

## Kinetics of Thermal Polymerization of Shellac. Part III. Reaction Mechanism of Gelation

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### Synopsis

The present investigation pertains to the reaction mechanism of gelation. The pre-gelation stage comprises the acetal formation reaction (an intermolecular reaction), while the post-gelation phase involves the formation of three-dimensional network structures (an intramolecular reaction) from the linear hemiacetal polymers (formed in the pre-gelation stage) through esterification and etherification. Further, the dependences of the rate of gelation  $R_g$  on functional groups and of the branching coefficient  $\alpha$  on time are also indicated in the paper.

### INTRODUCTION

Though some suggestions were made in the previous paper<sup>1</sup> on the mechanism of polymerization of shellac, they still call for further investigation. It was proposed that either ether or acetal formation is the main reaction of the pregelation stage, but these viewpoints lacked experimental proof. According to a recent report<sup>2</sup> there are changes only in hydroxyl and carbonyl values, favoring the formation of acetals in the pregelation stage. According to Kamath,<sup>3</sup> the adjacent hydroxyls combine to produce an unsaponifiable linkage, i.e., a cyclic acetal. However, Gidvani<sup>4</sup> has pointed out that the pregelation stage involves the formation of macromolecules by linear growth through esterification which becomes more rapid in the early post-gelation phase and then shows a decelerating trend. Further formation of crosslinkages is rendered possible through etherification. Since no change in acid value in the pregelation stage has been reported,<sup>2,5</sup> however, the above postulate seems improbable. Moreover, Nagel and Baumann<sup>6</sup> claimed that some lac acids are present as lactones which on heating exhibit a strong tendency to aggregate, and splitting off of water is due to a small amount of anhydride formation. Ranganathan and Aldis<sup>7</sup> also supported the anhydride formation theory, but Gidvani<sup>4</sup> opposed the possibility of this type of reaction on the basis of the fact that when all hydroxyl groups of lac are esterified with saturated acids like butyric, caprylic, and lauric acid the resulting products do not polymerize, even on heating at 175°C. for 14 days, though carboxyl groups of lac are free to react.

In view of incomplete information in the literature on the gelation process, an attempt has been made here to illustrate the reaction scheme of gelation as far as possible.

### EXPERIMENTAL

For the investigation, various dried and desiccated samples of dewaxed, decolorized shellac (about 10 g. each) were cured for longer periods at 150°C. by a method already described.<sup>1</sup> The chemical constants of these polymer samples, as a whole, were determined by standard procedures<sup>8</sup> and the results are given in Table I. The rate of gelation  $R_g$  was computed from the weight fraction of gel, and its dependence on time is depicted in Figure 1.

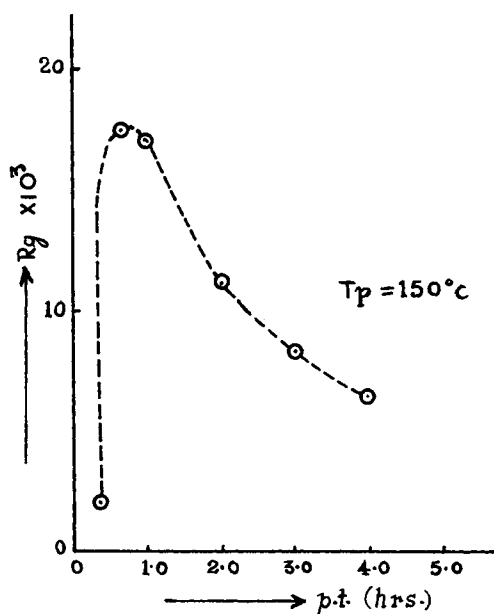


Fig. 1. Variation of  $R_g$  with time of curing.

TABLE I  
Variation of Chemical Constants and Rate of Gelation with Time at  $T_p$  150°C.

Curing time p.t., hr.	$R_g \times 10^3$	Acid value A.V.	Hydroxyl value H.V.	Iodine value I.V.
0		71.4	260.2	13.98
1/3	2.08	62.7	238.0	16.51
2/3	17.54	53.6	215.7	17.76
1	17.00	44.7	152.6	19.00
2	11.22	35.9	130.4	20.40
3	8.34	22.4	103.5	20.62
4	6.46	17.9	71.9	21.63

## RESULTS AND DISCUSSION

From Figure 1, it is evident that gelation starts before the intermolecular reaction (i.e., acetal formation) is complete and rapidly approaches a maximum velocity. Afterwards it slows down steadily.

According to Nagel and Körnchen,<sup>9</sup> the decreased velocity may be ascribed to reduced mobility of the larger molecules already formed as well as to the reduction in the number of reactive groups. In this connection, it may be also mentioned that in the common polycondensations, the absolute velocity becomes vanishingly slow due to the low concentration of the available reactant species and this effect is more pronounced with higher orders of reactions.<sup>11</sup> Moreover, the bulk viscosity of the reaction medium does not exert any appreciable effect on the rates of reaction of very large molecules. The explanation for this lack of response to viscosity lies in the relatively high activation energies of the common condensation reactions as well as in considerable degrees of mobility associated with the reactive chain ends, even at high bulk viscosity and in gel phase.

Moreover, the rate of reaction is proportional to the concentration of transitory activated complex which always remains in chemical equilibrium with the reactants;<sup>12</sup> therefore, the rate of reaction will not be affected by the mobility of the molecules, the diffusion rate, and the viscosity.

### Dependence of $R_g$ on Functional Groups

Since the fraction of material in gel form is a linear function of the fraction of the reacted groups in the entire system,<sup>13</sup> it was thought worthwhile to investigate the dependence of the rate of gelation  $R_g$  on the concentrations of various functional groups (viz.,  $-\text{COOH}$ ,  $-\text{OH}$ , and  $-\text{C}=\text{C}-$ ) left unconsumed in the reacting system. With this view in mind, the rate of gelation at a particular instant was plotted against the corresponding concentrations of carboxyl, hydroxyl, and unsaturation groups as shown in Figures 2-4. The nature of variation of the  $R_g$  with the concentration of various unreacted functional groups as well as with time are identical. Hence it can be inferred that the rate of gelation is proportional to the concentrations of unreacted functional groups present in the entire system. Hence the rate of gelation  $R_g$  can be expressed by eq. (1):

$$R_g = K[\text{COOH}][\text{OH}][-\text{C}=\text{C}-] \quad (1)$$

On taking logarithms the equation is transformed to the form:

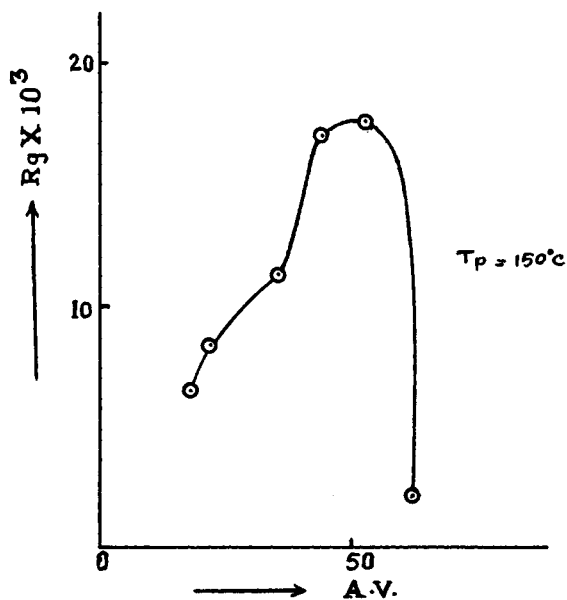
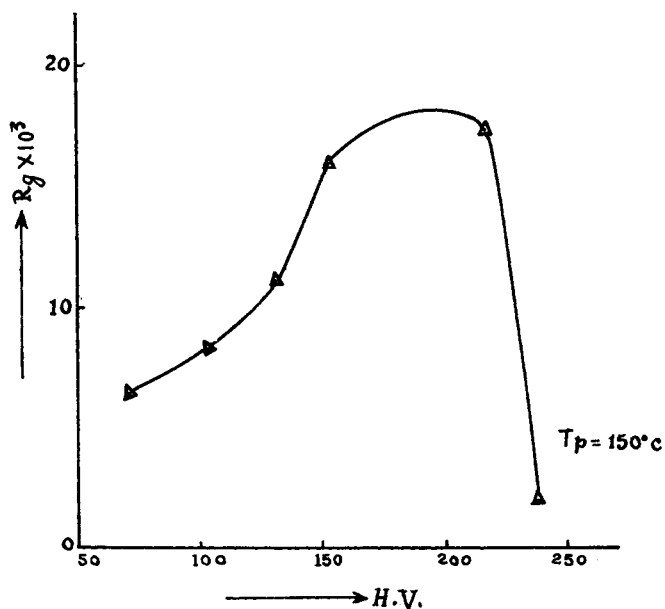
$$\log R_g = \log K + \log [\text{COOH}] + \log [\text{OH}] + \log [-\text{C}=\text{C}-]$$

or

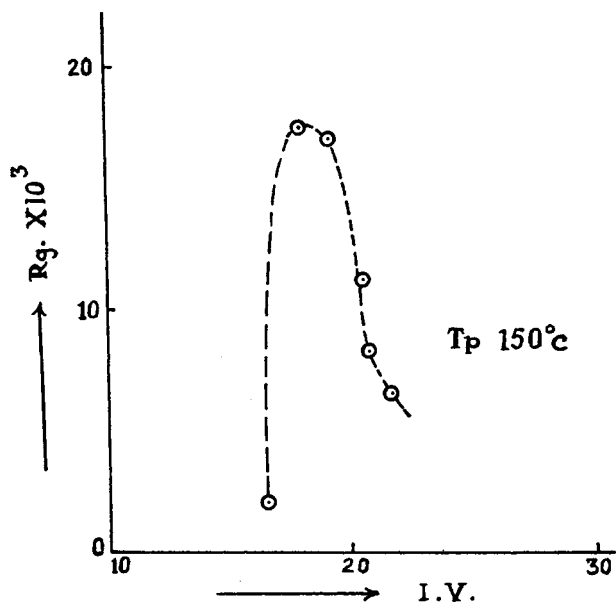
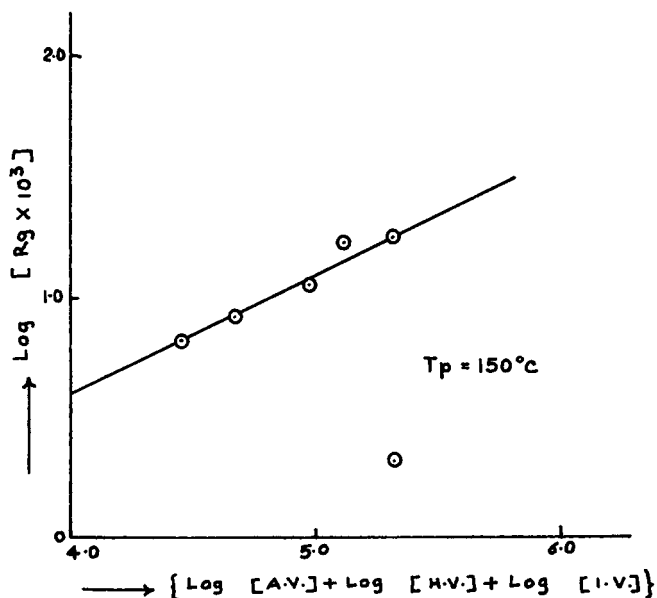
$$\log R_g = \log K + \log (\text{A.V.}) + \log (\text{H.V.}) + \log (\text{I.V.}) \quad (2)$$

where A.V., H.V., and I.V. are the acid value, hydroxyl value, and iodine value, respectively.  $K$  would evidently represent the gelation constant.

If the above assumptions are correct, a plot of  $\log R_g$  against the sum of

Fig. 2.  $R_g$  vs. acid value.Fig. 3.  $R_g$  vs. hydroxyl value.

logarithms of acid, hydroxyl, and iodine values would yield a straight line. Such plot of data is shown in Figure 5, in which all points except the initial one fall on a straight line, giving sufficient ground for the validity of the above relationship. The deviation of first initial point may be ascribed

Fig. 4.  $R_g$  vs. iodine value.Fig. 5. Dependence of rate of gelation  $R_g$  on the concentration of functional groups.

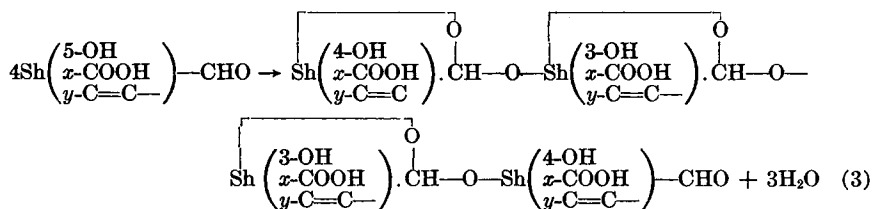
to the interference of intermolecular (i.e., acetal formation) and intramolecular (three-dimensional network formation) reactions. Moreover, from eq. (1), it is evident that the rate of gelation  $R_g$  follows a third-order reaction scheme.

### Intermolecular Reaction in Pregelation Stage

Since it has been reported that only hydroxyl and carbonyl groups are affected in the pregelation stage,<sup>2</sup> it is evident that the acetal formation is the main reaction of the polymerization process.

Since the simpler alcohols and aliphatic and certain aromatic aldehydes in the presence of a catalyst give linear acetals, whereas hydroxy aldehydes invariably give anhydro compounds of the half-acetals, i.e., cyclic acetals or lactolides, and many-membered cyclic acetals are often obtained in polymeric form,<sup>14</sup> it is obvious that in polymerization of polyhydric shellac, the formation of cyclic acetals is most likely.

It was reported in the previous communication<sup>1</sup> that the intermolecular reaction of the pregelation stage is of zero order; i.e., the rate of reaction is constant. The rate of intermolecular reaction, calculated from  $\Delta H.V./\Delta t$  and  $\Delta C.V./\Delta t$  on the basis of the data in literature,<sup>2</sup> has also been found to be constant. This lends support to the previous finding. Moreover, it was also reported that out of five hydroxyl groups present in shellac, only three are present in the branching unit. Therefore, the intermolecular reaction in the pregelation stage can be represented by eq. (3):



because only tetramers are formed prior to the gel point.<sup>1</sup> The chemical formula (3) cannot represent the exact planar conformation of the polymer molecule, however, because the nature of the hydroxyl groups reacted is unknown, that is to say, it is not known whether the hydroxyl groups reacted belong to the branch unit or not. Therefore the structure is purely conjectural, since the molecular structure of shellac (a heterogeneous mixture of several large molecular species) as well as the positions of the hydroxyl groups in the molecule are unknown. Moreover, it may be stated that a superimposition of the intramolecular reaction over intermolecular reaction in the later phase of the pregelation stage cannot be excluded as reported earlier.<sup>1</sup>

### Intramolecular Reaction in the Post-Gelation Phase

The intramolecular reaction in the condensation polymerization involves the formation of infinite networks.<sup>12</sup> These networks contain many circuitous connections and hence there is a netlike structure of the gel fraction. Hence, gelation (a continuous process of sol to gel conversion) is a consequence of the polyfunctional nature of the reactants.

Before considering the trends of intramolecular reactions involved in gelation, mention may be made of the fact that the intermolecular reaction of the pregelation stage is not complete at the gel point.<sup>2</sup>

To determine when this intermolecular reaction reaches completion, the carbonyl value C.V. was plotted against the time of reaction  $t$ , and the straight line obtained was extrapolated to zero carbonyl value. From the graph, it was observed that complete consumption of carbonyl groups takes place after about 100 min. curing at 150°C. and is independent of the intramolecular reaction.

With a view to probing the various chemical processes involved in gelation, it was thought worthwhile to study the comparative consumption of various functional groups in the course of gelation. Decreases in units of carboxyl, hydroxyl, carbonyl, and hydroxyl equivalent of iodine values during a given reaction time were computed, the results are listed in Table II. In this connection it should be mentioned that the hydroxyl

TABLE II  
Decrease in Units of Functional Groups with Time

$t$ , hr.	$\Delta$ H.V.	$\Delta$ A.V.	$\Delta$ C.V. <sup>a</sup>	$\Delta$ U.V. <sup>b</sup>	$\Delta$ H.V. - ( $\Delta$ A.V. + $\Delta$ U.V.)
1/8	22.2	8.7	12.10	5.5	8.0
2/8	44.5	17.8	14.64	8.5	18.2
1	107.6	26.7	17.24	11.0	69.9
2	129.8	35.5	22.04	14.0	80.3
3	156.7	49.0	22.04	14.5	93.2
4	188.3	53.5	22.04	17.0	117.8

<sup>a</sup> Computed from the C.V.- $t$  plot.

<sup>b</sup> Computed from the relation U.V. = 2.2 (I.V.).

group can react with carbonyl, carboxyl, and hydroxyl groups as well as with a hydrogen atom attached to the adjacent carbon atom to give hemiacetal, ester, ether, and unsaturation. The hemiacetal bond or ring is formed as a result of an interaction between carbonyl and hydroxyl groups present on the same molecule and is accompanied by subsequent formation of a fresh hydroxyl group on the aldehydic carbon atom. However, during heat hardening of shellac, such hemiacetal units first formed are further interconnected to yield a polymer chain (on account of dehydration reaction between the freshly generated and potential hydroxyl groups present on these units). Obviously, this reaction is responsible for decreases in the hydroxyl value in the pregelation stage.

Further decreases in hydroxyl value result from the reactions (a) between the carboxyl and hydroxyl groups, (b) between the hydroxyl group and the hydrogen atom attached to the adjacent carbon atom, and (c) between two hydroxyl groups.

Since the changes in acid and hydroxyl equivalent of iodine values are positive, possibilities of reactions (a) and (b) are thus confirmed.

From Table II it is evident that the decrease in units of hydroxyl value is in excess of the sum of decreases in units of carboxyl and hydroxyl equivalent of iodine values. Therefore, the decrease in units of hydroxyl group in excess of this sum in a given reaction time would be the amount attributable to ether formation, i.e., reaction (c).

Furthermore, a critical review of the data of Table II reveals that the formation of a three-dimensional infinite network structure is the direct consequence of the simultaneous processes of esterification and etherification, starting just prior to gel point and continuing throughout the process of gelation. These points will be more clear if estimations of ester and ether linkages present in infinite networks are attempted by means of alkaline and acid hydrolyses.

Now considering the presence of various active points, i.e., functional groups in each monomer unit present in the linear polymer formed in the pregelation stage as pictured above, the possibility of the tremendous formation of intramolecular linkages through esterification and etherification can be well estimated.

Moreover, it may be added that the fractions of carboxyl and hydroxy groups consumed in 4 hr. curing at 150°C. are 0.75 and 0.76, respectively.

### Dependence of Branching Coefficient on Time

The branching coefficient  $\alpha$  is defined as the probability that a given functional group of a branch unit leads via a chain to another branch unit.<sup>12</sup> Evidently when this probability approaches a value of unity, all branch units are linked together by chains and the formation of an infinite network structure is complete. To examine this point, the dependence of

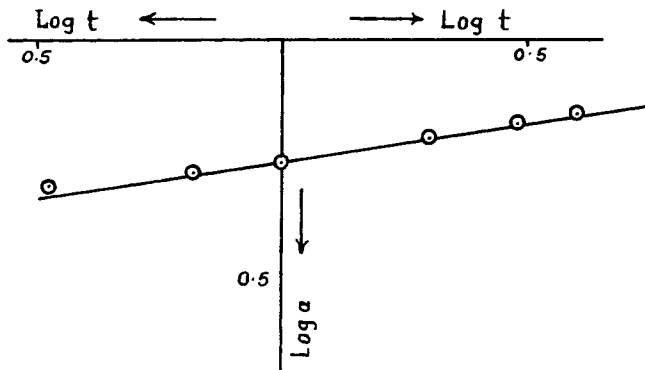


Fig. 6. Dependence of branching coefficient on time.



$\alpha$  (computed from weight fraction of gel) on time was sought. From the graphical study of the nature of variation of  $\alpha$  with time it was found that:

$$\log \alpha = \log A + B \log t \quad (4)$$

A plot of  $\log \alpha$  against  $\log t$  is shown in Figure 6. Equation (4) will vanish when  $t = 0$ , because, in that case,  $\alpha$  would be also equal to zero. Again, when  $t = 1$ ,  $\log \alpha = \log A$ , and, when  $\alpha = 1$ ,  $\log t = -\log A/B$ . The latter equation would enable us to predict the time of complete gelation. From the graph,  $\log A = -0.245$  and  $B = 1/6$ . Hence,  $t = \text{antilog } 1.47 = 29.5$  hr.; that is, the gelation of shellac at  $150^\circ\text{C}$ . would be complete only after 29.5 hr.

### Role of Unsaturation in Gelation

From Table I it is evident that there is a gradual increase (prior to gelation and onwards) in iodine value (i.e., in unsaturation) which is responsible for the onset of gelation as discussed above, but since incorporation of unsaturation into the sol or gel-fraction is uncertain (on account of the possibility of solid-liquid phase reaction) it is very difficult to predict anything about the role in gelation. However, in general the rate of polymerization increases with increasing unsaturation, and this effect is enhanced by conjugation and other relative positions of unsaturated linkages.<sup>15</sup> In the present case it is very difficult to locate the position of new unsaturation linkages formed. However, it may be added that the double bond may remain as such in the polymer throughout the entire process or may cause addition polymerization in the later stages by providing some active points in the polymer molecule. All these points can be determined only if the gelation study is extended to still longer periods and the amounts of unsaturation in sol and gel phases are examined separately.

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### Résumé

Cette communication traite du mécanisme de réaction de la gélification. L'étape de pré-gélification comprend la réaction de formation d'un acétal, c'est-à-dire, une réaction intermoléculaire, tandis que l'étape de post-gélification implique la formation de structures tridimensionnelles (c'est-à-dire une réaction intra-moléculaire), à partir des polymères linéaires à fonction hémicétal (formés dans l'étape de pré-gélification) par estérification et étherification. On mentionne également dans cette communication la dépendance de la vitesse de gélification ( $R_p$ ) en fonction des groupements fonctionnels et celle du coefficient de ramification  $\alpha$ , vis à vis du facteur temps.

### Zusammenfassung

Die vorliegende Untersuchung behandelt den Reaktionsmechanismus der Gelbildung. Die Vorgelphase umfasst die Acetalbildungsreaktion, d.h. eine intermolekulare Reaktion, während die Nachgelphase in der Bildung dreidimensionaler Netzwerkstrukturen (d.h. Intramolekulare Reaktion) aus dem linearen Hemiacetalpolymeren (in der Vorgelphase gebildet) durch Veresterung und Verätherung besteht. Weiters wurden in der Arbeit Angaben über die Abhängigkeit der Gelbildungsgeschwindigkeit  $R_p$  von den funktionellen Gruppen und des Verzweigungskoeffizienten  $\alpha$  vom Zeitfaktor gemacht.

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