Molecular Size Distribution in Three Dimensional Polymers.   II.   Trifunctional Branching Units

By Paul J. Flory[1]

Having annunciated and examined the critical conditions for incipient formation of infinite networks in three dimensional polymerizations in general,[2] a detailed statistical analysis of the composition of a particular class of three dimensional polymers, namely, those in which the branch units are trifunctional, will be presented in this paper. Equations will be derived to express the relative quantities of species of various complexities and sizes. These distribution equations are equally applicable before gelation, at the gel point[3] and after a portion of the polymer, calculable from the equations, has been converted to infinite networks (gel).

As in the preceding paper,[2] the analysis is limited to cases where all units are joined together at random or where previously formed linear chains are linked together at random through reaction of their terminal functional groups with tri-functional units. It is assumed that intramolecular reactions do not occur in species of finite size. This, of course, is not strictly true.[2]

The probability that a chain[4] starting from a branch unit would end in another branch was the only probability pertinent to the development in the preceding paper. Here we are concerned also with the probability that a chain starting with an unreacted group will end in a branch. In order to simplify the analysis which follows, these probabilities are assumed to be the same, and the same symbol α is used for both. In other words, the probability α that at one end of a chain there is a branch is assumed to be independent of the status of the other end of the chain. This is equivalent to the limiting case of long chains, discussed in the preceding paper.[5] Although application of the results of this paper is somewhat restricted by

the assumptions, there can be little doubt that the main conclusions can be applied without restraint to all three dimensional polymers in which units of functionality not greater than three are joined together randomly.

Theoretical

Derivation of the Fundamental Recurrence Relationship.—The statistical treatment evolves from the scheme for representing the "plan" of a three dimensional polymer molecule depicted in Fig. 1 of the preceding paper.[2] The first task is to find the probability W_n that a chain selected at random from the polymeric mass is a part of a network composed of z chains combined by n trifunctional branch units, where $z = 2n + 1$. The probability that both ends of the chain selected at random lead to branch units is α^2. The probability that there is a branch at one end (not at either of the ends) and an unreacted terminal group at the other end is $\alpha(1 - \alpha)$. A branch unit at an end of the chain gives rise to two new chains, each of which furnishes an additional chain end. The probability that these two additional chain ends lead to networks containing a total of n' additional branch units is $W_{n'}$. It follows that

$$W_n = \alpha(1 - \alpha) W_{n-1} + \alpha^2 W_{n-2}W_0 + \alpha^2 W_{n-3}W_1 + \ldots + \alpha^2 W_0 W_{n-2} + \alpha(1 - \alpha)W_{n-1}$$

or, letting $W_{-1} = (1 - \alpha)/\alpha$

$$W_n = \alpha^2 \sum_{i=0}^{n} W_{n-i-1} W_{i-1} \qquad (1)$$

This is the recurrence relationship upon which all subsequent deductions depend.[6]

Solution of the Recurrence Relationship.[7]— Let a function $\varphi(\xi)$ be defined by

$$\varphi(\xi) = \sum_{n=0}^{\infty} W_{n-1} \xi^n \qquad (2)$$

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(3) In view of the results of the preceding paper, we shall use the terms "gel point" and "critical point" (for formation of three dimensional networks) synonymously.

(4) As the terminology used here is identical with that of the preceding paper, no attempt will be made to restate definitions.

(5) See case 4 of ref. 2. It will be obvious that the statistical treatment presented here could be modified to include the case where the two probabilities discussed above differ from each other. For the sake of simplicity, this more complex situation is not dealt with in this paper.

(6) For situations in which it is not permissible to consider that α is an independent probability (independent of the fate of the other end of the chain; see footnote (5)) it will be necessary merely to modify W_{-1} appropriately.

(7) The author is indebted to Professor William C. Taylor of the Mathematics Department of the University of Cincinnati for the solution of the recurrence relationship (1) which is presented in this section.

Then

$$[\varphi(\xi)]^2 = \sum_{n=0}^{\infty} \xi^n \sum_{i=0}^{n} W_{n-1-i} \, W_{i-1}$$

$$= 1/\alpha_2 \sum_{n=0}^{\infty} W_n \, \xi^n$$

$$= \varphi(\xi)/\alpha^2 \xi - W_{-1}/\alpha^2 \xi \qquad (3)$$

The solution of (3) is

$$\varphi(\xi) = \frac{1 \pm \sqrt{1 - 4\alpha^2 \, \xi \, W_{-1}}}{2\alpha^2 \xi}$$

Substituting $W_{-1} = (1 - \alpha)/\alpha$ and letting $\alpha(1 - \alpha) = \beta$

$$\varphi(\xi) = \frac{1 \pm \sqrt{1 - 4\beta\xi}}{2\alpha^2 \xi} \qquad (3.1)$$

Binomial expansion of $(1 - 4\beta\xi)^{1/2}$ gives

$$1 + \sum_{n=1}^{\infty} \frac{(-1) \cdot 1 \cdot 3 \cdot 5 \cdots (2n - 3)(2\beta\xi)^n}{n!} =$$

$$1 - 2 \sum_{n=0}^{\infty} \frac{(2n)! \, (\beta\xi)^{n+1}}{n!(n + 1)!}$$

Substituting this expression in (3.1), where we reject the alternate positive sign as it leads to probabilities which are negative

$$\varphi(\xi) = 1/\alpha^2 \sum_{n=0}^{\infty} \frac{(2n)! \, \beta^{n+1} \xi^n}{n!(n + 1)!} \qquad (4)$$

Comparing (4) with (2) we obtain the distribution function

$$W_n = (1 - \alpha)^2 \frac{(2n + 2)! \, \beta^n}{(n + 1)! \, (n + 2)!} \qquad (5)$$

Equation (5) expresses the probability that a chain selected at random is a part of a network containing n branch units. Since, according to
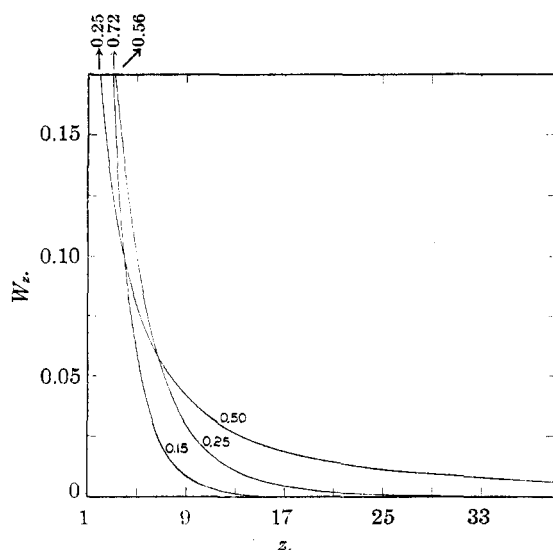

Fig. 1.—Weight fractions of species of various complexities z for the values of α indicated.

the assumptions, the length of an individual chain is totally independent of the size of the network of which it is a part, W_n is also the weight fraction of networks possessing n branch units. The weight fraction W_z of networks composed of z chains ($z = 2n + 1$) is

$$W_z = \frac{(1 - \alpha)^2 \, (z + 1)! \, \beta^{(z-1)/2}}{[(z + 1)/2]! \, [(z + 3)/2]!} \qquad (5.1)$$

where z, of course, is restricted to odd integral values. The quantity z will be referred to as the *molecular complexity*.

Some of the properties of the functions for W_n, or W_z, are grasped more readily when they are replaced by the approximate expressions obtained by introducing Stirling's formula, $n! \cong \sqrt{2\pi n} \, (n/e)^n$, together with other approximations appropriate when n is large. Then

$$W_n \cong \frac{1 - \alpha}{\alpha \sqrt{\pi}} \frac{(4\beta)^{n+1}}{(n + 1)^{3/2}} \qquad (5.2)$$

Distribution of Species with Respect to Complexity (z).—Three features of the function W_n are particularly important to the subsequent discussion. First, W_n approaches zero as $n \to \infty$ for all values of β in the physically significant range 0 to 1/4. Second, the series $\sum_{n=0}^{\infty} W_n$ converges for all values of β in the same range (including $\beta = 1/4$), in compliance with physical necessity. Finally, W_n may be expressed in the form

$$W_n = (1 - \alpha)^2 F(\beta, n) \qquad (5.3)$$

As α increases starting from zero, β increases from zero to a maximum of 1/4 when $\alpha = 1/2$, and then returns to zero as α proceeds to unity. The point $\alpha = 1/2$ (*i. e.*, $\beta = 1/4$) represents the gel point as deduced in the preceding paper.

It is obvious from (5.3) that for every value of β ($\beta = 1/4$ excepted) there will be two values of W_n, one for $\alpha < 1/2$ and one for $\alpha' = (1 - \alpha) > 1/2$. The distribution of finite species in the polymeric mixture after gelation has occurred ($\alpha > 1/2$) is identical with that for the same value of β before gelation ($\alpha < 1/2$), except for the constant factor $(1 - \alpha)^2$ in (5) and (5.1). That is, the ratio of the weight fractions of each finite species in the two distributions is given by $(1 - \alpha)^2/\alpha^2$.

In Fig. 1 W_z calculated from (5.1) is plotted against z for several values of α in the region up to the gel point. Although only odd integral values of z are significant, continuous curves have been drawn. By appropriately altering the ordi-

nate scale, the same curves may be applied to the sol fractions (cf. seq.) in gelled polymers. The curve for $\alpha = 0.25$ represents the complexity distribution for the sol fraction when $\alpha = 0.75$, provided that ordinate values are multiplied by one-ninth. The curve for $\alpha = 0.15$ represents $\alpha = 0.85$ when ordinates are multiplied by 0.0311. In every case the weight fraction decreases continuously toward zero as the complexity increases, the rate of decrease becoming less as α approaches $1/2$. For all values of α a considerable fraction of the material is present as single chains ($z = 1$). For $\alpha = 0.15$, 0.25 and 0.50 the weight fractions for $z = 1$ are 0.72, 0.56 and 0.25, respectively. Never is any large fraction of the material found in finite species of great complexity.

The Sol–Gel Ratio.—The sum of the weight fractions of all *finite* species is given by

$$W_s = \sum_{n=0}^{\infty} W_n = \varphi(1) - W_{-1}$$

Substituting (3.1) for $\varphi(1)$

$$W_s = \frac{1 - \sqrt{1 - 4\beta} - 2\beta}{2\alpha^2}$$

where the minus sign has been chosen for the reason previously mentioned. When $\alpha < 1/2$

$$\sqrt{1 - 4\beta} = 1 - 2\alpha$$

When $\alpha > 1/2$

$$\sqrt{1 - 4\beta} = 2\alpha - 1$$

Hence

$$W_s = 1 \qquad \alpha \leqq 1/2$$
$$W_s = (1 - \alpha)^2/\alpha^2 \qquad \alpha > 1/2 \qquad (6)$$

All of the polymeric material is accounted for by summing all weight fractions W_n given by (5) when α does not exceed $1/2$. Beyond the gel point, where α exceeds $1/2$, some of the material is not included in the sum of all W_n's.

It should be recalled in this connection that in the derivation of the recurrence relationship (1) only molecular species containing n branch units and $n + 2$ unreacted terminal groups are reckoned with. Infinite networks which continue to branch out indefinitely through the polymeric mixture are excluded from consideration by the nature of the procedure employed. A value of $\sum W_n$ less than unity means, therefore, that some of the material is not present in finite networks. The weight fraction W_g of infinite networks may be found by difference. That is

$$W_g = 1 - W_s = (2\alpha - 1)/\alpha^2 \qquad (7)$$

Equations (6) and (7) give the weight fractions of

sol (finite molecular weight) and gel (infinite molecular weight) in the polymer beyond the gel point.[8] The sol-gel ratio is given by the ratio of W_s to W_g.

In Fig. 2 the weight fraction of gel is plotted against α. The gel fraction makes its appearance abruptly when α exceeds $1/2$, increases rapidly with α at first, and then gradually approaches unity as α goes to unity. According to the results of the preceding section, as α increases beyond the critical value, the complexity of the sol fraction decreases. This is the result of preferential conversion of complex species to infinite networks as α continues to increase.
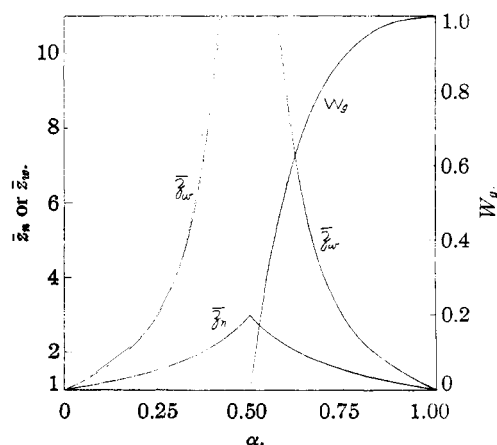

Fig. 2.—Weight fraction of gel (W_g), and number average and weight average complexities ($\bar{z}_n$ and $\bar{z}_w$, respectively) as functions of α. The $\bar{z}_n$ and $\bar{z}_w$ curves beyond $\alpha = 0.5$ refer to the sol fraction only.

Number Average and Weight Average Complexity.—Since high polymers are almost invariably composed of mixtures of molecules of various sizes, it is necessary to employ average molecular weights in the interpretation of their properties. However, it is always important to select the appropriate average. For colligative properties one must use the ordinary *number average* molecular weight $\overline{M}_n$, which is the ratio of total weight of material to total number of molecules. For the interpretation of viscous behavior of polymers and their solutions the

(8) The probability that a gambler, possessing initially a units of money, will be ruined in the course of an unlimited number of games against an infinitely rich opponent (each stake equals one unit of money) is discussed in "Introduction to Mathematical Probability," by J. V. Uspensky, McGraw-Hill Book Co., Inc., New York, N. Y., 1937, p. 143. By a method entirely different from that given above, it is shown that the probability that the gambler eventually will be ruined is $[(1 - \alpha)/\alpha]^a$ where α is the chance ($>1/2$) that he will win any one game. Equation (6) for an analogous situation, with $a = 2$, agrees with this expression. See footnote (20) of the preceding paper.

weight average molecular weight $\overline{M}_w = \sum w_x M_x$ must be used,[9,10] where w_x is the weight fraction of species having molecular weight M_x.

If N_0 is the number of chains and Y is the number of branches, and it is assumed that no intramolecular reaction occurs, then the total number of networks, or molecules, equals $N_0 - 2Y$ or $N_0(1 - 4\alpha/2)$. The number average number of chains per molecule, or the number average complexity, is

$$\bar{z}_n = 1/(1 - 4\alpha/2) \qquad (8)$$

The weight average number of chains per molecule, or weight average complexity, is given by

$$\bar{z}_w = \sum_{n=0}^{\infty} (2n + 1)W_n \qquad (9)$$

For large n, introducing (5.2)

$$\bar{z}_w \cong \frac{2(1 - \alpha)}{\alpha\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(4\beta)^{n+1}}{\sqrt{n + 1}} \qquad (9.1)$$

The series in (9.1) is convergent for all values of β up to the critical point $\beta = 1/4$. At the critical point $\bar{z}_w$ reaches infinity, although, according to the preceding discussion, no infinite networks are present until β exceeds $1/4$. Beyond the gel point, $\bar{z}_n$ and $\bar{z}_w$ for the sol fraction are given by the above expressions with α ($>1/2$) replaced by $1 - \alpha$.

In Fig. 2, $\bar{z}_n$ and $\bar{z}_w$ are plotted against α; beyond $\alpha = 1/2$, the values refer to the sol fraction. The curve for $\bar{z}_w$ has been calculated by carrying out numerical evaluation of the lower terms in (9), supplemented, for higher values of n, with an evaluation of the integral corresponding to the series in (9.1).[11]

During a polymerization process in which bi- and trifunctional units are joined together at random, as in a condensation polymerization, not only does the degree of branching α increase as the reaction progresses, but the chains increase in length as well. Equations (8) and (9) do not reflect, therefore, the true course of the corresponding average molecular weights; as the polymerization proceeds, the average molecular weights will increase more rapidly than the corresponding complexities z. However, it can be shown that

the ratio of the two average molecular weights will vary approximately as $\bar{z}_w/\bar{z}_n$. This ratio increases with $\alpha(\alpha < 1/2)$ and becomes infinite at the gel point.

From another point of view, it can be shown that at the gel point the number average molecular weight $\overline{M}_n$ is only three-halves what it would have been at the same extent of reaction had the trifunctional units been replaced *stoichiometrically* with bifunctional units. Although the branch units impart no great increase in $\overline{M}_n$, they may produce a very marked increase in $\overline{M}_w$, particularly if α is near the critical value $1/2$. The exceptional condition of infinite disparity between weight and number average is encountered when $\alpha = 1/2$.

It has been shown recently that viscosities of certain molten linear polymers are related to their weight average molecular weights $\overline{M}_w$ by the simple formula[10]

$$\log \eta = A + C\overline{M}_w^{1/2}$$

Although this relationship without modification cannot be expected to hold for three dimensional polymers, the viscosities of the latter probably depend upon the weight average in such a way that the viscosity will increase without limit as $\overline{M}_w$ increases. The course of the viscosity increase[12] during three dimensional polymerization finds immediate explanation if viscosity is assumed to depend on $\overline{M}_w$ in this way. The viscosity increases very slowly at first, but as the gel point is approached the rate of viscosity rise becomes increasingly rapid. Since $\overline{M}_w$ becomes infinite at the critical point, the viscosity should become infinite also.

Distribution of Species with Respect to Size.— Figure 1 offers a rough idea of the distribution of polymer among species of various sizes, provided that it is understood that the weight fraction of species of each complexity z should be replaced by a distribution of molecules ranging in size from very much less to very much more than z times the average molecular weight per chain. The greater the value z, the sharper this distribution will be and the more nearly the size distribution curve will resemble the complexity curve shown in Fig. 1. The following quantitative derivation of the actual size distribution affords a more accurate representation of the composition of a three dimensional polymer formed by random linking together of bi- and trifunctional units.

(9) E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

(10) P. J. Flory, This Journal, **62**, 1057 (1940).

(11) This integral is $\int_{n+1}^{\infty} \frac{(4\beta)^{n+1}}{(n + 1)^{1/2}} dn$, where the n-th term is the last included in the numerical summation according to (9). A change of variable to $y = [-2(n + 1)\ln(4\beta)]^{1/2}$ yields the error function $\int_{y}^{\infty} e^{-y^2/2} dy$ which can be evaluated from tables.

(12) See Fig. 2 of the preceding paper.

Let q represent the probability of continuation of a chain; that is, q is the mean probability that a given functional group has condensed with a functional group of a bifunctional unit. Then

$$q = p\frac{(G - 3Y)}{G} \qquad (10)$$

where G is the total number of functional groups, Y is the number of trifunctional branch units and p is the extent of reaction, or the fraction of the G groups which have condensed. The probability that a chain selected at random contains y units is given by[13] $(1 - q)q^{y-1}$. The probability that there are x units in a network of z chains selected at random is

$$Q_{zz} = \sum [(1 - q)q^{y_1-1}(1 - q)q^{y_2-1} \dots (1 - q)q^{y_z-1}]$$

where the summation is over all values of the y's consistent with

$$y_1 + y_2 + \dots y_z = x$$

Then

$$Q_{zz} = q^{z-z}(1 - q)^z \frac{(x - 1)!}{(z - 1)!(x - z)!} \qquad (11)$$

Since the average number of units per chain is $1/(1 - q)$, the average number of units in a z chain network is $z/(1 - q)$. Of the total quantity of z-chain species, the weight fraction composed of x units is

$$x\,Q_{zz}(1 - q)/z$$

Of the total polymer, the weight fraction composed of x-unit, z-chain species is given by

$$w_{zz} = xW_zQ_{zz}(1 - q)/z$$

The weight fraction of x-unit species, regardless of the number of chains is

$$w_x = \sum_{z=1,3,5\dots}^{\infty} xW_zQ_{zz}(1 - q)/z$$

Replacing z with $2n + 1$, and substituting (5) for W_n and (11) for Q_{zz}

$$w_x = 2(1 - \alpha)^2(1 - q)^2q^{x-1}\sum_{n=0}^{\infty}\frac{h^n x(x - 1)\dots(x - 2n)}{(n + 2!)n!}$$

where $h = \beta(1 - q)^2/q^2$. $\qquad (12)$

Since the summation in (12) converges rapidly, except when x is very large, it has been possible to carry out the necessary numerical calculations for the construction of the curves for w_x plotted against x, as in Fig. 3. Here q has been taken equal to 0.98; hence, the average chain length is 50 units. Curves for $\alpha = 0$, 0.25 and 0.50 (critical point) are shown for a comparison of the dependence of the nature of the distribution on

(13) P. J. Flory, THIS JOURNAL, **58**, 1877 (1936).

branching. The area under each curve extended to infinity is the same. The position of the maximum is shifted comparatively little by an increase in α, although the height of the maximum decreases rapidly as α increases. The quantity of high molecular weight material increases at the expense of the low molecular weight species in such a way that the distribution curve is flattened as α increases. The curve for $\alpha = 0.25$ in Fig. 3 is also applicable to the sol fractions in gelled polymers when $\alpha = 0.75$.
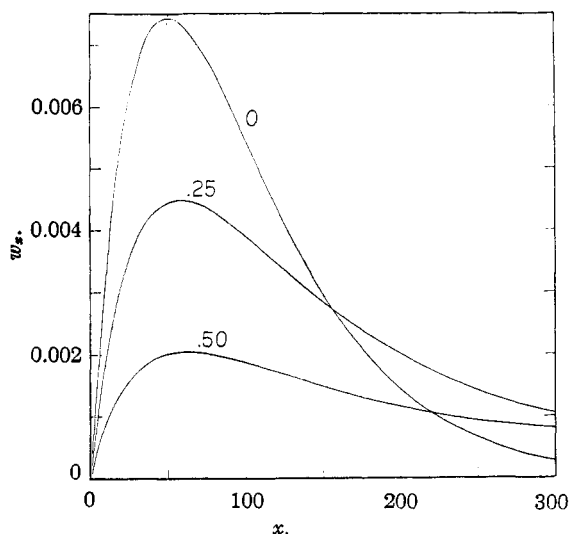

Fig. 3.—Weight fraction distributions according to size for $q = 0.98$ (average chain length = 50) and $\alpha = 0$, 0.25 and 0.50, respectively. The integrated area under each curve extrapolated to infinity is unity.

These curves do not represent the quantities of various species at successive stages of the polymerization, in as much as both q and α increase as the reaction progresses (see eq. (10)). They are merely intended to show the dependence of the shape of the distribution curve on the degree of branching α.

Summary

The distribution of molecular species of various complexities in three dimensional polymers in which the chain branching units are trifunctional has been investigated by statistical methods. It is assumed that the polymer is formed through random linking together of bi- and trifunctional units. The results are somewhat in error due to the further assumption, inherent in the method employed, that no intramolecular reactions occur in molecular species of finite size.

In a condensation polymerization of a large

number of bifunctional units and a small number of trifunctional units, for example, the number of chain branches (trifunctional units) is fixed, but the number of unreacted functional groups decreases as intermolecular condensation of the functional groups proceeds. The average chain length, where a chain is defined as the linear portion of the molecule bounded by branching units or unreacted terminal groups at both ends, increases as the reaction progresses. The statistical analysis shows that although increasing quantities of complex species are formed as the reaction proceeds, simple single chains (containing no branch units) are always in abundance. Even at the critical point for the formation of infinite networks, i. e., at the gel point, one-fourth of the polymer by weight is composed of single chain species.

At the gel point the number average molecular weight $\overline{M}_n$ is merely three-halves what it would have been if the trifunctional units had been replaced stoichiometrically with bifunctional units; in other words, at the gel point the trifunctional units are responsible for a decrease of only one-third in the total number of molecules. On the other hand, the size distribution of species is broadened markedly by the presence of the branch units. This effect on the distribution is reflected by the rapid rise in the weight average molecular weight $\overline{M}_w$ as the gel point is approached. In contrast with $\overline{M}_n$, $\overline{M}_w$ reaches infinity at the critical point

$\alpha = \frac{1}{2}$, although no infinite networks are present until α exceeds $\frac{1}{2}$ (α equals the probability of a branch at the end of a given chain.) Since the viscosities of polymers depend on their weight average molecular weights, an explanation is provided for the observed increase in viscosity without limit as the gel point is approached.

The simultaneous presence of sol (soluble polymer) and gel (insoluble polymer) after gelation, is shown by the statistical treatment to be the direct consequence of random distribution of branch units in the polymer. It is in no way dependent upon different chemical properties of the ingredients from which the sol and gel fractions are formed.

In harmony with the results of the preceding paper, infinite networks (gel) make their appearance suddenly when α exceeds $\frac{1}{2}$. For greater values of α the weight fraction of sol is given by $(1 - \alpha)^2/\alpha^2$. The weight fraction of gel can be calculated by difference.

Highly branched species are preferentially converted to gel as the reaction continues beyond the gel point. Consequently, the average complexity in the sol fraction decreases as the polymerization proceeds beyond gelation.

The situations dealt with in this paper and the one preceding find obvious analogies in certain gas phase chain reactions.

Molecular Size Distribution in Three Dimensional Polymers. III. Tetrafunctional Branching Units

BY PAUL J. FLORY[1]

Three dimensional polymers in which the branch units are tetrafunctional are particularly important. They include copolymers of styrene with divinylbenzene,[2,3] analogous copolymers of other vinyl and divinyl compounds,[4] raw rubber, vulcanized rubber and condensation polymers composed of bifunctional and tetrafunctional units. Certain protein gels, e. g., those of egg al-

bumin,[5] probably should be included if one considers secondary valence bonds as the cross linkages. In this paper the size distributions in tetrafunctionally branched polymers will be investigated by a statistical method unlike that which has been applied to trifunctionally branched polymers in the preceding paper.[6]

The particular case under consideration is that of long chains of uniform length, some of which are connected with one another by randomly distributed tetrafunctional units, or cross linkages. The probability that any particular unit in a poly-

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