The Gelation Point of Alkyd Resins

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INTRODUCTION

The quantitative treatment of gelation has been dealt with by Flory and Stockmayer[1,2] who independently and by different means deduced formulas relating the gel points of polyfunctional systems with the extent of reaction of the functional groups. These treatments, as is well known, are based on two assumptions, one of which is occasionally valid and the other of which is probably never valid; namely, that all functional groups of the same kind in the system are equally reactive and that intramolecular reaction is excluded. Provided the first of these assumptions is valid, as it is with certain systems, the calculated gel point agrees closely with the observed gel point, the discrepancy (2–5%) being probably caused by some intramolecular reaction. It is the purpose of this communication to apply Flory's[1] quantitative treatment to the polyesterification reaction that occurs in the making of oil-modified alkyd resins, and to deduce an expression for the gel point, taking into account the different reactivities that exist between the functional groups in this particular and industrially important system.

THE BASIC GEL POINT EQUATION

We will first of all deduce the gel point for the general case of the alkyd resin which may contain any or all of three different types of polyhydric alcohol—dihydric and two polyhydric of functionality 3 or more—one dibasic acid or anhydride and one monobasic acid, assuming for the time being that all functional groups of a kind are equally reactive, and excluding intramolecular reaction.

Schematically, the monomer units may be represented by

B—B dihydric alcohol, $g = 2$

polyhydric alcohol, functionality $g_1 \geqslant 3$

polyhydric alcohol, functionality $g_2 > g_1$

A—A dibasic acid or anhydride, functionality $= 2$
—A monobasic acid, functionality $= 1$
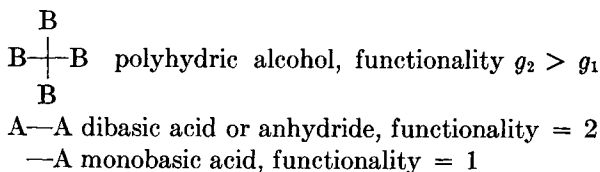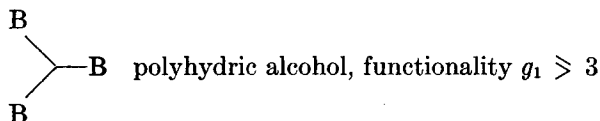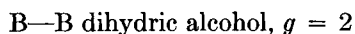
In these schemes, B = hydroxyl group, A = carboxyl group.

The stoichiometry of the system is represented by the following symbols:

$$\rho = \frac{\text{B's belonging to B—B}}{\text{total B's}}$$

$$\lambda = \frac{\text{A's belonging to A—}}{\text{total A's}}$$

and

$$\epsilon = \frac{\text{total B's}}{\text{total A's}}$$

The treatment of Flory[1] is used here; that is, we seek α, the probability that any B group, belonging to a branch unit (polyalcohol of functionality $g > 2$) and selected at random, is connected via a chain to another branch unit.

This state of affairs may come about in four possible ways shown in Figure 1.

The probability, α, is equal to the sum of the four individual probabilities of each of these four cases occurring in any selection taken at random, each case being equally valid for the purpose of
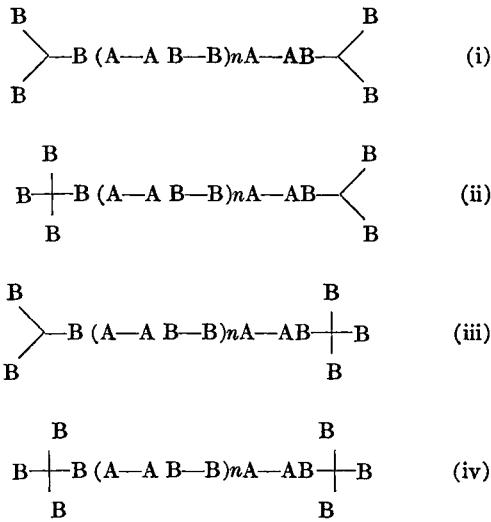
Fig. 1. Showing the four possible ways whereby, in the system under discussion, branch unit may be linked to branch unit. n is any integer from 0 to ∞.

evaluating α. If P_A, P_B are the fractions of A, B groups, respectively, that have reacted, then these four probabilities are:

$$\alpha_{(i)} = \sum_{n=0}^{\infty} P_B \left(\frac{1 - \rho - \theta}{1 - \rho}\right) [(1 - \lambda)\rho P_A P_B]^n$$
$$\times (1 - \lambda) P_A (1 - \rho - \theta)$$

$$\alpha_{(ii)} = \sum_{n=0}^{\infty} P_B \left(\frac{\theta}{1 - \rho}\right) [(1 - \lambda)\rho P_A P_B]^n$$
$$\times (1 - \lambda) P_A (1 - \rho - \theta)$$

$$\alpha_{(iii)} = \sum_{n=0}^{\infty} P_B \left(\frac{1 - \rho - \theta}{1 - \rho}\right) [(1 - \lambda)\rho P_A P_B]^n$$
$$\times (1 - \lambda) P_A \theta$$

$$\alpha_{(iv)} = \sum_{n=0}^{\infty} P_B \left(\frac{\theta}{1 - \rho}\right) [(1 - \lambda)\rho P_A P_B]^n$$
$$\times (1 - \lambda) P_A \theta$$

and the sum of these four probabilities, α, is:

$$\alpha = \sum_{n=0}^{\infty} P_A P_B (1 - \lambda)(1 - \rho)[P_A P_B (1 - \lambda)\rho]^n$$

Evaluating the summation:

$$\alpha = \frac{P_A P_B (1 - \lambda)(1 - \rho)}{1 - P_A P_B (1 - \lambda)\rho} \qquad (1)$$

Now at the gel point, it was shown by Flory[1] that $\alpha = 1/(g - 1)$ where g is the functionality of the branch unit. If there is more than one branch

unit, g in this expression must be replaced by the appropriate average.

Thus, in this system where for each *branch unit* hydroxyl group there is $(1 - \rho - \theta)/(1 - \rho)$ g_1-ol hydroxyl groups and $\theta/(1 - \rho)$, g_2-ol hydroxyl groups, the average value of g is:

$$\left(\frac{1 - \rho - \theta}{1 - \rho}\right) g_1 + \left(\frac{\theta}{1 - \rho}\right) g_2$$

so that instead of $\alpha = 1/(g - 1)$ we write:

$$\alpha = \frac{1}{\left(\dfrac{1 - \rho - \theta}{1 - \rho}\right) g_1 + \left(\dfrac{\theta}{1 - \rho}\right) g_2 - 1}$$

therefore

$$\alpha = \frac{(1 - \rho)}{g_1(1 - \rho - \theta) + g_2\theta - (1 - \rho)}$$

Thus the final gel point equation is

$$\frac{1 - \rho}{g_1(1 - \rho - \theta) + g_2\theta - (1 - \rho)}$$
$$= \frac{P_A P_B (1 - \lambda)(1 - \rho)}{1 - P_A P_B (1 - \lambda)\rho} \qquad (2)$$
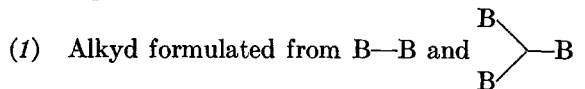
Rearranging, we have:

$$(P_A P_B)_{gel}$$
$$= \frac{1}{(1 - \lambda)[g_1(1 - \rho - \theta) + g_2\theta + 2\rho - 1]} \qquad (3)$$

where $(P_A P_B)_{gel}$ signifies that the particular values of P_A and P_B are those at gelation.

This same eq. (3) may be derived also by applying Stockmayer's generalized gel point equation[2] for this system using the same symbols as defined above.
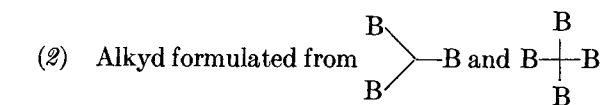
In practice, of course, it may be unlikely that three polyhydric alcohols are present at the same time. It is common, however, for an alkyd to be made with a dihydric alcohol and a polyhydric of functionality >2, two polyhydric alcohols of functionality >2, or one polyhydric alcohol of functionality >2.

For each of these special individual cases the general equation reduces to:

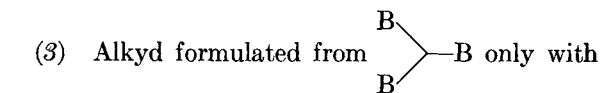*(1)* Alkyd formulated from B—B and $\begin{smallmatrix} B \\ \diagdown \\ \diagup \\ B \end{smallmatrix}$—B

with A—A and A—:

$$\therefore \theta = 0$$

$$(P_A P_B)_{gel} = \frac{1}{(1 - \lambda)[g(1 - \rho) + 2\rho - 1]} \qquad (4)$$

(2)   Alkyd formulated from $\diagdown\!\!\!\!\diagup$—B and B—$|$—B

with A—A and A—:

$$\therefore \rho = 0$$

$$(P_A P_B)_{gel} = \frac{1}{(1 - \lambda)[g_1(1 - \theta) + g_2\theta - 1]} \quad (5)$$

(3)   Alkyd formulated from $\diagdown\!\!\!\!\diagup$—B only with

A—A and A—:

$$\therefore \rho = \theta = 0$$

$$(P_A P_B)_{gel} = \frac{1}{(1 - \lambda)(g - 1)} \quad (6)$$

In these equations P_A is related to P_B by the equation

$$P_A = \epsilon P_B \quad (7)$$

so that any of these gel point expressions can readily be expressed in terms either of P_A or P_B alone. Thus, for the general case

$$(P_A)_{gel} =$$

$$\left[\frac{\epsilon}{(1 - \lambda)\{g_1(1 - \rho - \theta) + g_2\theta + 2\rho - 1\}} \right]^{1/2} \quad (3a)$$

$$(P_B)_{gel} =$$

$$\left[\frac{1}{\epsilon(1 - \lambda)\{g_1(1 - \rho - \theta) + g_2\theta + 2\rho - 1\}} \right]^{1/2} \quad (3b)$$

Note that eqs. (3) to (6) assume that all the re-actants—monobasic and dibasic acids, polyhydric alcohols—are present from the start of the reaction, and are not added in stages. This reservation is of importance in alkyd technology because there are two main ways of making alkyd resins—the so-called "fatty acid" method and the so-called "monoglyceride" method. In the former method, all reactants are present at the start of the reaction, and eqs. (3) to (6) strictly apply only when this method is used. In the "monoglyceride" method, the fatty acid is in effect completely reacted with the polyalcohol before the dibasic acid is reacted (in practice triglyceride and polyalcohol are alco-holyzed first to equilibrium, giving a random mix-ture of mono-, di-, and triglycerides and glycerol, and the corresponding esters of the other polyal-cohol in case there are two polyalcohols present), and eqs. (3) to (6) would apply only if the reaction were completely reversible and equilibrium were

attainable within the time of the reaction. As it has been proved that equilibrium is established quite slowly under these conditions, eqs. (3) to (6) cannot be applied to "monoglyceride" alkyds, but a modification can be used, and this modification is dealt with in the Appendix to this paper. For the present, however, this reservation is unimpor-tant since the primary purpose of this paper is to derive a gel point formula for cases of unequal reac-tivity, and as will be seen, it will be assumed that the monobasic acid is completely reacted as in the case of "monoglyceride" alkyds, whatever method of manufacture is employed. The above treatment was given mainly to introduce and illustrate the mathematical approach that is being used. This modified gel point, which mainly concerns alkyds in which phthalic anhydride is used as the dibasic acid, is derived in the next section.

THE MODIFIED GEL POINT EQUATION

In this section we consider an alkyd whose mono-mer units are the same as were considered in the previous section, and are represented by the same symbols. This time, however, we differentiate be-tween the different degrees of reaction of the various carboxyl groups, it being assumed for the time being that the hydroxyls are all of equal reactivity. Thus:

$$P_\lambda = \frac{\text{monobasic acid A's reacted}}{\text{total monobasic acid A's}}$$

$$P_{\delta_1} = \frac{\text{primary dibasic acid A's reacted}}{\text{total primary dibasic acid A's}}$$

$$P_{\delta_2} = \frac{\text{secondary dibasic acid A's reacted}}{\text{total secondary dibasic acid A's}}$$

These are clearly related to P_A, the overall de-gree of reaction of the acid groups, by the equation:

$$P_A = \lambda P_\lambda + [(1 - \lambda)/2](P_{\delta_1} + P_{\delta_2}) \quad (8)$$

As before, we seek the probability of occurrence of each of the four possible routes from branch unit to branch unit as given in Figure 1. This time, however, we have to bear in mind the different probabilities of reaction of the three distinct types of carboxylic group; P_λ, P_{δ_1}, and P_{δ_2}.

Considering first of all the possibility (1) of Figure 1, the probability that the left-hand B group is reacted is P_B. The probability that it is

from the particular branch unit $\diagdown\!\!\!\!\diagup$—B is
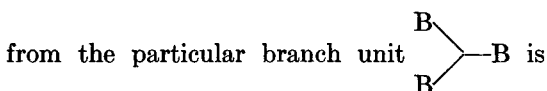
$$P_B[(1 - \rho - \theta)/(1 - \rho)]$$

where the fraction $[(1 - \rho - \theta)/(1 - \rho)]$ is the function of

B\
  >—B type B groups from all branch
B/

unit B groups.

The probability that the B group is reacted with a dibasic acid carboxyl group is

$$P_B[(1 - \rho - \theta)/(1 - \rho)][1 - \lambda(P_\lambda/P_A)]$$

$(1 - \lambda)$ being the fraction of dibasic acid carboxyl groups present in the system, and the fraction P_λ/P_A expressing the relative reactivity of the monobasic acid carboxyl groups compared with all other types of carboxyl groups. This correction for λ is necessary in this case because we are expressing the probability of reaction of a dibasic acid carboxyl group as 1 minus the probability of reaction of a monobasic acid carboxyl group, and since the carboxyl groups all have different reactivities we must allow for this in our expression.

Thus the probability that the left-hand B group has reacted with a dibasic acid carboxyl group is:

$$P_B\left(\frac{1 - \rho - \theta}{1 - \rho}\right)\left(1 - \lambda\frac{P_\lambda}{P_A}\right)$$

The probability that it is a *primary* carboxyl group that has reacted with the left-hand B group is this last expression multiplied by P_{δ_1}/P_A, representing the relative reactivity of primary carboxyls compared with other types of carboxyl groups, that is

$$P_B\left(\frac{1 - \rho - \theta}{1 - \rho}\right)\left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}}{P_A}$$

The probability that the other carboxyl groups (the secondary carboxyl group) has reacted is P_{δ_2}, and so the probability that the left-hand B group, for the possibility (i) of Figure 1, has reacted as far as the secondary carboxyl group of the first A—A unit is:

$$P_B\left(\frac{1 - \rho - \theta}{1 - \rho}\right)\left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}}{P_A}P_{\delta_2}$$

In order to obtain the probability that this latter carboxyl group is reacted with a B group from a B—B unit, we multiply by ρ the fraction of all such B groups present in the system, and the probability that the second B group on this unit is also reacted is obtained by multiplying by P_B. Hence the probability that the system is reacted as far as
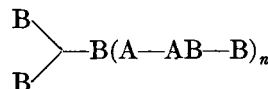
B\
  >—BA—AB—B
B/
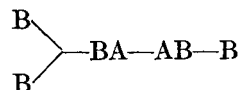
is given by:

$$P_B\left(\frac{1 - \rho - \theta}{1 - \rho}\right)\left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}P_{\delta_2}P_B}{P_A}$$

As there may be anything from 0 to n such A—AB—B units, we must raise to the power of n all such probabilities as concern the possibility of formation of A—AB—B, and put in a summation sign, so that the expression:

$$\sum_{n=0}^{\infty} P_B\left(\frac{1 - \rho - \theta}{1 - \rho}\right)\left[\left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}P_{\delta_2}P_B\rho}{P_A}\right]^n$$

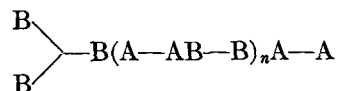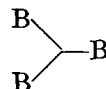gives the probability that the system has reacted as far as

B\
  >—B(A—AB—B)$_n$
B/

Proceeding as above, we now multiply by

$$\left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}}{P_A}P_{\delta_2}$$

to give the probability that the system has reacted as far as

B\
  >—B(A—AB—B)$_n$A—A
B/

and finally we multiply by $(1 - \rho - \theta)$ to signify that we have reached another branch unit, the particular branch unit being the

B\
  >—B
B/

hence the total probability of formation of possibility (i) of Figure 1, is:

$$\alpha_{(i)} = \sum_{n=0}^{\infty} P_B\left(\frac{1 - \rho - \theta}{1 - \rho}\right)$$
$$\times \left[\left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}P_{\delta_2}P_B\rho}{P_A}\right]^n$$
$$\times \left(1 - \lambda\frac{P_\lambda}{P_A}\right)\frac{P_{\delta_1}P_{\delta_2}}{P_A}(1 - \rho - \theta)$$

The argument for deriving $\alpha_{(ii)}$, $\alpha_{(iii)}$, and $\alpha_{(iv)}$ is quite similar; the results are:

$$\alpha_{(ii)} = \sum_{n=0}^{\infty} P_B \left(\frac{\theta}{1-\rho} \right)$$

$$\times \left[\left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2} P_B \rho}{P_A} \right]^n \left(1 - \lambda \frac{P_\lambda}{P_A} \right)$$

$$\times \frac{P_{\delta_1} P_{\delta_2}}{P_A} (1 - \rho - \theta)$$

$$\alpha_{(iii)} = \sum_{n=0}^{\infty} P_B \left(\frac{1 - \rho - \theta}{1-\rho} \right)$$

$$\times \left[\left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2} P_B \rho}{P_A} \right]^n \left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2}}{P_A} \theta$$

$$\alpha_{(iv)} = \sum_{n=0}^{\infty} P_B \left(\frac{\theta}{1-\rho} \right)$$

$$\times \left[\left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2} P_B \rho}{P_A} \right]^n \left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2}}{P_A} \theta$$

Summing the four α's, we have:

$$\alpha = \sum_{n=0}^{\infty} P_B (1 - \rho) \left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2}}{P_A}$$

$$\times \left[\left(1 - \lambda \frac{P_\lambda}{P_A} \right) \frac{P_{\delta_1} P_{\delta_2} P_B \rho}{P_A} \right]^n$$

evaluating the summation:

$$\alpha = \frac{\dfrac{P_{\delta_1} P_{\delta_2} P_B}{P_A} (1 - \rho) \left(1 - \lambda \dfrac{P_\lambda}{P_A} \right)}{1 - \dfrac{P_{\delta_1} P_{\delta_2} P_B \rho}{P_A} \left(1 - \lambda \dfrac{P_\lambda}{P_A} \right)} \quad (9)$$

at the gel point $\alpha = 1/(g-1)$; as before, g in this expression is given by

$$[g_1(1 - \rho - \theta) + g_2\theta]/(1 - \rho)$$

as explained in the preceding section; hence at gelation:

$$\frac{(1 - \rho)}{g_1(1 - \rho - \theta) + g_2\theta - (1 - \rho)}$$

$$= \frac{\dfrac{P_{\delta_1} P_{\delta_2} P_B}{P_A} (1 - \rho) \left(1 - \lambda \dfrac{P_\lambda}{P_A} \right)}{1 - \dfrac{P_{\delta_1} P_{\delta_2} P_B \rho}{P_A} \left(1 - \lambda \dfrac{P_\lambda}{P_A} \right)} \quad (10)$$

This simplifies to:

$$\frac{P_{\delta_1} P_{\delta_2} P_B}{P_A} \left(1 - \lambda \frac{P_\lambda}{P_A} \right)$$

$$= \frac{1}{g_1(1 - \rho - \theta) + g_2\theta + 2\rho - 1} \quad (11)$$

or, if we put $g_e = g_1(1 - \rho - \theta) + g_2\theta + 2\rho$, so that g_e has the same significance as the g_e defined by Stockmayer,[2] we have:

$$P_{\delta_1} P_{\delta_2} P_B / P_A = 1/(g_e - 1) \left(1 - \lambda \frac{P_\lambda}{P_A} \right) \quad (12)$$

Equation (12) is quite rigidly deduced, no assumptions at all being made except that all B groups are equally reactive and intramolecular reaction is excluded [this last assumption being explicit in equating α with $1/(g - 1)$].

Equation (12) can only be used, however if P_{δ_1} and P_{δ_2} and P_λ are known—P_A and P_B being known from the "acid value" and "hydroxyl value," respectively, of the system. The exact knowledge of P_{δ_1}, P_{δ_2}, and P_λ will certainly be extremely difficult to obtain; however, in the alkyd case, using C_{18} fatty acids as the monobasic acid and phthalic anhydride as the dibasic acid, the following assumptions will not introduce too much error:

(1) $\qquad\qquad P_{\delta_1} \cong 1$

Phthalic anhydride is well known to react completely to the half-ester, very rapidly even at 100°C. At 250°C., which is the normal working temperature for making alkyds, the assumption would appear to be quite valid.

(2) $\qquad\qquad P_\lambda \cong 1$

This assumption is not quite so justified, but providing the value of P_A is over 0.80 then P_λ will be close enough to unity as a first approximation. The greater P_A is, the better will the approximation be, and in the range of $P_A > 0.90$ the error is expected to be negligible. Of course, the range of $P_A > 0.90$ is the most interesting in alkyd technology.

Rewriting eq. (8) with $P_{\delta_1} = P_\lambda = 1$:

$$P_{\delta_2} = \frac{2(P_A - \lambda)}{1 - \lambda} - 1$$

$$\therefore P_{\delta_2} = \frac{2P_A - 1 - \lambda}{1 - \lambda} \quad (13)$$

and substituting in eq. (12), in which P_{δ_1} and P_λ are also put equal to 1:

$$P_{\delta_2} P_B / P_A = 1/\{(g_e - 1)[1 - (\lambda/P_A)]\} \quad (14)$$

and putting $P_B = P_A/\epsilon$:

$$P_{\delta_2} = \epsilon/\{(g_e - 1)[1 - (\lambda/P_A)]\} \quad (15)$$

and introducing eq. (13):

$$\frac{2P_A - 1 - \lambda}{1 - \lambda} = \frac{\epsilon}{(g_e - 1)\,[1 - (\lambda/P_A)]} \quad (16)$$

On solving eq. (16) for P_A, we have:

$$(P_A)_{gel} = \frac{1}{4}\left[\frac{\epsilon(1-\lambda)}{g_e - 1} + 1 + 3\lambda\right]$$

$$+ \frac{1}{4}\left[\left\{\frac{\epsilon(1-\lambda)}{g_e - 1} + 1 + 3\lambda\right\}^2 - 8\lambda(1+\lambda)\right]^{1/2} \quad (17)$$

This is the modified gel point equation, giving the gel point in terms of the *overall* degree of reaction of the acid groups (as may be determined from "acid value" measurements) and the formulation variables.

Note that in eq. (17)

$$g_e = g_1(1 - \rho - \theta) + g_2\theta + 2\rho$$

Clearly, eq. (17) may be used for phthalic anhydride alkyds irrespective of the method of manufacture (fatty acid or monoglyceride.) It is important to stress however, that it is *only* valid for the case when phthalic anhydride is used as the dibasic acid. It does not apply if either isophthalic acid or adipic acid are used as the dibasic acid. In these cases, the reactivity differences between the carboxyl groups are of a much smaller order and eqs. (3) to (6) are applicable. In this case allowance must be made for mode of manufacture, i.e., fatty acid or monoglyceride.

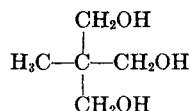## THE CASE OF UNEQUAL HYDROXYL REACTIVITY

The above treatment has assumed that all the hydroxyl groups are of equal reactivity. One could presumably take into account the possibility of differently reactive hydroxyl groups by methods similar to those indicated in the previous section. Flory[1] has already indicated how it may be done in the case of the primary and secondary hydroxyl groups of glycerol. No attempt has been made to allow for these different reactivities in this case, however, and it is the purpose of this section to justify this omission.

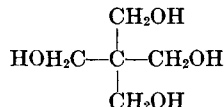The polyhydric alcohols that are industrially of importance include:

Glycerol
Pentaerythritol
Dipentaerythritol
Ethylene glycol
1,2,6-Hexanetriol
Trimethylol ethane
Trimethylol propane

With the exception of the case of the primary and secondary hydroxyl groups of glycerol, it is extremely unlikely that the reactivities differ very much, since the hydroxyl groups are mainly primary, the —CH_2OH group being part of quite a small molecule, and many are similar in type.

Thus, trimethylolethane

$$\begin{array}{c} CH_2OH \\ | \\ H_3C-C-CH_2OH \\ | \\ CH_2OH \end{array}$$

and pentaerythritol

$$\begin{array}{c} CH_2OH \\ | \\ HOH_2C-C-CH_2OH \\ | \\ CH_2OH \end{array}$$

have the same skeleton. None of these —OH groups are affected by steric hindrance and the reaction of one would be considered unlikely to affect the reactivity of another one. Such differences as these are will be due mainly to slight structural differences, affecting the *size* of the molecule more than anything else. The belief in the similarity of reactivity of these polyhydric alcohols is supported by the general similarity in reaction velocity when these substances are used interchangeably. Thus pentaerythritol alkyds do not process very much faster than glycerol alkyds and what differences there are is attributable to the β-hydroxyl group of glycerol, which is known to react at one-quarter the rate of the α-hydroxyl groups.

Now it can be established both practically and theoretically that despite this 4-fold difference in reactivity between the primary and secondary hydroxyl groups of glycerol, the gel point of phthalic/glycerol alkyds or adipic/glycerol alkyds is little affected thereby. Having established that a 4-fold difference can be ignored so far as gel point calculation is concerned, we argue that the much smaller order of difference that occurs between the reactivity of the different polyalcohols enumerated above can certainly be ignored.

The practical evidence is as follows: An alkyd whose formulation was 1 mole adipic acid, 1 mole stearic acid, 1 mole trihydric alcohol was prepared

in the laboratory and esterified to the gel point. When glycerol was used as the polyhydric alcohol gelation occurred at $P_A = 0.900$. Using trimethylol ethane as the polyhydric alcohol, gelation occurred at $P_A = 0.910$. Since all hydroxyl groups are equivalent in the latter alcohol, one can conclude that the gel point is unaffected by the unequal reactivities of the glycerol hydroxyls. (For the theoretical evidence the writer is indebted to Dr. D. F. Rushman and colleagues of the Paint Research Station.)

In his original paper on gelation, Flory[1] showed that, in the reaction between glycerol and a dibasic acid in equivalent amounts, the value of α is given by:

$$\alpha = \theta_3/(1 - \theta_2) \tag{18}$$

where

$$\theta_2 = [2PP_\alpha^2(1 - P_\beta) + 2PP_\alpha P_\beta(1 - P_\alpha)$$
$$+ 2PP_\alpha P_\beta (1 - P_\alpha)]/(2P_\alpha + P_\beta) \tag{19}$$

and

$$\theta_3 = 3PP_\alpha^2 P_\beta/(2P_\alpha + P_\beta) \tag{20}$$

In these expressions:

$$P_\alpha = \frac{\alpha\text{-hydroxyl groups reacted}}{\alpha\text{-hydroxyl groups present initially}}$$

$$P_\beta = \frac{\beta\text{-hydroxyl groups reacted}}{\beta\text{-hydroxyl groups present initially}}$$

$$P = \frac{\text{carboxyls reacted}}{\text{carboxyls present initially}}$$

$$P = \frac{2}{3}P_\alpha + \frac{1}{3}P_\beta$$

since stoichiometric amounts are used.

Now, as a result of studies on the relative amounts of α- and β-monoglycerides at equilibrium, Dr. Rushman[3] and his colleagues at the Paint Research Station[3] were able to show that

$$P_\beta(1 - P_\alpha)/2P_\alpha(1 - P_\beta) = 0.125 \tag{21}$$

The expression on the left-hand side is the ratio of monoglycerides found at equilibrium after alcoholyzing glycerol with triglyceride oil. The 0.125 is the experimental ratio. This expression follows from the fact that at equilibrium, moles of α-monoglycerides per mole glycerol used is

$$2P_\alpha(1 - P_\beta)(1 - P_\alpha)$$

and moles β-monoglyceride per mole glycerol used is

$$P_\beta(1 - P_\alpha)^2$$

This ratio gives eq. (21).

Now using the equation:

$$P = \frac{2}{3}P_\alpha + \frac{1}{3}P_\beta$$

in conjunction with eq. (21), it is possible to solve for P_α and P_β, thus:

$$P_\alpha = \frac{1}{3}[2.25(p + 1)$$
$$\pm (5.062P^2 - 7.875P + 5.062)^{1/2}] \tag{22a}$$

$$P_\beta = \frac{1}{3}[9P - 4.5(P + 1)$$
$$\pm (20.248P^2 - 31.504P + 20.248)^{1/2}] \tag{22b}$$

and using these values of P_α and P_β, and fitting the results into eqs. (18), (19), and (20), one can determine the value of α at any value of P for the case when the α and β hydroxyls differ in reactivity to the extent that they are observed in practice to differ. The results are given in Table I.

TABLE I
Variation with P, the Proportion of All Carboxyls That Have Reacted, of P_α, P_β, and α in the Glycerol/Dibasic Acid Reaction (Equivalent Amounts Taken)[a]

P	P_α	P_β	α
0.2	0.260	0.080	0.00576
0.3	0.383	0.134	0.0225
0.4	0.499	0.202	0.0628
0.5	0.609	0.282	0.1433
0.6	0.709	0.382	0.279
0.7	0.800	0.500	0.4735
0.8	0.879	0.642	0.686
0.9	0.944	0.812	0.863

[a] P_α and P_β are proportion of α- and β-hydroxyl groups, respectively, that have reacted, for the case when the α-hydroxyl group is 4 times as reactive as the β-hydroxyl group.

The relationship between α and P for the case when reactivity differences are ignored is given by $\alpha = P^2$.

A graph of α vs. P^2 for the case where $\alpha = P_2$ and for the results given in Table I is given in Figure 2; the critical value of α at gelation for this system is $\alpha = 0.5$. The two curves cross very near to this point. To be precise, the gel point, neglecting reactivity differences, is at $P = 0.707$, and from the graph of the results in Table I it is at $P = 0.713$. It can be shown that significant divergencies of the gel point from $P = 0.707$ do not commence until the order of the reactivity difference between the two groups is about 20 times.

Since this most interesting theoretical evidence is supported by the practical result quoted above,
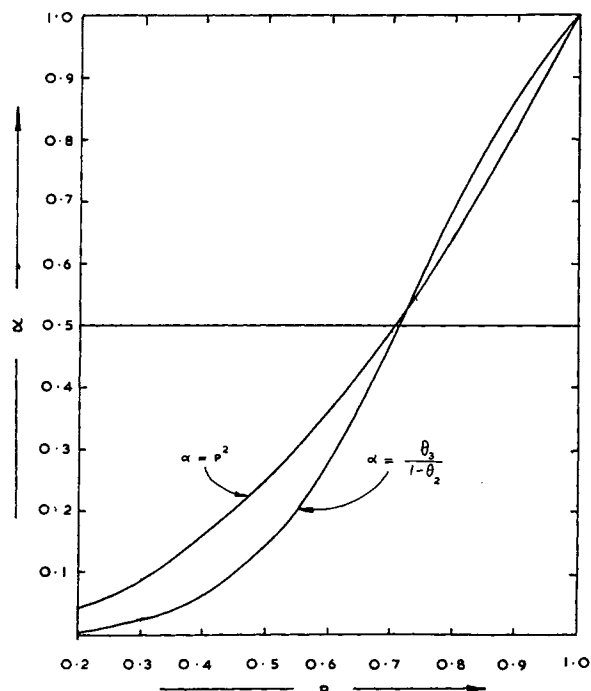
Fig. 2. Showing the variation of α with P for the glycerol/dibasic acid reaction (stoichiometric amounts of reactants). The graph of α vs. P^2 is for the case of equal reactivity of all hydroxyl groups. The graph of α vs. $\theta_3/(1 - \theta_2)$ is for the case where the α-hydroxyl groups are 4 times as reactive as the β-hydroxyl groups. Note how the two graphs cross very nearly at $\alpha = 0.5$, indicating that the gel point for this reaction is only very slightly affected by such differences in hydroxyl reactivity as are observed in practice.

it is contended that no serious errors are likely to be introduced if reactivity differences between the hydroxyl groups of the polyhydric alcohols of importance in alkyd technology are ignored. Of course, any other polyhydric alcohols that may be used or proposed must be considered in this connection "on their merits." The above remarks apply only to those polyhydric alcohols enumerated at the commencement of this section.

Equation (17), then, may safely be used to deduce gel points of alkyds which are based on fatty acids, phthalic anhydride, and up to 2 polyhydric alcohols of functionality equal to or greater than 3 and not more than 1 dihydric alcohol. Whereas reactivity differences between hydroxyl groups are unlikely to exceed a factor of 4, which as shown above may be neglected for gel point calculation purposes, it can be shown that between the carboxyl groups of a fatty acid and the secondary carboxyl group of phthalic acid there is a reactivity difference which is of a much higher order. Thus, Bhide and Sudborough[4] showed that whereas the rate

constant of esterification for C_{12} to C_{18} fatty acids (esterification with ethanol in $0.1N$ HCl) was about 0.27, that for benzenoid carboxylic acids, under similar conditions, was in the range 0.002 to 0.007, i.e., the former is 100 to 1000 times more reactive. The rate constant of esterification for adipic acid, pimelic acid, and suberic acid however, under similar conditions was found to be in the range 0.26–0.3, i.e., of the same order as for the fatty acids. The conclusion is that by using dibasic acids, such as adipic acid, no correction for reactivity need be applied, and the gel paint will be given by eqs. (3) to (6). With phthalic anhydride, however, eq. (17) must be used.

Before passing on to the next section, in which experimental results are discussed, it is as well to point out that eqs. (3a) and (17) make no allowance for fatty acid dimerization that occurs as a result of the action of heat with unsaturated fatty acid such as are used in air-drying alkyds. Any tendency to dimerize would, of course, alter the value of λ in both equations, and presumably, if the amount of dimerization were known, it could be allowed for. However, for practical purposes this limitation is less serious than it may seem because if the formulation of an industrial alkyd is such that it is likely to gel, it will in practice usually do so at some value of P_A less than 0.96–0.97. In most formulations this corresponds to an "acid value" of 10 or more, which, under the usual industrial conditions (230–260°C.) and with good water removal will be attained in quite a short time from the start of the reaction and before any serious quantity of dimerization has occurred. It is only with the so-called "long oil" alkyds containing 60% or more of fatty acid and with a gel point (true) corresponding to a value of $(P_A)_{gel}$ of more than 0.97 that considerable dimerization may occur, because of the much longer times needed to process an alkyd, in practice, to an "acid value" of less than 10 compared with the usually quite short time needed to attain a value of 10. Those alkyds are hard to gel in any case, and it certainly is true that if they do, fatty acid dimerization is mainly responsible.

CORRECTION FOR INTRAMOLECULAR CONDENSATION

Equations (3) to (6), and eq. (17), if used in the correct circumstances, predict gel points that are somewhat earlier than those observed in practice. It is the purpose of this final section to indicate some

TABLE II

Gel Points, Calculated by Means of Eqs. (3a) or (17) as Appropriate, Compared with the Observed Gel Points, in a Few Selected Cases

| Polyhydric alcohol | Moles of reactants per mole of polyhydric alcohol | | λ | ϵ | (P_A) gel calculated from | | (P_A) gel observed | % discrepancy |
	Fatty acid	Dibasic acid			Eq. (3a)	Eq. (17)		
Trimethylolethane	1.000	1.000 of adipic acid	0.333	1.000	0.866	—	0.908	4.8
$g = 3$	1.100	0.950 of adipic acid	0.317	1.000	0.889	—	0.935	5.2
	1.000	1.000 of phthalic anhydride	0.333	1.000	—	0.926	No gel @ 0.97	>5.0
Glycerol	0.849	1.015 of phthalic anhydride	0.295	1.042	—	0.918	0.964	5.0
$g = 3$	1.000	0.936 of phthalic anhydride	0.348	1.045	—	0.944	0.973	3.0
Pentaerythritol	1.426	1.290 of phthalic anhydride	0.375	1.051	—	0.879	0.953	8.5
$g = 4$	1.25	1.375 of phthalic anhydride	0.312	1.000	—	0.839	0.91	8.5
	1.25	1.375 of isophthalic acid	0.312	1.000	0.696	—	0.76	9.2

practical results obtained in the laboratory, to examine the discrepancy that exists between these observed gel points and the theoretical gel point, and to explain this discrepancy, which is quite small, on the basis of intramolecular reaction, which has been ignored up to now.

All workers on the subject of gelation have observed that intramolecular reaction, or "ring closure," occurs. This will inevitably delay the gelation of the system, since reaction between two functions on the same molecule cannot increase molecular size whereas reaction between two functions on different molecules inevitably increases molecular size. Thus Kienle, van der Meulen and Petke[5] in their classical work on the glycerol-dibasic acid reaction observed a discrepancy between the number-average molecular weight as observed and as calculated from loss of functional groups that could be explained if it was assumed that about 5% of the ester links were intramolecular. Flory[1] observed a discrepancy of 2.5 to 5% between the observed and calculated gel points (calculated according to the equivalent of eq. (3a) and when $\lambda = 0$) in reaction between a glycol, a dibasic acid, and a tribasic acid. Stockmayer[6] obtained some interesting results in the reaction between pentaerythritol and adipic acid. The theoretical gel point is $P_A = 0.577$. The observed gel point was higher than this, and increased in proportion to the dilution. Extrapolation to zero dilution (or "infinite concentration") when ring closure should be suppressed entirely gave $(P_A)_{gel} = 0.578 \pm 0.005$ in perfect agreement with theory. More recently, Price, Gibbs, and Zimm, have produced similar results in the reaction between adipyl chloride, trimethylolethane, and neopentyl glycol[7]

and with polyalkoxysilanes.[8] These results correlate well with the theory of Kilb,[9] in which an attempt was made to account statistically for intramolecular reaction. Unfortunately, the theory of Kilb, though applicable to alkyd resins, requires a constant to be determined experimentally and this constant can only be obtained by observing the actual gel point. In Table II are given some results obtained by observing the gel point of actual alkyds prepared in the laboratory.

Two facts stand out clearly from the results given in Table II. First, the extent of the discrepancy between the observed and the calculated gel point is similar for those cases where eq. (3a) was applicable and for those cases where eq. (17) was applicable; that is to say, the gel point calculated using the unmodified formula, if used where applicable (in this work with adipic acid and isophthalic acid alkyds) is as close to the observed gel point as the gel point calculated using the formula modified to allow for reactivity differences, applicable when phthalic anhydride was used. This is put forward as evidence in support of the modified gel point formula, eq. (17).

Second, when the polyalcohol or branch unit has a functionality of 3, the per cent discrepancy is of the order of 3–5%, and when it has a functionality of 4, the percentage discrepancy is of the order of 8–9%. It is interesting to note that in Flory's original work,[1] in which the branch unit was trifunctional, the observed discrepancy between the observed and calculated gel points was in the range of 2.5–6%, whereas with tetrafunctional pentaerythritol Stockmayer[6] observed a discrepancy of 9%. This was for the reaction carried out without solvent, as in the case of industrial alkyds. This

seems to confirm the suspicion that the tendency to intramolecular condensation increases with the functionality of the branch unit, which is perhaps not very surprising since the greater the functionability and hence degree of branching, the greater is the chance that a function will react with another function on the same molecule.

It is hoped in a later communication to provide further and more definite evidence in support of the theories presented here. The experimental evidence given in Table II was mainly obtained from preliminary trials. In all cases the reactions were carried out in 2 liter round-bottomed flasks, heated by means of electric heating mantles. The mass was stirred and maintained at the reaction temperature (230 or 250°C.) to an accuracy of ±5°C. Xylene was added and water of esterification was removed as the azeotrope using Dean and Stark type of separator. As the gel point approached, periodic samples were taken for "acid value determination" (titration of a weighed sample, dissolved in toluene/ethanol, with $0.1N$ alcoholic KOH, using phenolphthalein) and the acid value at gelation deduced by extrapolation. From the acid value, the degree of reaction is readily calculated. The gel point is sharp and easy to determine. In any case, in the examples quoted here, the acid value was changing quite slowly at the gel point, and so experimental error would not be very large.

APPENDIX

Modification of Eq. (3a) for "Monoglyceride" Alkyds

Consider an alkyd formulated from 1 mole glycerol a moles monobasic acid and $^1/_2(3/\epsilon - a)$ moles dibasic acid. In this alkyd $\lambda = a\epsilon/3$ but for present purposes it is more convenient to use the parameter a. If this alkyd is prepared by the "monoglyceride" method, the fatty acid and glycerol will first be completely reacted to give a random mixture of mixed glycerides. Assuming complete randomness the distribution of glycerides will be, per mole of glycerol used:

$(a/3)^3$ moles triglyceride, $g = 0$
$3(a/3)^2[1 - (a/3)]$ moles diglyceride, $g = 1$
$3(a/3)[1 - (a/3)]^2$ moles monoglyceride, $g = 2$
$[1 - (a/3)]^3$ moles free glycerol, $g = 3$

and this mixture of glycerides will constitute the polyalcohol that reacts with the dibasic acid.

Working out the gel point for this case, using the same method as was used to derive eq. (3) and as-

suming that the fatty acid distribution remains unaltered and that no free fatty acid is liberated during the esterification, it is easy to show that in that case

$$(P_A{}^*P_B{}^*)_{gel} = \frac{3}{2(3 - a)} \qquad (A1)$$

or including the parameter g, which in this case equals 3:

$$(P_A{}^*P_B{}^*)_{gel} = \frac{g}{(g - 1)(g - a)} \qquad (A2)$$

$P_A{}^*$ and $P_B{}^*$ differ from the P_A and P_B of eq. (3) in referring only to the extent of esterification *after* complete reaction of the monobasic acid. As in the case of P_A and P_B, $P_A{}^*$ and $P_B{}^*$ are related by the equation

$$P_B{}^* = P_A{}^*/\epsilon^* \qquad (A3)$$

Where ϵ^* has the same significance as ϵ, but with no account being taken of those A and B group that are reacted in the mixed glycerides, i.e.:

$$\epsilon^* = \frac{3 - a}{3/\epsilon - a}$$

Therefore:

$$\epsilon^* = \frac{(3 - a)\epsilon}{(3 - a\epsilon)} \qquad (A4)$$

thus

$$P_B{}^* = \frac{P_A{}^*(3 - a\epsilon)}{(3 - a)\epsilon} \qquad (A5)$$

and incorporating eq. (A5) into (A1) we have:

$$(P_A{}^*)_{gel} = \left[\frac{3\epsilon}{2(3 - a\epsilon)}\right]^{1/2} \qquad (A6)$$

or if $g = 3$:

$$(P_A{}^*)_{gel} = \left[\frac{g\epsilon}{(g - 1)(g - a\epsilon)}\right]^{1/2} \qquad (A7)$$

Converting back to the use of the parameter λ by means of the relation $\lambda = a\epsilon/g$, we have:

$$(P_A{}^*)_{gel} = \left[\frac{\epsilon}{(1 - \lambda)(g - 1)}\right]^{1/2} \qquad (A8)$$

which is exactly the same as eq. (3a) for the case where $\theta = \rho = 0$. In this case, however, whereas eq. (3a) is in terms of P_A, eq. (A8) is in terms of $P_A{}^*$.

The above treatment refers only to the case when $g = 3$. By a similar process it can be shown to be

valid for the case when $g = 4$ or when there is present two polyols g_1 and g_2 as defined above, i.e., whatever the value of g, the gel point for the "fatty acid" case is the same as the gel point for the "monoglyceride" case, the two values of P_A having the different significance discussed above.

It remains to convert eq. (A8) to give the gel point in terms of P_A, the overall degree of reaction. Since the monobasic acid is 100% esterified, the component of P_A for this constituent is equal to 1.000. Hence the overall degree of reaction is the mean of 1.00 and P_A^* given by eq. (A8) weighted according to the amounts of each monobasic acid and dibasic acid present, thus:

$(P_A)_{gel}$ = [1 × equivalents of monobasic acid + P_A^* × equivalents of dibasic acid]/total acid equivalents

or, in the symbols used here:

$$(P_A)_{gel} = \frac{a\epsilon}{g} + \left(1 - \frac{a\epsilon}{g}\right)(P_A^*)_{gel} \quad \text{(A9)}$$

or using λ and the other parameter defined earlier:

$$(P_A)_{gel} = \lambda + (1 - \lambda)(P_A^*)_{gel} \quad \text{(A10)}$$

In eq. (A10), $(P_A^*)_{gel}$ is given by eq. (3a).

It is then quite a simple matter to correct for the case when the monobasic acid is completely reacted before the dibasic acid is added. The difference between the gel points observed for an alkyd made by the two processes will only reflect the difference between eqs. (3a) and (A10) if the monobasic acid remains fully reacted during the second stage and is not liberated by acidolysis. Of course, with phthalic anhydride alkyds the modification of eq. (7) implies that "fatty acids" and "monoglyceride" alkyds should have the same gel point. If adipic acid, or some other acid of similar reactivity to fatty acids is used as the dibasic acid, then there should be some difference in the gel point between alkyds made by the two processes. It is hoped to test this point experimentally in the future.

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Synopsis

Using Flory's basic method, an equation is derived for the gelation point of oil-modified alkyd resins in which account is taken of the different reactivities of the various carboxyl groups. The resultant modified equation is useful when phthalic anhydride is used as the dibasic acid because of the widely differing carboxyl group reactivities which occur in this case. If adipic or isophthalic acid is used as the dibasic acid, the gel point equation deduced by Flory's original method, which takes no account of reactivity differences, may be used. In such a case the difference between the observed and calculated gel point is about 5% when the polyhydric alcohol used is trifunctional and 8–9% when the polyhydric alcohol used is tetrafunctional. The modified gel point equation, applicable when phthalic anhydride is used as the dibasic acid, is shown to predict gel points with similar degrees of accuracy, discrepancies being also greater for alkyds using tetrahydric alcohols than for alkyds using trihydric alcohols. The discrepancy is believed to be due to the occurrence of intramolecular condensation, and it is contended that the degree of such intramolecular condensation in branching systems is proportional to some function of the branch unit functionality.

Résumé

En employant la méthode de base de Flory, on obtient une équation pour le point de gélification des huiles à base de résines alkydes modifiées dans lesquelles on tient compte des différentes réactivités des différents groupes carboxyles. L'équation modifiée résultante est utile lorsqu'on utilise l'anhydride phthalique comme acide bibasique à cause des réactivités très divergentes des groupes carboxyles se produisant dans ce cas. Si on utilise l'acide adipique ou l'acide isophtalique comme acide bibasique, on peut employer pour le point de gélification l'équation déduite par la méthode originale de Flory qui ne tient pas compte des différences de réactivité. Dans un tel cas, la différence entre le point de gélification observé et calculé est d'environ 5% lorsque l'alcool polyvalent utilisé est trifonctionnel et 8–9% lorsque l'alcool polyvalent utilisé est tétrafonctionnel. L'equation modifiée pour le point de gélification, applicable lorsque l'anhydride phtalique est utilisé comme acide bibasique, montre qu'il est possible de prévoir les points de gélification avec un degré de précision semblable, le désaccord étant également plus grand pour des alkydes issus d'alcools tétravalent que pour des alkydes issus d'alcools trivalents. Le désaccord semble être dû à une condensation

intramoléculaire et on admet que le degré d'une telle condensation intramoléculaire dans des systèmes ramifiés est proportionnel à une fonction quelconque de la fonctionnalite de l'alcool.

Zusammenfassung

Mit Hilfe der von Flory entwickelten Methode wird eine Gleichung für den Gelpunkt von öl-modifizierten Alkydharzen abgeleitet, in welcher der unterschiedlichen Reaktivität der verschiedenen Karboxylgruppen Rechnung getragen wird. Die erhaltene, modifizierte Gleichung kann auf Phthalsäureanhydrid als zweibasische Säure mit Vorteil angewendet werden, da in diesem Fall zwei stark unterschiedliche Reaktivitäten der Carboxylgruppen auftreten. Bei Verwendung von Adipinsäure oder Isophthalsäure als zweibasische Säure, kann die nach der ursprünglichen Methode von Flory abgeleitete Gelpunkts-Gleichung verwendet werden, welche Unterschiede in der Reaktivität nicht berücksichtigt. In einem solchen Fall beträgt der Unterschied zwischen beobachtetem und berechneten Gelpunkt für einen trifunktionellen, mehrwertigen Alkohol 5% und für einen tetrafunktionellen 8–9%. Es wird gezeigt, dass die modifizierte, für die Benützung von Phthalsäureanhydrid als zweibasische Säure anwendbare Gleichung, die Festlegung von Gelpunkten mit ähnlicher Genauigkeit gestattet, wobei ebenfalls die Unstimmigkeit bei Alkyden mit vierwertigen Alkoholen grösser als bei solchen mit dreiwertigen Alkoholen ist. Es wird angenommen, dass diese Unstimmigkeit durch das Auftreten einer intramolekularen Kondensation verursacht wird und dass das Ausmass einer solchen intramolekularen Kondensation in Systemen mit Verzweigung von der Funktionalität der Verzweigungseinheit abhängig ist.