Modelling of resole type phenol formaldehyde polymerization

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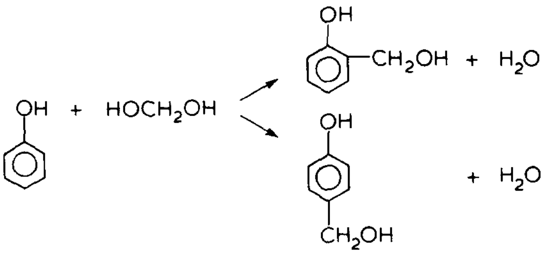
The kinetics of polymerization of phenol formaldehyde has been modelled to account for the formation of highly-branched resole molecules. The conversions of phenol and formaldehyde, number-average chain length, degree of branching and the concentrations of internal and external *ortho* and *para*-H atoms are obtained as functions of time, for several values of the various rate constants and the initial phenol to formaldehyde ratios. The conversions of phenol and formaldehyde are found to be most sensitive to the rate constant associated with the reaction between the external *para*-H atom with $-CH_2OH$ groups. The condensation between two $-CH_2OH$ groups prevents complete depletion of formaldehyde and leads to highly-branched, high molecular weight final products at large reaction times. Our studies show that at low values of the initial phenol to formaldehyde ratio, small amounts of lightly-branched, low molecular weight polymer with a high degree of substitution by $-CH_2OH$ groups is obtained. At some intermediate initial phenol to formaldehyde ratio, highly-branched, high molecular weight product is obtained and at high values of this feed ratio, larger amounts of lightly-branched, lower average molecular-weight product is obtained.

INTRODUCTION

Even though the polymerization of phenol-formaldehyde has been reported as early as in 1907, detailed experimental studies of the kinetics and the chemistry of the several reactions involved were not carried out until much later[1-5]. This is probably because of the complex nature of the kinetic scheme and the complication introduced by the dependence of the rate constants on the pH of the reaction medium. In an acidic medium, when the initial molar ratio of phenol to formaldehyde is larger than unity, the reactions lead to relatively linear molecular structures called novolacs, whereas under basic conditions, and with the initial phenol to formaldehyde ratios less than unity, short, highly-branched molecular structures are produced, called resoles.

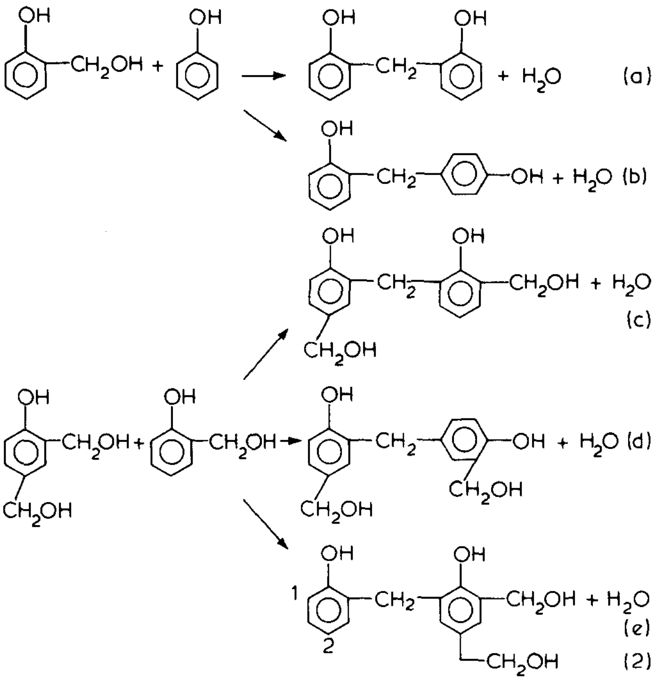
In an aqueous medium, formaldehyde exists as a difunctional species, $HOCH_2OH$, and this can react with phenol at the two *ortho* and one *para* positions[6] to give *ortho*- and *para*-methylol phenol respectively:



(1)

These products can react with a molecule of $HOCH_2OH$ to give two disubstituted, mononuclear (i.e., containing a single phenolic ring) products which, in turn, can react further to give the trisubstituted, mononuclear product.

The formation of dinuclear species can take place by the condensation of the $-CH_2OH$ group on the mononuclear species and the $-H$ atom at the *ortho* or *para* positions of either phenol or another mononuclear molecule. Five of the several reactions are shown below, to illustrate the variety of possibilities:



(2)

In addition to this, dinuclear species can also be formed by the condensation of two $-CH_2OH$ groups on different mononuclear species. One such possible reaction is shown below for illustration:

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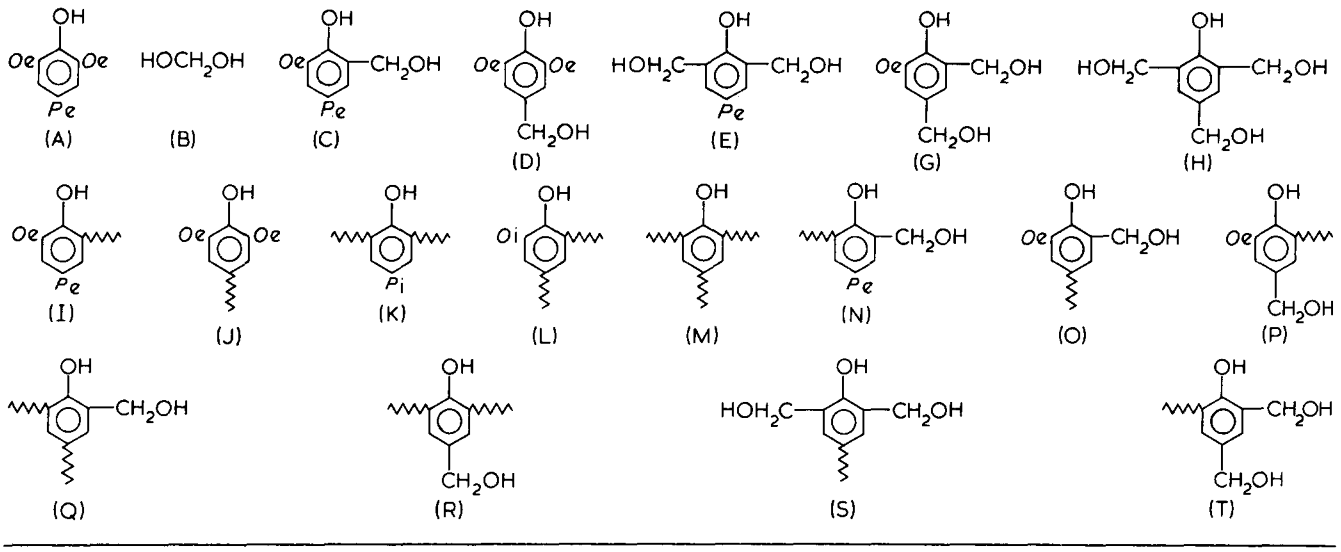
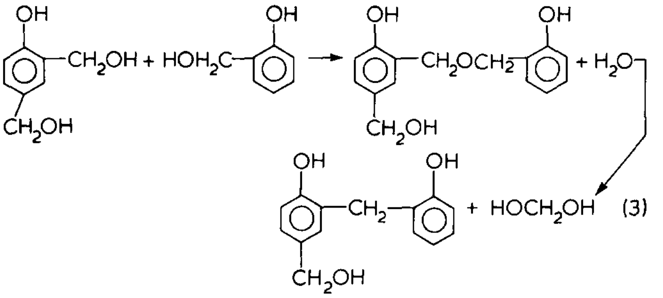
Table 1 Basic entities required for this study, alongwith an indication of type of $-H$ group. mm represents linkage to another phenolic ring via a $-CH_2-$ or $-CH_2OCH_2-$ group




(3)

The –H atom at the *ortho* and *para* positions of the dinuclear species, for example, sites 1 and 2 in equation 2e, can react with $HOCH_2OH$ to give higher $-CH_2OH$ substituted dinuclear compounds.

Multinuclear compounds having *n* phenolic rings can be formed by the reaction of *i*-ringed compounds with those having *n-i* rings, where *i* can take a value from 1 to *n*-1, and the corresponding reactions can be written in analogy with the above equations. In general, a crosslinked molecular structure may form.

Little work has been reported on the mathematical modelling of phenol formaldehyde polymerization. Novolac formation has been studied by Drumm and LeBlanc[6] but they simplified the kinetic scheme considerably and assumed that molecules having two or more CH_2OH groups per chain do not exist in the system. In order to keep their equations simple, they had to omit several reactions which are actually present in reality. Kumar *et al.*[7] incorporated these reactions. They considered four types of sites (i.e. –H positions on phenolic rings)—the *ortho* and *para* sites on the phenolic rings at the ends of any chain (called *ortho* and *para* external) and the *ortho* and *para* –H sites on the interior phenolic rings (called *ortho* and *para* internal), and solved the mass-balance equations numerically to give the conversions of phenol and formaldehyde as functions of time. Recently, they extended this work to give[8] the molecular weight distribution (*MWD*) of chains. Their mathematical model, however, cannot be applied to resole formation because of the assumption of one or no CH_2OH units per chain.

In this work, a theoretical model is presented which can account for branching in resole systems. Mass balance equations are solved numerically to give the conversion, average molecular weight, degree of branching, etc. as a function of time in terms of the various rate constants, which have been treated as parameters.

FORMULATION

In the kinetics of ARB-type polycondensations characterized by the equal-reactivity hypothesis, instead of focussing attention on the individual molecular species, as for example, $A-(RBA)_{\overline{n-1}}-RB$, it is easier to study the progress of the reaction in terms of a different 'basic entity', namely, the functional groups A or B[9]. As the polymerization becomes more complex, more such basic entities are required for study, as was found in the case of linear polycondensations not following the equal reactivity hypothesis[10–14]. For the case of phenol–formaldehyde polymerization, it is found that nineteen such basic entities are required to account for both the formation of branches as also the unequal reactivities of external and internal ortho and para positions. These basic entities are listed in *Table 1*.

The entire course of the polymerization can now be represented in terms of several elementary reactions between these basic entities. Each of the elementary reactions can be associated with an appropriate rate constant chosen from among the following:

(i) k_1, the rate constant for the reaction between an external *ortho* –H site (o_e) on a phenolic ring and a $-CH_2HO$ group, either on $HOCH_2OH$ or on a phenolic ring;

(ii) k_2, that for the reaction between an internal *ortho* –H site (o_i) and a $-CH_2OH$ group;

(iii) k_3, between an internal *para* –H site (p_i) and a $-CH_2OH$;

(iv) k_4, between an external *para* –H site (p_e) and a $-CH_2OH$; and

(v) k_5, that for the reaction between two $-CH_2OH$ groups giving a $-CH_2-$ linkage and a $HOCH_2OH$ molecule.

It is assumed that the rate constants are independent of the units on which the –H atom (other than its position

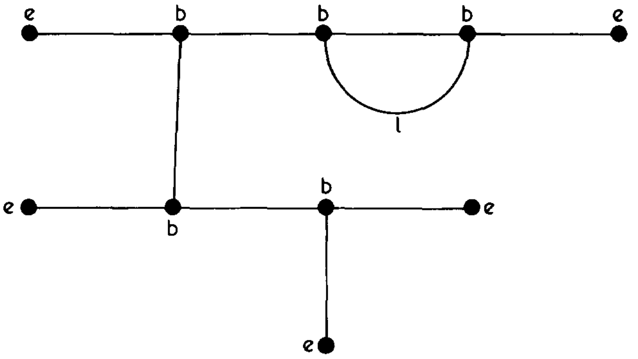


Figure 1 Typical branched molecule with a loop

relative to the $-OH$) and the $-CH_2OH$ groups are located. This approximation is analogous to that used in the equal reactivity hypothesis. Also, the two-step process shown in equation 3 has been compressed into a single step with an overall rate constant k_5 which is assumed to be independent of the units attached to the two $-CH_2OH$ groups. It is anticipated that the rate of reaction between $-CH_2OH$ groups on external phenolic rings will be higher than that associated with either an external and an internal $-CH_2OH$ group or two internal $-CH_2OH$ groups but this difference is neglected at present to keep the number of parameters reasonable. The 360 possible elementary reactions between the nineteen basic entities along with the associated rate constants are given by Pal *et al.*[15] and can be supplied on request. It must be remembered that appropriate factors (1/2, 1,2,4, etc.) must be incorporated along with the rate constants k_1 to k_5, to take care of the total number of ways the sites are involved in reaction. For example, in the reaction between A and C to give two I's, the $-CH_2OH$ of entity C can attack two o_e sites on A and so the rate constant is $2k_1$. In the reactions between two basic entities of the same type, as for example between G and G to give P and T, an extra factor of one-half is used in the reaction rate constant computed by the above method to prevent counting of intermolecular collisions twice, as discussed by Gupta *et al.*[13,14] and Kumar and Gupta[16].

Mass balance equations for an isothermal batch reactor are written and nondimensionalized in terms of the following variables:

$$X=k_1t[B]_0,\quad X_2=k_2/k_1,\quad X_3=k_3/k_1,\quad X_4=k_4/k_1,\quad X_5=k_5/k_1$$

$$A'=[A]/[B]_0,\ B'=[B]/[B]_0,\ \text{etc.} \tag{4}$$

where [ ] represents the concentration, t the time and subscript 0, the initial conditions. It is assumed that only phenol and formaldehyde are taken as the starting materials. The equations are then solved numerically on a DEC 1090 computer using a fourth-order Runge Kutta algorithm to give the dimensionless concentrations as a function of X. The increment in the dimensionless time, ΔX, was reduced in the first few runs until it made little difference in the final results. This value of ΔX of 0.01 was used in all the runs. The computer time per run, for X of about 1.5, was approximately 5 s. Several checks were made on the computer program, one of these being a comparison of the total number of phenolic rings in the system computed at any time with the initial number of phenol molecules.

The number-average degree of polymerization, $\overline{DP}_n$, can also be obtained for this system. It is given by the ratio of the original number of phenolic rings, $[A]_0$, to the total number of polymer molecules (including the single ring species) at any time, as:

$$\overline{DP}_n=\frac{[A]_0}{[X_p]+[A]+[C]+[D]+[E]+[G]+[H]} \tag{5}$$

where $[X_p]$ is the concentration of polymer molecules containing two or more phenolic rings. $[X_p]$ can, in turn, be written in terms of the concentration of the 'end' rings, $[X_e]$, $(=[I]+[J]+[N]+[O]+[P]+[S]+[T])$, the concentration of 'loops' (cyclic chains within polymer molecules), $[X_1]$, and the concentration of branch points, $[X_b]$ $(=[M])$. A study of a typical chain structure containing branches and loops (*Figure 1*) shows that the presence of every branch point not associated with a loop, increases the number of end phenolic rings by unity. The presence of a loop, however, wastes two branch points. $[X_p]$ can thus be written as

$[X_p]$ = concentration of end rings-concentration of branch points not leading to a loop/2

$$=([X_e]-\{[X_b]-2[X_1]\})2 \tag{6}$$

Loops can be formed by intramolecular linkages of various types. Using a typical reaction between basic entities I and N as an illustration, the rate of loop formation because of this reaction can be written as

$$\frac{d}{dt}[X_1]_{I,N}=$$

$$k_1[I][N]\times\frac{\text{number of linkages formed that are intramolecular}}{\text{total number of linkages formed}} \tag{7}$$

The term in brackets can be expressed in terms of $[X_p]$, the concentration of polymer molecules of chain-length of two and above, as: fraction of intramolecular I–N type links = average number of I in a polymer molecule × average number of N in a polymer molecule × number of polymer molecules per unit volume/total number of I per unit volume × total number of N per unit volume:

$$=\frac{\left\{\frac{[I]}{[X_p]}\right\}\times\left\{\frac{[N]}{[N_p]}\right\}\times\{[X_p]\times N_{av}\ddagger}{\dagger[I]\times N_{av}\}\times\{[N]\times N_{av}\}}=\frac{1}{[X_p]N_{av}} \tag{8}$$

where N_{av} is the Avogadro number. Thus, the rate of loop formation can be obtained by a proper summation over the appropriate reactions:

$$\begin{aligned}N_{av}[X_p]\frac{d}{dt}[X_1]=\{&k_1+k_4)[I]+2k_1[J]+k_3[K]\\&+k_2[L]\}\{[N]+[O]+[P]+[Q]+[R]\\&+2[S]+2[T]\}+[N]\{k_1([O]+[P])\\&+k_4([N]+[O]+[P]+[Q]+[R]\\&+2[S]+2[T])\}+k_1[O]\{[O]+2[P]\\&+[Q]+[R]+2[S]+2[T]\}+\\k_1[P]\{[P]+[Q]+[R]+2[S]+2[T]\}&+k_5\{[N](\frac{[N]}{2}\\&+[O]+[P]+[Q]+\end{aligned}$$

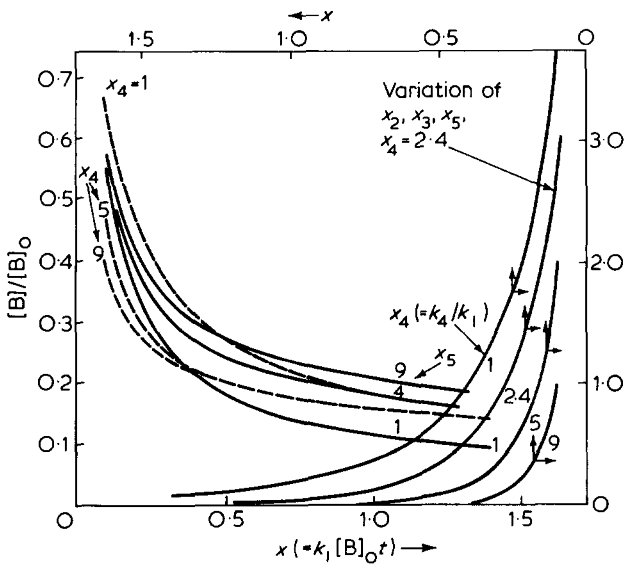


Figure 2 Dimensionless phenol concentration vs. time for various values of X_4 (solid lines with arrows, use upper and right hand scales). Dimensionless formaldehyde concentrations for various values of X_4 (broken lines) and X_5 (solid) (use left-hand and lower axes). Values of other parameters as in Equation 10

$$\begin{aligned}&[\mathrm{R}]+2[\mathrm{S}]+2[\mathrm{T}])+[\mathrm{O}](\frac{[\mathrm{O}]}{2}+[\mathrm{P}]+[\mathrm{Q}]+[\mathrm{R}]+2[\mathrm{S}]\\&\qquad+2[\mathrm{T}])\\&+[\mathrm{P}](\frac{[\mathrm{P}]}{2}+[\mathrm{Q}]+[\mathrm{R}]+2[\mathrm{S}]+2[\mathrm{T}])\\&+[\mathrm{Q}](\frac{[\mathrm{Q}]}{2}+[\mathrm{R}]+2[\mathrm{S}]+2[\mathrm{T}])+[\mathrm{R}](\frac{[\mathrm{R}]}{2}+2[\mathrm{S}]+2[\mathrm{T}])\\&+2[\mathrm{S}]([\mathrm{S}]+2[\mathrm{T}])+2[\mathrm{T}][\mathrm{T}]\}\end{aligned} \tag{9}$$

The initial value of $[X_1]$ is zero. Equations 6 and 9 need to be solved simultaneously, along with the mass balance equations for the various basic entities.

RESULTS AND DISCUSSION

The four dimensionless rate constants, X_2 to X_5, and the initial phenol to formaldehyde ratio, have been treated as parameters, varying around the following set of reference values one at a time

$$X_2=0.125;\ X_3=0.3;\ X_4=2.4;\ X_5=3.0;\ [\mathrm{A}]_0/[\mathrm{B}]_0=0.7 \tag{10}$$

The values of X_2, X_3 and X_4 are typical of those characterising novolac formation[6] and represent a useful starting point for studies on resole formation since these parameters are not available for the latter system. The value of X_5 is somewhat arbitrarily taken as three since it has been reported that condensation between $-CH_2OH$ groups is fairly rapid in resole formation. This does not represent a drawback in our study since a detailed variation of each of these values is explored. The $[A]_0/[B]_0$ value has been taken as 0.7, which is usually encountered in resole manufacture.

Figure 2 shows the dimensionless concentrations of phenol and formaldehyde as a function of the dimensionless time, X, for different values of the rate parameters. It is found that the variation of the rate parameters X_2, X_3 and X_5 has little effect on the phenol concentration. This is consistent with the fact that phenol has neither an internal -H site nor a $-CH_2OH$ group on it. However, the parameter X_4 $(=k_4/k_1)$ is important and as the reactivity of the *para* position on the phenol increases, its depletion becomes faster. The formaldehyde concentrations are found to be less sensitive to X_2 and X_3, the parameters characterizing the internal -H sites, as compared with X_4 and X_5. An interesting aspect of the formaldehyde concentration is that it does not deplete to zero. This is because of the generation of formaldehyde in the later stages of the reaction by the condensation of two $-CH_2OH$ groups and as k_5 is increased, the final value of formaldehyde concentration increases. The effect of increasing k_4, however, is primarily felt in the initial stages of the reaction, the asymptotic value being relatively unchanged.

X_2 and X_5 are found to be the most important parameters which influence branching as shown in *Figure 3*. The concentration of branch points, [M], rises slowly at first, but when a sufficient number of polynuclear species have been generated, it increases rapidly. *Figure 3* shows the relative importance of the condensation between $-CH_2OH$ and -H sites in determining branching over the condensation between two $-CH_2OH$ groups. It is also found that X_3, which represents the reactivity of p_i, influences branching much less than does X_2, which corresponds to the reactivity of o_i. A possible reason for this is the relative abundance of o_i available, compared with the p_i, due to the high value of X_4 of 2.4. The effect of X_4, on branching, similarly, is small, as shown in *Figure 3*. However, the crossing over of the graphs for different values of X_4 is due to two opposing factors—the depletion of p_i and the preponderance of o_i as X_4 increases and secondly, the relatively slower rate of reaction of the o_i.

The effect of parameter variation on the number average chain length, $\overline{DP}_n$, is shown in *Figure 4*. A comparison of *Figures 3* and *4* reveals that the sharp increase in $\overline{DP}_n$ above values of X of about 0.5 is associated with a similar sharp rise in the branching. The sensitivity of $\overline{DP}_n$ to the various rate constants is thus similar to that for branching.

Figures 5 and *6* show dimensionless concentrations of the various reaction sites as X_4 and $[A]_0/[B]_0$ are varied. These concentrations do not include phenol. As X_4 is increased, the o_i increase at the expense of p_i. The reason is

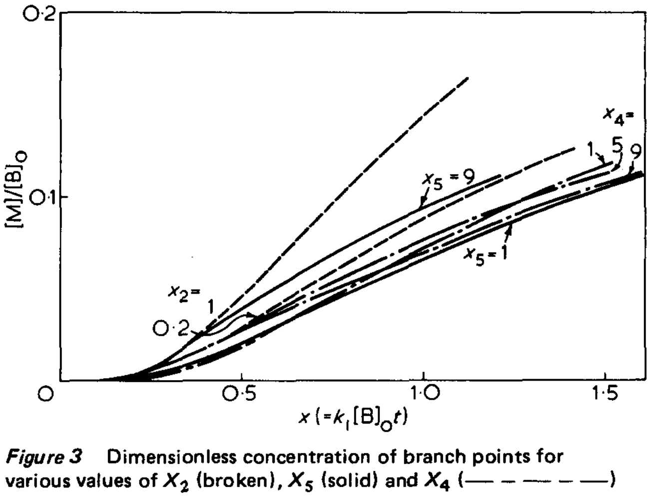


Figure 3 Dimensionless concentration of branch points for various values of X_2 (broken), X_5 (solid) and X_4 (— — — — —)

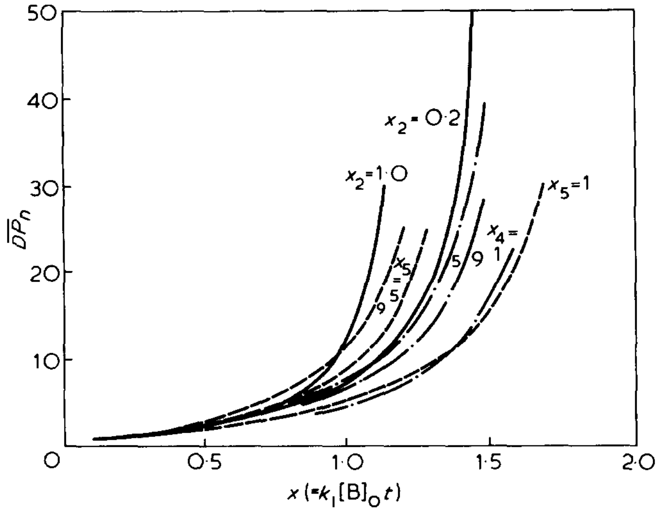


Figure 4 Number average chain length as a function of the dimensionless time. Parameters changed are X_2 (——), X_5 (– – – –) and X_4 (— - — - —)

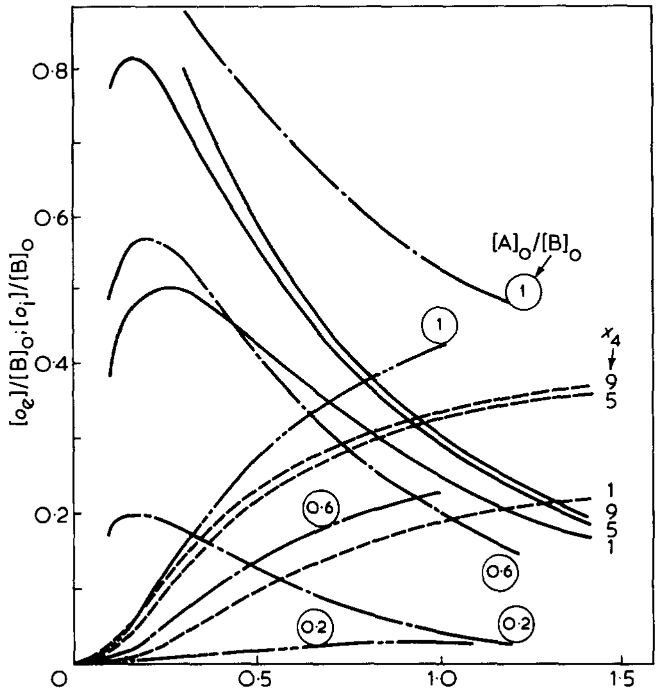


Figure 5 Dimensionless concentrations of external ortho sites with X_4 varied (——) and with $[A]_0/[B]_0$ varied (— - — -) and of internal ortho sites with X_4 varied (– – – –) and $[A]_0/[B]_0$ varied (— - — - —). Values of $[A]_0/[B]_0$ are circled. Values of other parameters are as given in equation 10

the same as for branching. Similarly, as the relative reactivity of the p_e site is increased, the concentration of p_e decreases substantially whereas that for o_e increases slightly. The peak observed in the external site concentrations is due to the exclusion of phenol in the definition of the site concentrations. In the early stages of the reaction, p_e and o_e are first generated, as formaldehyde reacts with the phenol. Thereafter, these sites are consumed with the addition of $-CH_2OH$ groups and the formation of polynuclear compounds.

The effect of X_2 and X_3 variation on the site concentrations are minimal except for $[o_i]/[B]_0$ for X_2 and $[p_i]/[B]_0$ for X_3 which decrease substantially as X_2 and X_3 are increased respectively. The effect of increasing X_5 is an increase in the internal sites at the expense of the external sites, because the condensation reaction between two $-CH_2OH$ groups, at most, transforms external sites to internal ones. The increase in internal *para* sites with X_5, is less because of the preponderance of *ortho* sites in the system.

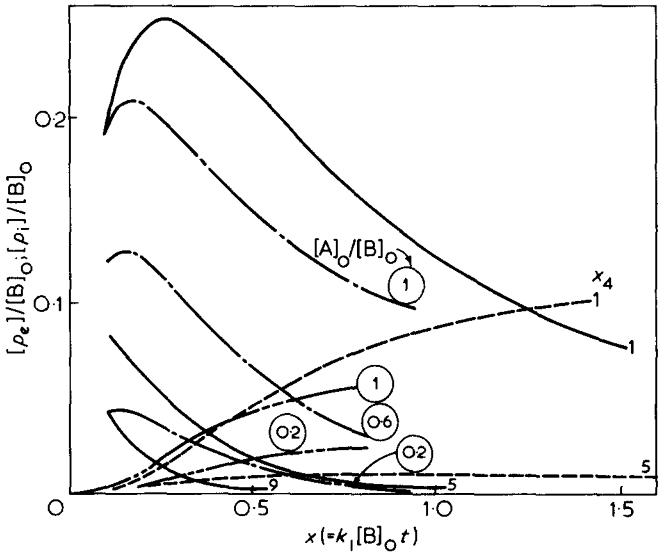


Figure 6 Dimensionless concentrations of external *para* sites with X_4 varied (——) and with $[A]_0/[B]_0$ varied (— - — -) and of internal *para* sites with X_4 varied (– – – –) and with $[A]_0/[B]_0$ varied (— - — - —). $[A]_0/[B]_0$ values circled. Other parameters are as given in equation 10

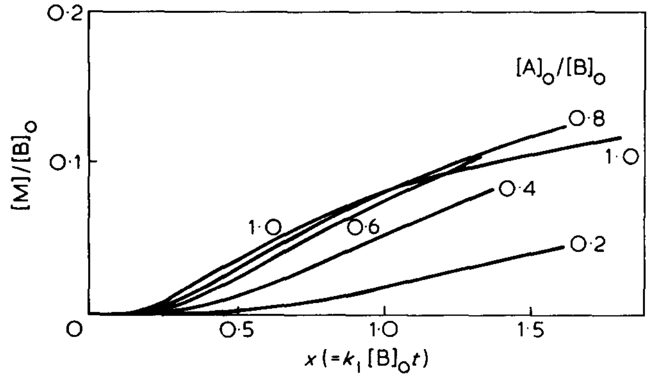


Figure 7 Dimensionless concentration of branch points for various initial phenol to formaldehyde ratios. Values of equation 10 used for the rate constants

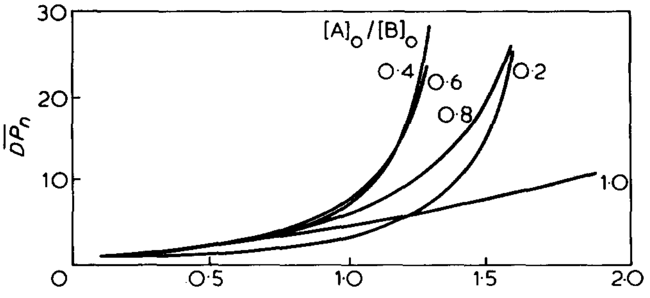


Figure 8 $\overline{DP}_n$ for various initial phenol to formaldehyde ratios. Values of equation 10 used for the rate constants

The effect of varying the initial phenol to formaldehyde ratio using the reference values of X_2 to X_5 (equation 10) are shown in *Figures 7* and *8*. The degree of branching and $\overline{DP}_n$ first increase as $[A]_0/[B]_0$ is increased from 0.2 to about 0.6 and thereafter, they decrease. The decrease is more marked for $\overline{DP}_n$ than for the degree of branching. It is observed from *Figures 5–8* that at low $[A]_0/[B]_0$, short polymer molecules having $-CH_2OH$ at most of the sites are formed, as indicated by the low values of $[p_i]/[B]_0$, $[p_e]/[B]_0$, $[o_e]/[B]_0$ and $[o_i]/[B]_0$. These chains are far removed from each other and further reaction between them to give high molecular weight polymer, cannot take place. As $[A]_0/[B]_0$ is increased this restriction is no longer present and highly branched molecular structures with high $\overline{DP}_n$ are produced. However, as the initial phenol to formaldehyde ratio is increased further, insufficient formaldehyde is available and several, less highly branched polymer molecules are formed. The total concentration of branch points does not decrease too much. At a $[A]_0/[B]_0$ ratio of about 0.6, the number of branch points per polymer molecule and $\overline{DP}_n$ are at the highest. It is interesting to observe that $[A]_0/[B]_0$ values for real polymerizations lie close to this theoretically predicted value.

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