

# Modelling of Condensation Polymerization of Novolac-Type Phenol-Formaldehyde in Homogeneous, Continuous-Flow, Stirred-Tank Reactors

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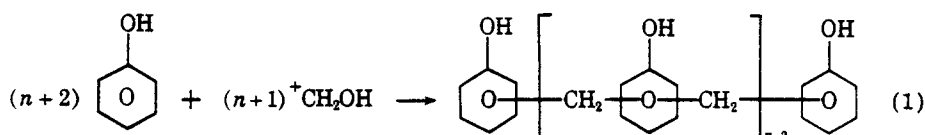
## Synopsis

A detailed kinetic model for the novolac-type phenol-formaldehyde polymerization has been proposed in terms of five reactive sites. These sites have been shown to have different reactivities. Mass-balance equations for homogeneous, continuous-flow, stirred tank reactors (HCSTR) for each of the species have been written, and these have been solved numerically. A comparison of the results with those for the batch reactor shows that, for a given residence time, smaller but more polydispersed and branched chains are formed.

## INTRODUCTION

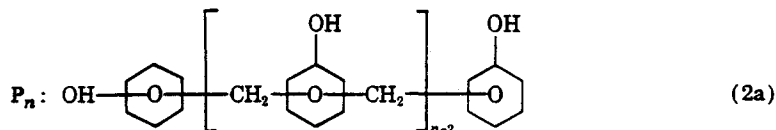
Even though the polymerization of phenol and formaldehyde is one of the oldest known reactions (first reported in 1907), very little modeling of the reaction system exists because of its complexity.<sup>1,2</sup>

Experimental studies have revealed that formaldehyde in the reaction mass exists solely as OH-CH<sub>2</sub>-OH, exhibiting a functionality of 2. A molecule of phenol, on the other hand, has three reactive sites, two ortho and one para, which can undergo chemical reactions with free formaldehyde as well as those reacted once with polymer chains. It has been experimentally demonstrated that the ortho and para sites have different reactivities.<sup>2-5</sup> In view of this, the equal reactivity hypothesis does not hold and, representing the polymerization as



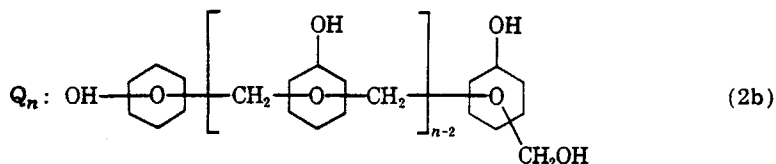
is a considered oversimplification.

To account for the different reactivities of the sites, it is noted that there are the following two kinds of molecular species besides unreacted phenol and formaldehyde:



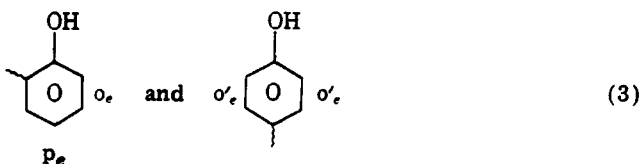
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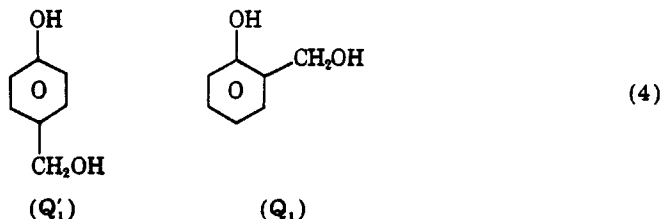


$P_n$  differs from  $Q_n$  by the extra  $\text{CH}_2\text{OH}$  on the latter. The study of gelation reveals that the functionality of phenol is slightly less than 3, and the polymer molecule is largely found to grow by the reaction of end groups. In view of this, Drumm and LeBlanc assume that the reactivity of internal sites is less than that of the end group sites.<sup>2</sup>

In our earlier work,<sup>1</sup> we proposed a three-parameter kinetic model for novolac formation in terms of the reaction of sites based upon the fundamental characteristics of the polymerization as discussed above. Molecules of chain length 2 and above are distinguished from the remainder of the species and we proposed the following four sites located upon them: (a) ortho external  $o_eT$ , (b) ortho internal  $O_i$ , (c) para external  $p_e$ , (d) para internal  $p_i$ . Different rate constants were assumed to be associated with each of these. Further, ortho external sites,  $o_eT$ , can arise due to the following two distinct endings:



where the wavy line represents the remainder of the polymer molecule. The structures in eq. (3) are distinguished from each other for convenience of mass balance, even though they react at the same rate. In addition to this, when phenol (P) reacts with formaldehyde (F), it forms the following two distinct species ( $Q_1$  and  $Q'_1$ )

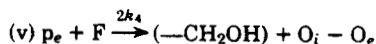
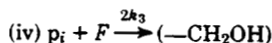
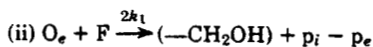
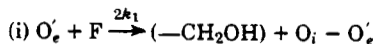


In Table I, different reactions occurring in novolac formation are given. The rate constants for each of these have been written in terms of the rate constants involving the site and  $\text{---OH}$  group.<sup>3</sup> For example, in reaction 1(i), F has two  $\text{---OH}$  groups and the reaction progresses with rate constant  $2k_1$ . Similarly, in reaction 4(i), P has two  $o_e$  sites and F two  $\text{---OH}$  groups, and therefore it progresses with rate constants  $4k_1$ . The rates of consumption of the different species have been derived for batch reactors with the help of Table I, and the results are summarized in Table II.

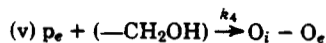
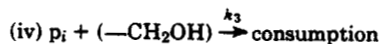
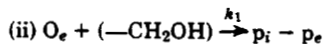
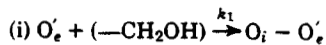
As the throughput of the reactor increases, the economics of increasing capacity

TABLE I  
Reactions of  $O_e$ ,  $O'_e$ ,  $p_i$ ,  $O_i$ , and  $p_e$

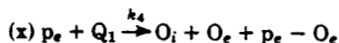
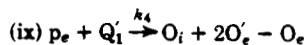
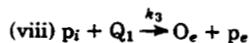
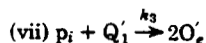
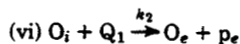
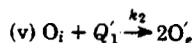
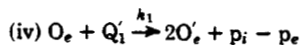
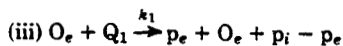
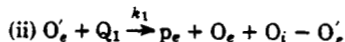
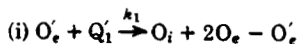
(1) With formaldehyde



(2) With bound formaldehyde ( $-CH_2OH$ )

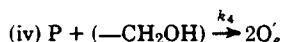
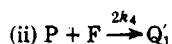
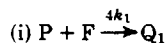


(3) With  $Q'_1$  and  $Q_1$

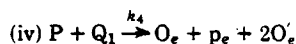
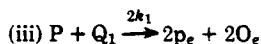
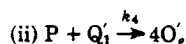
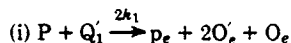


(4) Reaction of P with F and ( $-CH_2OH$ )

TABLE I. (Continued from previous page.)



(5) Reactions of P with  $Q_1$  and  $Q'_1$



favors the use of continuous reactors like tubular reactors or homogeneous continuous-flow stirred tank reactors (HCSTRs).<sup>6</sup> Indeed, recently several processes manufacturing novolac have been patented in which HCSTRs have been used.<sup>7</sup>

Homogeneous, continuous-flow, stirred tank reactors (HCSTR) have definite advantages over batch (or flow) reactors,<sup>8-10</sup> and, in several commercial applications, a HCSTR followed by a flow reactor is used.<sup>3</sup> In this paper, an HCSTR-forming Novolac-type polymer has been simulated and a sensitivity analysis has been carried out. The effect of different parameters upon the conversion of these sites have been examined, and the results have been compared with the corresponding batch reactor performance.

### MASS BALANCE EQUATIONS FOR HCSTR

It is assumed that the feed to the HCSTR is a mixture of phenol and formaldehyde only. Since the reactive sites  $o_e$ ,  $o'_e$ ,  $o_i$ ,  $p_i$ , and  $p_e$  have been defined to exist on molecules with chain length  $n \geq 2$ , the concentration of these in the feed would be zero, and therefore the mass balance equations for HCSTRs are given by

$$0 = y_i + x \left( \frac{dy_i}{dt} \right)_{\text{batch,exit}}, \quad i = 1-7 \quad (5)$$

where  $x$  is the dimensionless residence time,  $y_1$ - $y_7$  are the dimensionless concentrations of  $O_e$ ,  $O'_e$ ,  $O_i$ ,  $p_i$ ,  $p_e$ , and  $Q'_1$ , respectively,  $(dy_i/dt)_{\text{batch,exit}}$  above are the rate expressions for the different species given in Table II, whose right-hand

TABLE II  
Balance Equations for Batch Reactor for Different Sites and Species of Table I

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(1) $\frac{d[O'_e]}{dt}$	$= -2k_1[O'_e]\{[Q_1] + 2[F] + [CH_2OH]\} + [Q'_1]\{2k_1[O_e] + 2k_2[O_i] + 2k_3[p_i] + 2k_4[p_e] + 4(k_1 + k_4)[P]\} + 2k_4[P]\{[Q_1] + [CH_2OH]\}$
(2) $\frac{d[O_e]}{dt}$	$= [Q_1]\{k_1[O'_e] + k_2[O_i] + k_3[p_i] + (4k_1 + k_4)[P]\} - [Q'_1]\{k_1[O_e] + k_4[p_e] - 2k_1[P]\} - 2[F]\{k_1[O_e] + k_4[p_e]\} - [CH_2OH]\{k_1[O_e] - 2k_1[P]\}$
(3) $\frac{d[O_i]}{dt}$	$= [Q_1]\{k_1[O'_e] - k_2[O_i] + k_4[p_e]\} + [Q'_1]\{k_1[O'_e] - k_2[O_i] + k_4[p_e]\} + 2[F]\{k_1[O'_e] - k_2[O_i] + k_4[p_e]\} + [CH_2OH]\{k_1[O'_e] - k_2[O_i] + k_4[p_e]\}$
(4) $\frac{d[p_i]}{dt}$	$= k_1[O_e]\{[Q_1] + [Q'_1] + 2[F] + [CH_2OH]\} - k_3[p_i]\{[Q_1] + [Q'_1] + 2[F] + [CH_2OH]\}$
(5) $\frac{d[p_e]}{dt}$	$= [Q_1]\{k_1[O'_e] + k_2[O_i] + (4k_1 + k_4)[P] + k_3[p_i]\} + [Q'_1]\{2k_1[P] - k_1[O_e] - k_4[p_e]\} - 2[F]\{k_1[O_e] + k_4[p_e]\} + [CH_2OH]\{2k_1[P] - k_4[p_e]\}$
(6) $\frac{d[Q_1]}{dt}$	$= 4k_1[F][P] - (2k_1 + k_4)[Q_1][P] - [Q_1]\{k_1[O'_e] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - 2(k_1 + k_4)[Q_1]^2 - (3k_1 + k_4)[Q_1][Q'_1] - (k_1 + k_4)[Q_1][CH_2OH]$
(7) $\frac{d[Q'_1]}{dt}$	$= 2k_4[P][F] - (2k_1 + k_4)[Q'_1][P] - [Q'_1]\{k_1[O'_e] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - 4k_1[Q'_1]^2 - (3k_1 + k_4)[Q_1][Q'_1] - 2k_1[Q'_1][CH_2OH]$
(8) $\frac{d[F]}{dt}$	$= -2[F]\{(2k_1 + k_4)[P] + k_1[O'_e] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\}$
(9) $\frac{d[P]}{dt}$	$= -(2k_1 + k_4)[P]\{[Q_1] + [Q'_1] + 2[F] + [CH_2OH]\}$
(10) $\frac{d[CH_2OH]}{dt}$	$= 2[F]\{k_1[O'_e] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - [CH_2OH]\{k_1[O'_e] + k_1[O_e] + k_2[O_i] + k_3[p_i] + k_4[p_e]\} - (k_4 + 2k_1)[P][CH_2OH]$

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sides have been evaluated at the exit concentrations of the HCSTR. Similar balance equations can be written for phenol ( $y_8$ ), formaldehyde ( $y_9$ ), and bound formaldehyde— $CH_2OH$  ( $y_{10}$ ) as follows:

$$y_{8,0} = y_8 + x \left( \frac{dy_8}{dt} \right)_{\text{batch,exit}} \quad (6a)$$

$$y_{9,0} = y_9 + x \left( \frac{dy_9}{dt} \right)_{\text{batch,exit}} \quad (6b)$$

$$0 = y_{10} + x \left( \frac{dy_{10}}{dt} \right)_{\text{batch,exit}} \quad (6c)$$

where the subscript 0 stands for feed concentrations.

When the rate expressions from Table II are substituted in eqs. (5) and (6), 10 nonlinear algebraic expressions are obtained involving  $y_1$ – $y_{10}$ . In principle, they can be solved for a given residence time and specified input conditions.

NUMERICAL TECHNIQUE

In the Gauss-Jordan technique of numerical solution, one must provide a good initial guess of solution and a Jacobian matrix which consists of an array of partial derivative of the algebraic functions with respect to the independent variables. To provide the former is always a problem, whereas the derivation of the latter is time consuming.

To overcome both these difficulties, the Brown's technique, as described in Figure 1 was employed.<sup>11</sup> In this method, an initial guess must also be provided, and the results for batch reactors were used as the one.

Results for HCSTR were obtained starting from  $x = 0.1$ , at which the first guess solution corresponded to that of batch (or tubular) reactor of the same time of polymerization. The  $x$  for this HCSTR was then changed by 0.01, and the guess solution for the CSTR with immediately lower residence time was used to calculate the effect of  $x$  upon the performance of the CSTR. This solution procedure proved to be very efficient, and results always converged in less than three iteration.

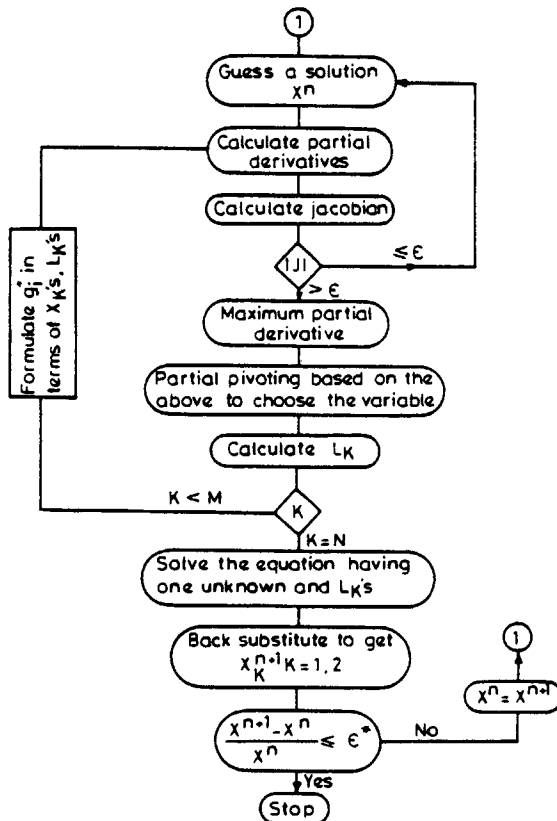


Fig. 1. The flow chart giving the Brown's technique.

## RESULTS AND DISCUSSION

For a given value of  $R_3$ ,  $y_1$ - $y_{10}$  were calculated as a function of  $x$  and in Figures 2 and 3, the dimensionless concentrations of ortho external sites ( $y_1 + y_2$ ) and para external sites  $y_5$  vs.  $x$  have been plotted. As  $x$  is varied, these curves quickly rise to an asymptotic value for large  $x$ . The variation in  $R_3$  can be obtained by changing the reaction temperature and the effect of increasing  $R_3$  is found to give a sharper rise and larger asymptotic value. In the same figure, results for the batch reactors are also given and they are always found to be larger than those for an HCSTR for a given  $R_3$ .

In Figures 4 and 5, the concentration of  $O_i$  and  $p_i$  have been plotted as a function of  $x$ , and the results for the batch reactor are also included. As  $R_3$  in-

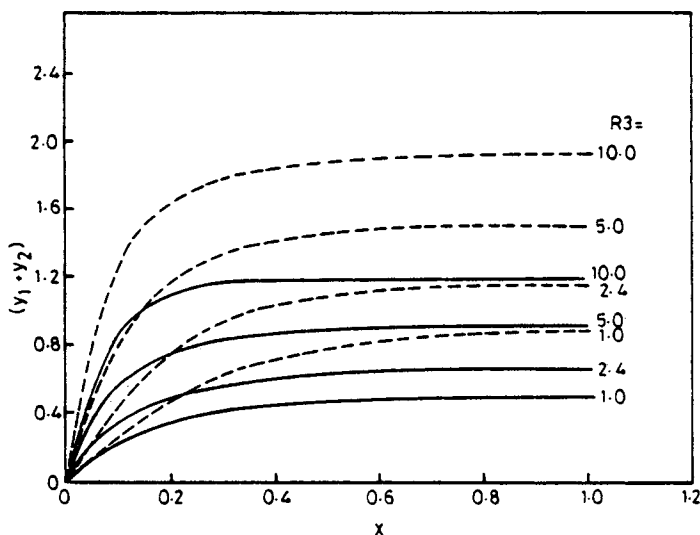


Fig. 2. Effect of  $R_3$  on  $O_e$  as a function of time.  $R_1 = 0.125$ ,  $R_2 = 0.30$ ,  $[P]_0/[F]_0 = 1.67$ . (---) Batch; (—) CSTR.

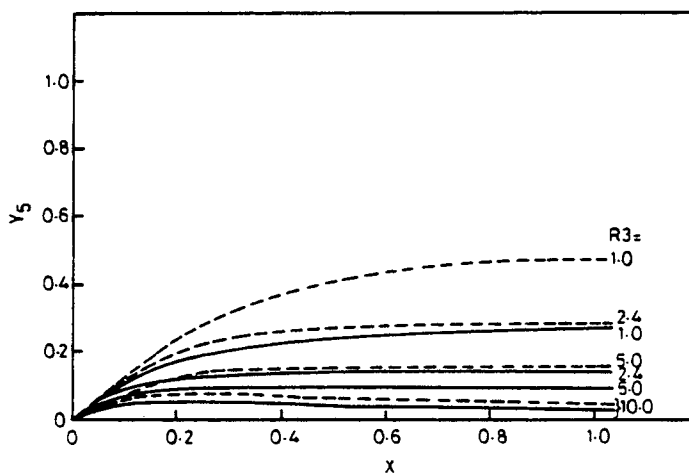


Fig. 3. Effect of  $R_3$  on  $p_e$  as a function of time.  $R_1 = 0.125$ ,  $R_2 = 0.30$ ,  $[P]_0/[F]_0 = 1.67$ . (---) Batch; (—) CSTR.

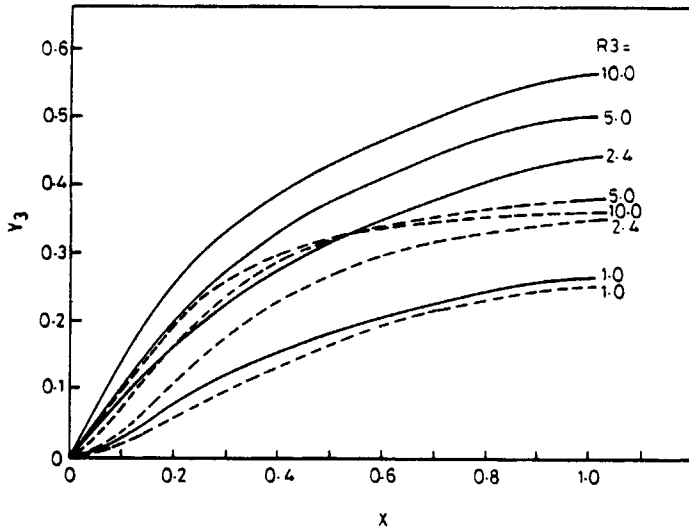


Fig. 4. Effect of  $R_3$  on  $O_i$  as a function of time.  $R_1 = 0.125$ ,  $R_2 = 0.30$ ,  $R_3 = 2.40$ ,  $[P]_0/[F]_0 = 1.67$ . (---) Batch; (—) CSTR.

creases, the rise of  $y_3$  becomes sharper and the curve settles to higher asymptotic value for HCSTRs. In the case of a batch reactor, the asymptotic value of  $y_3$  was first found to increase and then decrease, and this phenomena was explained through the fact that very large  $R_3$  favored the dimer formation.<sup>1</sup> As opposed to this, in the range of values of  $R_3$  studied for HCSTRs, the average molecular weight of the polymer formed continues to increase.

Dimensionless concentrations of phenol and formaldehyde ( $y_8$  and  $y_9$ ) vs.  $x$  have been plotted in Figures 6 and 7. As expected, the conversions for HCSTR are always lower than those for batch reactors. Therefore, the average molecular weight of the polymer formed must be smaller. In view of results of Figures 2-5, it means that the polymer formed in HCSTR is highly polydispersed.

The variation of  $R_1$  and  $R_2$  for a given  $R_3$  is found to have a small effect upon  $y_1$ - $y_{10}$  for HCSTRs. Their functional behavior remains identical to those shown

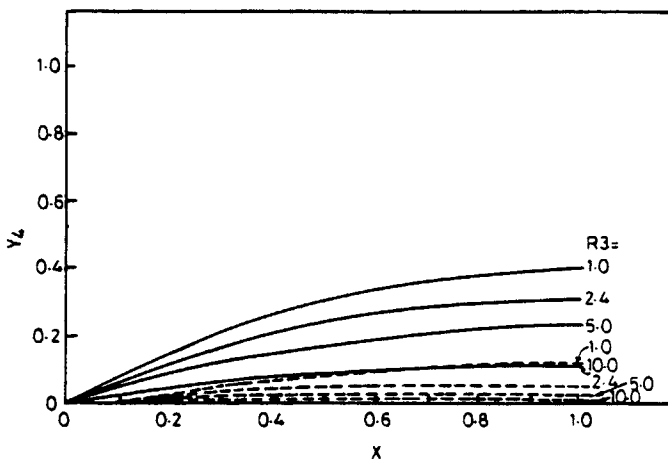


Fig. 5. Effect of  $R_3$  on  $p_i$  as a function of time.  $R_1 = 0.125$ ,  $R_2 = 0.30$ ,  $[P]_0/[F]_0 = 1.67$ . (---) Batch; (—) CSTR.



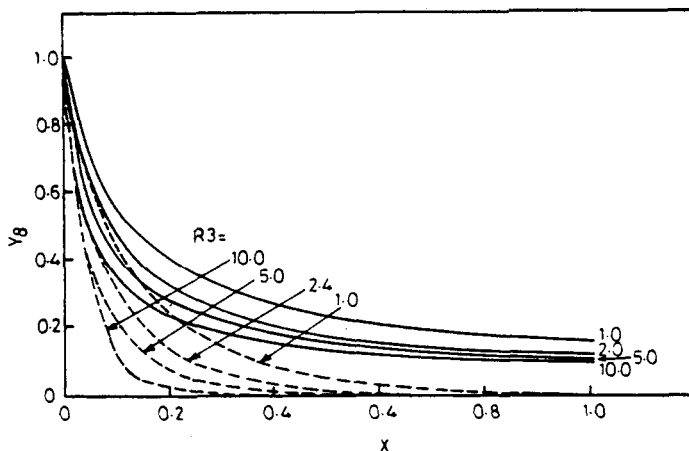


Fig. 6. Effect of  $R_3$  on phenol as a function of time.  $R_1 = 0.125$ ,  $R_2 = 0.30$ ,  $[P]_0/[F]_0 = 1.67$ . (---) Batch; (—) CSTR.

in Figures 2-7, except for slight numerical changes. The asymptotic values of some of these variables for different values of  $R_1$  have been given in Table III to confirm this. This insensitivity is attributed to the fact that the concentrations of  $O_i$  and  $p_i$  in HCSTRs are small for all possible choices of residence times and in the rate expressions given in Table II, the terms involving  $R_1$  and  $R_2$  remain essentially unaffected when  $R_1$  and  $R_2$  are varied.

In our previous work,<sup>1</sup> we noted that all chemical reactions at  $O_i$  and  $p_i$  would lead to branching and the rate of branching for batch reactors,  $\dot{B}_{\text{batch}}$ , was derived to be

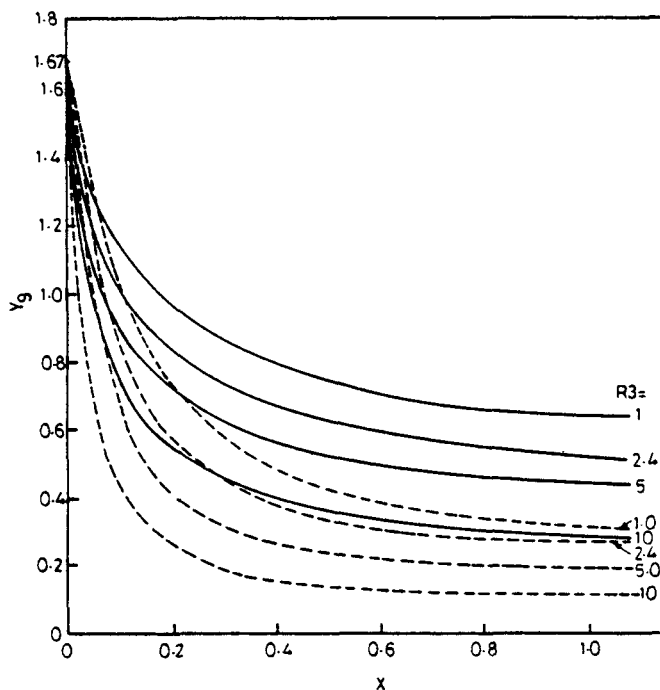


Fig. 7. Effect of  $R_3$  on formaldehyde as a function of time.  $R_1 = 0.125$ ,  $R_2 = 0.30$ ,  $[P]_0/[F]_0 = 1.67$ . (---) Batch; (—) CSTR.

TABLE III  
 Effect of  $R_1$  on Different 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.	$R_1$	$y_1$	$y_2$	$y_3$	$y_4$	$y_5$	$y_6$	$y_7$	$y_8$	$y_9$
1	0.05	(i) <sup>a</sup>	0.5207	0.1516	0.4108	0.2082	0.1683	0.1334	0.5568	
		(ii) <sup>a</sup>	0.8863	0.2778	0.3479	0.0633	0.2928	0.0013	0.2725	
2	0.15	(i)	0.5238	0.1530	0.3907	0.2068	0.1697	0.1312	0.5622	
		(ii)	0.8879	0.2786	0.3418	0.0630	0.2936	0.0013	0.2741	
3	0.25	(i)	0.5266	0.1542	0.3729	0.2055	0.1709	0.1293	0.5671	
		(ii)	0.8894	0.2795	0.3359	0.0638	0.2943	0.0013	0.2756	
4	0.35	(i)	0.5290	0.1553	0.3569	0.2043	0.1720	0.1276	0.5715	
		(ii)	0.8908	0.2803	0.3302	0.0625	0.2950	0.0012	0.2771	
5	0.50	(i)	0.5321	0.1567	0.3357	0.2027	0.1734	0.1254	0.5773	
		(ii)	0.8929	0.2814	0.3220	0.0622	0.2961	0.0011	0.2793	
6	0.8	(i)	0.5370	0.1590	0.3010	0.2000	0.1757	0.1219	0.5869	
		(ii)	0.8966	0.2835	0.3068	0.0616	0.2979	0.0010	0.2835	

<sup>a</sup> (i) HCSTR; (ii) batch.

TABLE IV  
Effect of  $[P]_0/[F]_0$  on Different Sites and P and F at Large Times ( $x = 1.0, R_1 = 0.125, R_2 = 0.30, R_3 = 2.40$ )

No.	$[P]_0/[F]_0$	$y_1$	$y_2$	$y_3$	$y_4$	$y_5$	$y_8$	$y_9$
1	0.5	(i) <sup>a</sup> 0.0432	0.0114	0.0702	0.0364	0.0115	0.5416	0.0836
		(ii) <sup>a</sup> 0.0283	0.0037	0.0934	0.0132	0.0046	0.4630	0.0017
2	1.0	(i) 0.2167	0.0609	0.2216	0.1176	0.0639	0.2529	0.2605
		(ii) 0.2668	0.0598	0.2883	0.0469	0.0687	0.0840	0.0320
3	1.67	(i) 0.4896	0.1514	0.2876	0.1520	0.1610	0.1981	0.6663
		(ii) 0.8875	0.2784	0.3433	0.0631	0.2934	0.0013	0.2737
4	2.0	(i) 0.6685	0.1970	0.4715	0.2452	0.2227	0.1065	0.7108
		(ii) 1.1115	0.3755	0.3088	0.0585	0.3880	0.0001	0.4892
5	3.0	(i) 1.090	0.3256	0.6903	0.3537	0.3818	0.0678	1.162
		(ii) 1.486	0.5505	0.2154	0.0425	0.5569	0.0000	1.315
6	4.0	(i) 1.496	0.4494	0.9027	0.4586	0.5379	0.0499	1.610
		(ii) 1.664	0.6390	0.1628	0.0327	0.6428	0.0000	2.234

<sup>a</sup> (i) HCSTR; (ii) batch.

$$\dot{B}_{\text{batch}} = (R_2 y_4 + R_1 y_3)(y_6 + y_7 + y_8 + y_{10}) \quad (7)$$

The total number of branches  $B_e$  formed can be obtained by a simple number balance on HCSTRs as

$$B_e = x \dot{B}_{\text{batch}} \quad (8)$$

For small residence times, the term  $(R_2 y_4 + R_1 y_3)$  in eq. (7) is small whereas for large residence times, the term  $(y_6 + y_7 + y_8 + y_{10})$  becomes small. Therefore,  $\dot{B}_{\text{batch}}$  is small for all  $x$  and therefore the degree of branching  $B_e$  in eq. (8) remains small for all  $x$ . The fact that  $(y_6 + y_7 + y_8 + y_{10})$ ,  $y_3$ , and  $y_4$  for HCSTRs are always larger than those for a batch reactor, the degree of branching  $B_e$  for the former is always larger. Thus a homogeneous continuous-flow stirred tank reactor would form fewer but larger and more highly branched polymer chains.

In Table IV, the effect of  $[P]_0/[F]_0$  upon the asymptotic values of  $y_1$ - $y_{10}$  has been examined for HCSTRs, and the results are compared with those for batch reactors. For the former,  $y_3$  and  $y_4$  keep increasing as  $[P]_0/[F]_0$  is increased whereas for batch reactors these first increase and then decrease. In the table, the unreacted formaldehyde and phenol,  $y_8$  and  $y_9$ , are always found to be larger than those for the batch reactor.

## CONCLUSIONS

Based upon our kinetic model for novolac formation from acid-catalyzed polymerization of phenol and formaldehyde,<sup>1</sup> mass balance equations for homogeneous continuous-flow stirred tank reactors have been written. This results in 10 nonlinear algebraic equations, and Brown's technique for their numerical solution was found to be successful.

The parameter  $R_3$  was found to have a profound effect upon the exit concentration of  $y_1$ - $y_{10}$  in HCSTRs. For a given  $R_3$ , concentrations of different sites ( $O_e$ ,  $O'_e$ ,  $O_i$ ,  $p_i$ , and  $p_e$ ) rises, ultimately reaching an asymptotic value. These terminal concentrations keep increasing as  $R_3$  is increased. This result is in contrast to what is observed for batch reactors and can be explained by the fact that the polydispersity index  $\rho$  of the polymer formed for the same  $x$  in an HCSTR is higher. Since the conversion of phenol and formaldehyde in an HCSTR is lower, it would also imply that the average molecular weight of the polymer formed is small. The analysis on branching shows that polymer chains are more highly branched in HCSTRs.

## NOMENCLATURE

$\dot{B}$	Branching rate for batch reactors
$[F]_0$	inlet formaldehyde concentration to the HCSTR
$k_1$ - $k_4$	rate constants as defined in Table I
$O_e, O'_e$	ortho external sites on chains with $n \geq 2$
$O_i$	ortho internal sites on chains with $n \geq 2$
$p_i$	para internal sites on chains with $n \geq 2$
$p_e$	para external sites on chains with $n \geq 2$
P	phenol molecule
$R_1$	$k_2/k_1$
$R_2$	$k_3/k_1$
$R_3$	$k_4/k_1$

$t$	residence time of HCSTR
$y_1$	$[O_e]/[F]_0$
$y_2$	$[O_e]/[F]_0$
$y_3$	$[O_i]/[F]_0$
$y_4$	$[p_i]/[F]_0$
$y_5$	$[p_e]/[F]_0$
$y_6$	$[Q_1]/[F]_0$
$y_7$	$[Q_1]/[F]_0$
$y_8$	$[P]/[F]_0$
$y_9$	$[F]/[F]_0$
$y_{10}$	$[CH_2OH]/[F]_0$

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