

Kinetics of Thermal Polymerization of Shellac.

Part I. Kinetics and Gelation Studies

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Synopsis

In the present investigation the kinetics of thermal polymerization of shellac has been studied. A linear relationship between the intrinsic viscosity $[\eta]$ and the time of polymerization has been observed up to a certain extent of reaction followed by a sharp rise in value of $[\eta]$ near the gel point. After gelation the intrinsic viscosity of the sol fraction again falls abruptly. Besides, an attempt has also been made to understand the nature of gelation from the weight fractions of gel formed after prolonged curing at different temperatures.

INTRODUCTION

Though much work has been done on the effect of heat for hardening of shellac for improvement of its curing properties, the polymerization process is still shrouded with uncertainty. Negal and his collaborators¹ were first to report the effect of heat on shellac and claimed that water is split off on heating and the shellac becomes increasingly insoluble in alcohol but 5-10% of the constituents always remain in a thermoplastic state, acting as a natural plasticizer for the rest of the material. Similar claims were also made by other workers.²

Gidvani³ suggested that the elimination of water can take place either (a) by a reaction of carboxyl group with a hydroxyl group present in shellac, or (b) by a reaction of two carboxyl groups to form acid anhydrides, or (c) by a reaction of two hydroxyl groups to form ethers, or (d) by a reaction of hydroxyl group with the hydrogen atom attached to the adjacent carbon atoms to form a double bond. But the possibilities of reactions a, b, and c are eliminated, as Bhattacharjee⁴ and Gidvani³ have claimed that acid and iodine values do not change during polymerization. Furthermore, the findings of Bhattacharjee⁴ that there is gradual decrease in hydroxyl value of shellac on heating and of Kamath et al.⁵ that the polymerized shellac has zero carbonyl value lead us to believe that the polymerization process involves either formation of ethers or a reaction between hydroxyl groups and carbonyl group forming acetal, hemiacetal, etc., but definite evidence is still awaited in this direction.

Attempts have also been made to explore the polymerization process by physical methods, but data are very scarce. However changes in fluidity,⁶

melting point,⁷ and melt⁸ and solution⁴ viscosity of shellac have been observed with the progress of polymerization, but, no elaborate studies have so far been made in a systematic investigation. The present paper deals with a detailed study of solution viscosity of shellac polymers as well as the weight fractions of gel.

EXPERIMENTAL

Polymerization

For the investigation a 20-g. portion of dewaxed decolorized shellac was weighed out and dried at 42°C. for 6 hr. Then it was placed in a desiccator and left overnight in vacuum. The polymerization was carried out in an oil bath, thermostatically controlled to $\pm 0.1^\circ\text{C}$. For polymerization the weighed amount of shellac was first transferred to a polymerization tube (6×1 in.). The tube, in turn, was suspended from the rack of the oil bath through a cork in such a way that the column of shellac remained under oil. The upper surface of the shellac was pressed against the bigger circular flattened end ($7/10$ in. diameter) of a glass rod (9 in. long and $3/10$ in.

TABLE I
Variation of the Intrinsic Viscosity and the Axis Ratio with Time of Polymerization
($T_p = 125^\circ\text{C}$.)

Polymerization time p.t., min.	$[\eta]$	f	$K' \times 10^6$
0	0.071	7.8	
10	0.075	8.1	6.7
20	0.078	8.3	5.8
30	0.083	8.6	6.7
40	0.086	8.8	6.2
50	0.091	9.1	6.7
60	0.094	9.2	6.4
70	0.099	9.5	6.7
80	0.109	10.1	
90	0.125	11.0	
			Avg. 6.5

diameter) by exerting a slight pressure of the thumb on the upper circular end ($2/5$ in. diameter) of the rod. The time at which the shellac was completely melted was treated as initial time. The contents of the tube were constantly stirred by the glass rod and after a certain interval of time the polymerization tube was taken out from the oil bath and the molten shellac was scooped out of the test-tube and spread over a galvanized sheet to stop the reaction. The mass solidified quickly. The polymerizations were carried out at temperatures of 125, 135, 150, and 175°C. for different intervals of time. The solid masses so obtained were crushed and passed through 100 mesh sieve and retained for viscosity measurements.

Viscosity Measurements

A 2% solution of each polymerized shellac sample was prepared in 100% alcohol. The solution was filtered clear of suspended impurities in each case and concentration was checked by measuring aliquots to tared weighing bottle and evaporating the solvent and weighing to constant weight.

TABLE II
Variation of the Intrinsic Viscosity and the Axis Ratio with Time of Polymerization
($T_p = 135^\circ\text{C}.$)

Polymer- ization time p.t., min.	$[\eta]$	f	$K' \times 10^5$
0	0.071	7.8	
10	0.077	8.2	1.0
20	0.082	8.5	
30	0.089	8.9	
40	0.097	9.5	
50	0.108	10.0	
60	0.145	11.7	1.08
70	0.123	10.7	
			Avg. 1.0

TABLE III
Variation of the Intrinsic Viscosity and Axis Ratio with Time of Polymerization
($T_p = 150^\circ\text{C}.$)

Polymer- ization time p.t., min.	$[\eta]$	f	$K' \times 10^5$
0	0.071	7.8	
5	0.075	8.1	1.3
10	0.080	8.4	
15	0.084	8.6	
20	0.090	9.0	
25	0.102	9.7	
30	0.128	11.1	1.6
			Avg. 1.45

TABLE IV
Variation of the Intrinsic Viscosity and Axis Ratio with Time of Polymerization
($T_p = 175^\circ\text{C}.$)

Polymer- ization time p.t., min.	$[\eta]$	f	$K' \times 10^5$
0	0.071	7.8	
3	0.076	8.2	2.8
6	0.081	8.5	
9	0.090	9.0	
12	0.118	10.5	2.8
15	0.104	9.9	
			Avg. 2.8

The viscosity measurements were carried out in a completely cleaned Ubbelohde dilution viscometer at $30 \pm 0.1^\circ\text{C}$. From the data the reduced specific viscosity η_{sp}/c was calculated and plotted against c and the intrinsic viscosity $[\eta]$ determined. The results are given in Tables I-IV.

Determination of Weight Fractions of Gel

To determine the weight fractions of gel, several 10-g. samples of completely dried shellac were polymerized for longer periods in similar manner at different temperatures and their percentages of insolubles were determined by a modified USG method⁹ as outlined below.

About 0.2 g. of dried and desiccated polymer sample was weighed in a 100 cc. Pyrex beaker and 20 cc. of methanol was added. This mixture was stirred well and then allowed to stand for some time to dissolve. After that it was boiled for 5 min. on a water bath and the contents of the beaker were quantitatively emptied into a tared sintered glass crucible with the help of boiling methanol, and filtered under vacuum and weighed after drying. The results are summarized in Table V.

TABLE V
Dependence of the Weight Fraction of Gel W_g on the Time and Temperature of Polymerization

Polymer- ization time p.t., hr.	125°C.		150°C.		175°C.	
	$W_g \times 100$	α	$W_g \times 100$	α	$W_g \times 100$	α
1/6					2.5	0.50
1/4					28.2	0.53
1/3			2.5	0.50		
2/3			42.1	0.54		
1	2.0	0.50	61.2	0.56	86.1	0.66
2	47.6	0.55	80.8	0.63	95.2	0.73
3	62.3	0.58	90.1	0.68	99.3	0.84
4	70.2	0.60	93.1	0.71		
5	75.8	0.62				

RESULTS AND DISCUSSION

The plots of η_{sp}/c against c of all the polymers are shown in Figures 1-4. The variation of $[\eta]$ as a function of the time of polymerization at four different temperatures is presented in Figures 5-8. From the critical examination of these, it is evident that there exists a linear relationship between the intrinsic viscosity and the time of polymerization up to a certain extent of reaction. Hence the initial stage of reaction could be expressed as

$$[\eta] = A + mt \quad (1)$$

when $t = 0$, $[\eta] = [\eta]_0$. Thus,

$$[\eta] = [\eta]_0 + mt$$

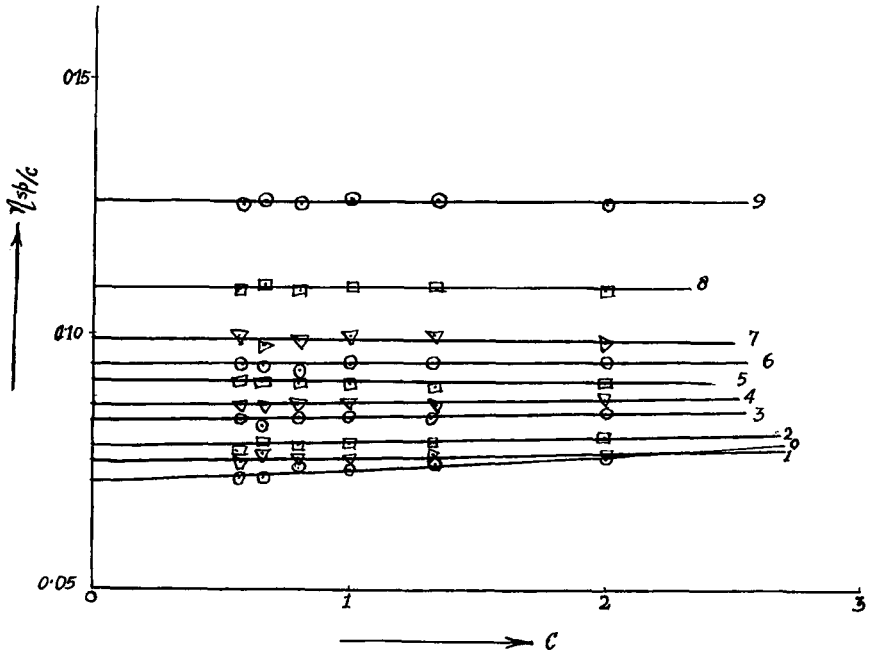


Fig. 1. Plot of reduced viscosity vs. concentration, $T_p = 125^\circ\text{C}$.

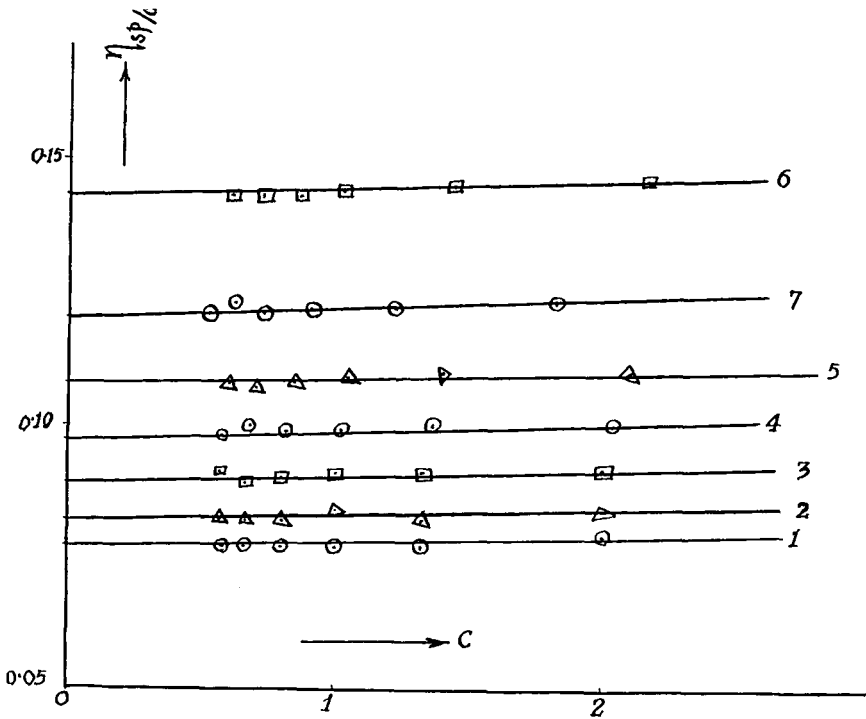


Fig. 2. Plot of reduced viscosity vs. concentration, $T_p = 135^\circ\text{C}$.

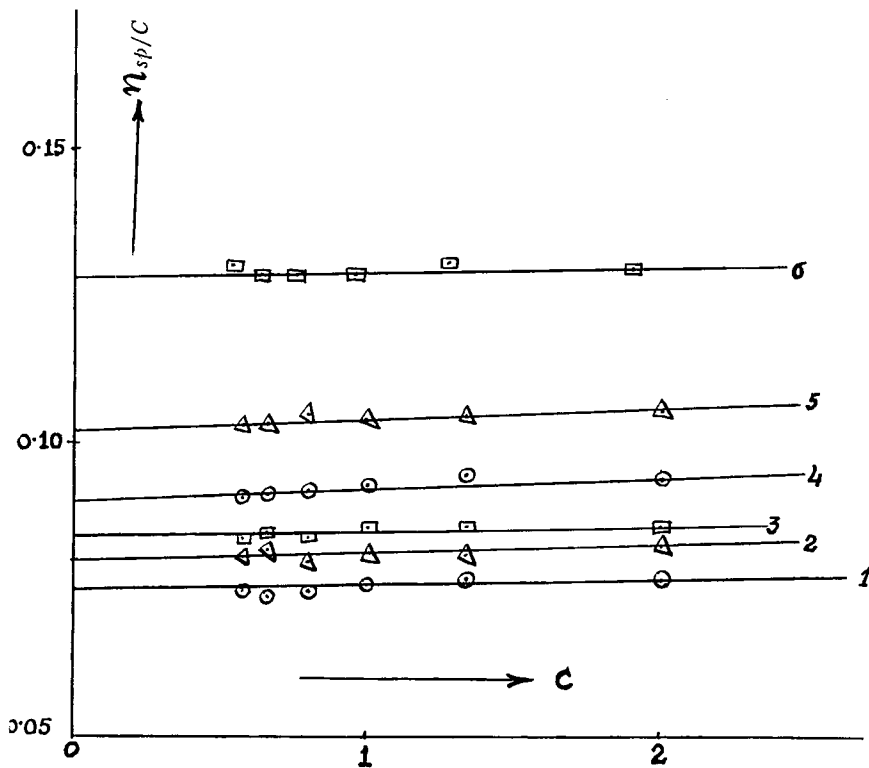


Fig. 3. Plot of reduced viscosity vs. concentration, $T_p = 150^\circ\text{C}$.

or

$$m = \{[\eta] - [\eta]_0\}/t \quad (2)$$

By differentiating eq. (1) with respect to time it could be expressed in the following equation:

$$d[\eta]/dt = m$$

Therefore

$$d[\eta]/dt = (\{[\eta] - [\eta]_0\}/t) \quad (3)$$

Now

$$[\eta] = k_m M_2^\alpha$$

$$[\eta]_0 = k_m M_0^\alpha$$

Thus

$$\begin{aligned} [\eta] - [\eta]_0 &= k_m M_2^\alpha - k_m M_0^\alpha \\ &= k_m M_0^\alpha [(M_2/M_0)^\alpha - 1] \\ &= K_m M_0^\alpha [(\overline{DP}_n)^\alpha - 1] \\ &= K_m M_0^\alpha [(1-p)^{-\alpha} - 1] \\ &= K_m M_0^\alpha p \end{aligned}$$

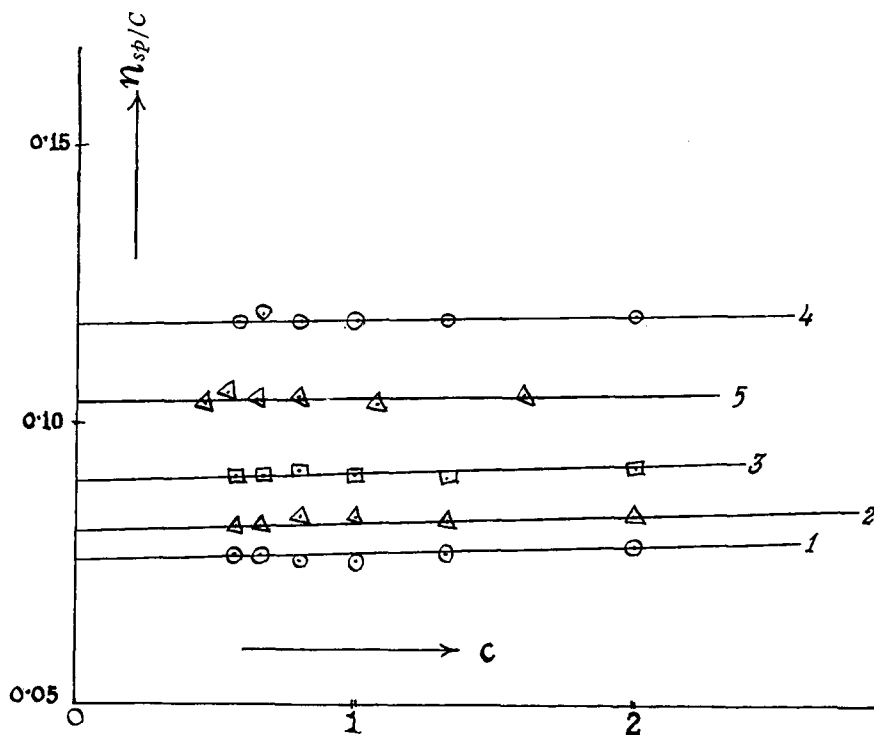


Fig. 4. Plot of reduced viscosity vs. concentration, $T_p = 175^\circ\text{C}$.

Thus relative change in intrinsic viscosity in relation to time of polymerization is just a representation of the extent of reaction, p

Now

$$[\eta] - [\eta]_0 = K_m M_0^\alpha \alpha p.$$

By differentiation we have

$$d[\eta] = K_m M_0^\alpha \alpha dp \quad (4)$$

or

$$d[\eta]/dt = K_m M_0^\alpha \alpha. (dp/dt)$$

or

$$dp/dt = (1/K_m M_0^\alpha \alpha) (d[\eta]/dt) \quad (5)$$

Let

$$y = K_m M_0^\alpha \alpha$$

and

$$\log y = \log K_m + \alpha \log M_0 + \log \alpha \quad (6)$$

The value of Gidvani³ of k_m is:

$$k_m = 5.89 \times 10^{-4}$$

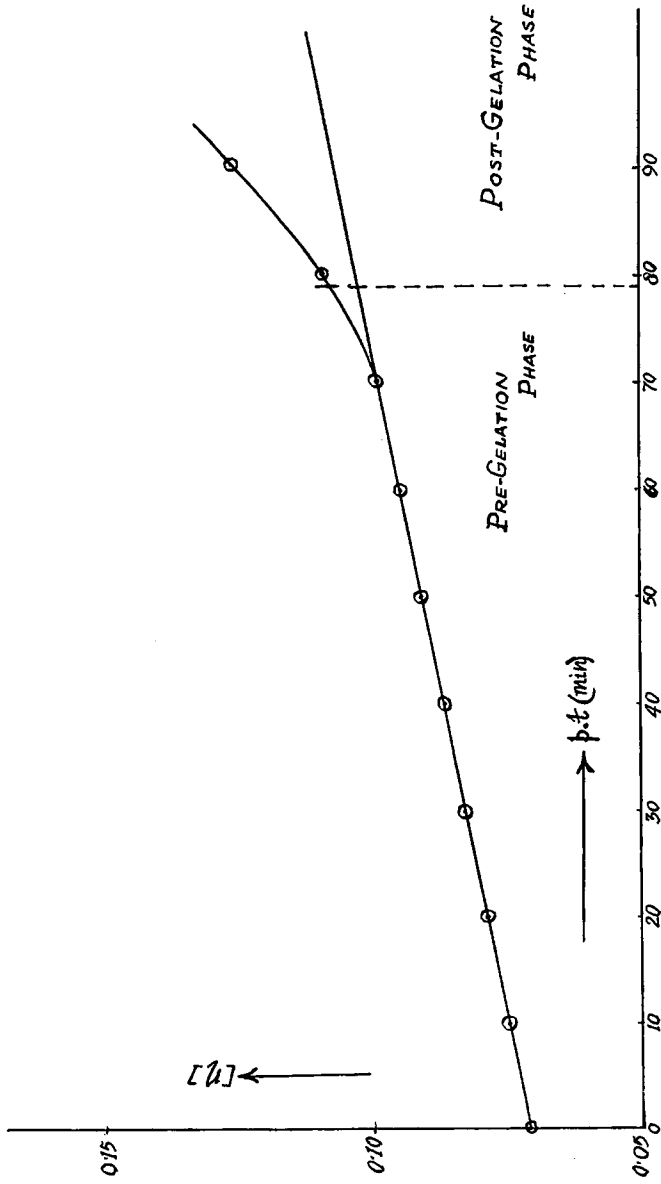


Fig. 5. Variation of intrinsic viscosity with time of polymerization, $T_p = 125^\circ\text{C}$.

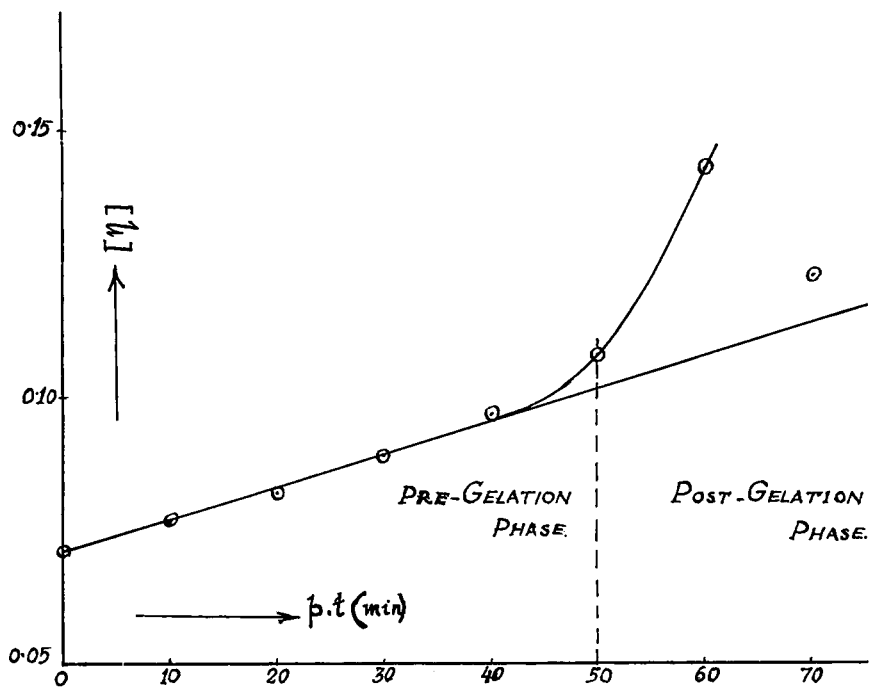


Fig. 6. Variation of intrinsic viscosity with time of polymerization, $T_p = 135^\circ C$.

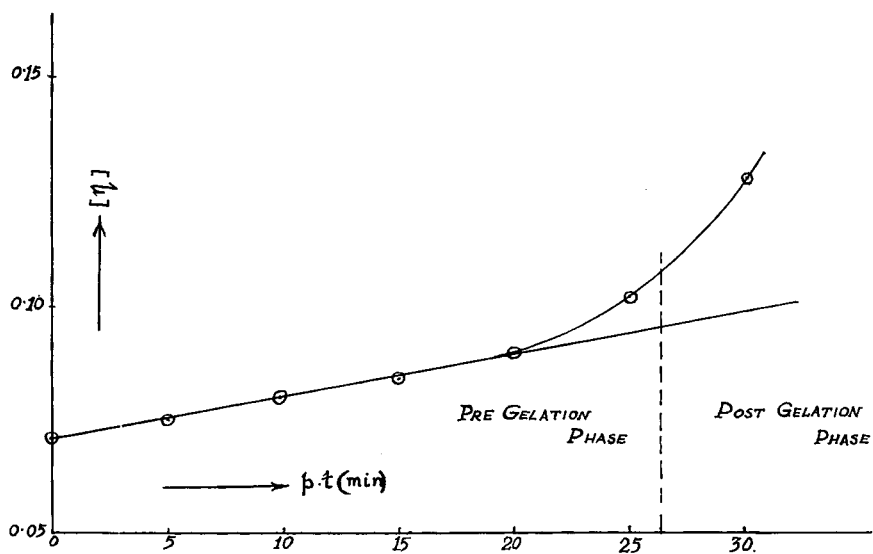


Fig. 7. Variation of intrinsic viscosity with time of polymerization, $T_p = 150^\circ C$.

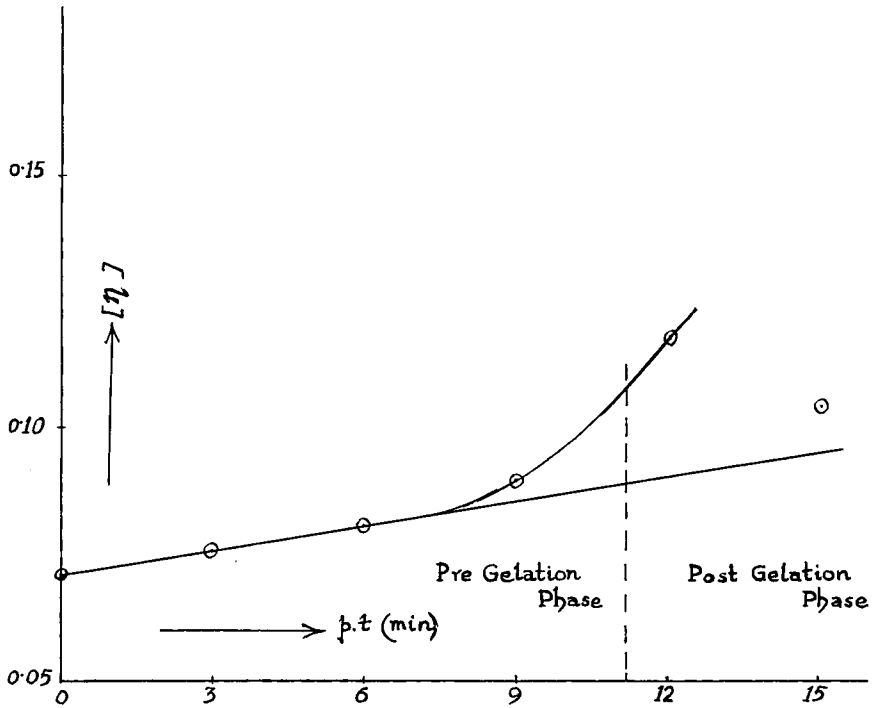


Fig. 8. Variation of intrinsic viscosity with time of polymerization, $T_p = 175^\circ\text{C}$.

(Since the solvent has not been specified, the value of k_m must be confirmed by osmotic pressure measurements in 100% alcohol.)

$$\text{Now } [\eta]_0 = K_m M_0^\alpha$$

or

$$0.071 = 5.89 \times 10^{-4} \times 1000^\alpha$$

or

$$\log 0.071 = \log 5.89 - 4 + 3\alpha$$

or

$$\alpha = 0.694$$

Substituting the value of α and k_m in eq. (6) we have

$$\begin{aligned} \log y &= \log k_m + \alpha \log M_0 + \log \alpha \\ &= \log 5.89 \times 10^{-4} + 0.694 \log 10^3 + \log 0.694 \end{aligned}$$

Thus

$$y = 0.0494$$

$$k_m M_0^\alpha \alpha = 0.0494$$

$$d[p]/dt = (1/0.0494) (d[\eta]/dt) = 20.24 (d[\eta]/dt)$$

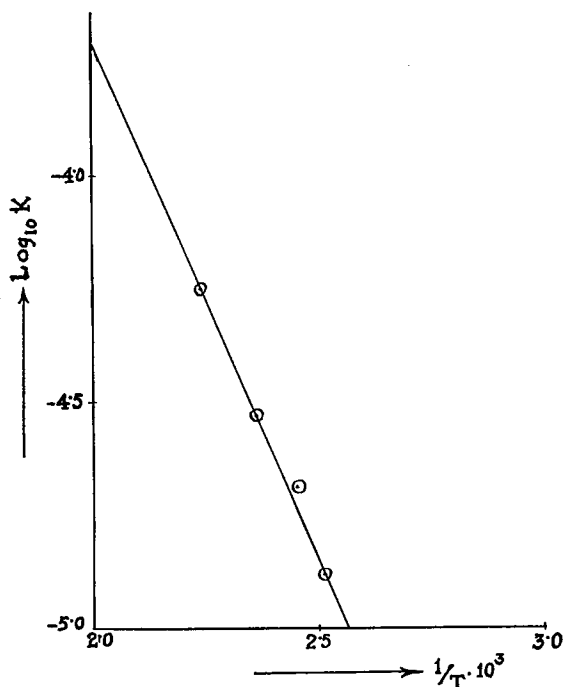


Fig. 9. Plot of $\log K$ vs. the reciprocal temperature.

But $d[\eta]/dt = \text{const.} = K'$ for a given extent of reaction at all temperatures of polymerization. Therefore, $R_p = (dp/dt) = 20.24 (d[\eta]/dt) = 20.24 K' = K$.

Thus the overall rate of polymerization R_p remains constant up to a certain extent of reaction and follows a zero-order scheme. The values of K' and K at various temperatures of polymerization are given in Table VI. The values of $\log K$ and the reciprocals of the temperatures of polymerization in absolute units are also included in the same table.

TABLE VI
Relationship between the Rate Constant and the Temperature

Temperature, °C. (°K.)	$(1/T) \times 10^3$	K' (mean)	K (mean)	$\log K$
125 (398)	2.51	6.5×10^{-6}	1.32×10^{-4}	-4.88
135 (408)	2.45	1.0×10^{-5}	2.02×10^{-4}	-4.69
150 (423)	2.36	1.45×10^{-5}	2.93×10^{-4}	-4.53
175 (448)	2.24	2.8×10^{-5}	5.67×10^{-4}	-4.25

From the plot of $\log K$ against $(1/T), \times 10^3$ (Fig. 9), E has been found to be 10.0 kcal. This may be ascribed to the energy of activation of polymerization plus the energy of activation of viscous flow. The value of A has been found to be 2.04×10^{-4} , which may be recognized as the algebraic

sum of frequency factors for polymerization reaction and the viscous flow. The linear part of the intrinsic viscosity $[\eta]$ and polymerization time (p.t.) plots may be ascribed to the intermolecular reaction, i.e., the reaction between the functional groups to form linear polymers. After this, there is a sharp rise in value of $[\eta]$ with the time of polymerization, indicating the superimposition of intramolecular reaction over the intermolecular reaction which culminates finally in gelation as a result of the formation of infinite networks of three-dimensional structures.

It is also evident from the graph that after gelation the intrinsic viscosity $[\eta]$ decreases very much on account of the preferential conversion of the larger, more complex species to the network fraction.

Critical Conditions for Gelation

The intrinsic viscosity of polymer solutions is a measure of the effective volume of polymer molecules,¹⁰ which also includes the volume of the enmeshed solvent. The latter, in its turn, is dependent on the degree of entanglement of coiled polymer molecules. It has been seen in the present case that gelation (as determined by visual solubility test, i.e., by the detection of a very small amount of very gelatinous precipitate suspended in the filtered solution) starts when $[\eta]$ approaches a fixed value, that is to say, when a critical molecular dimension or axis ratio is reached.

From a careful examination of the data of the Tables I-IV it is evident that as soon as the value of the axis ratio for shellac polymer at any temperature of polymerization exceeds 10, the gelation starts, and this may be considered as the critical condition for onset of gelation in the case of polymerization of shellac by heat.

The axis ratio has been calculated from Simha's equation:

$$[\eta] = 2 \times 10^{-3} f^{1.73}$$

or

$$f = \text{antilog} \left(\frac{\log [\eta] + 2.6990}{1.73} \right)$$

Thus the critical condition for the onset of gelation in shellac is axis ratio = 10, i.e., $[\eta] = 0.108$.

We know that

$$[\eta] - [\eta]_0 = k_m M_0^\alpha \alpha \cdot p = 0.0494 p$$

At the critical point, $[\eta] = 0.108$, and therefore

$$0.108 - 0.071 = 0.0494 p_c$$

and

$$p_c = 0.749$$

Thus it is evident that the gelation starts when 75% conversion has been completed

$$\overline{DP}_n = \frac{1}{1-p_c} = \frac{1}{1-0.75} = 4$$

or

$$M_n/M_0 = 4$$

or

$$M_n = 4 M_0$$

It is also clear now that the gelation starts only when tetramers are formed.

Dependence of the Time of Gelation on Temperature

The time of gelation t_g at each temperature of polymerization T_p was determined from $[\eta]$ and polymerization time graphs by taking the value of polymerization time corresponding to the value 0.108 for $[\eta]$. The values are tabulated in Table VII. By plotting the logarithm of t_g against

TABLE VII
Relationship between the Time of Gelation and Temperature

Temperature, °C. (°K.)	t_g , sec.	$\log t_g$
125 (398)	4740	3.68
135 (408)	3000	3.48
150 (423)	1584	3.20
175 (448)	666	2.82

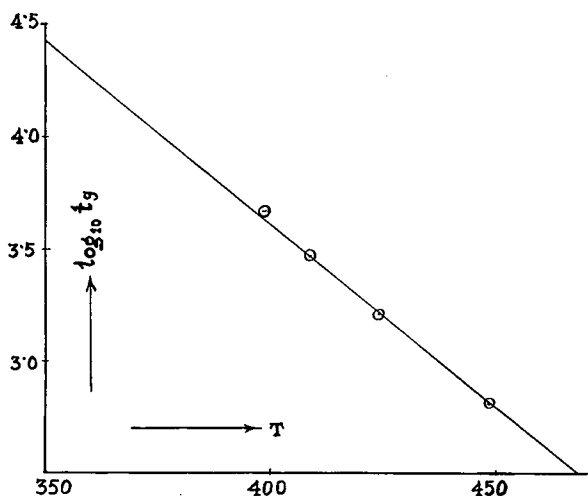


Fig. 10. Plot of the logarithm of the gelation time vs. temperature.

T_p , a straight line was obtained (Fig. 10). Hence, we can express t_g in terms of temperatures of polymerization by the following equation:

$$t_g = A e^{-\alpha T_p}$$

or

$$\log t_g = \log A - (\alpha/2.303) T_p$$

From the graph, $A = 26.92 \times 10^3$ and $\alpha = 0.038$. These values are in conformity with those of Gidvani and others.¹¹

Flory's Equation for Critical Conditions of Gelation

It is a well known fact that the gelation occurs at a critical extent of reaction which is independent of temperature and catalyst concentration,¹² and which is solely dependent on the functionality and proportions of the ingredients¹³ and involves the formation of infinitely large polymer networks.¹⁴ Besides it has been also found that the gelation occurs long before the completion of intermolecular reaction. For the gel point Flory¹⁴ has suggested the following relationship:

$$\alpha_c = 1/(f-1)$$

Here α_c represents the critical value of the branching coefficient (the branching coefficient α is defined as the probability of a given functional group on a branch unit connected to another branch unit) and f is the functionality of the monomer. α is given by the equation:

$$\alpha = p_A p_B \rho / [1 - p_A p_B (1 - \rho)]$$

where $p_A p_B = p$ = total extent of the reaction and ρ = the ratio of A 's (reacted and unreacted) belonging to branch units to the total number of A 's in the mixture.

Now the five hydroxyl groups of shellac may only function as the branching unit, but the question remains to be answered as to how many hydroxyl groups are present in the branching unit. Probably there may be either three or four or all of them present in the branching unit.

Let us consider all these cases one by one.

(1) When all the hydroxyl groups are present in the branching unit, then

$$\rho = 5/5 = 1$$

Therefore, $\alpha_{c(\text{expt})} = p_A p_B = p_c = 0.75$; and $\alpha_{c(\text{theor})} = 1/(5-1) = 0.25$. In view of the above facts, this does not seem possible.

(2) When four out of five hydroxyl groups are present in branching unit, then

$$\rho = 4/5 = 0.8$$

Therefore, $\alpha_{c(\text{expt})} = 0.7$ and $\alpha_{c(\text{theor})} = 1/(4-1) = 0.33$. Since these two values do not tally, it is also not possible.

(3) When three out of five hydroxyl groups are present in the branching unit, then

$$\rho = \frac{3}{5} = 0.6$$

Therefore, $\alpha_{c(\text{exp})} = 0.64$, and $\alpha_{c(\text{theor})} = 1/(3-1) = 0.5$. It is therefore evident that three out of the five hydroxyl groups present in shellac are in the branching unit. Though there exists some discrepancy between the theoretical and experimental values, this discrepancy could be explained by the fact that the intramolecular reactions in the theory have been ignored. According to Flory¹⁴ some of the interunit linkages are damaged during the formation of intramolecular bindings, and the reaction continues further to reach the critical point and consequently the observed gel point appears at a higher extent of reaction than the theoretical expectation.

Nature of Gelation

It is also a well known fact that the onset of gelation causes a separation of the reaction mixture into two phases, the gel (infinite net work structure) which is insoluble in all nondegrading solvents and the sol, which is soluble and separable from the former. The simultaneous presence of sol and gel after gelation is the direct consequence of random distribution of branch units in the polymer. It is in no way dependent on different chemical

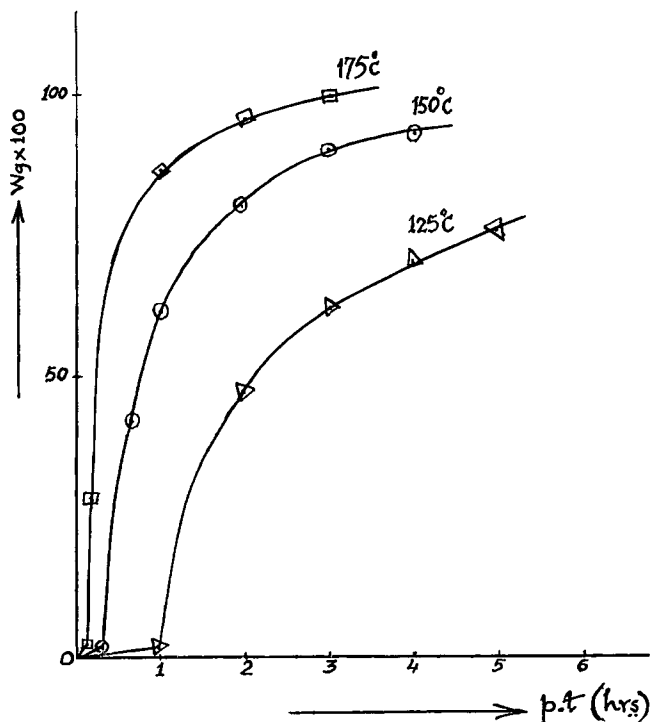


Fig. 11. Variation of the weight fraction of gel W_g with time at different temperatures.

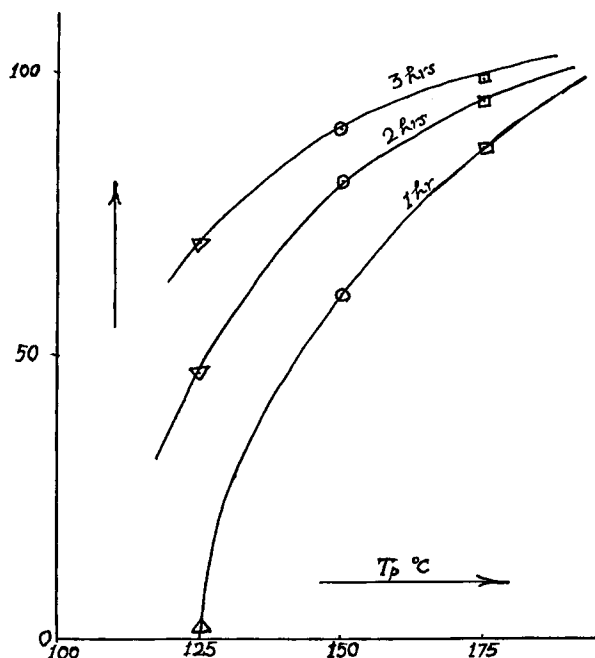


Fig. 12. Dependence of the weight fraction of gel on the time of polymerization at various temperatures: (Δ) 125°C.; (O) 150°C.; (\square) 175°C.

properties of the ingredients¹⁵ from which the sol and gel fractions are formed. As soon as the polymerization crosses the gel point, the amount of gel increases at the expense of the sol and the polymers formed become more tough and less extensible. This fact has been exploited to explain the nature of gelation.

It is evident from the data of Table V and Figure 11 that just prior to gelation shellac remains practically soluble in methanol or any solvent (the percentage of insolubles being 0.2 only) and as soon as the gel point is passed, shellac becomes gradually insoluble in all solvents, the amount of insolubles being dependent solely on time and temperature of polymerization (Fig. 12).

Moreover, it is interesting to report that just after polymerization time, the gel formation begins at a very rapid rate and then slackens. Similar observations have been made by Verman and Bhattacharya.¹⁶ According to Negel and Koernchen,¹⁷ the decreased velocity of polymerization may be ascribed to the reduced mobility of larger molecules formed and also to the reduction in the number of reactive groups. Mention has also been made of the fact¹⁰ that shellac is rendered increasingly insoluble in alcohol on heating but 5–10% of it always remains in thermoplastic state, acting as a natural plasticizer for the rest of the material. In the course of the present investigation it has been observed that shellac can be rendered completely insoluble in alcohol as is the case of other three-dimensional polymers.

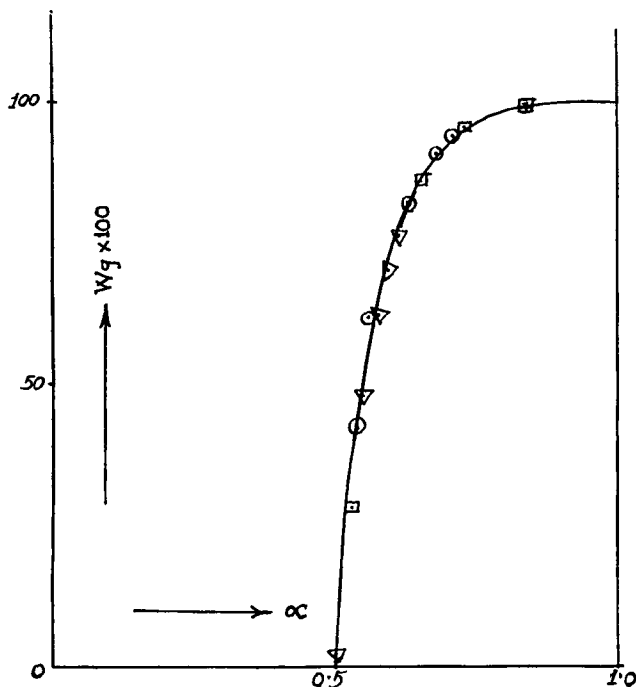


Fig. 13. Plot of the weight fraction of gel vs. the branching coefficient α .

This controversy may be ascribed to the probability of degradation of some of the polymers formed during hot extraction.

Flory and Stockmayer¹⁴ have deduced the following equation for the sum of the weight fractions of gel for the trifunctional case:

$$W_g = 1 - (1 - \alpha)^3 / \alpha^3$$

From the preceding, it is known that the functionality of the branching unit responsible for formation of three-dimensional networks of shellac is three. The above equation was employed to compute the values of α from weight fractions of gel; results are shown in Table V and Figure 13.

It is evident from extrapolation of the plot of Figure 13 that the gel formation takes place when α assumes a value of 0.5, which is in agreement with Flory's equation for gel point. This lends support to the previous findings that only three out of five hydroxyl groups are present in the branching unit and aid in the formation of the three dimensional network structure.

Number-Average and Weight-Average Degrees of Polymerization and Complexities at the Gel Point

In condensation polymerization¹³

$$DP_n = 1 / (1 - \alpha f / 2)$$

and

$$DP_w = \sum - W_x = (1+\alpha)/[1 - (f-1)\alpha]$$

By inserting the values of α and f in the above equations it could be shown that DP_n and DP_w become four and infinity, respectively, at the gel point.¹³

Evidently, the ratio, DP_w/DP_n (an index of the heterogeneity of polymers) would be infinite at the gel point. This indicates an extreme heterogeneity of three-dimensional polymers formed at gel point.

Moreover, in the case of condensation polymerization, not only does the degree of branching increase as the reaction progresses, but also chains increase in length.¹⁵ The number of chains in a molecule Z , also referred to as a molecular complexity, is indicated by the following equation:¹³

$$Z = f^n - n + 1$$

regardless of intramolecular reactions. The number- and weight-average values are given as follows:

$$(Z_n)_{AV} = 1/[1 - 2\alpha(f-1)/f]$$

$$(Z_w)_{AV} = [1 + (f-1)\alpha]/[1 - (f-1)\alpha]$$

By substituting the values of α and f in the above equations, $(Z_n)_{AV}$ and $(Z_w)_{AV}$ become equal to three and infinity, respectively, at the gel point. According to Flory¹⁵ the average molecular weights increase more rapidly as the polymerization proceeds than the corresponding complexities. The ratio of the two molecular weights vary approximately as the ratio of these two complexities (Z_w/Z_n), which in turn, increases with α and becomes infinite at the gel point. This behavior has also been observed in the present case, thus supporting the validity of theory postulated by Flory for three-dimensional polymerization.

CONCLUSIONS

From the data of the experiments it is evident that only three out of five hydroxyl groups of shellac are present in the branching unit and help in the formation of three-dimensional polymers.

The whole polymerization process could be divided into three distinct stages namely, A, B, and C.

The ordinary shellac is in the A stage, when it is fusible and soluble in alcohol.

In the B stage it becomes rubbery, but still remains soluble in alcohol. The time of conversion from A to B stage is called as polymerization time or life under heat and involves the formation of macromolecules of linear type comprising four monomer units. This may be ascribed to intermolecular reaction.

Just after the B stage, gelation or the C stage starts, which involves the formation of three-dimensional network structures by association or crosslinking of linear polymers; this is an intramolecular reaction. In

the C stage shellac gradually loses its solubility in various solvents as the molecules become more gigantic, more rigid, and more compact and ultimately it is rendered completely insoluble in all nondegrading solvents.

On further heating these networks lose their plastic properties to a large extent and become brittle on account of formation of low molecular weight material.

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Résumé

Dans le présent travail on étudie la cinétique de la polymérisation thermique du shellac. On observe une relation linéaire entre la viscosité intrinsèque $[\eta]$ et la durée de polymérisation (p. t.) pour un certain degré de réaction suivi par une rapide augmentation de $[\eta]$ près du point de gélification. Après la gélification la viscosité intrinsèque de la fraction sol tombe de nouveau brusquement. En outre, on essaye de comprendre la nature de la gélification à partir des fractions pondérales de gel formé après un traitement prolongé à différentes températures.

Zusammenfassung

In der vorliegenden Arbeit wurde die Kinetik der thermischen Polymerisation von Schellack untersucht. Bis zu einem bestimmten Umsatz besteht eine lineare Beziehung zwischen Viskositätszahl $[\eta]$ und Polymerisationsdauer ($p. t$), dann folgt ein scharfer Anstieg von $[\eta]$ in der Nähe des Gelpunktes. Nach der Gelbildung nimmt die Viskositätszahl der Solfraktion wieder stark ab. Zusätzlich wurde versucht, aus den Gewichtsbruchteilen des nach längerer Härtung bei verschiedenen Temperaturen gebildeten Gels Einblick in die Natur der Gelbildung zu gewinnen.

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