}{\mathrm{d}t} = &-(2k_1+k_4)[P]\sum_2^{\infty}[Q_n]- \\ &CN\sum_2^{\infty}[Q_n]+\frac{2[F]}{SUM}\left(CN\sum_2^{\infty}[P_n]+CM[P_2]\right)+ \\ &(k_1+k_4)[Q_1]^2+(3k_1+k_4)[Q_1][Q'_1]+ \\ &2k_1[Q_1]^2\end{aligned}\tag{26}$$

A similar mass balance can be made on P_n. It is noted that P_n is formed when P_{n-1} reacts with Q_1 or Q'_1 and P_{n-i} reacts Q_i. It is consumed when it reacts with formaldehyde and any Q_m. The balance gives:

$$\begin{aligned}\frac{\mathrm{d}[P_n]}{\mathrm{d}t} = &\frac{CN}{SUM}[P_{n-1}]([Q_1]+[Q'_1])+ \\ &\sum_{i=2}^{n-3}\frac{CN}{SUM}[P_{n-i}][Q_i]+\frac{CN}{SUM}[P_2][Q_{n-2}]+ \\ &(2k_1+k_4)[P][Q_{n-1}]-\frac{2CN}{SUM}[P_n][F]- \\ &\frac{CN}{SUM}[P_n]\left(\sum_2^{\infty}[Q_m]+[Q_1]+[Q'_1]\right) \qquad n\geqslant 5\end{aligned}\tag{27}$$

The above equation is valid only for $n\geqslant 5$ and therefore balances for P_2, P_3 and P_4 are written as:

$$\begin{aligned}\frac{\mathrm{d}[P_2]}{\mathrm{d}t} = &(2k_1+k_4)[P]([Q_1]+[Q'_1])-\frac{2CM}{SUM}[P_2][F] \\ &-\frac{CM}{SUM}[P_2]\left(\sum_2^{\infty}[Q_m]+[Q_1]+[Q'_1]\right)\end{aligned}\tag{28}$$

$$\begin{aligned}\frac{\mathrm{d}[P_3]}{\mathrm{d}t} = &\frac{CM}{SUM}[P_2]([Q_1]+[Q'_1])+(2k_1+k_4)[P][Q_2]- \\ &\frac{2CN}{SUM}[P_3][F]-\frac{CN}{SUM}[P_3]\left(\sum_2^{\infty}[Q_m]+[Q_1]+[Q'_1]\right)\end{aligned}\tag{29}$$

$$\begin{aligned}\frac{\mathrm{d}[P_4]}{\mathrm{d}t} = &\frac{CN}{SUM}[P_3]([Q_1]+[Q'_1])+\frac{CM}{SUM}[P_2][Q_2]+ \\ &(2k_1+k_4)[P][Q_3]-\frac{2CN}{SUM}[P_4][F]- \\ &\frac{CN}{SUM}[P_4]\left(\sum_2^{\infty}[Q_m]+[Q_1]+[Q'_1]\right)\end{aligned}\tag{30}$$

On summation of equations (27)–30), one obtains:

$$\begin{aligned}\frac{\mathrm{d}\sum_2^{\infty}[P_n]}{\mathrm{d}t} = &(2k_1+k_4)[P]\sum_2^{\infty}[Q_n]+(2k_1+k_4)[P]([Q_1]+ \\ &[Q'_1])-\frac{2[F]}{SUM}\left(CN\sum_3^{\infty}[P_n]+CM[P_2]\right)\end{aligned}\tag{31}$$

When equations (26) and (31) are added, one obtains:

$$\begin{aligned}\frac{\mathrm{d}(SUM)}{\mathrm{d}t} = &(2k_1+k_4)[P]([Q_1]+[Q'_1])+(k_1+k_4)[Q_1]^2 \\ &+3(k_1+k_4)[Q_1][Q'_1]+2k_1[Q'_1]^2-CN\sum_2^{\infty}[Q_n]\end{aligned}\tag{32}$$

To calculate the molecular weight distribution, equations (4)–(12), (26), (28) and (32) must be solved simultaneously and substituted in equations (23) and (27) to obtain $[P_n]$ and $[Q_n]$ as a function of time. These equations are written in dimensionless form using the

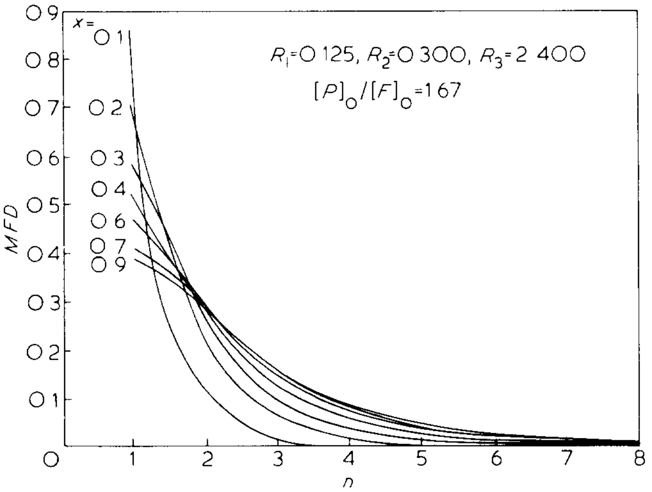


Figure 1 Mol fraction distribution of p_i for different times

following variables:

$$y_1=\frac{[O'_e]}{[F]_0} \qquad (33a)$$

$$y_2=\frac{[O_e]}{[F]_0} \qquad (33b)$$

$$y_3=[O_t]/[F]_0 \qquad (33c)$$

$$y_4=[p_i]/[F]_0 \qquad (33d)$$

$$y_5=[p_e]/[F]_0 \qquad (33e)$$

$$y_6=[Q_1]/[F]_0 \qquad (33f)$$

$$y_7=[Q'_1]/[F]_0 \qquad (33g)$$

$$y_8=[F]/[F]_0 \qquad (33h)$$

$$y_9=[P]/[F]_0 \qquad (33i)$$

$$y_{10}=[\mathrm{CH_2OH}]/[F]_0 \qquad (33j)$$

$$y_{11}=[P_2]/[F]_0 \qquad (33k)$$

$$y_{12}=\sum_{2}^{i}[P_n]/[F]_0 \qquad (33l)$$

$$y_{13}=SUM/[F]_0 \qquad (33m)$$

$$x=k_1[F]_0t \qquad (33n)$$

$$y_{P_i}=[P_i]/[F]_0 \quad i=3,4,\ldots \qquad (33o)$$

$$y_{Q_i}=[Q_i]/[F]_0 \quad i=2,3,\ldots \qquad (33p)$$

$$R_1=(k_2/k_1) \qquad (33q)$$

$$R_2=(k_3/k_1) \qquad (33r)$$

$$R_3=(k_4/k_1) \qquad (33s)$$

The mole fraction distributions $MFD\ P_i$ and $MFD\ Q_i$ of species P_i and Q_i respectively have been obtained from:

$$MFD\,P_i=\frac{[P_i]}{\sum_{i=2}^{i}[P_i]+[P]} \quad i=1,2,3,\ldots \qquad (34a)$$

and

$$MFD\,Q_i=\frac{[Q_i]}{\sum_{i=1}^{\infty}[Q_i]+[Q'_1]} \quad i=1,2,\ldots \qquad (34b)$$

In the above equation for $i=1$ in $MFD\ Q_i$, $[Q_{1,i}]$ equal to $([Q_1]+[Q'_1])$ has been used in the calculation. As opposed to this, in the weight fraction distributions, $WFD\ P_i$ and $WFD\ Q_i$ of P_i and Q_i, the total weight of the reaction mass at the time of interest has been made as the basis:

$$WFD\,P_i=\frac{WP_i}{\sum_{i=2}^{i}WP_i+\sum_{i=1}^{i}WQ_i+WP+WQ'_1} \qquad (35a)$$

$$WFD\,Q_i=\frac{WQ_i}{\sum_{i=2}^{i}WP_i+\sum_{i=1}^{i}WQ_i+WP+WQ'_1} \qquad (35b)$$

where WP_i, WQ_i, WP and WQ'_1 are the weights of species P_i, Q_i, P and Q'_1 respectively.

RESULTS

Equations (4)–(12), (26), 28) and (32) have been solved using the Runge–Kutta method of order IV. The value of Δx was changed and stable solutions were obtained for Δx as 10^{-4}. For $R_1=0.125$, $R_2=0.300$ and $R_3=2.400$ (experimental quantities[1]) $[P_i]$ and $[Q_i]$ have been calculated and the mol fraction distribution shown in *Figures 1* and *2* for different times of reaction x. *Figures 1* and *2* show that they decrease monotonically and the mol fraction of P_9 (or Q_9) and beyond is essentially zero. As time increases, the mol fraction distribution becomes broader and broader. The weight fraction distribution was similarly calculated from the knowledge of P_i and Q_i and it was found that they do not undergo a maximum in contrast to what is predicted by the Flory's equation which is valid when the equal reactivity hypothesis holds[2].

In the kinetic model presented in this work, the molecular weight distribution is found to depend upon four parameters: R_1, R_2, R_3 and $[P]_0/[F]_0$. In *Figure 3*, the effect of R_3 on the mol fraction distribution of P_i for a given $x=(=0.802)$ has been examined. In this plot, $i=1$ corresponds to phenol and a maximum at $i=2$ appears for values of R_3 greater than 5. As R_3 increases, the reaction at the *para* position becomes preferential giving P_2 of the

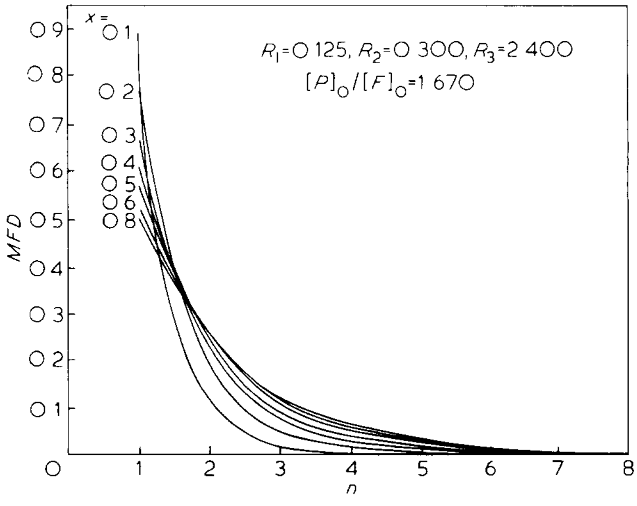


Figure 2 Mol fraction distribution of Q_i for different times. $(Q_1+Q'_1)$ has been reported at $i=1$ times

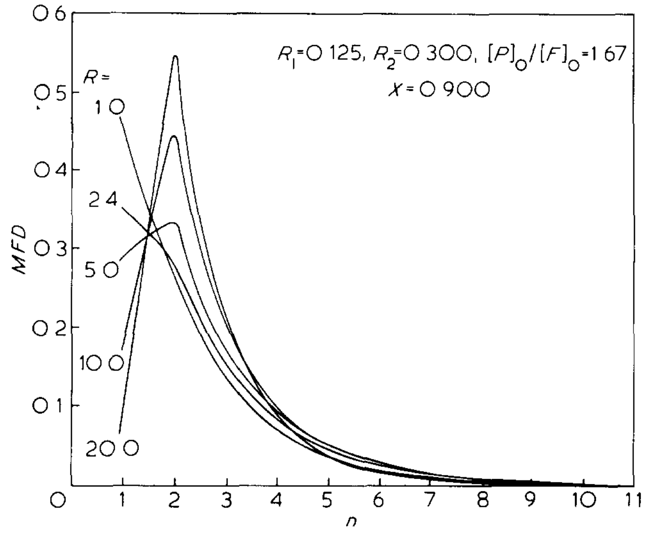


Figure 3 Effect of R_3 upon mol fraction distribution of p_j at x = 0.802

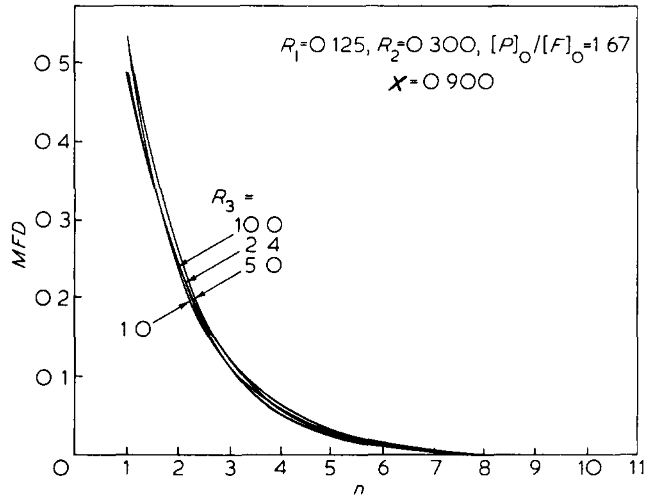


Figure 4 Effect of R_3 upon mol fraction distribution of Q_j at X = 0.802

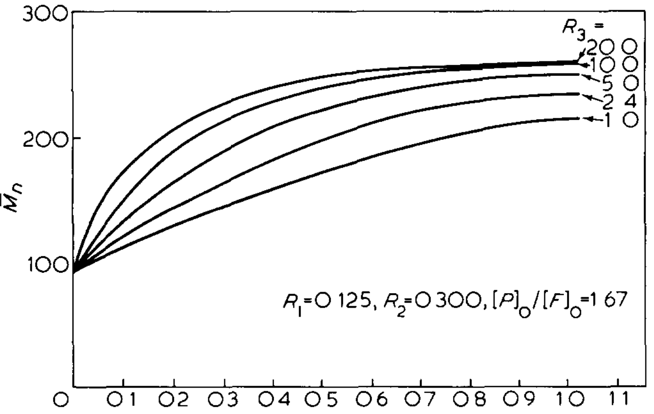
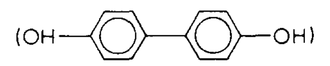


Figure 5 Effect of R_3 upon the number average molecular weight as a function of time

molecular structure (OH——OH) in a higher concentration as shown in *Figure 3*. *Figure 4* gives the distribution of Q_i for $x = 0.90$ and surprisingly no such maximum is found. The distribution of these becomes sharper and sharper as R_3 is increased.

In the calculation of the number ($\bar{M}_n$) and weight ($\bar{M}_w$) average molecular weights, P_t and Q_t have been combined. The effect of R_3 upon $\bar{M}_n$ and $\bar{M}_w$ have been examined in *Figures 5* and *6* respectively. $\bar{M}_n$ in *Figure 5* increases sharply for small x, but considerably slowly later on. The asymptotic value reached is found to increase as R_3 is increased. As opposed to this, the asymptotic value of $\bar{M}_w$ in *Figure 6* increases first and for values of R_3 beyond 5, it starts decreasing. This can be explained by carefully examining *Figures 3* and *4*. The distribution of P_t broadens first for R_3 between 1 and 5 but for values beyond 5, becomes very sharp. As seen from *Figure 4*, the distribution of Q_t remains fairly unchanged for variation in R_3. This implies that the overall polydispersity first increases and then falls with increasing R_3 which is indeed what is reflected in the behaviour of $\bar{M}_w$ for large time periods.

The effect of $[P]_0/[F]_0$ on the *MFD* of P_i and Q_i has been examined in *Figures 7* and *8*. In *Figure 7*, as this ratio is increased from 0.5, the *MWD* of P_i broadens slightly

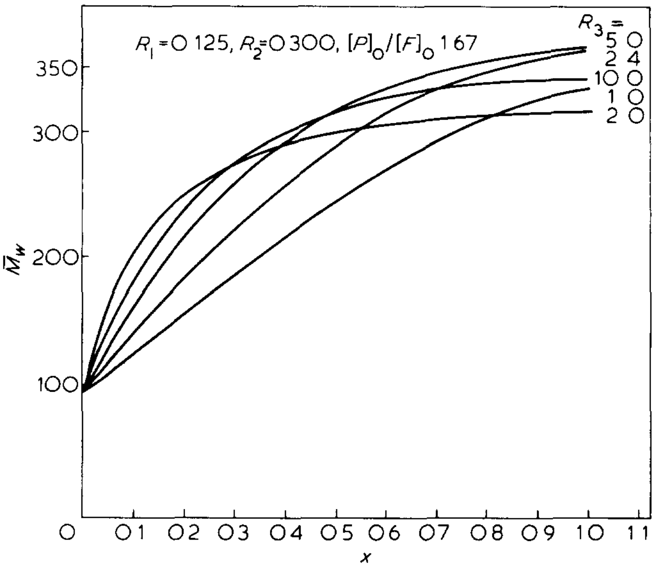


Figure 6 Effect of R_3 upon the weight average molecular weight as a function of time

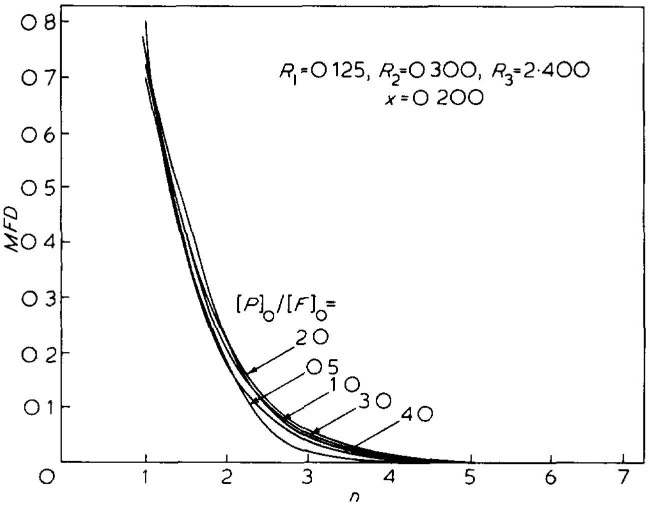


Figure 7 Effects of $[P]_0/[F]_0$ upon mol fraction distribution of p_i for x = 0.200

and for values greater than 1.75, it once again becomes sharp. For $[P]_0/[F]_0$ beyond 3, the dimer is preferentially formed as shown in *Figure 7*. The broadening occurs because the increase in total number of sites would lead to increased polymerization rate in the reactor thus giving the production of larger chains. This would give rise to a broader *MWD*. However, as $[P]_0/[F]_0$ is increased beyond a certain value the curves start becoming sharper because of the reduced formaldehyde concentration in the reaction mass and for values more than 3, dimers are formed in large quantities as seen in *Figure 7*. Similar behaviour, of the first broadening and then becoming sharper later on, is found for Q_i in *Figure 8* as $[P]_0/[F]_0$ is increased. These curves, however, do not give a maximum at $i=2$.

R_1 and R_2 were systematically varied and their effects upon the *MFD*'s of P_i and Q_i examined. *Table 3* gives the variation of *MFD* of P_i for $x=0.802$ due to changes in R_1 and the results confirm the lower sensitivity of *MFD* to this parameter. The dimensionless forms of equations (5) and (6) are

$$\frac{dy_3}{dx}=(-R_1y_3+R_3y_5+y_1)(y_6+y_7+y_8+y_{10}) \quad (36a)$$

and $$\frac{dy_4}{dx}=(y_2-R_2y_4)(y_6+y_7+y_8+y_{10}) \quad (36b)$$

For shorter times, polymer chain lengths are small and for large times $(y_6+y_7+y_8+y_{10})$ is depleted due to polymerization. As a result, y_3 and y_4 remain small for all the time in the reaction mass. Consequently, their contribution to the molecular weight distribution remains small.

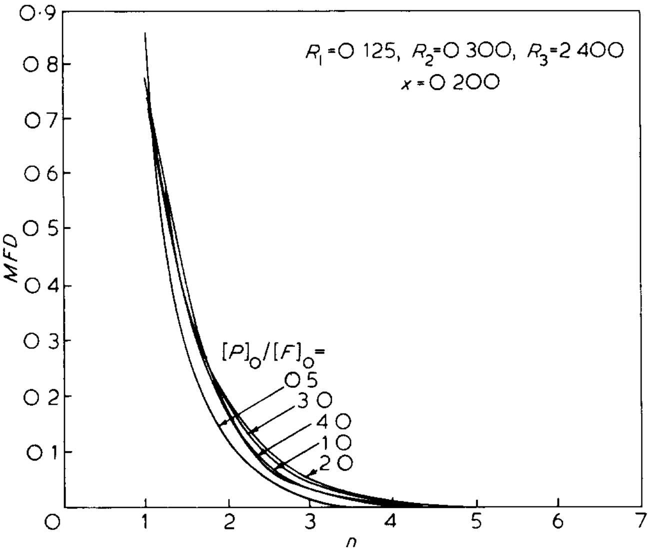


Figure 8 Effect of $[P]_0/[F]_0$ upon mol fraction distribution of Q_i for $x = 0.200$

CONCLUSIONS

There are two kinds of species in the reaction mass of novolac type phenol-formaldehyde polymerization:

(a) molecular species P_i which does not contain any bound formaldehyde (–CH_2OH): and

(b) molecular species Q_i which has bound formaldehyde.

A given molecule of Q_i is assumed to have no more than one bound CH_2OH, the assumption justified from our earlier studies[3]. The molecular weight distribution for batch reactors has been modelled and solved numerically.

The model involves four parameters, R_1, R_2, R_3 and $[P]_0/[F]_0$ and the sensitivity analysis reveals that among these, the *MWD* is extremely sensitive to R_3 and $[P]_0/[F]_0$. As R_3 is increased, the mol fraction distribution of P_i undergoes a maximum at $i=2$ for large time because the *para* positions of phenol preferentially react to form dimers. As $[P]_0/[F]_0$ ratio is increased the distribution of P_i is found to broaden first but then becomes sharper for higher values. The broadening occurs because the increasing number of sites increases the polymerization rate thus giving the formation of higher oligomers. These curves subsequently become sharper because the formaldehyde concentration has reduced considerably in the reaction mass and dimers are preferentially formed giving a maximum in the *MWD* at $i=2$. The *MWD* for Q_i behaves similarly except that it does not have a maximum for any $[P]_0/[F]_0$ ratio.

The *MWD* results are found to be less sensitive to the variations of R_1 and R_2. This is because chain lengths of polymer molecules are small and consequently there is small number of internal sites in the reaction mass. As a result, their contribution to the *MWD* is small.

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Table 3 Effects of R_1 on the mol fraction of P_n for $R_2 = 0.30$, $R_3 = 2.41$, $X = 0.802$, $\frac{[P]_0}{[F]_0} = 1.67$

R_1	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9
0.05	0.2725	0.2012	0.1099	0.0583	0.0309	0.0163	0.0086	0.0045	0.0024
0.15	0.2741	0.2012	0.1092	0.0581	0.0308	0.0163	0.0086	0.0046	0.0024
0.25	0.2756	0.2013	0.1084	0.0580	0.0308	0.0163	0.0087	0.0046	0.0024
0.35	0.2771	0.2014	0.1077	0.0576	0.0307	0.0163	0.0087	0.0046	0.0024
0.50	0.2793	0.2014	0.1066	0.0573	0.0306	0.0164	0.0087	0.0046	0.0025
0.80	0.2835	0.2016	0.1047	0.0566	0.0305	0.0164	0.0088	0.0047	0.0025