Modelling of phenol—formaldehyde polymerization reaction

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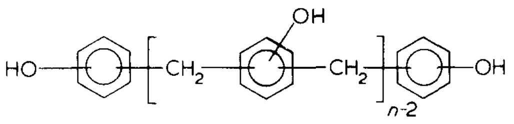
In the condensation polymerization of phenol and formaldehyde, the *ortho* and *para* positions exhibit different reactivities. In addition, along a polymer chain, internal reactive sites have lower reactivity, possibly due to shielding phenomena[1,2]. A detailed kinetic model for novalac formation has been proposed accounting for all these factors. Five different kinds of reactive sites have been shown to exist on a polymer chain and the reactivity of a given reaction has been assumed to be governed completely by the reactive site involved in it. A mass balance has been written for each site and the equations have been solved numerically to examine the effect of different parameters on the course of the condensation polymerization. The model predicts polymer chains with small levels of branching, which is consistent with experimental observations.

INTRODUCTION

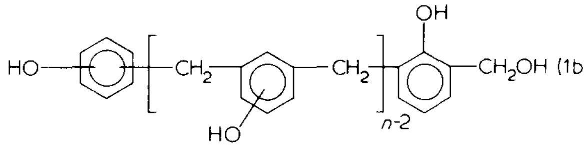
There are several classes of polycondensation reaction which do not obey the equal reactivity hypothesis[1-5]. In these cases, differential equations for the mass balance of each species have to be solved numerically to obtain the conversion, polydispersity index and molecular weight distribution as a function of time. In earlier studies, two simplified models, consistent with experiemntal findings were proposed and the equations solved numerically[3-5]. Results were found to be significantly different from the cases where the equal reactivity hypothesis holds.

The polymerization of phenol and formaldehyde belongs to the class of reactions which do not obey the equal reactivity hypothesis, but a one parameter model is inadequate to describe its kinetics. Even though this is a well-established reaction, there have been very few attempts at the theoretical modelling of the polymerization process[1].

Phenol has three sites, two *ortho* and one *para*, which can undergo chemical reactions. Thus its functionality is three. Formaldehyde exists as HO–CH$_2$–OH in aqueous solution and therefore exhibits a functionality of two. Several experimental studies on novalac polymer have been made[6-9] which have established that the *para* position has a significantly higher reactivity than the *ortho* positions. At any time, the reaction mass consists of the following two kinds of molecular species[1] besides unreacted phenol and formaldehyde:

P_n:


(1a)

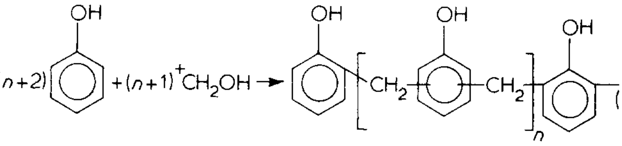
Q_n:


(1b)

Q_n differs from P_n by virtue of the $-CH_2OH$ group.

A study of gelation reveals that the effective functionality of phenol is slightly less than three[1]. In addition, molecular growth is found to occur mainly, though not completely, by the reaction of the end-groups[1]. Based on these observations, Drumm and LeBlanc[1] assume that the reactivity of internal (or branching) sites is less than that of end sites. In fact, they treat the ratio of the reactivities of the internal sites to that of the external sites as a curve-fitting parameter and find that a value of this ratio of about 0.125 explains some of their limited experimental data on molecular weight distributions. A possible explanation for this effect is molecular shielding.

In view of the above discussion, the overall polymerization reaction, written as:



(2)

is a considerably oversimplified representation for any kinetic analysis and a more detailed model is necessary.

In the kinetic model proposed by Drumm and LeBlanc, the reaction is assumed to occur between P_n and F and P_n and Q_m as follows

$$P_n + F \xrightarrow{k_a} Q_n \tag{3a}$$

$$P_n + Q_m \xrightarrow{k_c} P_m + n \tag{3b}$$

where the reaction rate constants k_a and k_c, are taken as proportional to the total number of sites on P_n, suitably weighted to account for the reactivity differences between internal and end sites. Even though chain branching is per-

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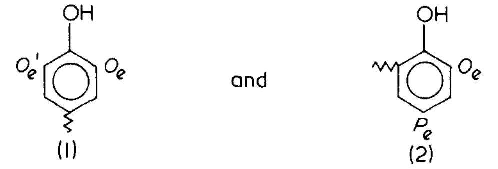
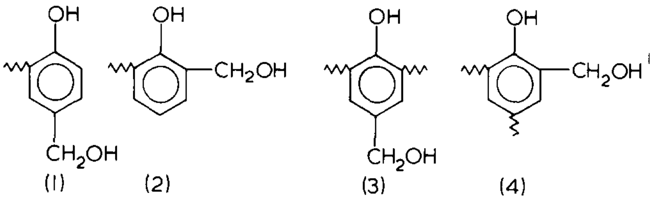
Table 1 Some of the reactions of polymer chains of length greater than 2

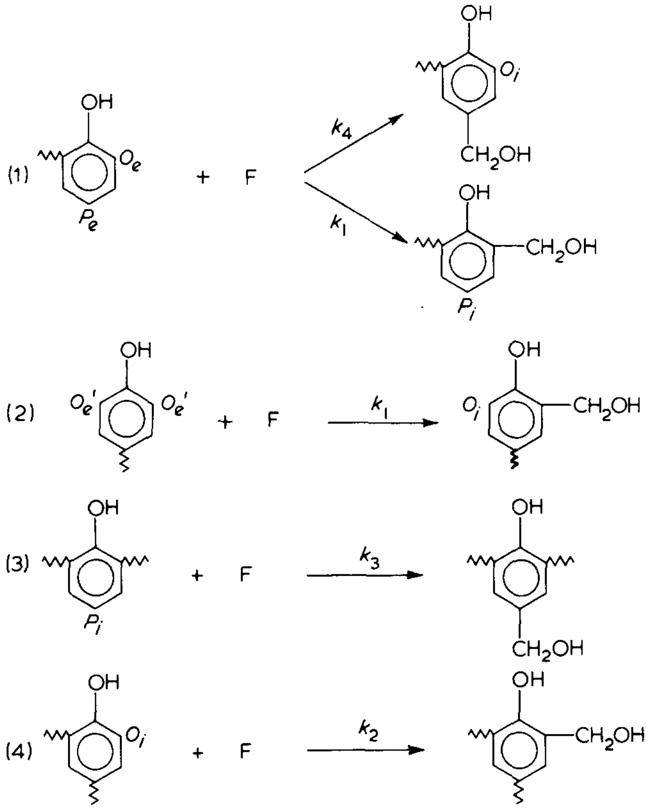
(a) Distinct molecular species having an *ortho* external position



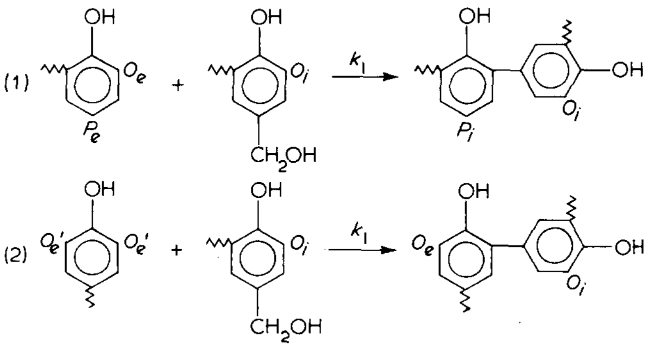
Distinct molecular species having $-CH_2OH$

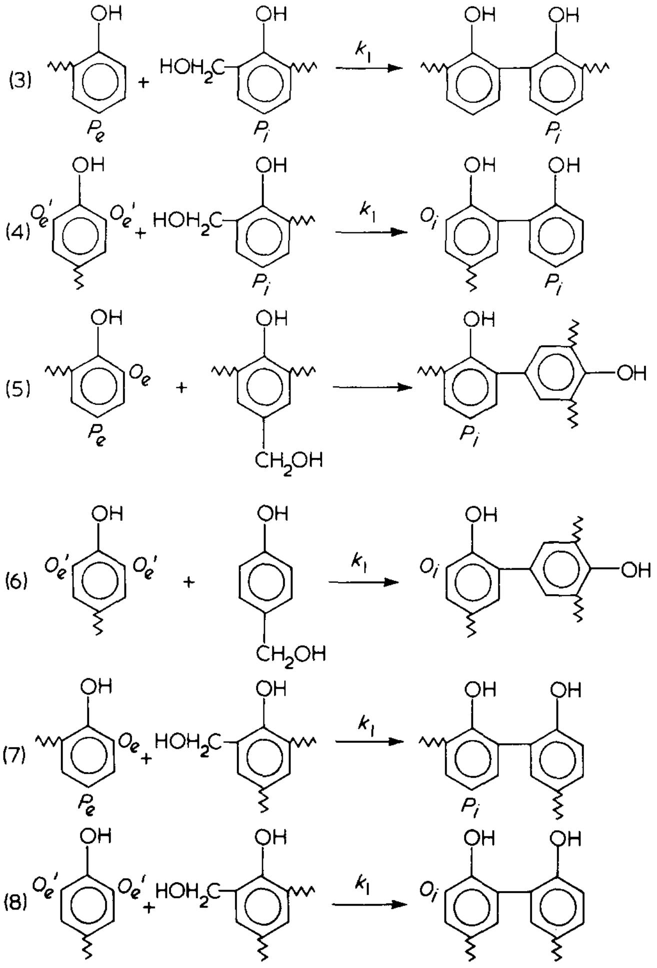


(b) Formation of $-CH_2OH$



(c) Different reactions of O_e and O_e' with $-CH_2OH$





mitted through reaction (3b) in calculating the total number of sites, the chains were assumed linear. In the model, the details of the molecular reactions at the *ortho* and *para* positions have been smeared out by defining overall rate constants k_a and k_c. In addition, $-CH_2OH$ on Q_m can react with a reaction site on Q_n and this has not been accounted for in the model of Drumm and Le Blanc.

The kinetic model developed in the present work relaxes the assumptions of Drumm and LeBlanc and starts from the fact that the *ortho* and *para* positions of a phenyl ring have different reactivities. It builds in all the experimental features of the formation of novalac. It assumes that the external positions have higher reactivity compared to that of the internal ones and also that the *ortho* positions are less reactive than the *para* positions. This is a three parameter model and in this work a sensitivity analysis has been presented to examine the effect of the various parameters on the conversion of the reactive species.

Kinetic model

Polymer chains have been assumed to include all molecules in the reaction mass with length, n, greater than or equal to 2. All the reactive sites situated at chain ends are regarded as external, whereas the remainder are considered internal.

There are four kinds of site along a polymer chain: *para* external (p_e), *para* internal (p_i), ortho internal (O_i) and *ortho* external (O_{eT}) positions. *Table 1a* shows that there are two distinct molecular species carrying an *ortho* external position and these have been denoted as O_e' and O_e, the sum of these being O_{eT}. All these positions can react with formaldehyde (F) as shown in *Table 1b* and are schematically written as:

$$O_e' + \mathrm{F} \xrightarrow{k_1} (\mathrm{-CH_2OH}){-}O_e' + O_i \quad (4a)$$

$$O_e + \mathrm{F} \xrightarrow{k_1} (\mathrm{-CH_2OH}){-}p_e + p_i \quad (4b)$$

$$O_i + \mathrm{F} \xrightarrow{k_2} (\mathrm{-CH_2OH}) \quad (4c)$$

$$p_i + \mathrm{F} \xrightarrow{k_3} (\mathrm{-CH_2OH}) \quad (4d)$$

$$p_e + \mathrm{F} \xrightarrow{k_4} (\mathrm{-CH_2OH}){-}O_e + O_i \quad (4e)$$

In equations (4a), (4b) and (4e), $-O_e'$, $-p_e$ and $-O_e$ represent the fact that the simultaneous loss of these species are associated with the reactions of O_e', O_e and p_e, respectively. ($-$CH$_2$OH) indicates that a formaldehyde molecule is attached to the polymer chain with length equal to or greater than two. There are five distinct molecular species formed due to these reactions as shown in *Table 1b*, but they are not distinguished from each other because the reactivities of all the reactions have been assumed to be entirely governed by reacting sites only.

In *Table 1c*, different reactions of bound formaldehyde with O_e and O_e' are given. There are eight possible reactions. If all polymer chains with bound formaldehyde are represented by ($-$CH$_2$OH) and are not distinguished, then its reaction with different reactive sites can be schematically written as:

$$O_e' + \mathrm{-CH_2OH} \xrightarrow{k_1} O_i - O_e \quad (5a)$$

$$O_e + \mathrm{-CH_2OH} \xrightarrow{k_1} p_i - p_e \quad (5b)$$

$$O_i + \mathrm{-CH_2OH} \xrightarrow{k_2} \text{Consumption} \quad (5c)$$

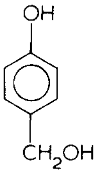
$$p_i + \mathrm{-CH_2OH} \xrightarrow{k_3} \text{Consumption} \quad (5d)$$

$$p_e + \mathrm{-CH_2OH} \xrightarrow{k_4} O_i - O_e \quad (5e)$$

In the above representation, the reactivity of a given reaction is once again assumed to be governed by the reactive sites involved in it. Also, $-O_e'$ in reaction 5a, $-p_e$ in reaction 5b and $-O_e$ in equation 5e imply a simultaneous removal of these sites when an O_e', O_e and p_e undergoes chemical reaction, respectively.

The schematic representation of equation (5), however, is not valid for reactions of phenol. When phenol reacts with formaldehyde, the following two distinct species are formed:

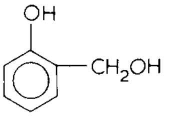
Q_1':



(6a)

(6)

Q_1:



(6b)

Reactions of Q_1' and Q_1 are also not included in equation (5) and should be accounted for separately. *Table 2* gives all the possible reactions of phenol (P), Q_1 and Q_1' with different reactive sites and F and with its help, the following schematic reactions are written.

(a) Reactions of P with F and $-$CH$_2$OH

$$\mathrm{P} + \mathrm{F} \xrightarrow{2k_1} \mathrm{Q_1} \quad (7)$$

$$\mathrm{P} + \mathrm{F} \xrightarrow{k_4} \mathrm{Q_1'} \quad (8)$$

$$\mathrm{P} + \mathrm{-CH_2OH} \xrightarrow{2k_1} p_e + O_e \quad (9)$$

$$\mathrm{P} + \mathrm{-CH_2OH} \xrightarrow{k_4} 2O_e' \quad (10)$$

(b) Reactions of P with Q_1 and Q_1'

$$\mathrm{P} + \mathrm{Q_1'} \xrightarrow{2k_1} p_e + 2O_e' + O_e \quad (11)$$

$$\mathrm{P} + \mathrm{Q_1'} \xrightarrow{k_4} 4O_e' \quad (12)$$

$$\mathrm{P} + \mathrm{Q_1} \xrightarrow{2k_1} 2p_e + 2O_e \quad (13)$$

$$\mathrm{P} + \mathrm{Q_1} \xrightarrow{k_4} O_e + p_e + 2O_e' \quad (14)$$

(c) Reactions of Q_1 and Q_1' with reactive sites

$$O_e' + \mathrm{Q_1'} \xrightarrow{k_1} O_i + 2O_e' - O_e' \quad (15)$$

$$O_e' + \mathrm{Q_1} \xrightarrow{k_1} p_e + O_e + O_i - O_e' \quad (16)$$

$$O_e + \mathrm{Q_1} \xrightarrow{k_1} p_e + O_e + p_i - p_e \quad (17)$$

$$O_e + \mathrm{Q_1'} \xrightarrow{k_1} 2O_e' + p_i - p_e \quad (18)$$

$$p_i + \mathrm{Q_1} \xrightarrow{k_3} O_e + p_e \quad (19)$$

$$p_i + \mathrm{Q_1'} \xrightarrow{k_3} 2O_e' \quad (20)$$

$$O_i + \mathrm{Q_1'} \xrightarrow{k_2} 2O_e' \quad (21)$$

$$O_i + \mathrm{Q_1} \xrightarrow{k_2} O_e + p_e \quad (22)$$

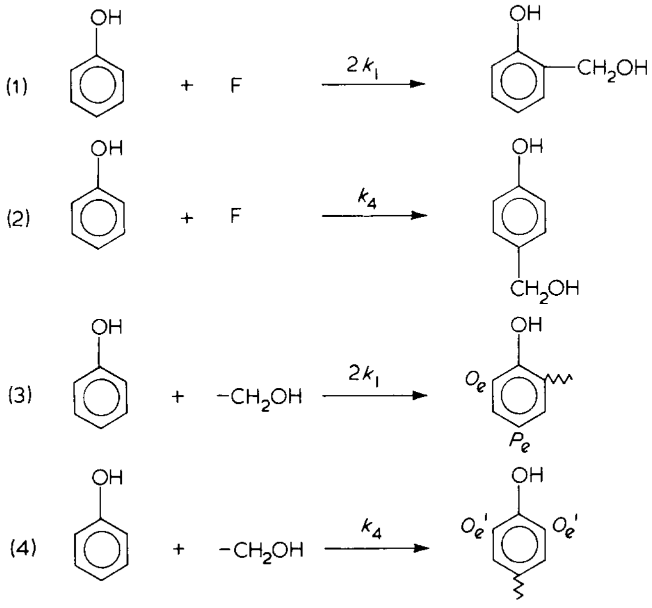
$$p_e + \mathrm{Q_1} \xrightarrow{k_4} O_i + O_e + p_e - O_e \quad (23)$$

$$p_e + \mathrm{Q_1'} \xrightarrow{k_4} O_i + 2O_e' - O_e \quad (24)$$

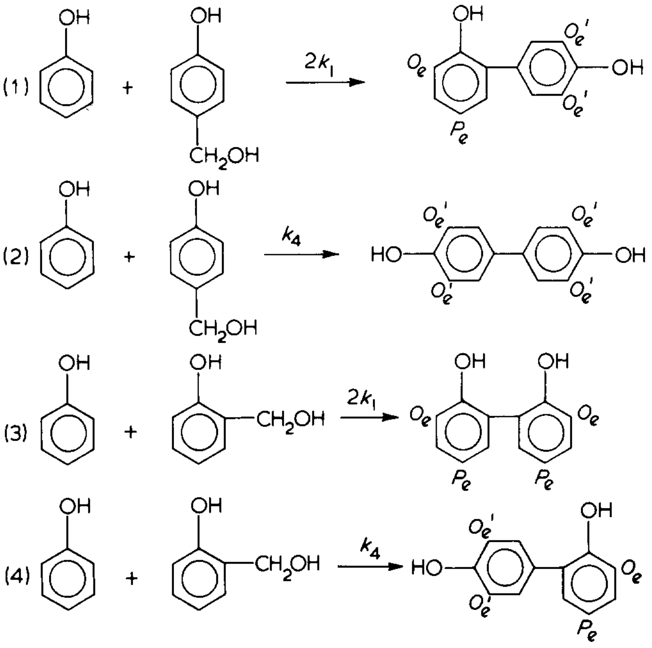
While considering the reactivity of the molecular species P in equation (9), it is noted that it has two *ortho* positions and therefore would react twice as fast. The rate constant for this reaction has been written as $2k_1$. In the scheme

Table 2 Reactions of phenol, Q_1 and Q_1' with F and $-CH_2OH$

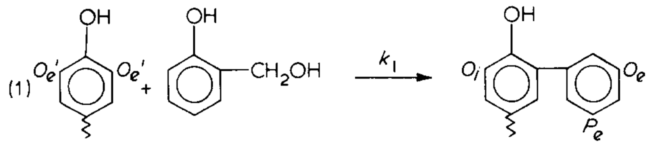
(a) Reaction of phenol (P) with F and $-CH_2OH$

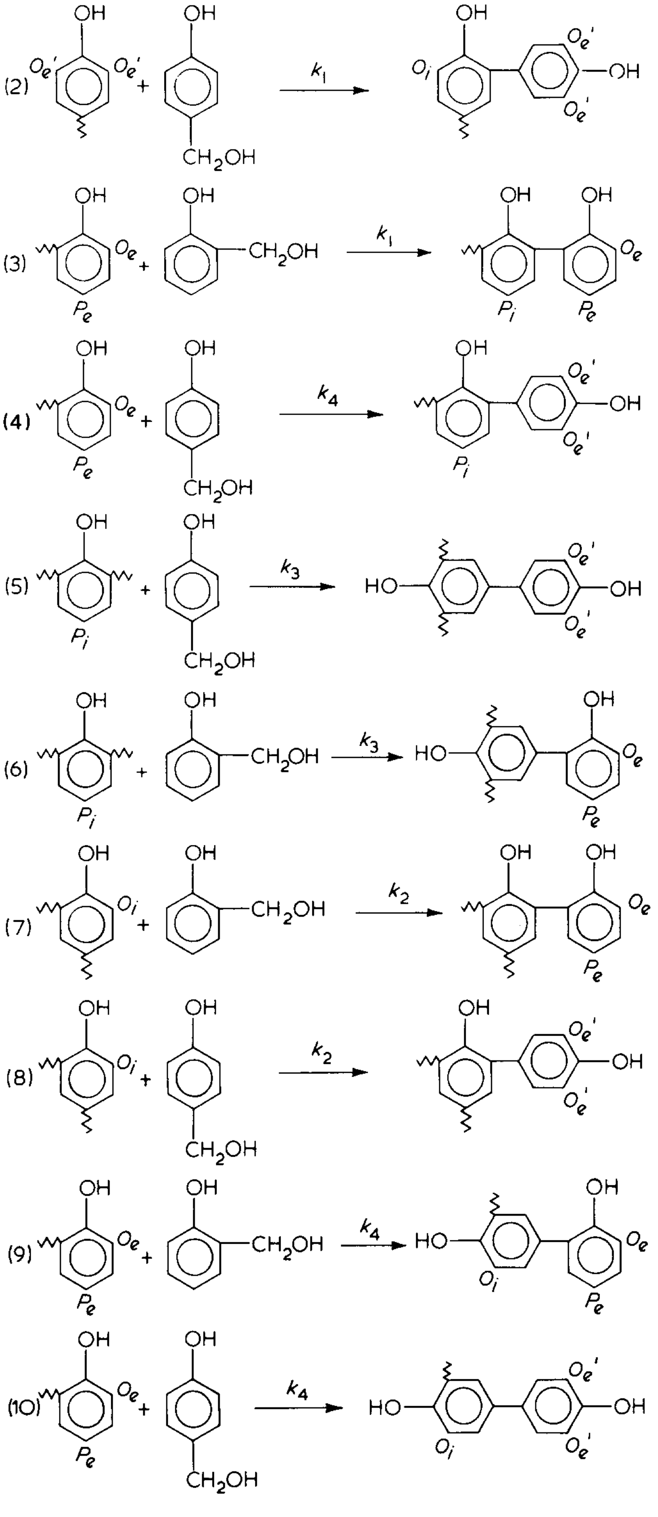


(b) Reaction of P with Q_1 and Q_1'



(c) Reactions of Q_1 and Q_1' with O_e', O_e, O_i, p_i and p_e





above, the reactions between Q_1 and Q_1' have been neglected

In the reaction mass there are ten molecular species, O_e', O_e, O_i, p_i, p_e, P, F, Q_1, Q_1' and $-CH_2OH$; a mass balance of each of these is written to obtain equations (25)–(34):

$$\frac{d[O_e']}{dt} = -k_1[O_e'][F] - k_1[-CH_2OH][O_e'] + 2k_4[P][-CH_2OH] + 4k_1[P][Q_1'] + 2k_4[P][Q_1] + 4k_4[P][Q_1']$$
$$+ k_1[O_e'][Q_1'] + 2k_1[O_e][Q_1'] + 2k_4[p_e][Q_1'] + 2k_2[O_i][Q_1'] + 2k_3[p_i][Q_1'] - k_1[O_e'][Q_1] - k_1[O_i'][F]$$
$$- k_1[-CH_2OH][O_e'] - k_1[O_e'][Q_1'] - k_1[O_e'][Q_1] \qquad (25)$$

$$\frac{\mathrm{d}[O_e]}{\mathrm{d}t} = -k_1[O_e][\mathrm{F}] - k_1[O_e][-\mathrm{CH_2OH}] + 2k_1[\mathrm{P}][-\mathrm{CH_2OH}] + 4k_1[\mathrm{P}][\mathrm{Q_1}] + 2k_1[\mathrm{P}][\mathrm{Q_1'}] + k_4[\mathrm{P}][\mathrm{Q_1}]$$
$$+ k_1[O_e'][\mathrm{Q_1}] - k_1[O_e][\mathrm{Q_1'}] + k_4[p_e][\mathrm{Q_1}] + k_2[O_i][\mathrm{Q_1}] + k_3[p_i][\mathrm{Q_1}] - k_4[p_e][\mathrm{F}] - k_4[p_e][-\mathrm{CH_2OH}]$$
$$- k_4[p_e][\mathrm{Q_1'}] - k_4[p_e][\mathrm{Q_1}] \tag{26}$$

$$\frac{\mathrm{d}[O_i]}{\mathrm{d}t} = k_1[O_e'][\mathrm{F}] - k_2[O_i][\mathrm{F}] + k_4[p_e][\mathrm{F}] + k_1[O_e'][-\mathrm{CH_2OH}] - k_2[O_i][-\mathrm{CH_2OH}] + k_4[p_e][-\mathrm{CH_2OH}]$$
$$+ k_1[O_e'][\mathrm{Q_1'}] + k_1[O_e'][\mathrm{Q_1}] + k_4[p_e][\mathrm{Q_1'}] + k_4[p_e][\mathrm{Q_1}] - k_2[O_i][\mathrm{Q_1'}] - k_2[O_i][\mathrm{Q_1}] \tag{27}$$

$$\frac{\mathrm{d}[p_i]}{\mathrm{d}t} = k_1[O_e][\mathrm{F}] - k_3[p_i][\mathrm{F}] + k_1[O_e][-\mathrm{CH_2OH}] - k_3[p_i][-\mathrm{CH_2OH}] + k_1[O_e][\mathrm{Q_1'}] + k_1[O_e][\mathrm{Q_1}] -$$
$$- k_3[p_i][\mathrm{Q_1'}] - k_3[p_i][\mathrm{Q_1}] \tag{28}$$

$$\frac{\mathrm{d}[p_e]}{\mathrm{d}t} = -k_4[p_e][\mathrm{F}] - k_4[p_e][-\mathrm{CH_2OH}] + 2k_1[\mathrm{P}][-\mathrm{CH_2OH}] + 4k_1[\mathrm{P}][\mathrm{Q_1}] + 2k_1[\mathrm{P}][\mathrm{Q_1'}] + k_4[\mathrm{P}][\mathrm{Q_1}]$$
$$+ k_1[O_e'][\mathrm{Q_1}] + k_1[O_e][\mathrm{Q_1}] - k_4[p_e][\mathrm{Q_1'}] + k_2[O_i][\mathrm{Q_1}] + k_3[p_i][\mathrm{Q_1}] - k_1[O_e][\mathrm{F}] - k_1[O_e][-\mathrm{CH_2OH}]$$
$$- k_1[O_e][\mathrm{Q_1'}] - k_1[O_e][\mathrm{Q_1}] \tag{29}$$

$$\frac{\mathrm{d}[Q_1']}{\mathrm{d}t} = k_4[\mathrm{P}][\mathrm{F}] - 2k_1[\mathrm{P}][\mathrm{Q_1'}] - \{k_1[O_e'] + k_1[O_e] + k_4[p_e] + k_2[O_i] + k_3[p_i]\}[\mathrm{Q_1'}] - k_4[\mathrm{P}][\mathrm{Q_1'}] \tag{30}$$

$$\frac{\mathrm{d}[\mathrm{Q_1}]}{\mathrm{d}t} = 2k_1[\mathrm{P}][\mathrm{F}] - 2k_1[\mathrm{P}][\mathrm{Q_1}] - k_4[\mathrm{P}][\mathrm{Q_1}] - \{k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\}[\mathrm{Q_1}] \tag{31}$$

$$\frac{\mathrm{d}[\mathrm{F}]}{\mathrm{d}t} = -2k_1[\mathrm{P}][\mathrm{F}] - k_4[\mathrm{P}][\mathrm{F}] - \{k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\}[\mathrm{F}] \tag{32}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = -2k_1[\mathrm{P}][\mathrm{F}] - k_4[\mathrm{P}][\mathrm{F}] - (2k_1 + k_4)[\mathrm{P}][-\mathrm{CH_2OH}] - \{2k_1[\mathrm{Q_1}] + 2k_1[\mathrm{Q_1'}] + k_4[\mathrm{Q_1}] + k_4[\mathrm{Q_1'}]\}[\mathrm{P}] \tag{33}$$

$$\frac{\mathrm{d}[-\mathrm{CH_2OH}]}{\mathrm{d}t} = [\mathrm{F}]\{k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - [-\mathrm{CH_2OH}]\{k_1[O_e'] + k_1[O_e] + k_2[O_i]$$
$$+ k_3[p_i] + k_4[p_e]\} - (k_4 + 2k_1)[\mathrm{P}][-\mathrm{CH_2OH}] \tag{34}$$

Equations (25) to (34) can be rearranged and written in terms of the following dimensionless groups:

$$x = k_1 t[\mathrm{F}]_0 \tag{35}$$

$$R_1 = k_2/k_1,\ R_2 = k_3/k_1 \text{ and } R_3 = k_4/k_1 \tag{36}$$

$$y_1 = [O_e']/[\mathrm{F}]_0 \tag{37}$$

$$y_2 = [O_e]/[\mathrm{F}]_0 \tag{38}$$

$$y_3 = [O_i]/[\mathrm{F}]_0 \tag{39}$$

$$y_4 = [p_i]/[\mathrm{F}]_0 \tag{40}$$

$$y_5 = [p_e]/[\mathrm{F}]_0 \tag{41}$$

$$y_6 = [\mathrm{Q_1}]/[\mathrm{F}]_0 \tag{42}$$

$$y_7 = [\mathrm{Q_1'}]/[\mathrm{F}]_0 \tag{43}$$

$$y_8 = [\mathrm{F}]/[\mathrm{F}]_0 \tag{44}$$

$$y_9 = [\mathrm{P}]/[\mathrm{F}]_0 \tag{45}$$

$$\text{and } y_{10} = [-\mathrm{CH_2OH}]/[\mathrm{F}]_0 \tag{46}$$

Equations (25) to (34) are coupled differential equations and are solved using the Runge–Kutta method of fourth order with Δx as 10^{-3}.

RESULTS AND DISCUSSION

Equations (25) to (34) were solved numerically using the Runge–Kutta 4th order technique as a function of x with R_1, R_2, R_3 and $[\mathrm{P}]_0/[\mathrm{F}]_0$ as parameters. The value of the increment, Δx, was adjusted numerically until stable solutions were obtained.

Among the different parameters studied, R_3 was found to be the most important one. *Figures 1* to *6* give $(y_1 + y_2)$,

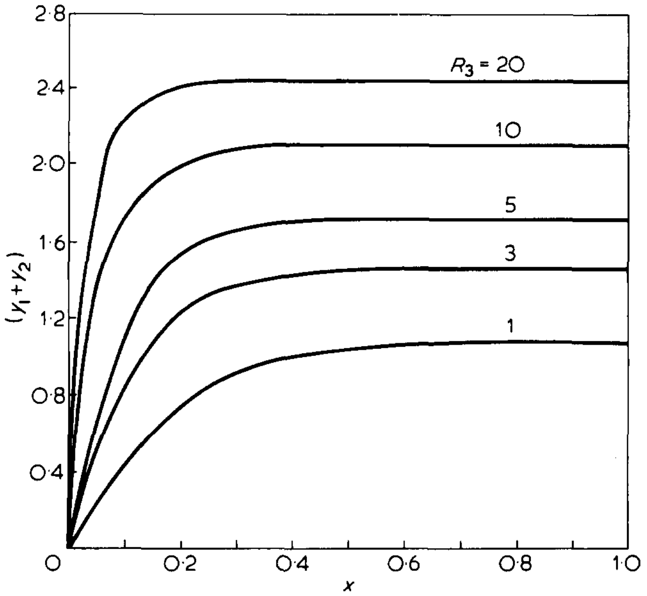


Figure 1 $(y_1 + y_2)$ as a function of x with R_3 as parameter. (R_1 = 0.125, R_2 = 0.30 and $[P]_0/[F]_0$ = 1.67)

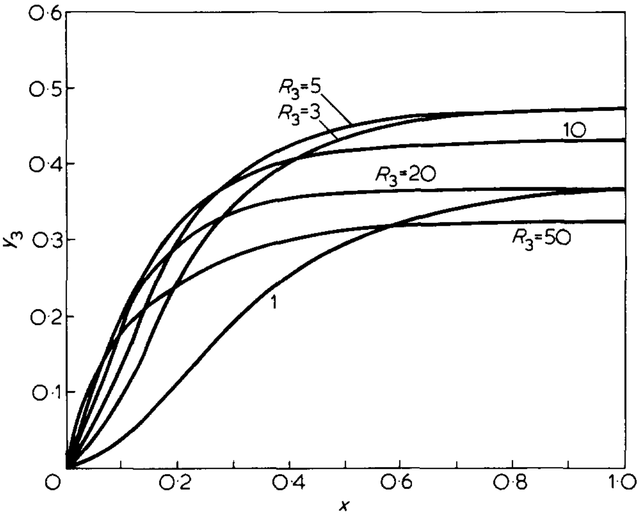
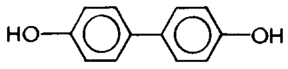


Figure 2 y_3 as a function of x with R_3 as parameter (R_1 = 0.125, R_2 = 0.30 and $[P]_0/[F]_0$ = 1.67)

y_3, y_4, y_5, y_8 and y_9 as a function of x for different values of R_3. In these, $[P]_0/[F]_0$, R_1 and R_2 were taken as 1.67, 0.125 and 0.30, respectively, as used in ref 1.

Figure 1 gives the total number of *ortho* positions in the reaction mass and it is found to increase rapidly with x, reaching an asymptotic value which increases as R_3 increases. In addition, as the value of R_3 increases, the asymptotic values of $(y_1 + y_2)$ are reached in shorter and shorter times. Calculations also show that y_1 becomes larger than y_2. This result is expected because preferential reaction of p_e would mean that several short chains are formed instead of fewer large molecules. This would give a higher concentration of external *ortho* positions.

Figures 2 and *3* give the concentrations of O_i and p_i with time. As found for $(y_1 + y_2)$, y_3 also first increases rapidly, but for large x it attains an asymptotic value, $y_{3,\mathrm{asy}}$. As R_3 increases, $y_{3,\mathrm{asy}}$ first increases but for $R_3 > 3$, begins to fall; this is explained as follows. For $R_3 < 3$, *para* positions react preferentially as R_3 increases leading to an increase in *ortho* internal positions and a corresponding decrease in *para* internal positions (*Figure 3*). However, as R_3 is increased further, polymer chains have fewer *para* external positions thus leading to their reduced capability of further reaction. As the phenol molecule has *para* external, increasing R_3 would imply its preferential reaction and ultimately lead to complete elimination of reactions (4a), (5a), (15) and (16). In the limit as R_3 tends to a large value, only dimers would be formed with the molecular structure



in which case y_3 would be zero.

Figures 4, 5 and *6* give the concentration of *para* external positions, formaldehyde and phenol as a function of time. y_5 reaches an asymptotic value for large x for a given R_3;

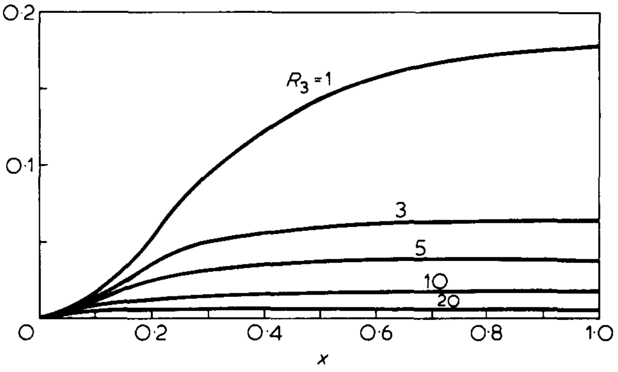


Figure 3 y_4 as a function of x with R_3 as parameter (R_1 = 0.125, R_2 = 0.30 and $[P]_0/[F]_0$ = 1.67)

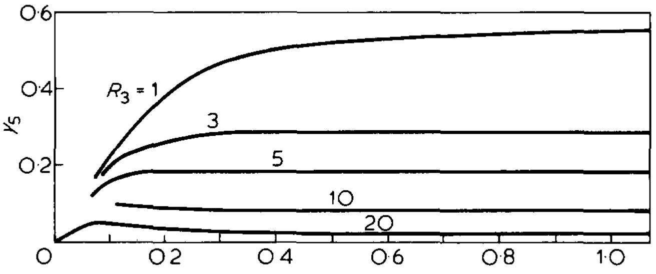


Figure 4 y_5 as a function of x with R_3 as parameter (R_1 = 0.125, R_2 = 0.30 and $[P]_0/[F]_0$ = 1.67)

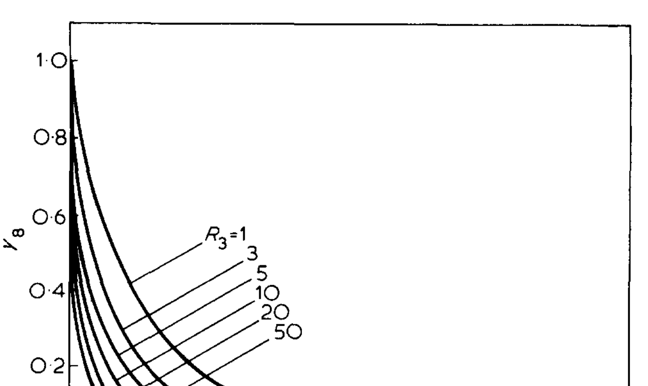


Figure 5 y_8 as a function of x with R_3 as parameter (R_1 = 0.125, R_2 = 0.30 and $[P]_0/[F]_0$ = 1.67)

however, its terminal value monotonically reduces as R_3 increases. *Figure 5* gives y_8 and the different curves start from unity and approach zero for large x. This approach becomes sharper and sharper as R_3 increases in value. This is also expected physically because as the reactivity of the *para* external position increases, formaldehyde is being consumed at higher rates. Similarly in *Figure 6*, y_9 has been plotted and it is found that its asymptotic value is not zero. This indicates that a large quantity of unreacted phenol remains in the reaction mass and this reduces as R_3 increases. As has been explained earlier, preferential reaction at the *para* external positions gives polymer molecules of lower chain length. Due to the fact that these polymer molecules have fewer *para* external positions, phenol molecules become more preferred sites of chemical reaction. In view of this, the terminal value of y_9 reduces as R_3 increases, as observed in *Figure 6*.

Subsequently, numerical results were generated for different R_1 and R_2 with R_3 fixed at the value of 2.4 (the value reported in the literature[1]). Shapes of the curves obtained for $(y_1 + y_2)$, y_3, y_4, y_5, y_8 and y_9 remain exactly the same as shown in *Figures 1* to *6*; the conclusion is reached that the results are insensitive to parameters R_1 and R_2. In generating *Table 3*, R_1 was varied from 0.05 to 1 with R_2 and R_3 fixed at values of 0.30 and 2.4, respectively. Asymptotic values of y_1 to y_5, y_8 and y_9 have been given and it is observed that they are little affected by the variation of R_1. Similar results were obtained when R_1 and R_3 were fixed and R_2 varied. This behaviour is explained as follows. The dimensionless forms of equations (27) and (28) are:

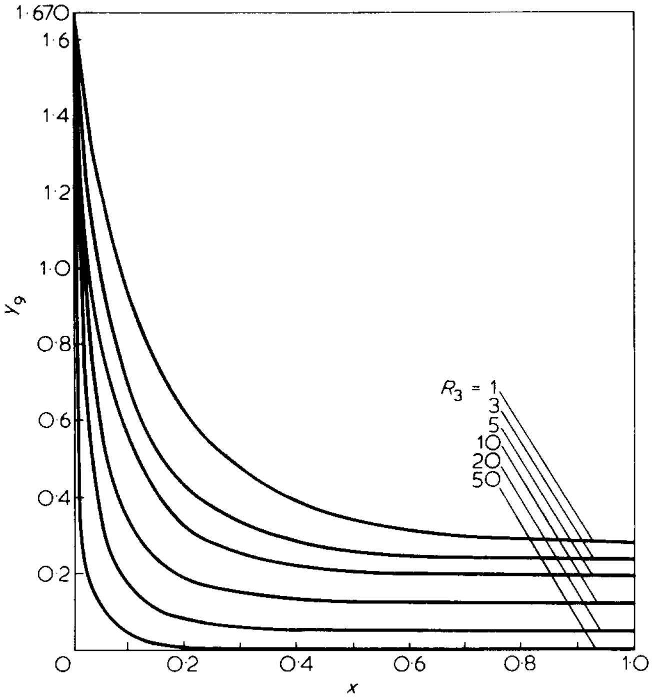


Figure 6 y_9 as a function of x with R_3 as parameter (R_1 = 0.125, R_2 = 0.30 and $[P]_0/[F]_0$ = 1.67)

$$\frac{dy_3}{dx} = (-R_1y_3 + R_3y_5 + y_1)(y_6 + y_7 + y_8 + y_{10}) \qquad (47)$$

and

$$\frac{dy_4}{dx} = (y_2 - R_2y_4)(y_6 + y_7 + y_8 + y_{10}) \qquad (48)$$

It is noted that for short times, the short chain lengths of polymer molecules give small values of y_3 and y_4. As a result of this, the term R_1y_3 in equation (47) and R_2y_4 in equation (48) are small because of low values of y_3 and y_4. By the time they become significant, the factor $(y_6 + y_7 + y_8 + y_{10})$ becomes very small due to the chemical reaction. Lastly, it may be added here that every reaction at O_i and p_i leads to branching of a polymer molecule, and in view of this the rate of branching, $\dot{B}$, would be the same as the rate of consumption of O_i and p_i. Or:

$$\dot{B} = (R_2y_4 + R_1y_3)(y_6 + y_7 + y_8 + y_{10}) \qquad (49)$$

For the reasons explained above, $\dot{B}$ remains small throughout the polymerization. It is an experimental fact that novalacs are linear molecules with small amounts of branching; this is confirmed by the model.

Numerical results were also generated for different initial ratios $[P]_0/[F]_0$). The functional behaviour of y_1 to y_{10} remains unchanged, except for the fact that the terminal phenol concentration increases as the ratio increases. Asymptotic values of y_1 to y_9 are given in *Table 4*. Terminal values of y_1 to y_9 are given in *Table 4*. Terminal values of y_3 and y_4 for $[P]_0/[F]_0 < 1$ are found to increase for the increasing ratio, but for $[P]_0/[F]_0 > 1$ they decrease. When formaldehyde is present in larger amount, (i.e. $[P]_0/[F]_0 <$ 1), branching is favoured; this should lead to a reduction in y_3 and y_4. As the initial molar ratio approaches one, a linear polymer chain would be the most probable configuration thus giving a maximum in y_3 and y_4. However, for initial molar ratios more than one, the chain length reduces with increasing $[P]_0/[F]_0$ which leads to reduction in y_3 and y_4.

In view of the fact that the results are insensitive to parameters R_1 and R_2, the internal *ortho* and *para* sites (O_i and p_i) can be assumed to react with the same rate constant as O_e and p_e. Then:

$$R_1 = 1 \qquad (50a)$$

Table 3 Effect of R_1 on concentrations of different reactive sites and P and F for large time (x = 1, R_2 = 0.30, R_3 = 2.4 and $[P]_0/[F]_0$ = 1.67)

No	R_1	y_1	y_2	y_3	y_4	y_5	y_8	y_9
1	0.05	1.0320	0.3338	0.4728	0.0873	0.3338	0.0005	0.2504
2	0.15	1.0334	0.3348	0.4627	0.0867	0.3348	0.0005	0.2528
3	0.25	1.0346	0.3358	0.4531	0.0862	0.3358	0.0005	0.2551
4	0.35	1.0358	0.3367	0.4438	0.0857	0.3367	0.0004	0.2574
5	0.50	1.0374	0.3380	0.4307	0.0850	0.3380	0.0004	0.2606
6	0.80	1.0402	0.3403	0.4069	0.0837	0.3403	0.0003	0.2665
7	1.00	1.0418	0.3416	0.3925	0.0829	0.3416	0.0003	0.2700

Table 4 Concentrations of different sites and P and F for large times (x = 1) as a function of initial phenol to formaldehyde ratio (R_1 = 0.125, R_2 = 0.30, R_3 = 2.40)

No	$[P_0]/[F]_0$	y_1	y_2	y_3	y_4	y_5	y_8	y_9
1	0.50	0.0362	0.0059	0.1935	0.0262	0.0059	0.4250	0.0003
2	0.80	0.1568	0.0305	0.4296	0.0642	0.0305	0.1590	0.0026
3	1.00	0.3260	0.0738	0.5421	0.0871	0.0738	0.0619	0.0123
4	1.67	1.0330	0.3346	0.4652	0.0869	0.3346	0.0005	0.2522
5	2.00	1.2418	0.4296	0.3885	0.0746	0.4296	0.0000	0.4786
6	3.00	1.5757	0.5918	0.2553	0.0508	0.5918	0.0000	1.3114
7	4.00	1.7349	0.6727	0.1896	0.0382	0.6727	0.0000	2.2305

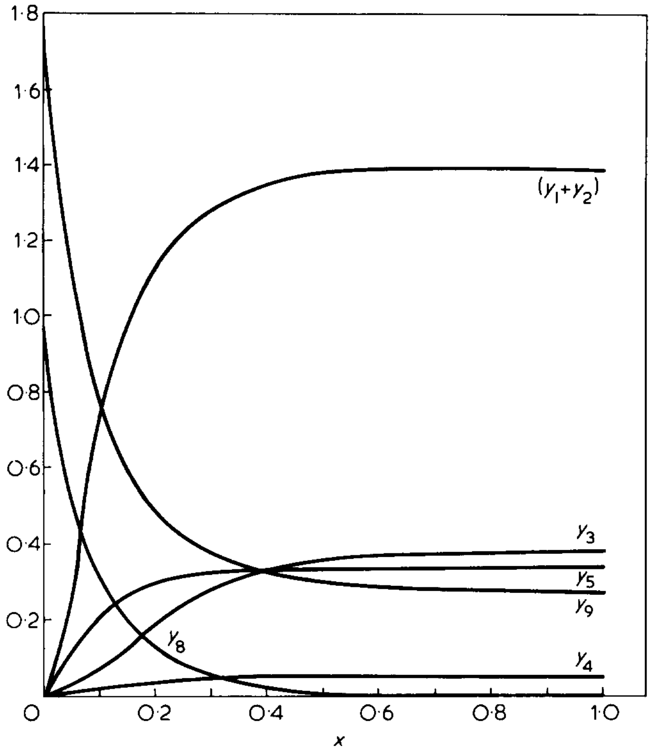


Figure 7 y_1 to y_5, y_8 and y_9 as a function of x with R_1 = 1 and $R_2 = R_3$ = 2.4

and

$$R_2 = R_3 = 2.4 \tag{50b}$$

and the kinetic model embodied in equations (25) to (34) involves a single parameter R_3. Results have been generated for this situation and plotted in *Figure 7*.

Lastly, concentrations of $-CH_2OH$ were calculated and found in every case to be small ($<10^{-3}$), thus justifying the assumption of the model that any given phenyl ring cannot have two formaldehyde molecules bound to it.

CONCLUSIONS

A kinetic model for novalac formation from the acid catalysed reaction of phenol and formaldehyde has been proposed. This accounts for the difference in reactivity of *ortho* and *para* positions and the effect of shielding on the reactivity of unreacted positions on polymer chains. The model involves 10 molecular species and the mass balance equation for each has been written. They have been solved numerically using the Runge–Kutta technique of 4th order.

The parameter involving the rate constant of the *para* external position, R_3, is the most important. As R_3 increases, the terminal value of $[O_{eT}]$ increases, $[p_e]$ reduces $[p_i]$ decreases and $[O_i]$ first increases and later starts decreasing. The increase of $[O_i]$ for $R_3 < 3$ is attributed to the fact that the preferential reaction of *para* position would give rise to increased *ortho* internal concentration. However, for $R_3 > 3$, chain lengths of the polymer are greatly reduced, leading to a decrease in the asymptotic value of O_i.

Variation in the reactivities of internal positions are found to have negligible effect upon the course of the polymerization, because polymer chains are smaller in length for short times giving rise to small $[O_i]$ and $[p_i]$. However, for large times when polymer molecules have grown in size and $[O_i]$ and $[p_i]$ are significant, the concentration of Q_1, Q_1', F and $-CH_2OH$ have considerably fallen. This implies that there is negligible branching which is consistent with experimental findings.

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