

Studies on the Formation of the Thermosetting Resins. XI. Computer Simulation on the Formation of Phenolic Resins

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ABSTRACT: The formation mechanisms of phenolic resins were studied by computer simulation. As an example, the process for the polymerization of *o*-methylolphenol is as follows: (1) the number of methylol groups and nuclear hydrogens of *o*- and *p*-position are stored, (2) a methylol group is selected, (3) a functional group of another molecule is selected to react with the methylol group previously selected, and (4) a molecule freshly formed is fed back into the computer. In this simulation, the reactivity of the functional group is represented by the probability that the group is selected. This procedure is iterated until the extent of reaction reaches to the same value as that of the practical reaction calculated from GPC chromatogram. Discussion about the reactivity of each functional group was made by comparison of the molecular weight distribution of the hypothetical product in the computer with that of the actual one. From these results, it is known that the formation of dimethylene ether linkage is negligibly small compared to that of the methylene linkage and a methylol group is more reactive with a nuclear hydrogen in the disubstituted phenol than in the monosubstituted phenol.

KEY WORDS Thermosetting Resin / Phenolic Resin / Computer Simulation
/ Gel-Permeation Chromatography / Methylolphenol / Methylenation /

It is well known that phenol-formaldehyde resins are formed by repetition of methylation and methylenation. But it is difficult to discuss the mechanisms of these reactions and to determine the properties and the structures of these resins owing to the lack of quantitative informations regarding the reactivity of *ortho*- and *para*-position in phenol, the influence of substitution on reactivity and the formation of dimethylene ether linkage besides methylation and methylenation.

In this paper, the computer-simulation technique is thus proposed as the method for discussing these reaction mechanisms. To simplify the treatment, methylolphenols are used as monomers. The molecular weight distributions calculated by computer simulation, giving several values of the reactivity ratio of a methylol group to a nuclear hydrogen and monosubstituted phenol to a disubstituted phenol are compared with those obtained from GPC measurements of the actually prepared resin. The value of the reactivity ratio which gives the most agreeable molecular weight distribution with that obtained from GPC is the most reasonable for the

practical reaction. The technique for generation of the random number, the Monte Carlo method, is used in this computer simulation.

EXPERIMENTAL

Materials

Ethanol and tetrahydrofuran (THF) were distilled. *o*-Methylolphenol was synthesized according to the reference¹. *o*-Methylol-*p*-cresol was synthesized as follows: 81 g of 37% formalin was slowly dropped into a cool mixture of 324 g of *p*-cresol and 160 g of 50% aqueous NaOH and the mixture was then stirred. The sodium salt of *o*-methylol-*p*-cresol was filtered off, washed with 500 cm³ of butanol and then dissolved in water and neutralized by adding acetic acid. The crude products were purified by recrystallization from water. *p*-Methylolphenol was synthesized as follows: 130 g of 50% aqueous KOH was slowly dropped into a cool mixture of 94 g of phenol and 81 g of 37% formalin; the mixture was then stirred and maintained at a temperature below 30°C. The mixture, containing the sodium salt of *o*-

methylolphenol was kept at the usual temperature for several days; following this acetic acid was added for neutralization.

For removal of the unreacted phenol and *o*-methylolphenol, the mixture was extracted with three 200 cm³ portions of chloroform. The residual solution was extracted with six 200 cm³ portions of ethyl ether, and then the ethyl ether solution was dried over anhydrous sodium sulfate and concentrated. The crude products were purified by recrystallization from benzene. These synthesized materials were identified by their melting points and the elemental analysis.

Polymerization

o-Methylol-*p*-cresol and *o*- and *p*-methylolphenol were used as monomers. In each case, the monomer was dissolved in 20 cm³ of ethanol in a three necked flask equipped with a reflux condenser. While adding hydrochloric acid as a catalyst, the flask was heated. A small amount of the reaction solution was collected several times during the reaction for measurement of GPC.

Gel-Permeation Chromatography (GPC)

A Japan Spectroscopic Co. Model-FLC-A700 GPC equipped with two 50 cm polystyrene-gel column (Shodex A803) was used. THF was used as the elution solvent at an ambient temperature, at a flow rate of 1.0 cm³/min. The samples were injected in 0.5% THF solution and detected by UV spectrum. From GPC chromatograms of these reaction products, the relationships between the molecular weight *M* and the elution volume *V* were obtained as follows.

$$\ln M = -AV + B$$

$$A = 0.5007 \quad B = 24.8565$$

for *o*-methylol-*p*-cresol polymer,

$$A = 0.3758 \quad B = 19.4702$$

for *o*-methylolphenol polymer,

$$A = 0.3721 \quad B = 19.3472$$

for *p*-methylolphenol polymer.

Using these relationships, the number- and the weight-average molecular weights, the molecular weight distribution and the extent of reaction were calculated. The extent of reaction in this paper is given by $(N_0 - N)/N_0$, where N_0 and N are the number of molecules in the initial system and in the sample collected, respectively.

COMPUTER SIMULATION

Principle of Hypothetical Reaction in Computer

Let us discuss the polymerization of the bifunctional monomers, A-A and B-B. In this polymerization, it is assumed that the reactions occur between any functional groups except in the case of intramolecular reactions. The concept of the computer simulation for this reaction is as follows. First, the number of the molecules and the functional groups of each species are stored in a computer. Since the probability that the functional group A or B will be selected, is utilized as the corresponding value of the reactivity in this simulation, the number of the functional groups stored is not the actual number but the hypothetical number by considering the reactivity. A functional group is selected by means of the technique of generation of random numbers called the Monte Carlo method. That is, numerics between 0 and 1 are, in advance, divided into two ranges which are proportional to the number of these functional groups stored. If a generated number belonging to the range of A, an A group is selected. Two functional groups thus selected are made to react hypothetically and the new molecule resulting is fed back into the computer. By repeating this procedure, the number of molecules stored in the computer decreases and the molecular weight distribution changes progressively. This procedure is repeated until the extent of reaction reaches to the same value calculated from GPC chromatogram of the actually prepared resin. The reactivity ratio of the functional group A to B, which gives the same molecular weight distribution as that of the practically prepared resin, is the suitable value for an actual reaction.

The assumptions used in the simulation for the polymerization of *o*-methylolphenol as example are as follows.

1. Only methylenation between methylol groups and nuclear hydrogens and the etherification between methylol groups themselves occur,
2. The reactivities of a methylol group and nuclear hydrogen are influenced by the nuclear position and the degree of substitution independently,
3. These reactivities are not effected by molecular size,
4. Intramolecular reactions do not occur.

The flow chart of the computer simulation of this

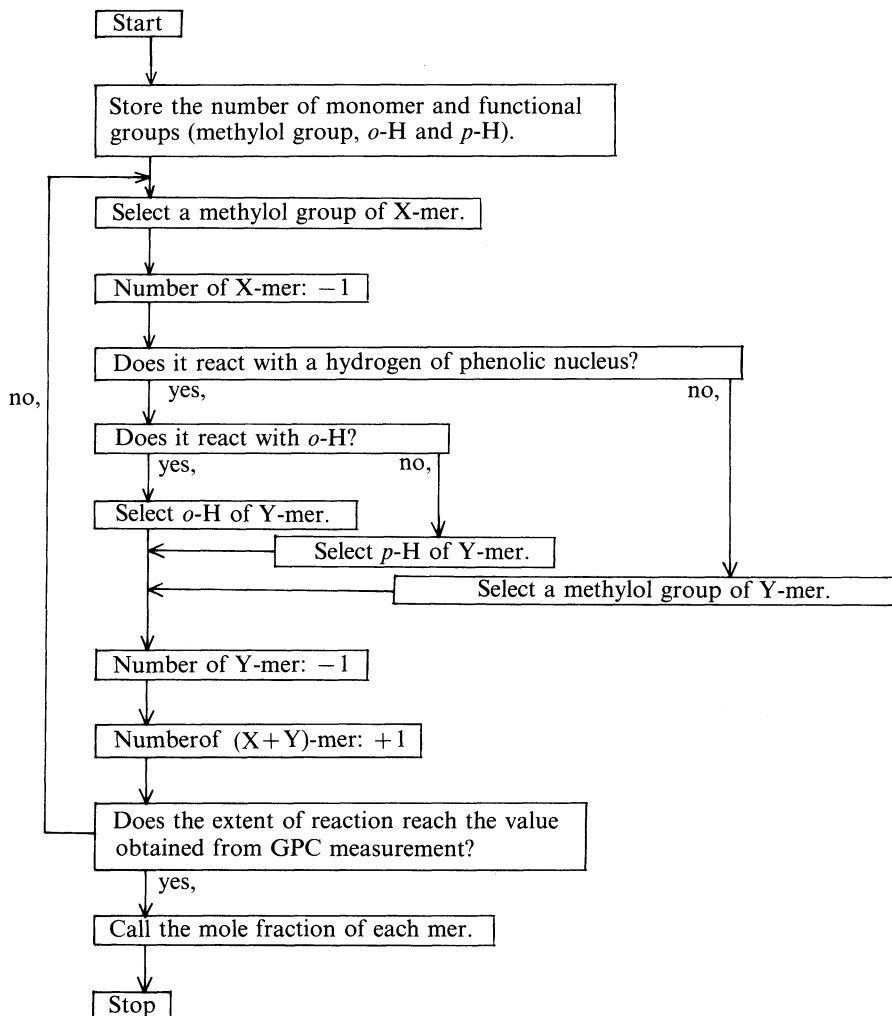


Figure 1. Flow chart of computer simulation for polymerization of *o*-methylolphenol. *o*-H and *p*-H represent the hydrogen at *ortho*- and *para*-position of phenolic nucleus.

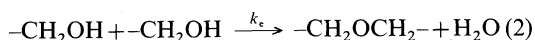
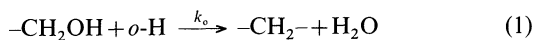
reaction is illustrated in Figure 1.

RESULTS AND DISCUSSION

Effects of Species of Functional Groups on Reactivity

a) Polymerization of *o*-Methylol-*p*-Cresol.

Designating the nuclear hydrogen at the *ortho*-position as *o*-H, the following reactions are considered.



and the rate of each reaction is represented as follows.

$$\frac{d[-\text{CH}_2-]}{dt} = k_o[\text{o-H}][-\text{CH}_2\text{OH}] \quad (3)$$

$$\frac{d[-\text{CH}_2\text{OCH}_2-]}{dt} = k_e[-\text{CH}_2\text{OH}]^2 \quad (4)$$

Since the reactivity of the functional group can be represented by the probability of selection of that functional group in this computer simulation as mentioned above, the stored number of *o*-H and $-\text{CH}_2\text{OH}$ are determined by multiplying the actual

number by the coefficients IO and IE, respectively. If the extent of reaction p is used instead of the reaction time t , the reaction rates are represented as follows.

$$\frac{d[-\text{CH}_2-]}{dp} = \text{IO}[o\text{-H}] \text{IE}[-\text{CH}_2\text{OH}] \quad (5)$$

$$\frac{d[-\text{CH}_2\text{OCH}_2-]}{dp} = \text{IE}[-\text{CH}_2\text{OH}] \text{IE}[-\text{CH}_2\text{OH}] \quad (6)$$

From these equations, the following formula are introduced,

$$\frac{d[-\text{CH}_2-]}{d[-\text{CH}_2\text{OCH}_2-]} = \frac{k_o[o\text{-H}]}{k_e[-\text{CH}_2\text{OH}]} = \frac{\text{IO}[o\text{-H}]}{\text{IE}[-\text{CH}_2\text{OH}]} \quad (7)$$

therefore, the following relation applies,

$$\frac{k_e}{k_o} = \frac{\text{IE}}{\text{IO}} \quad (8)$$

Comparison of the molecular weight distribution of *o*-methylol-*p*-cresol resin obtained from GPC measurements with that obtained from the computer

simulation giving $k_e/k_o=0$ and 1 are shown in Table I—III which indicate the effects of the reaction time, the reaction temperature and the concentration of HCl, respectively. Figure 2 shows examples of the GPC chromatograms of the samples appearing in Table I. We also examined similar treatments which gave several values of k_e/k_o . From these results, it is

Table I. Comparison of molecular weight distributions of the *o*-methylol-*p*-cresol resin obtained from GPC^a and computer simulation, giving k_e/k_o equal to 0 or 1

<i>N</i> -mer	Mole fraction		
	GPC	Simulation	
		$k_e/k_o=0$	$k_e/k_o=1$
Reaction time, 30 min ($p=0.294$)			
1	0.716	0.707	0.678
2	0.200	0.205	0.246
3	0.056	0.062	0.060
4	0.017	0.019	0.013
5	0.006	0.005	0.002
6	0.003	0.002	0.000
Reaction time, 160 min ($p=0.572$)			
1	0.422	0.426	0.307
2	0.271	0.246	0.335
3	0.139	0.141	0.194
4	0.085	0.081	0.092
5	0.027	0.044	0.043
6	0.016	0.028	0.019
7	0.013	0.015	0.006
8	0.010	0.011	0.004
9	0.005	0.003	0.001

^a Monomer, 0.05 mol; HCl, 0.012 mol.

Table II. Comparison of the molecular weight distributions of the *o*-methylol-*p*-cresol resin obtained from GPC^a and computer simulation, giving k_e/k_o equal to 0 or 1

<i>N</i> -mer	Mole fraction		
	GPC	Simulation	
		$k_e/k_o=0$	$k_e/k_o=1$
Reaction temp, 50°C ($p=0.446$)			
1	0.558	0.557	0.492
2	0.257	0.244	0.310
3	0.109	0.108	0.130
4	0.034	0.051	0.046
5	0.020	0.020	0.015
6	0.009	0.012	0.005
7	0.006	0.005	0.002
8	0.003	0.003	0.000
Reaction temp, 110°C ($p=0.432$)			
1	0.586	0.569	0.507
2	0.236	0.244	0.312
3	0.106	0.105	0.120
4	0.031	0.047	0.043
5	0.018	0.019	0.013
6	0.010	0.009	0.005
7	0.006	0.004	0.001
8	0.003	0.002	0.000

^a Monomer, 0.05 mol; HCl, 0.012 mol.

Table III. Comparison of the molecular weight distributions of the *o*-methylol-*p*-cresol resin obtained from GPC^a using a small amount of catalyst and from computer simulation, giving k_e/k_o equal to 0 or 1

<i>N</i> -mer	Mole fraction		
	GPC	Simulation	
		$k_e/k_o=0$	$k_e/k_o=1$
1	0.622	0.616	0.568
2	0.236	0.235	0.291
3	0.093	0.091	0.100
4	0.020	0.035	0.031
5	0.015	0.016	0.008
6	0.007	0.005	0.002
7	0.003	0.002	0.000

^a Monomer, 0.05 mol; HCl, 0.0001 mol; reaction temp, 110°C ($p=0.386$).

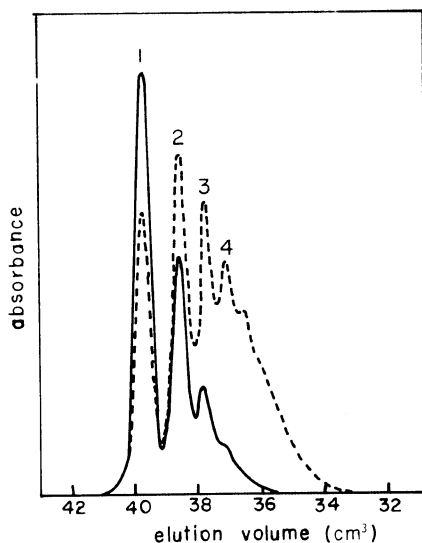


Figure 2. GPC chromatograms of *o*-methylol-*p*-cresol resin shown in Table I: solid line, reaction time, 30 min; dotted line, reaction time, 160 min. The numbers in the figure indicate the number of phenolic nuclei.

obvious that the molecular weight distributions obtained from the computer simulation, giving 0 or negligibly small values as k_e/k_o , agree with those of the resins synthesized under any sort of conditions. Because $k_e \ll k_o$, it is assumed that the dimethylene ether linkage is hardly formed.

b) Polymerization of *o*-Methylolphenol

If the nuclear hydrogen at *para*-position is designated as *p*-H, the rates of the formation of the methylene linkage and dimethylene ether linkage are expressed as follows.

$$\frac{d[-CH_2-]}{dt} = k_o[o-H][-CH_2OH] + k_p[p-H][-CH_2OH] \quad (9)$$

$$\frac{d[-CH_2OCH_2-]}{dt} = k_e[-CH_2OH]^2 \quad (10)$$

For the reaction in the computer, they are represented by eq 11 and 12.

$$\frac{d[-CH_2-]}{dp} = IO[o-H]IE[-CH_2OH] + IP[p-H]IE[-CH_2OH] \quad (11)$$

$$\frac{d[-CH_2OCH_2-]}{dp} = IE[-CH_2OH]IE[-CH_2OH] \quad (12)$$

From these equations, the following relation is introduced,

$$\frac{k_p}{k_o} = \frac{IP}{IO} \quad (13)$$

Assuming that the formation of the dimethylene

Table IV. Comparison of the molecular weight distributions of the *o*-methylolphenol resin obtained from GPC^a and computer simulation, giving k_p/k_o equal to 1 or 10

<i>N</i> -mer	Mole fraction		
	GPC	Simulation	
		$k_p/k_o=1$	$k_p/k_o=10$
1	0.704	0.627	0.602
2	0.144	0.210	0.234
3	0.062	0.085	0.091
4	0.033	0.039	0.039
5	0.024	0.017	0.018
6	0.012	0.010	0.009
7	0.007	0.005	0.004
8	0.005	0.002	0.003

^a Monomer, 0.025 mol; HCl, 0.012 mol; reaction temp, 50°C; reaction time, 300 min ($p=0.412$).

ether linkage can also be neglected in this reaction system, the computer simulation was performed for $k_p/k_o=1$ and 10 under several conditions and such results as in Table IV were obtained.

It is obvious from these results that the molecular weight distributions obtained from the simulation for both $k_p/k_o=1$ and 10 do not agree with those of GPC measurements for any set of reaction conditions. It is clear that this computer simulation is unsatisfactory for discussing the difference in the reactivity between *ortho*- and *para*-position of phenol.

Effects of the Degree of Substitution of Phenol on Reactivity

Assuming that the amount of dimethylene ether linkage in the products is negligibly small and that the reactivities of the nuclear hydrogen at *ortho*- and *para*-position of phenol are equal and by designating the nuclear hydrogens of mono- and di-substituted phenol as 1-H and 2-H and the rate constants of the reaction of methylol group with 1-H and 2-H as k_1 and k_2 , the reaction rates of *o*-methylolphenol may be expressed as follows.

$$\frac{d[-CH_2-]}{dt} = k_1[1-H][-CH_2OH] + k_2[2-H][-CH_2OH] \quad (14)$$

$$\frac{d[-CH_2OCH_2-]}{dt} = k_e[-CH_2OH]^2 \quad (15)$$

Using the factors I1 and I2 for 1-H and 2-H in a similar manner as the case of the factor IO for *o*-H, the rate equations 14 and 15 are expressed as follows.

$$\frac{d[-CH_2-]}{dp} = I1[1-H] IE[-CH_2OH] + I2[2-H] IE[-CH_2OH] \quad (16)$$

$$\frac{d[-CH_2OCH_2-]}{dp} = IE[-CH_2OH] IE[-CH_2OH] \quad (17)$$

Then the following equation is obtained,

$$\frac{k_2}{k_1} = \frac{I2}{I1} \quad (18)$$

Table V. Comparison of the molecular weight distributions of the *o*-methylolphenol resin obtained from GPC^a and computer simulation, giving k_2/k_1 equal to 2 or 1/5

N-mer	Mole fraction		
	GPC	Simulation	
		$k_2/k_1=2$	$k_2/k_1=1/5$
Reaction time, 90 min($p=0.250$)			
1	0.778	0.778	0.754
2	0.151	0.150	0.183
3	0.046	0.047	0.046
4	0.016	0.016	0.012
5	0.006	0.005	0.004
6	0.002	0.003	0.001
7	0.001	0.001	0.000
Reaction time, 300 min ($p=0.412$)			
1	0.704	0.695	0.601
2	0.144	0.138	0.230
3	0.062	0.079	0.097
4	0.033	0.036	0.040
5	0.024	0.020	0.018
6	0.012	0.012	0.009
7	0.007	0.008	0.003

^a Monomer, 0.025 mol; HCl, 0.012 mol; reaction temp, 50°C.

Table VI. Comparison of the molecular weight distributions of the *o*-methylolphenol resin obtained from GPC of resin^a synthesized at high temperature (110°C) and from computer simulation, giving k_2/k_1 equal to 5 or 1/5

N-mer	Mole fraction		
	GPC	Simulation	
		$k_2/k_1=5$	$k_2/k_1=1/5$
1	0.715	0.714	0.621
2	0.143	0.132	0.229
3	0.065	0.075	0.090
4	0.031	0.033	0.036
5	0.019	0.019	0.016
6	0.010	0.010	0.006
7	0.006	0.007	0.002

^a Monomer, 0.025 mol; HCl, 0.012 mol; reaction time, 10 min ($p=0.387$).

The simulation for polymerization of *o*-methylolphenol under several conditions was carried

out and the results, shown in Tables V and VI were obtained. The molecular weight distributions obtained from simulation in the case of $k_2 > k_1$ agree with that of the products for any reaction conditions. That is, the methylol group is more reactive with 2-H than with 1-H and the reactivity of 2-H increases with the increment of the extent of reaction. Similar results were obtained from simulation for the polymerization of *p*-methylolphenol.

From simulation, information about isomers can be also obtained. For example, the mole fractions of

isomers for each mer in the *o*-methylolphenol resin, obtained from the simulation giving $k_2/k_1 = 5$ as shown in Table VI, are listed in Table VII.

CONCLUSION

We propose computer simulation for determining the formation mechanism of phenolic resins and obtaining related information.

Applying this technique to the reaction of *o*-methylol-*p*-cresol, it was found that the phenolic nucleus was bonded mainly by methylene linkages and that the dimethylene ether linkage was hardly formed.

From the results of simulation for the reaction of *o*-or *p*-methylolphenol, it became evident that the reactivity of the nuclear hydrogen in di-substituted phenol with methylol group was larger than that in mono-substituted phenol. However, the difference of the reactivity between the nuclear hydrogen of *ortho*-position and *para*-position was not made clear.

Moreover, this technique can be used for calculating not only the molecular weight distribution but also the mole fraction of isomers of each mer.

We conclude that computer simulation is very convenient and useful for investigating of the formation of phenolic resins.

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Table VII. Mole fractions of isomers of each mer in *o*-merthylolphenol resin simulated under k_2/k_1 equal 5

<i>N</i> -mer	Number of 1-H	Number of 2-H	Mole fraction	Total
1	2	0	0.714	0.714
2	2	1	0.132	0.132
3	2	2	0.026	0.075
	4	0	0.049	
4	2	3	0.004	0.033
	4	1	0.029	
5	2	4	0.001	0.019
	4	2	0.010	
	6	0	0.008	
6	4	3	0.005	0.010
	6	1	0.005	
7	4	4	0.001	0.007
	6	2	0.004	
	8	0	0.002	