

Studies on Phenol Formaldehyde Gel Formation at a High Temperature and at Different pH

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Abstract

Gel formation characteristic of dilute phenol-formaldehyde solution in water is studied at an elevated temperature near 140⁰ C. It is experimentally found that at temperature range of 135⁰ C to 140⁰ C a solution containing 3.0% phenol with the phenol-formaldehyde mole ratio 1.0: 3.5 forms gel in a range of pH values of 9.6 to 12.0. The minimum gelling time is observed at a pH value of 10.4. The gel formation is found to be strongly depending on the pH at this elevated temperature. An explanation for the gelling behavior is presented which is based on an optimum ion concentration of Na⁺ to initiate the tri-methylol formation. It is hypothesize that subsequent gel formation begins when concentration of tri-methylol phenol attains a minimum threshold concentration value. The kinetics analysis provides a rationale for the proposed hypothesis. The observed dependence of gelling time has been explained.

Keywords: Phenol-Formaldehyde Monomer System, Methylolation, Gelation, Gelling-zone, High temperature gelling.

Introduction and Background Literature

A gel is a dispersion of a three dimensional network that entraps a solvent medium. Classification of gels is based on the type of links that creates the three dimensional structures, the size and shape of the gel configuration and the type of solvent. Gels can

form either by covalent bonding, called chemical gels or by physical interactions at colloidal level, called physical gels.

Gels find uses in many engineering applications. Gel formation technology has been implemented widely now for reduction of water produced along with oil from oil wells (Wu Lin., 2002; Dalrymple et al., 2000). Gel technology is also widely used in industries like pharmaceutical and food processing (Yosihito et al., 2001). Poly hydroxy-ethylene methacrylate gel has been used to make the soft contact lens. Super absorbent polymers are widely used in diapers for their property to lock absorbed water by forming gels.

Study of phenol formaldehyde polymer gel system is of both scientific and industrial interest. While the chemistry of reactions involved is reasonably well studied, the studies on the gel formation are scarce in literature. In this paper we report some new experimental findings on the formation of phenol formaldehyde gel that has potential gel applications in engineering areas such as water shut off in petroleum engineering at high temperature.

Methylol and Resole Formation during Gel Formation: Phenol-formaldehyde (P:F) aqueous system under go gel formation in presence of an alkaline catalyst. The reaction proceeds in two steps before gel can form, as given by Billmeyer, Jr. (1970). Initial reactions take place to form various methylol derivatives (-CH₂OH) of phenol. Methylol groups combine in either of the two '*ortho*'-positions or in '*para*'-position to hydroxyl group of phenol by addition reaction as shown in Figure-1. The reactions can proceed further through condensation and decomposition reactions in the presence of an alkaline catalyst and shown in Figure-2. With the formation of tri-functional *ortho*-

ortho-para methylol cross linking can initiate which can lead to the gel formation. Some important features of the chemistry of these reactions is briefly described in what follows:

- a) Methylol derivatives are formed by addition of methylol groups at *ortho* and *para* positions to the hydroxyl group.
- b) Condensation of methylol phenol molecules with either a phenol or another methylol phenol molecule to give a methylene bridge in the presence of alkaline catalyst with one molecule of water as condensation product.
- c) Condensation of two methylol groups to give an ether bridge.
- d) Decomposition of ether bridges to methylene bridges and formaldehyde.

Formaldehyde such released again reacts by step (a).

Reactions of step-(a) result in five methylol derivatives as described in Figure- 1. *Ortho-ortho-para* methylol derivative formation is favored when formaldehyde to phenol mole ratio is more than one ($F: P > 1$) and pH above 8.0 (Kentzen, 1969). A network formation can be initiated by *ortho-ortho-para* derivative as it has a functionality of three. It is possible that instead of the reacting system proceeding up to *o-o-p* methylol derivatives, under favorable conditions, undergo condensation reactions where intermediate *ortho-ortho* and *ortho-para* methylol derivatives condense either by methylene linkage formation or through ether linkages. While in the former case one molecule of water is liberated, in the latter case, one molecule of formaldehyde will form. Possible condensation products, known as resoles are shown in Figure- 2.

Network Formation and Gelation: Further polymerization of methylol with tri-functional *o-o-p* methylol will result in a network formation if a significant amount of

o-o-p methylol is formed. Phase transition for any monomer system to 'gel point' depends on solvent composition, temperature, pH value, ion compositions and also on the electrical field applied (Rossi et al, 1991). In phenol - formaldehyde system the reactions are catalyzed by stronger alkalis such as NaOH. With increase in pH value, Na^+ goes on increasing but beyond some stage of Na^+ concentration the catalytic action is stopped and the rate of formation of ortho methylol gets reduced.

Three dimensional cross linked structures are usually shown by using a lattice model. However, in reality the polymers can spread out or coiled up into a ball, depending on the relationship between them and their solvent, (Yamauchi, 2001). One such relationship is the solubility parameter. There are heterogeneous gels in which crosslinked units are locally concentrated and homogeneous gels with evenly distributed crosslinked units. Figure- 3 shows the different conceptual structure of gels.

The chemistry of methylol derivative formation in the Step-(a) has been studied by many researchers (Kentzen, 1969). Two probable mechanisms in *ortho* methylol formation are as follows:-

(a) Phenol assumes the anion form in equilibrium with NaOH catalyst that is followed by *ortho* substitution through the resonance formation.

(b) The other possibility is the formation of hemi-formals of phenol as the intermediate which quickly rearrange to phenol alcohol. Zavitsas has given a complete model for the reaction (Zavitsas and Beaulian, 1967).

On the other hand, reaction mechanism of *para* substitution would depend on the formation of an activated complex from the quinoid form (Yaddanapalli et al., 1959). Subsequently this reacts with phenol to give *para* derivatives.

Zavitsas et al, 1967 found that in presence of NaOH catalyst, the ratio of *ortho* to *para* substitution is a function of the dielectric constant of the medium.

Many more mono- and di-nuclear phenol alcohols can form in parallel (Martin, 1956). Martin had prepared and reported some 147 such alcohol products. Some of the phenol alcohols that can form are given in Table – 2. The order of the reactions for all the methylol formation is reported to be second order and depend on concentrations of monomeric formaldehyde and phenolic anions (Jones, 1946; Freeman and Lewis, 1954). While methyl groups combine in the ortho and para positions of phenol for both acidic and basic conditions, only a high pH value favors o-o-p methylol formation. The rate coefficients of the kinetics of methylation of phenol at 57° C are also reported (Zavitsas, 1966).

Experimental Studies:

Experiments have been conducted to study the formation of gels at different concentrations of phenol, at different pH of the solution and also at different phenol to formaldehyde mole ratios. Investigations have been carried out on the development and characterization of gels. A typical gel formation property of phenol formaldehyde system is presented. Studies that provided the basis to find the rate constant for gel formation is also presented here. Bulk gelation studies in glass ampoules, properly sealed and heating it to required temperature in an aging cell have been conducted and the gelling is monitored using Sydansk scale. TG and DTG of the gel have been carried out for chemical analysis.

Materials Used: All chemicals used were of analytical grade. Phenol solution of 88.0% concentration in water is prepared from phenol crystals (LR). Formaldehyde solution of

37~ 41% strength in water were obtained from Thomas Baker (Chemicals) Ltd, Mumbai, India. Sodium hydroxide pellets of lab grades were also obtained from Thomas Baker (Chemicals) Ltd, Mumbai, India.

Equipment Used: Following equipments / instruments were used in this study.

i) ageing Cells, S.S. 18-8 grade heavy duty, ii) 20 ml glass ampoules, iii) glass blowing arrangements for sealing the ampoules, iv) glass and acrylic made bottles for low temperature bulk gelation studies, v) Cyber Scan 1000 pH meter, vi) Metler PM 4000 weighing balance for coarse weighing (least count 1 mg), vii) Metler PM 10000, weighing balance (least count 0.01 mg), viii) Brook field viscometer, ix) electrically heated oven with temperature control.

Preparation of Gel Precursor Solution: Normally gel mixtures of 100 ml were prepared in each batch. Required amount of phenol was taken in a beaker and dissolved in a small quantity of distilled water. Formaldehyde solution was added to maintain a formaldehyde–phenol mole ratio of 3.5. Solution of 1.0 (N) NaOH was added and the initial pH of the mixture was taken in the range of 9.5 to 12.0. Distilled water was added as necessary to adjust concentration of ingredients and pH. Gel mixture of 20 ml was put in each ampoule and sealed.

Gelling Experiments: After 20 ml solution was put in each ampoule and sealed by flame torch and kept in ageing cells, the cells were placed in a oven for bulk gelation at 140⁰ C. Oxy-acetylene flame was used for sealing the ampoules. Five sealed ampoules were put in each ageing cell and four such ageing cells were used. Small quantity of water was placed in each ageing cell and the lids of the cells were tightly closed. As the cells were heated, steam generated inside the ageing cells was able to maintain a cell

temperature between 135⁰ to 140⁰ C. A schematic diagram of the ageing cell used is shown in Figure- 4.

The concentrations of phenol used were 2%, 2.5%, 3%, 3.5% and 4.0% by weight. Formaldehyde was added in two ratios, 3.0 and 3.5. Gelling was conducted at temperatures having a small range of 135⁰ C and 140⁰ C. Thus for each specific mole ratio sixteen sets of experiment were performed. For each of the sixteen experiments four ageing cells were used at a time with a holding capacity of 20 ampoules. From these experimental studies, it is found that gel formation takes place for range of pH 9.6 to 12.0. When samples were at pH less than 9.6 and above 12.0 no significant gel formation was observed in a rather long time period of sixteen hours.

Monitoring of gel formation: - Ampoules were taken out from the oven at an intervals of one hour and checked if the gel initiation had occurred. Four sets of similar samples were used at a time for data confirmation. Intermittent opening and closing of the cell was necessary to inspect the liquid characteristic inside ampoule. However, carefully reducing the opening and the closing time and adopting a suitable procedure minimized the occurrence of unnecessary perturbations.

Four ageing cells were marked AGC-1, AGC-2, AGC-3 and AGC-4. Distribution of ampoules was made as shown below, Table -1.

Sl. No.	Ageing Cell No.	Sample pH placed in ampoules
1	AGC-1	10.1, 10.3, 10.5, 10.7, 10.9
2	AGC-2	10.2, 10.4, 10.6, 10.8, 11.0
3	AGC-3	10.2, 10.3, 10.4, 10.5, 10.6

Ageing cells AGC-1 and 2 were first taken out, cooled quickly and opened for visual inspection. The ageing cells were re-packed and replaced in the oven after every inspection. Moment the first gel formation was observed, the third cell, AGC-3 was also opened for a cross checking. AGC-4 was used for one more cross checking. These experiments were repeated several times. When proper thickening of solution and gel formation was visually observed, the time was noted as the gel time. It was confirmed by tapping the inverted bottle. When gelled substance fall as a single piece on inversion it was considered as the gel formation has taken place. Gel strength was compared visually from 1 to 10 as practiced and given by Sydansk, (1999).

Experimental Results

Visual Observation on Gel Formation using Sydansk Scale: We report our visual observation on the various aspects of gel formation guided by Sydansk Scale. The aspects we have focused are the incubation time, the time of gelling and their dependence on the pH of the gelling solution. Time of gel formation is related to the kinetics of gelling. The kinetics of gelling, however, is not measured using a parameter such as viscosity and is a topic of our future study. The details of Sydansk scale which is used in petroleum engineering community is given else where (Sydansk, 1999). The incubation time for gelling as well as the time for gelling can be accurately obtained by this technique. The rate of gelling however can not be ascertained by this method. In this work, both incubation time and the gelling time are studied.

Gel strength is qualitatively characterized visually in Sydansk scale which is coded from one to ten. A ringing rigid gel having a tuning fork like mechanical vibration is

coded '10'. For no detectable gel formation which has same viscosity as the initial solution is coded as '0'. The intermittent conditions where flow ability of the fluid and deformability of semisolid substances are determined visually, coded from '1' to '9'. In this study, we have used code "0" and "10" for our analysis to make it reliable.

Based on a number of experimental observations, it is found that rate of gel formation is rapid in the vicinity of pH 10.4 and the gel formation time is 6 hours. It also has been found that both at below the pH of 10.3 and at above the pH of 10.5, the time of gelling is substantially higher than 6 hours. Furthermore, at pH below 9.5 no gelation was found to take place, even after 50 hours. Similarly, for pH of 10.8, the time of gelling is 11 hours. Beyond the pH of 12.0 no significant gelling was observed in our study.

The gelling data as represented by Sydansk scale are presented in Table- 4. From Table- 4 we can obtain the following two important characteristics of gelling.

- (i) locus of initiation of gel formation corresponding to each pH, and
- (ii) locus of completion of gel formation corresponding to each pH.

These findings are plotted as pH vs. time for gel formation in Figure- 5. From Figure- 5 we observe that the above mentioned loci result in two parabolic curves encompassing a crescent type region bounded by the curves one related to initiation of gelling and the other related to completion of gelling (Sydansk scale codes "0" to "10"). Therefore the figure can be divided into two distinct zones which are termed according to the gelling behavior as "No-Gelling" and "Gelling". The formation of gel begins and gets completed in the "gelling" zone as shown in the Figure- 5.

We further observe from the Figure- 5 that there is a sickle shaped area (crescent) formed by the "gelling" zone. This finding is being reported for the first time and has

significant practical importance. In the pH range of 10.1 to 10.7 the induction time is less but the time of gelling is higher, while at pH below and above this range, the induction time is high and the time of gelling is less. Importantly, we also observe that two ranges of pH on both sides of the pH value of 10.4 are not equal. It must be emphasized here that the concentration of phenol is an important parameter for the sickle zone formation and at concentrations of phenol below 2.5% and above 4.0%, this region does not appear.

The viscosity have been measured for some samples of gels (Sydansk scale codes “0” to “10”).

Evidence of o-o-p methylol Presence: A similar experimental procedure is followed as in Table 1. A set of ampoules with the specific phenol formaldehyde composition is put in the oven for gel formation. At every hour one ampoule was taken out and quickly quenched to sub zero temperature to arrest the reactions. The reactive mass is conserved in sub zero temperature. Samples of every-hour were subjected to thermogravimetric and differential-calorimetric analysis. Figures– 6 and 7 show Thermo Gravimetric (TG) & Differential TG of two samples taken from the regimes of “no gelling” and “gelling” composition. It is significant to note in DTG curve that percent mass loss per minute in “gelling” composition has a significant peak at 78° C. Table 2 shows that o-o-p methylol has the lowest melting point among all other methylols. An early mass loss observed at 78° C indicates the presence of *ortho-ortho-para* methylol. No such peak is seen in case of DTG curve for “no gelling” regime in Figure 7. It is expected that *ortho* methylol will be present in all stage of gel formation. *Ortho*-methylol presence corresponds to the peak at 86.9° C, which is agrees with the data

presented in Table 2. Two minor peaks observed beyond 90° C in ‘no gel’ composition signify the presence of *ortho-para*-methylol derivative. Therefore, it can be concluded that the formation and kinetics of *ortho-ortho-para*-methylol (tri-methylol) is key to the gel formation.

Chemical Kinetics Analysis:

Reaction Rate Constants: An analysis based on the rates of all relevant chemical reactions is conducted in this work. Prior to presentation of analysis, we describe here an approach used to determine the reaction rate constants at the experimental temperature. Rate constants of all reactions of Figure 1 reported in literature are at 57⁰ C. We need the values of rate constants at around 140⁰C for our kinetic analysis. To find the rate constant values at higher temperatures following experiments are conducted.

Similar experimental procedure described in previous sections are followed to study gel formation at temperatures 85⁰, 90⁰, 105⁰, 115⁰ and 130⁰ C. Gel initiation times (i.e. gel formation start points) are observed with phenol concentrations 1.5%, 2.0%, 2.25% and 2.5%. Phenol - formaldehyde ratio maintained as 1:3.5. For each concentration of phenol four sets of samples with pH values 9.5, 10, 10.5 and 11 are tested for finding gel time. The experimental data are shown in Table- 3. It has been noted that for solutions with 1.5% and for 2.5% phenol, gel formation was observed only at 90⁰ C. However, at 2.0% and 2.25% phenol gel formation was observed throughout the temperature range. The data at different experimental conditions indicate that temperature has significant effect on gel formation. It is observed that phenol concentration below 2.0% and above 2.25% the gel formation is not favored in this

temperature range. However, where gel formation is observed, the temperature rise results in a decrease in gel formation time. The temperature dependence of gelation can be represented by an Arrhenius equation (Silva R.F, 1999)

$$\ln(t_{gel}) = A + E / RT \dots\dots\dots(1)$$

Where, E is the activation energy for gelation and A is a constant in the equation.

Rate Constants for methylol Reaction:

The experimental data for pH values 2.25 and 2.5 are fitted into equation-1 to obtain the best-fit value of the parameters A and E for equation (1). Best fit lines for different pH value are shown in fig11. The slopes of the best fit lines at different pH values are almost constant. This leads to the conclusion that the slope i.e., the activation energy E for the phenol formaldehyde system is independent of the pH. Thus the major parameter that will decide the gel formation time is system temperature only. Rate constants of all reactions of Figure 1 reported in literature are for temperature range much below 100⁰ C. For our studies rate constants at elevated temperature of 140⁰C is thus evaluated.

Compositions from Rate Equations:

Besides the reactions presented in Figure -1, other compounds can form in parallel (Martin, 1956). Martin had prepared and reported some 147 such alcohol products. Some of the phenol alcohols that can form are given in Table -2.

With assumption of second order rate equations for all the reactions in Figure- 1, the rate equations can be written as follows: -

$$\frac{dC_O}{dt} = k_1 * C_{Ph} * C_{Fr} - k_3 * C_O * C_{Fr} - k_4 * C_O * C_{Fr} \dots\dots\dots(2)$$

$$\frac{dC_P}{dt} = k_2 * C_{Ph} * C_{Fr} - k_7 * C_P * C_{Fr} \dots\dots\dots (3)$$

$$\frac{dC_{OO}}{dt} = k_3 * C_O * C_{Fr} - k_5 * C_{OO} * C_{Fr} \dots\dots\dots (4)$$

$$\frac{dC_{OP}}{dt} = k_4 * C_O * C_{Fr} + k_7 * C_P * C_{Fr} - k_6 * C_{OP} * C_{Fr} \dots\dots\dots (5)$$

$$\frac{dC_{OOP}}{dt} = k_5 * C_{OO} * C_{Fr} + k_6 * C_{OP} * C_{Fr} \dots\dots\dots (6)$$

Where, C_{Ph} and C_{Fr} are the instantaneous concentration of phenol and formaldehyde. C_O , C_P , C_{OO} , C_{OP} , C_{OOP} are instantaneous concentration of *o*-methylol, *p*-methylol, *o-o* methylol, *o-p* methylol and *o-o-p* methylol respectively produced during the progress of the reactions.

The fractional yield of *o*- methylol with respect to phenol can be written as follows;-

$$\frac{dC_o}{dC_{Ph}} = \frac{k_1}{(k_1 + k_2)} + \left(\frac{k_3 + k_4}{k_1 + k_2} \right) * \frac{C_o}{C_{Ph}} \dots\dots\dots (7)$$

Thus at the very early stage of reaction when only methylation reaction is initiated fractional yield of *o*-methylol with respect to phenol is independent of formaldehyde concentration. Equation (6) correlates the concentration of *o*-methylol and the concentration of phenols, is a typical Bernoulli's integral equation of the form;-

$$\frac{dy}{dx} + P(x, y) = Q(x, y), \text{ which has a solution;- } y * e^{\int P dx} = \int Q * e^{\int P dx} dx + I$$

Solving this ODE with initial value condition as $t=0$ and $C_{Ph} = C_{Ph0}$ the value of C_O i.e. *o*-methylol concentration can be derived as given in equation (8);-

$$C_O = \frac{k_1}{p} \left[C_{Ph0}^{p/a} * C_{Ph}^{b/a} - C_{Ph} \right] \dots\dots\dots (8)$$

Where, $a = k_1 + k_2$, $b = k_3 + k_4$ and $p = a - b$.

Similarly concentrations of C_p i.e. *p*-methylol derivative can also be derived as presented in equation (9): -

$$C_p = \frac{k_2}{a - k_7} \left(C_{Ph_0}^{\frac{a-k_7}{a}} * C_{Ph_0}^{\frac{k_7}{a}} - C_{Ph} \right) \dots\dots\dots (9)$$

The fractional yield of other methylol derivatives with respect to phenol can also be found out through rigorous calculations.

For minimum gelling time found experimentally and given in Table- 4, the initial concentration of phenol and formaldehyde was 0.319 M and 1.157 M respectively. During gel formation, instantaneous concentrations of all methylol derivatives can be derived in terms of phenol concentration as given in equations (10) to (14);-

$$C_O = -2.53 * C_{Ph} + 1.853 * C_{Ph}^{0.727} \dots\dots\dots (10)$$

$$C_p = -0.3873 * C_{Ph} + 0.159 * C_{Ph}^{0.203} \dots\dots\dots (11)$$

$$C_{OO} = 3.256 * C_{Ph} - 8.09 * C_{Ph}^{0.727} + 5 * C_{Ph}^{0.613} \dots\dots\dots (12)$$

$$C_{OP} = 1.41 * C_{Ph} - 2.185 * C_{Ph}^{0.727} + 0.097 * C_{Ph}^{0.203} + 0.7873 * C_{Ph}^{0.532} \dots\dots\dots (12)$$

$$C_{OOP} = -2.74 * C_{Ph} + 8.42 * C_{Ph}^{0.727} - 5 * C_{Ph}^{0.613} - 0.256 * C_{Ph}^{0.203} - 0.782 * C_{Ph}^{0.532} \dots\dots\dots (14)$$

In Figure- 8 the above concentration relations are shown. From Figure- 8 it can be observed that the rise in tri-methylol concentration is rapid at high concentration of phenol and formaldehyde. With decrease in phenol and formaldehyde concentration *o*-*o*-*p* concentration slows down and asymptotically approaches to a very low value after a certain time period when concentration of phenol reduces to 0.05 M. We assume that the gelling begins at this point and therefore there exists an incubation period. The

complex kinetics leading to an end product, tri-methylol is the reason for the incubation period.

Discussion of Results

Description of a Mechanism of Gelation of Phenol Formaldehyde System at a High

Temperature: An incubation period of four and a half hours has been observed when gel formation took place at pH value 10.4. For this case the gelling period was observed as three hours as shown in Figure- 7. Figure- 7 also indicates that incubation period for other pH values are comparatively more. For example, at pH value less than 10.4 say, 9.8 the incubation period is twelve hours. Similarly at a higher pH value of 11.5 the incubation period is nine hours. It is also interesting to note that when incubation period is more the gelling period is in general short. Gelling time is hardly an hour when pH value is 9.8 and at pH value of 11.5 the gelling time is two hours. Such unique characteristic is explained qualitatively in what follows.

For the specific phenol formaldehyde solution the initial pH value of 10.4 gives an optimum Na^+ ion concentration that leads to a rapid formation of *o-o-p* methylol by all possible reaction routes as shown in Figure- 1. Minimum threshold concentration of *o-p* methylol is attained while free phenol molecules are still present in solution to form methylols and their resoles. The phenol formaldehyde solution being dilute the distances between the monomers are large. At the same time phenol molecules being small in size can access easily to the *o-o-p* molecules so formed. With the assumption that *o-o-p* remains uniformly distributed, a heterogeneous gel structure formation can initiate. While inter-molecular linking of resoles with gel points becomes difficult, intra-molecular crosslinking of every *o-o-p* molecule becomes more probable.

Crosslinked units are locally concentrated and a micro-gel in macro-gel structure is formed as shown in Figure- 4b. Possibility for a subsequent fuzz ball structure, as shown in Figure- 4c is also expected. Phenol molecules are more reactive than any other methylol molecules and they compete more readily to combine to the three active sites of tri-functional *o-o-p* methylol. Methylol formation is thus slowed down which in turn effect various resole formation. The overall effect is a longer gelling period of three hours. Though formation of *o-o* and *o-p* methylol proceeds in parallel the rates of formation become slower as phenol molecules join in the micro-gel structures initiated by tri-functional *o-o-p* methylol. Formation of other methylols and their resoles takes place while reaction rate for network formation proceeds in the micro-gel structure. The solution starts becoming viscous. More and more micro-gel points are developed and get inter connected. The gel formation is complete.

On the other hand, when pH value is different from 10.4, fast formation of *o-o-p* methylol is not favored. The various *o-o* and *o-p* methylol formation proceeds to a greater extent with their resole formation. The formation of threshold amount of *o-o-p* methylol is much delayed. But once *o-o-p* methylol attains threshold limit the network formation is rapid. This point is corresponding to incubation period. Available *o-o* and *o-p* methylols help *o-o-p* methylol to form network very quickly and reach gel point. As a result gelling period observed is comparatively short.

In pH values below and above 10.4, the *o-o-p* threshold concentration occurrence is delayed, but network formation starts more homogeneously in the presence of different methylols and very less phenol molecules left. Through out the solution *o-o-p* methylol molecules get favorable reaction conditions to undergo crosslinking. Equations 7 to 13

indicate how the composition of various methylols in the phenol-formaldehyde based gel system will be interrelated. Figure- 8 indicates the various methylol-concentration-relations when the initial solution contained 3.0 % phenol in water and phenol-formaldehyde mole ratio was 3.5. It can be observed from Figure- 8 that concentration of *o-o-p* methylol remains less than 0.02% while all other methylols i.e. *ortho*, *para*, *ortho-ortho*, *ortho-para* are significant. However, the concentration of *o-o-p* increases sharply while other concentration goes on reducing.

Future Scope of Work:

Further studies are required to develop a quantitative model to describe the observed gelling behavior, particularly at different pH values. The values of reaction of different pH are needed to carry out the chemical kinetic analysis to explain the observed results.

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Table – 2 Significant Phenolic Alcohols with their Melting Points (Martin, 1956)

Sl. No	Compound	Melting Points
1	<i>o</i> -methylolphenol	86
2	<i>p</i> -methylolphenol	124-126
3	2,4-dimethylolphenol	92-94
4	2,6-dimethylolphenol	95-101
5	2,4,6-trimethylolphenol	76-84
6	4-2,4-methylol- <i>o</i> -cresol	81-84
7	3-methylol-2-2'-dihydroxy- diphenylmethane	121-123
8	3-methylol-4-4'-dihydroxy- diphenylmethane	124-130

Table – 3 Gel Time at Different Temperatures

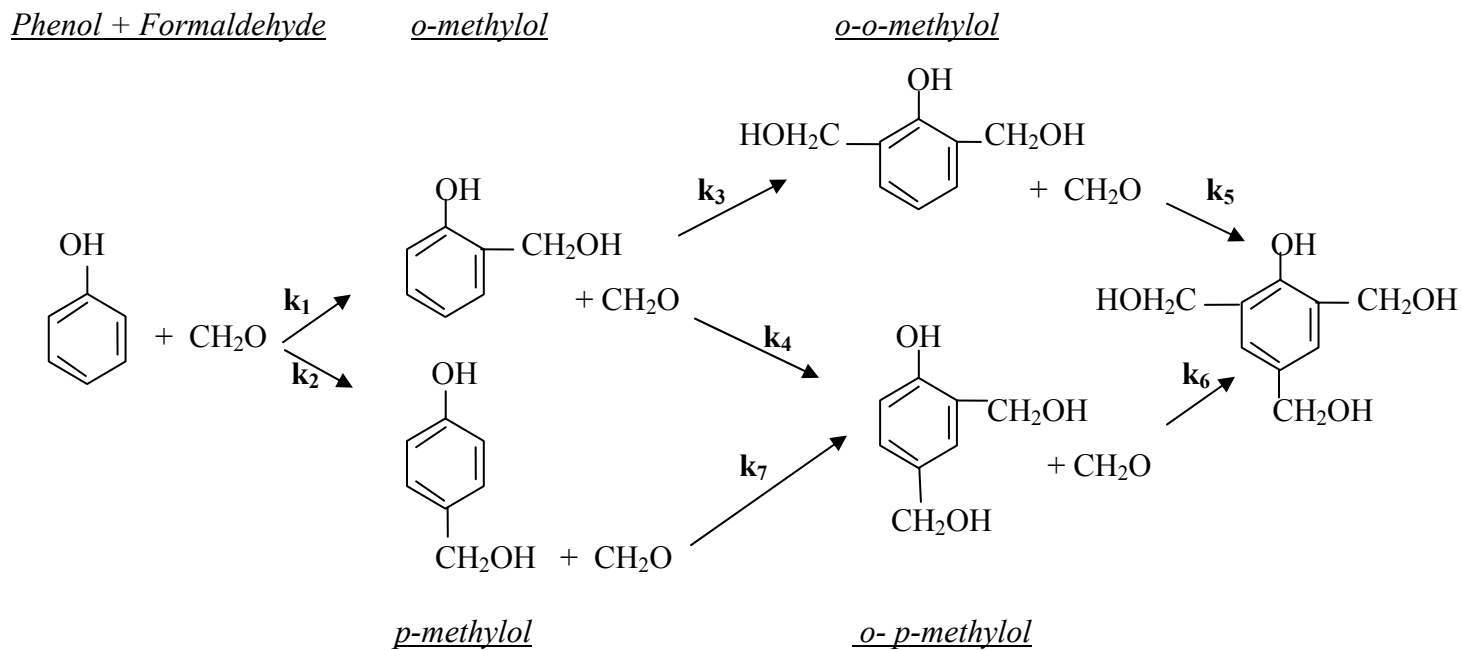
Gel Composition	pH	<i>Gel Start Point Time in Hours at Different Temperatures</i>				
		85 ⁰ C	90 ⁰ C	105 ⁰ C	115 ⁰ C	130 ⁰ C
1.5%Phenol	9.5	--	16	--	--	--
	10	--	28	--	--	--
	10.5	--	32	--	--	--
	11	--	60	--	--	--
2.0%Phenol	9.5	18	15	10	5	5.25
	10	22	18	15	11	5.25
	10.5	38	30	23	15	--
	11	62	50	45	15	--
2.25%Pheno	9.5	15	11	10	5	5.25
	10	19	14	12	9	4
	10.5	35	28	23	11	--
	11	50	45	34	13	--
2.5%Phenol	9.5	--	10	--	--	--
	10	--	13	--	--	--
	10.5	--	26	--	--	--
	11	--	44	--	--	--

Table – 4. Bulk Gelation Studies on Phenol – Formaldehyde system at 140°C (P : F = 1: 3.5)

SI No	Phenol gms	pH	Gel Strength build up with time in <i>Hrs.</i>																				
			4	5	6	7	8	9	10	11	12	13	14	15	16	18	20	22	24	26	28	30	
PF-01	3.000	9.5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
PF-02	3.000	10.0	1	1	1	1	1	1	1	1	1	9	10	10	10	10	10	10	10	10	10	10	10
PF-03	3.000	10.1	1	1	1	1	1	1	1	1	9	10	10	10	10	10	10	10	10	10	10	10	10
PF-04	3.000	10.2	1	1	1	1	1	4	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-05	3.000	10.3	1	1	1	4	8	10	10	0	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-06	3.000	10.4	1	1	1	4	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-07	3.000	10.5	1	1	1	1	8	8	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-08	3.000	10.6	1	1	1	1	8	8	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-09	3.000	10.7	1	1	1	1	1	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-10	3.000	10.8	1	1	1	1	1	1	8	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PF-10	3.000	10.9	1	1	1	1	1	1	8	10	10	10	10	10	10	10	10	10	10	10	10	10	10

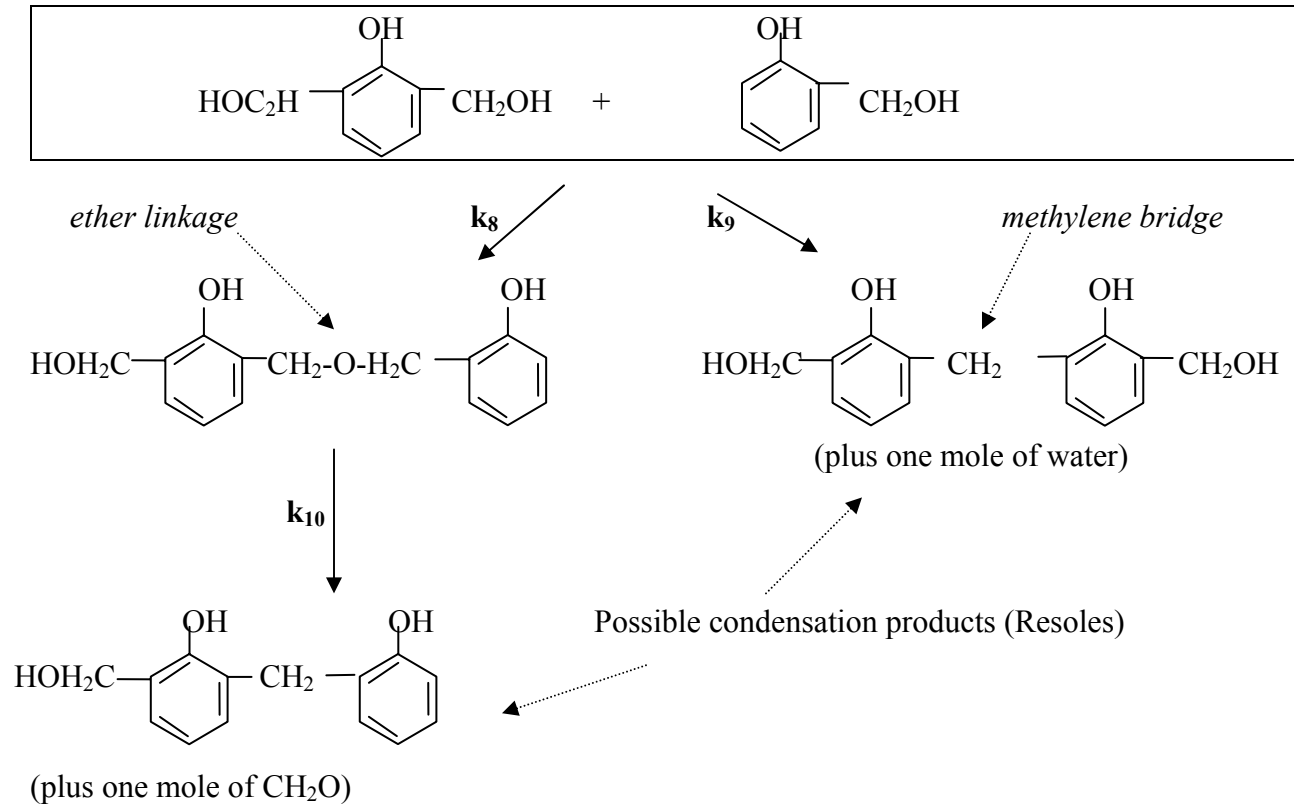
Gel Strength Measured as per Sydansk Scale

Figure – 1 Series-parallel reaction-steps for methylol formation (phase I)



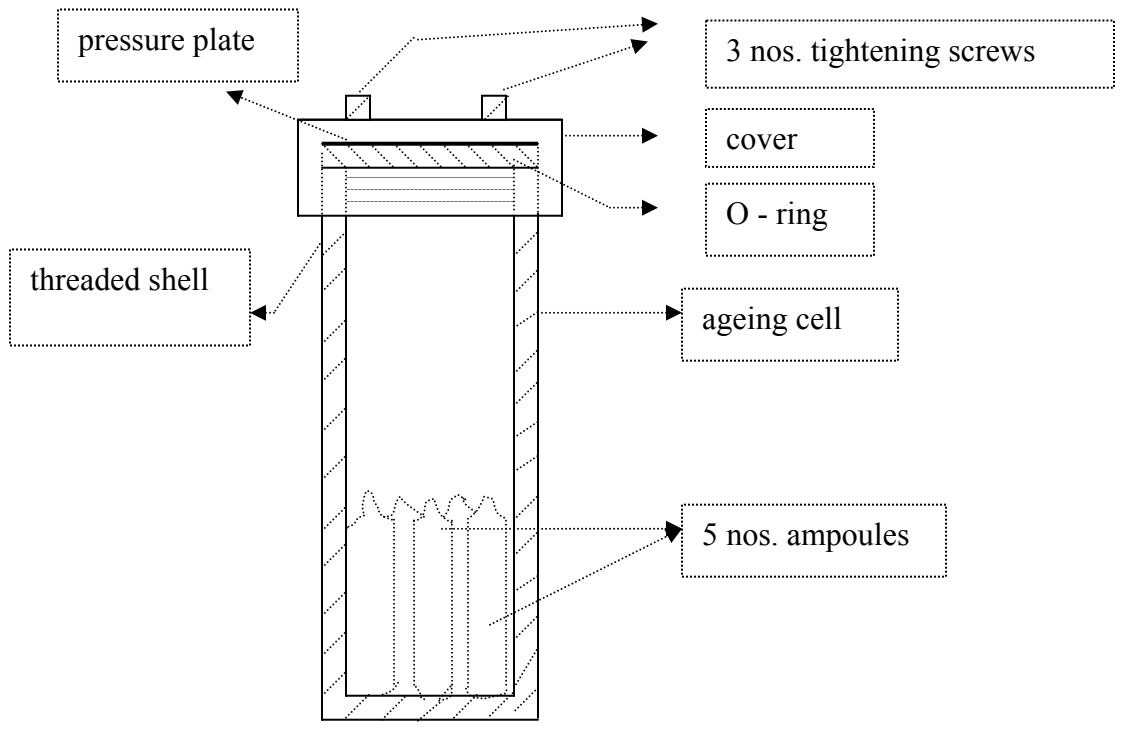
All k_i 's are reported in literature (Zavitsas, 1966).

Figure – 2 Resole formation through methylene linkages or ether linkages (phase II)

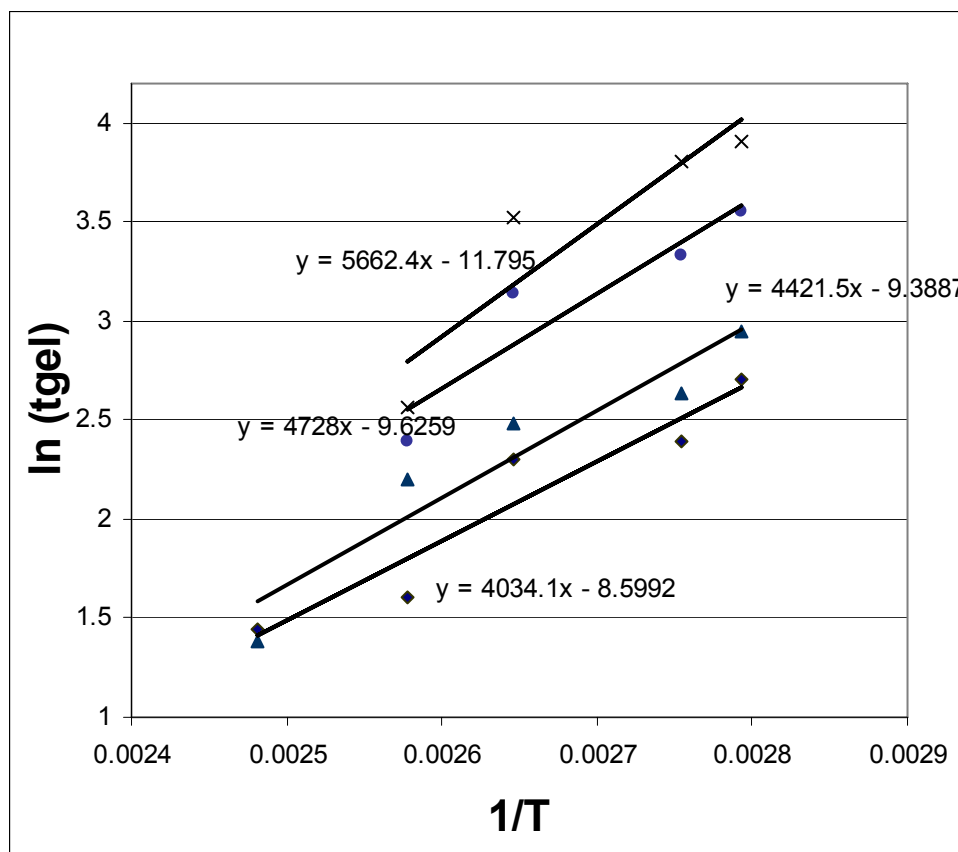


** The condensation reaction rates k_8 , k_9 and k_{10} are five to eight times faster than all k_1 to k_7 values (Kakiuchi et al, 1952).

Figure – 3 Schematic Diagram of an Ageing Cell



**Figure -4 Gel Time measured at Different Temperatures, Phenol 2.0%,
(F:P ratio 3.5:1 and pH values 9.5-10.0-10.5-11.0)**

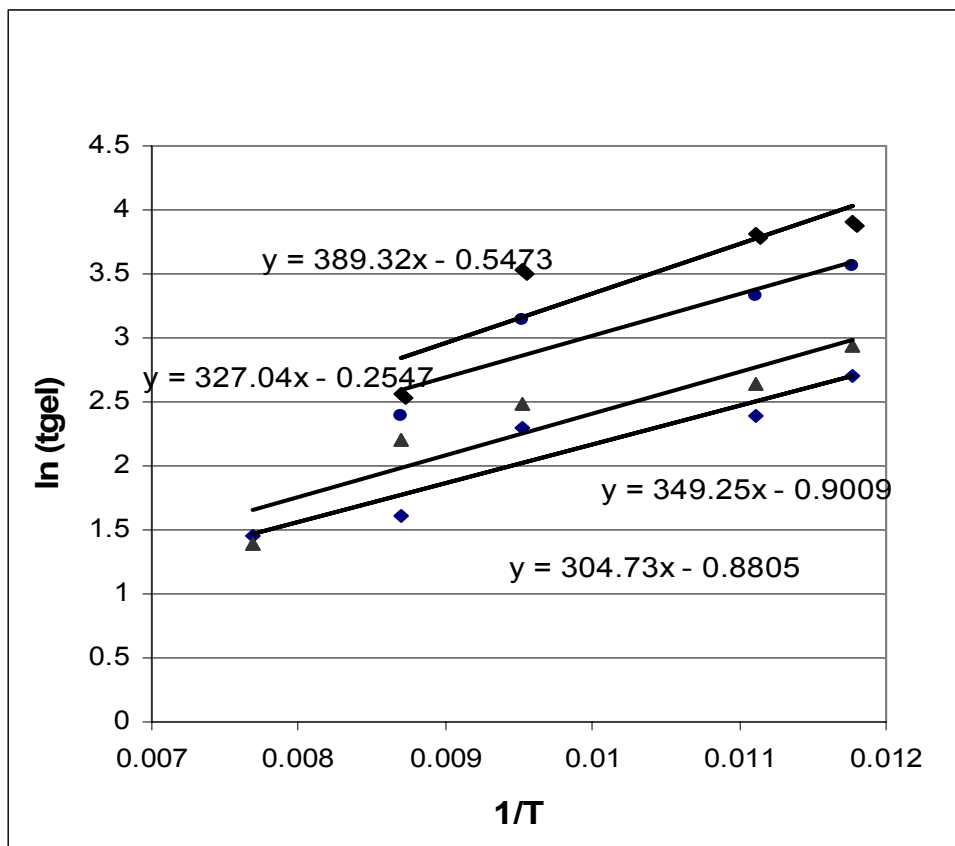


A linear variation of $\ln(t_{gel})$ with $1/T$ is observed. The Activation Energy ‘E’ calculated for four pH values are: -

Sl No	pH	E (Kcal/mole)
1.	9.5	9.86
2.	10.0	9.48
3.	10.5	7.88
4.	11.0	11.22

Figure -5 Gel Time measured at Different Temperatures, Phenol 2.25%

(F:P ratio 3.5:1 and pH values 9.5-10.0-10.5-11.0)

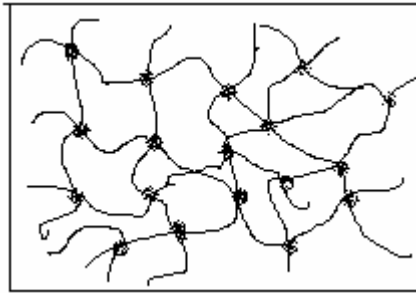


A linear variation of $\ln(t_{gel})$ with $1/T$ is observed. The Activation Energy 'E' calculated for four pH values are: -

Sl No	pH	E (Kcal/mole)
1.	9.5	8.088
2.	10.0	8.843
3.	10.5	9.456
4.	11.0	11.325

Figure- 6 Different Conceptual Structure of Gels

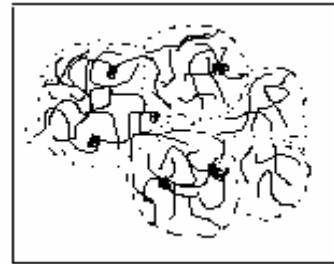
(Yamauchi A, 2001)



(a) Ideal Crosslinking (homogeneous gel)



(b) Heterogeneous gel Structure



(c) Polymer Floc ball

Figure-7 Gel Formation Time vs. Solution pH

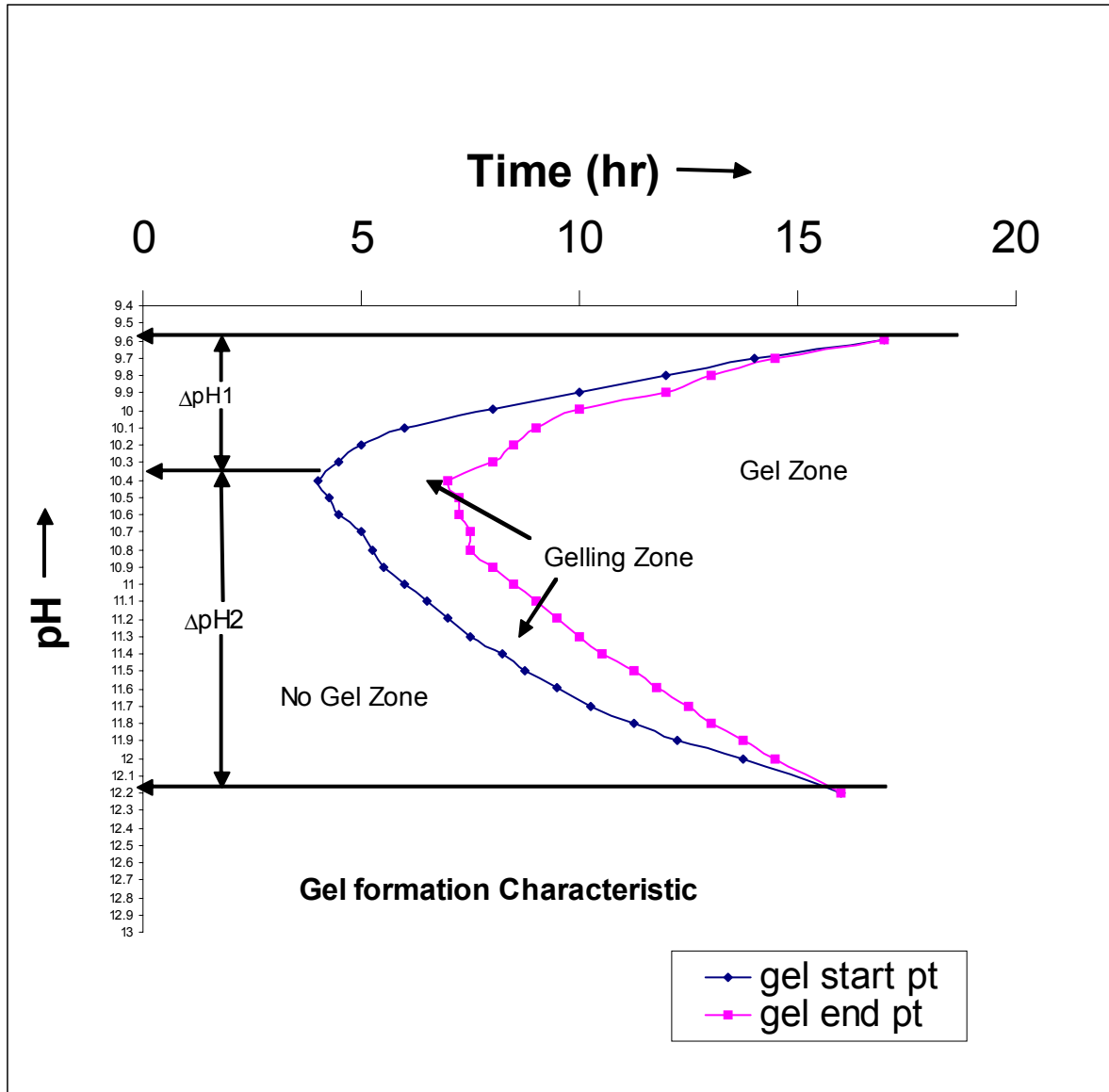


Figure-8 TG/ DTA of 'No-Gel' sample

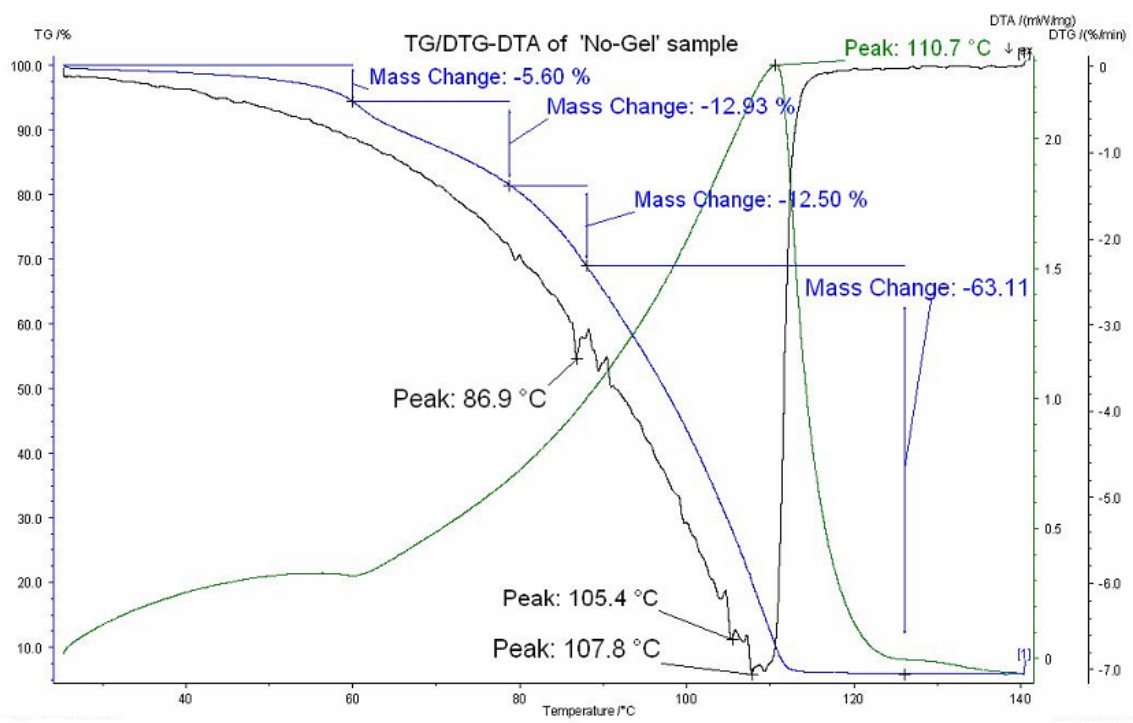


Figure- 9 TG/ DTA of ‘Gel-Formed’ sample.

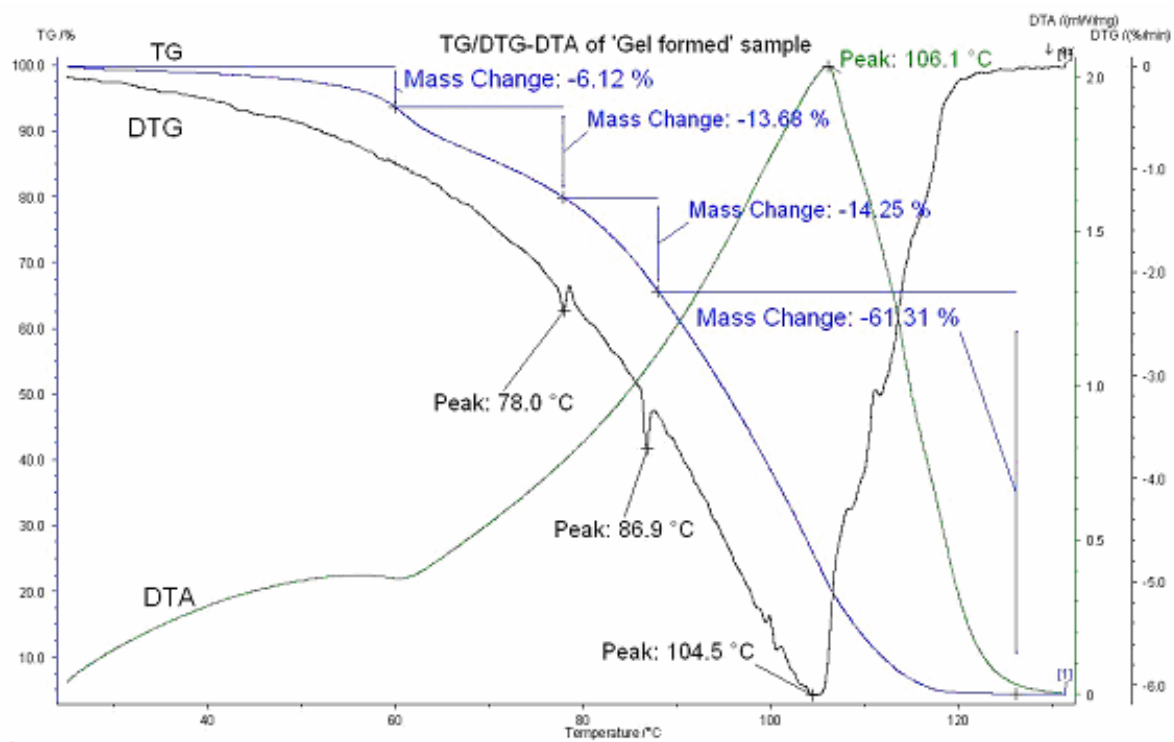
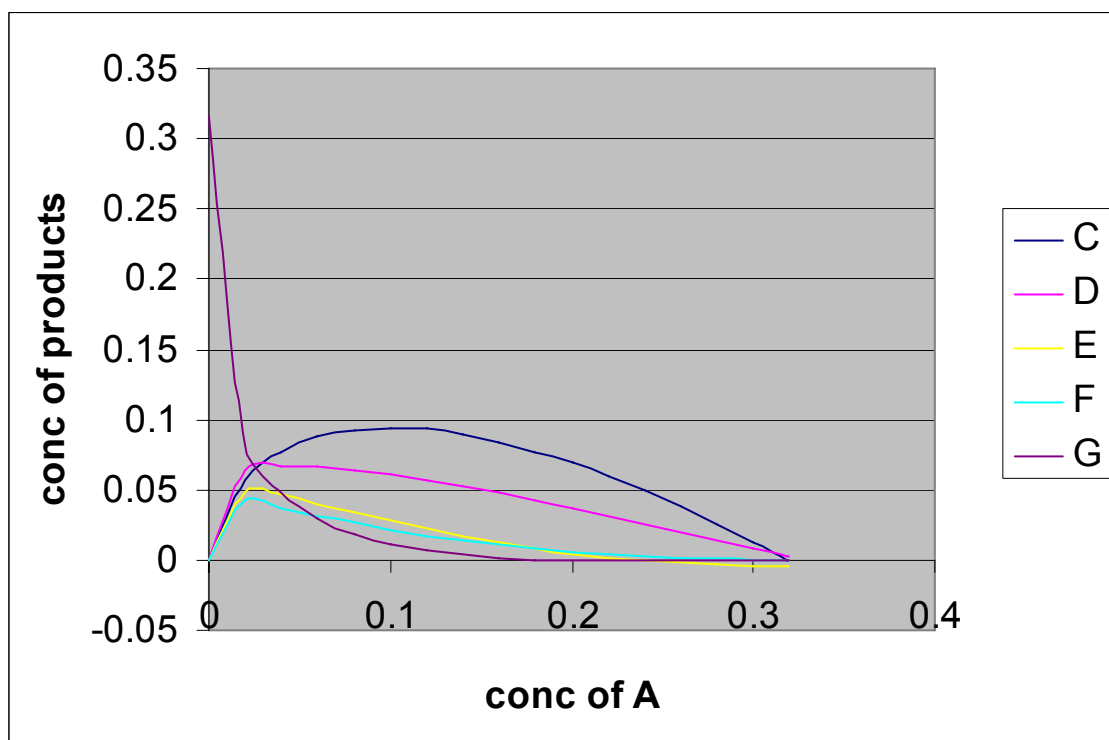


Figure- 10 Concentration Distribution of all
Methylols as Suggested from Kinetics



Where, C is Ortho-methylol derivative
D is Para-methylol derivative
E is Ortho-ortho-methylol derivative
F is Ortho-para-methylol derivative
G is Ortho-ortho-para-methylol derivative