

workers and indicate a slight negative solvent effect instead of the generally predicted positive one. Contrary to previous data there appears to

be no change of polarization with concentration in the more dilute region.

DURHAM, N. C.

RECEIVED AUGUST 1, 1941

[CONTRIBUTION FROM THE GRADUATE SCHOOL OF APPLIED SCIENCE OF THE UNIVERSITY OF CINCINNATI]

## Molecular Size Distribution in Three Dimensional Polymers. I. Gelation<sup>1</sup>

BY PAUL J. FLORY<sup>2</sup>

Polymerizations may be divided into two types: those which lead exclusively to soluble products regardless of the extent to which the reaction is carried toward completion, and those which lead to gelled, or insoluble, products provided that the reaction is carried far enough. The former behavior is characteristic of bifunctional systems, *e. g.*, the ethylene glycol-phthalic acid reaction, in which linear polymers are formed; the latter behavior is observed in systems of higher functionality where the reactants are functionally capable of producing indefinitely large three-dimensional molecules, *e. g.*, the glycerol-phthalic acid reaction. Since gelation occurs only when there is the possibility of unlimited growth in three dimensions, the conclusion that it is the result of the formation of infinitely<sup>3</sup> large molecules has been irresistible.<sup>4</sup> Carothers<sup>5</sup> pointed out that when one intermolecular linkage has been formed per initial monomeric molecule, all of the polymerizable material must be bound into one gigantic molecule, and possibilities for further *intermolecular* reaction are exhausted. In the reaction of two moles of glycerol with three of phthalic acid, for example, the extent of intermolecular reaction of the functional groups could not exceed  $\frac{5}{6}$ , or 83.3%, there being six potential linkages per five units. It was recognized by Carothers, however, that indefinitely large molecules might be formed at lower extents of reaction.<sup>6</sup> For example, a small fraction of the units might unite to form "infinite"<sup>3</sup> molecules, while the remaining

units yield comparatively small molecules. Gelation, in this case, if due to infinitely large molecules, would occur when fewer than one intermolecular linkage had been formed per unit of the entire polymer mixture. Interspersed with the networks of the infinite molecules there would be many smaller molecules of varying complexity. Common experience shows that gelation occurs in three dimensional polymerizations long before all of the material is bound together in one molecule. Usually it is possible to extract soluble material, the molecular weight of which is not extremely large, from the gelled polymer.

The existence of a sharply defined gel point at a certain critical extent of reaction (independent of temperature, amount of catalyst, etc.) is a significant characteristic of such polymerizing systems. Apparently, gelation occurs when a critical number of intermolecular linkages has been exceeded. Although this implication of numerous experimental results has been recognized for some time, quantitative formulation of the necessary conditions for gelation has not been attempted heretofore.

In the present paper (I) a method will be presented for deducing theoretically the critical conditions for the formation of infinitely large three dimensional molecules. The calculated critical points will be compared with experimental gel points for two types of polyesters. In II and III<sup>7,8</sup> of this series three dimensional polymers will be subjected to statistical treatment in an effort to gain some insight into their composition. It will be shown that the observed characteristics of multifunctional polymerizations are in harmony with the hypothesis that gelation is the result of the formation of infinitely large three dimensional networks.

It should be made clear at the outset that in the papers of this series the term "gel" is meant to include only those polymeric materials portions of which are insoluble in all solvents that do not

(1) Presented before the Organic Plastics Section of the Paint and Varnish Division at the Detroit Meeting of the American Chemical Society, September 10, 1940.

(2) Present address: Esso Laboratories of the Standard Oil Development Company, Elizabeth, New Jersey.

(3) The term "infinitely large molecule" refers to a molecule having dimensions of an order of magnitude approaching that of the containing vessel. Of course such molecules are finite in size, but by comparison with ordinary molecules they may be considered infinitely large.

(4) W. H. Carothers, *Chem. Rev.*, **8**, 402 (1931).

(5) W. H. Carothers, *Trans. Faraday Soc.*, **32**, 44 (1936). See in particular the Carothers functionality expression equation (2).

(6) See case (b), p. 46, ref. 5.

(7) P. J. Flory, *THIS JOURNAL*, **63**, 3091 (1941).

(8) P. J. Flory, *ibid.*, **63**, 3096 (1941).

destroy the primary polymer chain structure; the term "gel" will be applied in particular to that portion of such polymers which is insoluble in all solvents. The term "structurally insoluble gels" seems appropriate for such substances, but its introduction at this point would be an allusion to the hypothesis which this work will be shown to substantiate. The jelly-like masses which one obtains through the action of a swelling agent on a polymer, which in another solvent would dissolve completely, are not under consideration here.<sup>9</sup>

**Scope of the Present Statistical Treatment.**—The following treatment rests on the *primary condition* that during polymerization the functional groups of the polymerizing units unite in such a manner that the probability that any particular functional group has undergone reaction is an independent probability; *i. e.*, that it is independent of the number and configuration of other groups in the molecule of which the particular functional group is a part. Inasmuch as the reactivity of a polymer molecule ordinarily is independent of its size,<sup>10</sup> condensation polymerizations generally adhere to this condition. As a consequence of this fact, the size distribution in *linear* condensation polymers is represented by<sup>11</sup>

$$w_x = x(1 - p)^2 p^{x-1}$$

where  $w_x$  is the weight fraction of the species composed of  $x$  units and  $p$  is the fraction of the functional groups which have undergone reaction. This relationship is confirmed by its successful application to the treatment of viscosity<sup>12</sup> and degradation<sup>13</sup> in linear polyesters. The postulate that functional groups react at random in three dimensional condensation polymers should prove equally valid.

Some of the copolymers of vinyl and divinyl reactants<sup>14,15</sup> probably come

(9) For example, high molecular weight polystyrene is completely soluble in aromatic solvents. Polymerization of styrene in the presence of a small amount of divinyl benzene yields a product which is a gel of the type considered here; it swells, but does not dissolve completely in aromatic solvents (see H. Staudinger and E. Husemann, *Ber.*, **68**, 1618 (1935)). The jelly-like mass obtained by swelling ordinary polystyrene with propyl laurate (see J. N. Brønsted and K. Volqvartz, *Trans. Faraday Soc.*, **36**, 576 (1939)) is not a gel of the type discussed here. Failure of polystyrene to dissolve in propyl laurate can be attributed to inaptitude of the solvent, rather than to any intrinsic characteristic of the polymer.

(10) E. J. Flory, *THIS JOURNAL*, **61**, 3334 (1939).

(11) P. J. Flory, *ibid.*, **58**, 1877 (1936).

(12) P. J. Flory, *ibid.*, **62**, 1057 (1940).

(13) P. J. Flory, *ibid.*, **62**, 2255 (1940).

(14) H. Staudinger and E. Husemann, *Ber.*, **68**, 1618 (1935); *Trans. Faraday Soc.*, **32**, 323 (1936).

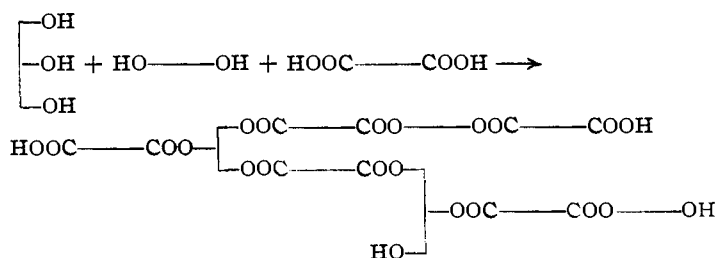
(15) R. G. W. Norrish and E. F. Brookman, *Proc. Roy. Soc.*, **A163**,

within the scope of the statistical treatment presented below. The primary condition stated above is fulfilled in such chain reaction polymerizations if the probability of termination of the growth of a given chain is independent of its length, and if the divinyl reactants enter the chains at random.<sup>16</sup>

The treatment is also applicable to linear polymers distributed in size according to (1), which become randomly cross-linked subsequent to formation of the main chains. It will not be applicable quantitatively to cross-linked chains of uniform length.<sup>8</sup>

Intramolecular reactions, that is, reactions between two functional groups of the same molecule, are neglected throughout this paper and the two that follow.<sup>7,8</sup> Results of Kienle and co-workers<sup>17</sup> on glycerol-dibasic acid polymers and of Bradley<sup>18</sup> on drying oil resins show that the decrease in the number of molecules is slightly less than the number of inter-unit linkages formed. Consequently, a small part of the reaction must be intramolecular. It is to be expected on this account that quantitative deductions from the present statistical analysis will be only approximately correct.

**Criteria for Incipient Formation of Infinite Networks.**—First, we consider systems which contain trifunctional units; in addition to these there also may be present units which are bifunctional (and monofunctional units also, for that matter). As an example, consider a glycerol-ethylene glycol-succinic acid mixture in which the formation of a typical polymer molecule is indicated by



The polymeric structures which are formed may

205 (1937); K. G. Blaikie and R. N. Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

(16) Under these conditions the *chain length* distribution is given by an expression equivalent to equation (1); see G. V. Schulz, *Z. physik. Chem.*, **B30**, 379 (1935), and P. J. Flory, *THIS JOURNAL*, **59**, 241 (1937).

(17) R. H. Kienle, P. A. van der Meulen and F. E. Petke, *ibid.*, **61**, 2258, 2268 (1939); R. H. Kienle and F. E. Petke, *ibid.*, **62**, 1053 (1940).

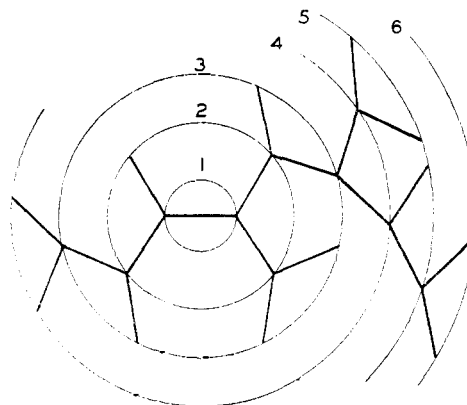
(18) T. F. Bradley, *Ind. Eng. Chem.*, **30**, 689 (1938); T. F. Bradley and H. F. Pfann, *ibid.*, **32**, 694 (1940).

be represented schematically as in Fig. 1. The portion of the molecule between two "branch" units, *i. e.*, trifunctional units (glycerol), or between a branch unit and a "terminal group" (unreacted OH or COOH), is represented by a straight line. Such a portion of a molecule will be called a "chain." The length of the chains will vary, but this is not important here. Even an unreacted functional group of a branch unit (*e. g.*, an unreacted OH of a glycerol unit) is to be considered as an end of a chain which extends from a branch to a terminal group (except in case 3, *cf. seq.*). For the present it is assumed that the functional groups of the branch unit are all equivalent. The network, or molecule, containing  $n$  branches possesses  $2n + 1$  chains.

Suppose the chain within the first circle in Fig. 1 has been selected at random from the polymer mixture. We wish to know the probability that this chain is a part of an infinite network. In the present paper we wish in particular to determine under what conditions this probability will be greater than zero. Our first concern is the fate of the ends of the particular chain selected at random. In Fig. 1 this chain gives rise to two branches, one at each end. The four new chains extending from these branches lead to three branches (on circle 2) and one terminal group. The resulting six chains lead to two branches on circle 3, etc. The network built about the chain selected at random in Fig. 1 could be designated 2, 3, 2, 2, 1, 0, where the figures indicate the numbers of branches found on successive circles.

Let it be assumed for the present that there exists a certain probability  $\alpha$  that any given one of the functional groups of a branch unit leads, via a sequence of bifunctional units, to another branch, rather than to a terminal group. That is,  $\alpha$  is taken to be the probability that any given chain extending outward from one of the circles in Fig. 1 ends in a branch on the next circle. It is obvious that  $\alpha$  will depend on the ratios of the various ingredients and on the extent of reaction of the functional groups. Details of the methods for calculating  $\alpha$ 's will be postponed until their critical values have been discussed.

If on the  $i$ -th circle there are  $Y_i$  branches, then the *expected number* of branches (arising from the  $2Y_i$  new chains) on the  $i + 1$  circle will be  $2\alpha Y_i$ . The actual number of branches on the  $i + 1$  circle probably will differ from the expected number, but by making  $Y_i$  sufficiently large the



2,3,2,2,1,0 molecule.

Fig. 1.—Schematic representation of a trifunctionally branched three-dimensional polymer molecule.

ratio of  $Y_{i+1}$  (*actual*) to  $Y_{i+1}$  (*expected*) can be made as near unity as we please.<sup>19</sup> Thus, if  $Y_i$  is sufficiently large,  $Y_{i+1}/Y_i$  will differ negligibly from  $2\alpha$ . Even though the network reaches circle  $i$  with a large value of  $Y_i$ , if  $\alpha < 1/2$  subsequent values  $Y_{i+1}, Y_{i+2} \dots Y_r$  will be less than  $Y_i$ . It becomes intuitively evident that eventually  $Y_r$  for some value of  $r > i$  must reach zero, whereupon further propagation of the network ceases. Thus, when  $\alpha < 1/2$ , infinite networks are impossible.<sup>20</sup>

When  $\alpha > 1/2$ , the expected value of  $Y_{i+1}$  exceeds  $Y_i$ . By analogous reasoning the conclusion is reached that the network may continue indefinitely, *i. e.*, infinite networks are possible. When  $\alpha = 1/2$  it can be shown by more elaborate methods<sup>7,20</sup> that the probability of an infinite network is zero. Therefore, when trifunctional branch units are involved, infinite networks are possible only when  $\alpha > 1/2$ .

(19) This statement is based on Bernoulli's theorem. See J. V. Uspensky, "Introduction to Mathematical Probability," McGraw-Hill Book Co., Inc., New York, N. Y., 1937, Chapter VI.

(20) The above development has been presented for its simplicity and the ease with which it can be generalized to include many situations. It is admittedly not rigorous, but its correctness is confirmed by the detailed analysis presented in the following paper.<sup>7</sup> Furthermore, the problems dealt with here are identical with certain classical problems concerning games of chance. For instance, when we wish to know the circumstance of a chain selected at random from a polymer containing trifunctional branches, the situation is analogous to a gambling game between a player who has initially two units of money (the two ends of the chain selected at random), and his infinitely rich opponent. The player and his opponent each stake one unit of money on each game, which the player always has the chance  $\alpha$  of winning. The question to be answered is this: is there a possibility that an infinite number of games may be played without the player's holdings ever being reduced to zero, thus ending the series of games? It can be shown (see ref. 19, Chapter VIII, in particular pp. 139-143) that the player is sure to lose his finite fortune to his infinitely rich opponent when  $\alpha \leq 1/2$ , provided that they play long enough. If, on the other hand,  $\alpha > 1/2$ , the player has a chance of continuing the games forever. However, he may lose his two units of money to his opponent, even if  $\alpha > 1/2$  but  $< 1$ .



If the branch unit is trifunctional, the extent of reaction which yields the critical value  $\alpha = 1/2$  is reached according to equation (4) when

$$p_A p_B = 1/(1 + \rho) \quad (5)$$

If A groups are present in excess ( $r > 1$ ),  $p_B = 1$  and  $p_A = 1/r$  when the reaction is complete. If B groups are in excess ( $r < 1$ ),  $p_B = r$  and  $p_A = 1$  at completion of the reaction. Hence, the critical value of  $\alpha$  can be reached only when  $r$  lies within the range

$$(1 + \rho) > r > 1/(1 + \rho)$$

which defines the quantities of excess of one functional group or the other which may be tolerated without rendering the critical value of  $\alpha$  inaccessible.

Similarly, if the branch units are tetrafunctional the critical value  $\alpha = 1/3$  is reached when

$$p_A p_B = 1/(1 + 2\rho) \quad (6)$$

3. So far it has been assumed that all functional groups of the same kind (A or B) are equally reactive. In one very important case, namely, the glycerol-dibasic acid reaction, the secondary hydroxyl group of the glycerol probably is somewhat less reactive than either primary hydroxyl. If we select one of the functional groups of a glycerol unit at random, without knowing whether it is a primary or a secondary group or whether or not other groups of the same unit have reacted, there is, of course, a definite probability  $p$  that it has reacted. However, in the evaluation of  $\alpha$  it is known beforehand that at least one of the hydroxyls of the glycerol must have reacted in order to terminate the chain from the preceding circle (see Fig. 1). If the primary hydroxyl groups are more reactive than the secondary one, there is less than one chance in three that the hydroxyl which is known to be esterified is the secondary one. Hence, with regard to the two remaining hydroxyl groups, the chance that one of them selected at random has reacted is some quantity  $\pi$  less than  $p$ . Furthermore, the probability that both remaining groups have reacted is less than  $\pi^2$ . From these considerations it follows that the probability  $\alpha$  that one of the two remaining functional groups of the branch unit leads to another branch is not independent of the fate of the other functional group of the branch. In other words  $\alpha$  is not an independent probability, and the method presented in the preceding section fails here.

The problem can be solved by the following

modification of previous procedure, provided that the relative reactivities of the primary and secondary groups are known. Only those glycerol units all three hydroxyls of which have reacted will be considered as branch units; if only two have reacted the glycerol unit will be considered to continue the chain, and if but one has reacted it will end the chain.

The particular example under consideration here is the reaction of two moles of glycerol with three of a dibasic acid. Let

$$\begin{aligned} p' &= \frac{[\text{Primary hydroxyls reacted}]}{[\text{Primary hydroxyls present initially}]} \\ p'' &= \frac{[\text{Secondary hydroxyls reacted}]}{[\text{Secondary hydroxyls present initially}]} \\ p &= \frac{[\text{Carboxyls reacted}]}{[\text{Carboxyls present initially}]} \\ p &= 2/3 p' + 1/3 p'' \end{aligned}$$

Presumably,  $p$  may be directly determined experimentally. If the relative reactivity of primary and secondary groups is known,  $p'$  and  $p''$  can be calculated from  $p$ .<sup>23</sup>

The probability that any particular carboxyl group is esterified by a primary hydroxyl group is  $2pp'/(2p' + p'')$ ; the probability that it is esterified by a secondary hydroxyl is  $pp''/(2p' + p'')$ . The probability that any particular carboxyl group is connected to a glycerol unit any two hydroxyl groups of which have reacted, while the third remains unreacted is

$$\begin{aligned} \theta_2 &= \frac{2pp'^2(1 - p'') + 2pp'p''(1 - p') + 2pp'p''(1 - p')}{(2p' + p'')} \\ &= \frac{2pp'(p' + 2p'' - 3p'p'')}{2p' + p''} \end{aligned}$$

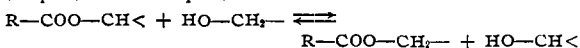
Similarly, the probability that the carboxyl group is connected to a completely esterified glycerol is

$$\theta_3 = 3pp'^2p''/(2p' + p'')$$

According to the above modification of the general procedure, the probability of chain continuation is  $\theta_2$ ; the probability of chain termination with a branch unit is  $\theta_3$ . By the preceding method

$$\begin{aligned} \alpha &= \sum_{n=0}^{\infty} \theta_2^n \theta_3 \\ &= \theta_3/(1 - \theta_2) \end{aligned} \quad (7)$$

(23) If the relative rates of reaction determine the relative proportions of primary and secondary groups esterified, it can be shown that  $(1 - p') = (1 - p'')k'/k''$ , where  $k'$  and  $k''$  are the rate constants for reaction of primary and secondary groups, respectively. In view of the rapidity with which ester interchange occurs in polyesters,<sup>13</sup> the position of the equilibrium



is probably the factor which determines  $p'$  and  $p''$ . If this is the case, then  $(1 - p'')/p'' = K(1 - p')/p'$  where  $K$  is the constant for the above equilibrium.

Thus,  $\alpha$ 's can be calculated when reactivities of the functional groups differ, provided that the necessary data are available for distinguishing  $p'$  and  $p''$ .

When  $p' = p'' = p$ , the case under consideration here becomes equivalent to that previously discussed under 2 when  $\rho = 1$  and  $r = 1$ . In this situation (7) reduces to

$$\alpha = p^3/[1 - 2p^2(1 - p)] \quad (7.1)$$

but equation (3) for the preceding case gives

$$\alpha = p^2 \quad (4.5)$$

The non-identity of these expressions is a consequence of the difference between the patterns, corresponding to Fig. 1, for describing the configuration of a given molecule according to which definition is used for a branching unit. However, both (4.5) and (7.1) lead to the same critical value of  $p = 1/\sqrt{2}$  when  $\alpha = 1/2$ .

4. In this section the limiting case of long chains will be discussed. According to our original definition,  $\alpha$  has been taken to be the probability that a chain *proceeding from a branch unit* will end with another branch;  $\alpha$  is not, in general, exactly equal to the probability that a chain which is terminated at one end by an unreacted functional group will lead to a branch at the other end.<sup>24</sup> In the limit of very long chains, *i. e.*, when both  $r$  and  $p$  approach unity, the latter probability and  $\alpha$  become identical. Furthermore,  $\alpha$  approaches the ratio of chain ends at branches to the total number of chain ends. That is

$$\alpha \cong \frac{f(\text{No. of branch units})}{f(\text{No. of branch units}) + (\text{No. of unreacted functional groups})} \quad (8)$$

Thus, when  $r = 1$  and  $p$  is near unity, appropriate series expansion of equation (4.4) leads to

$$\alpha \cong \rho/[\rho + 2(1 - p)] \quad (8.1)$$

which is equivalent to (8). This approximate relationship is particularly useful in a number of cases.

**The Number Average Degree of Polymerization.**—The number average number of units per molecule,  $DP_n$ , can be computed as follows. The number of A and B functional groups present ini-

(24) For example, according to (4.5)  $\alpha = p^2$  when  $r = 1$  and  $\rho = 1$ , using the definition of branch units as in 1 and 2 above. If one end of the chain is known to be an unreacted group, there are equal chances that this group is either A or B. In the former event a branch is inevitable, as the unit itself contains the branch; in the latter case the probability of a branch is  $p$ . Hence, the probability that a chain beginning with an unreacted functional group will end in a branch is  $(1 + p)/2$ , which differs decidedly from  $\alpha$ . This is an extreme case.

tially will be represented by  $N_A$  and  $N_B$ , respectively, where the branch unit of functionality  $f$  possesses functional groups of the type A. Then

$$\begin{aligned} \text{Total no. of units} &= \frac{1}{2}N_A(1 - \rho) + N_A\rho/f + N_B/2 \\ &= N_A[(1 - \rho)/2 + \rho/f + 1/2r] \end{aligned}$$

$$\text{Total no. of linkages} = N_A p_A$$

Assuming as above that all linkages are intermolecular

$$\text{No. of molecules} = (\text{no. of units}) - (\text{no. of linkages})$$


$$DP_n = \frac{\text{no. of units}}{\text{no. of molecules}} = \frac{f(1 - \rho + 1/r) + 2\rho}{f(1 - \rho + 1/r - 2p_A) + 2\rho} \quad (9)^{25}$$

Substitution in (9) of sets of values of  $p$ ,  $\rho$  and  $r$  corresponding to critical conditions shows that the number average molecular weight at this point is only several times that for a single chain.

### Experimental Results

For the purpose of comparing observed gel points with the critical points at which infinite networks become possible, experiments have been carried out with three dimensional polyesterifications in which either tricarballic acid or pentaerythritol was the branch unit. In the latter the four hydroxyls are exactly equivalent. In the former, one of the carboxyl groups is attached to a secondary carbon atom and the other two to primary carbons. The difference in their reactivities probably is negligible in view of the results obtained by Menshutkin<sup>26</sup> on rates and equilibria in the esterification of primary and secondary carboxylic acids.

In the theory given above it has been assumed that the reactivity of a functional group is unaffected by condensation of other groups of the unit. As is well known, such a condition is generally fulfilled satisfactorily if the functional groups are sufficiently far apart in the molecule. The carboxyl groups in tricarballic acid are separated by two atoms, as in succinic acid. In the latter it is known that the rate of esterification of one carboxyl group is not changed appreciably if the other has reacted.<sup>27</sup> In pentaerythritol the hydroxyl groups are separated by three carbon atoms, which probably is sufficient.

Finally, if A—A units are present in addition to the branch unit A , it is necessary that the A groups of both units be equally reactive. Results which follow indicate that this source of error is not important with the combinations which have been used.

**Materials.**—Purification and physical constants of the diethylene glycol,<sup>10</sup> adipic acid<sup>10</sup> and succinic acid<sup>12</sup> used here have been reported previously. Tricarballic acid and pentaerythritol were obtained from the Eastman

(25) Equation (9) is essentially equivalent to Carothers' functionality equation,<sup>5</sup> except that in the latter  $f$  denotes the average functionality of all units entering the polymerization. For the purpose of this paper it is more convenient to define  $f$  as the functionality of the branch units only.

(26) N. Menshutkin, *Ann. chim. phys.*, [5] **23**, 40-66 (1881).

(27) A. Kailan, *Z. physik. Chem.*, **85**, 706 (1913).

Kodak Company. The tricarballic acid was recrystallized twice from ethylene dichloride-dioxane mixtures and twice from ethylene dichloride-acetone mixtures; m. p. 160.0° (cor.); neut. equiv. 58.5, calcd. 58.7. Pentaerythritol was recrystallized from 90% alcohol; m. p. 256-258° (cor.).

**Procedure.**—Carefully weighed quantities of the pure ingredients were polymerized either in the presence of 0.2 to 0.4 equivalent per cent. of *p*-toluenesulfonic acid catalyst at 109° or in the absence of catalyst at 154°. The polymerization procedures have been adequately described previously.<sup>10,12</sup> From time to time during the reaction viscosities were measured<sup>12</sup> and samples were removed for titration of the unreacted carboxyl groups with 0.1 *N* alcoholic potassium hydroxide.

**Calculations.**—Since in all experiments the carboxyl group is the one which is determined experimentally, *p* will be used hereafter to represent  $p_{\text{COOH}}$ , the fraction of the carboxyl groups which have been esterified. Values of *p* have been calculated using the relationship<sup>28</sup>

$$1/(1 - p) = \frac{w - 18t}{(S + 190\gamma)t - \gamma w} \quad (10)$$

where

*w* = weight of sample in g.

*t* = titer in moles of potassium hydroxide

$\gamma$  = ratio of moles of *p*-toluenesulfonic acid monohydrate (mol. wt. = 190) to moles of carboxyl groups

*S* = (weight of mixture per mole of carboxyl groups) - (mol. wt. of water)

**Results.**—The results from one of the experiments with tricarballic acid, succinic acid and diethylene glycol are shown in Fig. 2. Values of *p* calculated using (10) from the titers of samples removed at intervals are plotted against time.<sup>29</sup> Using equations (4.1) and (9), respectively, the values of  $\alpha$  and  $DP_n$  shown in Fig. 2 were calculated from *p*,  $\rho$  and  $r$  (in this case  $r = 1$ ). Also included in Fig. 2 is the experimentally measured viscosity<sup>30</sup> which increases slowly at first, but very rapidly when the gel point is approached. This behavior is a well recognized characteristic of three-dimensional polymerizations.

There is no difficulty in locating the gel point. Within an interval of about two minutes, in a reaction such as the one portrayed by Fig. 2, the polymer loses completely its ability to flow in the viscometer and it becomes elastic. Samples removed just prior to gelation are completely soluble in chloroform or chloroform-dioxane mixture.

(28) See equation (6) of ref. 12.

(29) These results are not believed to be appropriate for kinetic interpretation. The water formed in the reaction may not have been removed fast enough, especially when the material became quite viscous, to prevent appreciable simultaneous hydrolysis.

(30) As the polymers begin to show elastic properties before the gel point is reached, it is probable that near the gel point rate of shear is not proportional to shearing stress, and the viscosity is not a characteristic constant independent of the method of measurement.

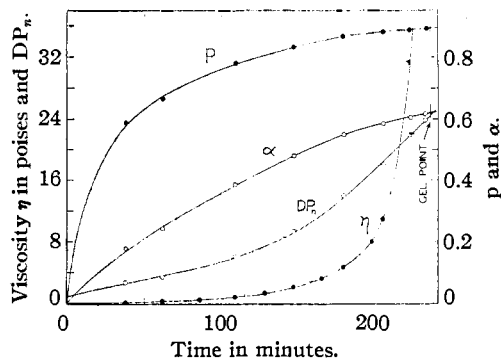


Fig. 2.—Results for the third experiment reported in Table I (109°; 0.20 equivalent per cent. *p*-toluenesulfonic acid catalyst).

Samples removed two or three minutes after gelation do not dissolve completely in such solvents, a small amount of very gelatinous precipitate remaining suspended in the solution. The rate of increase in  $\alpha$  near the gel point is so small that a negligible error is introduced by the brief extrapolation to the gel point from the data for the last sample titrated.

TABLE I  
GEL POINTS FOR POLYMERS CONTAINING TRICARBALLYLIC ACID

Additional ingredients, diethylene glycol and	$r = \frac{[\text{COOH}]}{[\text{OH}]}$	$\rho^a$	<i>p</i> at gel point obsd.	<i>p</i> at gel point calcd. <sup>b</sup>	$\alpha$ obsd. at gel point
Adipic acid	1.000	0.293	0.911	0.879	0.59
Succinic acid	1.000	.194	.939	.916	.59
Succinic acid	1.002	.404	.894	.843	.62
Adipic acid	0.800	.375	.9907	.955	.58

<sup>a</sup>  $\rho = 3 \times [\text{tricarballic acid}]/[\text{total carboxyl groups}]$ .

<sup>b</sup> Calcd. from (3.1) when  $\alpha = 1/2$ .

Data concerning gel points obtained in this way are presented in Table I. Observed critical values of  $\alpha$  in the last column have been obtained from  $r$ ,  $\rho$  and *p* (obs.) using equation (4.1). The calculated critical values of *p* have been obtained from  $r$ ,  $\rho$  and  $\alpha = 1/2$  using (4.1), which is based on the hypothesis that gelation is caused by formation of infinite networks, and on the assumption that no intramolecular reaction occurs.

Observed values of *p* and  $\alpha$  show that the reaction proceeds appreciably beyond the calculated critical point before gelation occurs. In the last experiment in the table possible differences in reactivities of various carboxyl groups could not vitiate the results, inasmuch as values of  $r$  and  $\rho$  were such that nearly all of the carboxyl groups had reacted before gelation occurred. Yet, the observed value of  $\alpha$  does not differ notably from

those in other experiments. In another experiment in which  $r = 0.800$  and  $\rho = 0.250$  and  $p$  (calcd.) = 1.000 for  $\alpha = 1/2$ , gelation did not occur even when the reaction was practically complete. The ultimate viscosity indicated that the polymer was not very near gelation. Thus, values of  $\alpha$  in excess of one-half prior to gelation are not due to unequal reactivities of the functional groups.

In the polymerization of pentaerythritol with an equivalent quantity of adipic acid ( $r = 1$ ,  $\rho = 1$ ), gelation occurred at  $p = 0.606$  which corresponds to  $\alpha = p^2 = 0.366$ , compared with  $\alpha$  (theor.) = 0.333 for tetrafunctional branch units.

Although the discrepancies between theory and experiment are well beyond the experimental error, there is sufficient correlation to lend support to the hypothesis that gelation is due to infinite networks. The discrepancies probably are no greater than may be attributed to the occurrence of some intramolecular reaction, which in the theoretical treatment has been neglected. Comparing observed and calculated values of  $p$ , it appears that if from 2 to 6% (depending on the ingredients and their ratios) of the inter-unit linkages are intramolecular, perfect agreement with theory is possible. In view of the results of Kienle and co-workers<sup>17</sup> and of Bradley<sup>18</sup> this is not unreasonable.

**Glycerol-Dibasic Acid Reactions.**—Kienle and co-workers<sup>17</sup> have determined the per cent. esterification ( $p \times 100$ ) at the gel point in reactions of glycerol with equivalent quantities of dibasic acids or their anhydrides. Overlooking the phthalic anhydride reaction where the results probably were vitiated by volatilization of the anhydride, Kienle and Petke<sup>17</sup> observed with succinic acid, or its anhydride, that gelation occurred approximately at  $p = 0.75$ . Assuming that the hydroxyls are equally reactive, according to equation (4.3),  $\alpha = p^2 = 0.56$ . If the secondary hydroxyl is less reactive than the primary ones, then according to the treatment set forth under 3 above,  $\alpha$  at the gel point must be somewhat less than 0.56. However, it is unlikely that this difference in reactivity is as great as would be required to bring  $\alpha$  down to the theoretical value, 0.50. The remaining discrepancy, which may be attributed to intramolecular reaction, seems to be in line with the results reported above.

The fact that cryoscopic measurements on samples removed on the verge of gelation yielded average molecular weights which were not large (ca. 1200) led Kienle and co-workers<sup>17</sup> to the con-

clusion that very large molecules could not be present. Cryoscopic measurements yield the number of molecules present in the sample, from which one calculates the number average molecular weight. Their results merely show that many molecules are present at the gel point; they do not give the slightest clue to the relative quantities of various species, nor do they exclude infinite networks beyond the gel point. The conclusion of Kienle and co-workers that gelation cannot be caused by the formation of infinitely large networks is entirely unjustified. Their results actually support the network hypothesis when interpreted as above.<sup>31</sup>

### Summary

A diagrammatic scheme has been presented for representing the structure of a three-dimensional polymer in a way which facilitates statistical analysis. It has been shown that the general condition for the formation of infinitely large molecules is expressed by  $\alpha > 1/(f - 1)$ , where  $f$  is the functionality of the branch units and  $\alpha$  is the probability of chain branching as opposed to chain termination. Methods have been presented for calculating  $\alpha$  from the number of branching units, the ratio of the two types of reactants (*e. g.*, OH and COOH), and the extent of reaction.

The analysis shows clearly that the number average molecular weight need not be very large when the statistical conditions for incipient formation of infinitely large three dimensional networks are fulfilled. Many smaller molecules are interspersed with the giant networks.

Experimentally observed gel points in three dimensional condensation polymerizations have been compared with theoretical critical points for the formation of infinite networks. The discrepancies are no larger than may be attributed to the formation of some intramolecular linkages, which are not accounted for in the theoretical treatment. These results provide additional support for the hypothesis that gelation is the result of the formation of infinitely large molecules.

The theory presented here should be applicable also to certain inorganic gels.

ELIZABETH, NEW JERSEY

RECEIVED JUNE 18, 1941

(31) Kienle and co-workers have attempted to deduce the approximate quantities of various polymeric species from measurements of three quantities: unesterified acid groups, water evolved and number average molecular weight. They recognize twelve possible species; actually there are many more which should not be excluded from consideration. The obvious impossibility of deducing twelve (or more) different quantities from three measurements renders their estimates purely fictitious.