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 $\alpha = {}^1/_2$, although no infinite networks are present until α exceeds ${}^1/_2$ (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 ${}^1/_2$. 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.

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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 albumin,[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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[2] H. Staudinger and W. Heuer, *Ber.*, **67**, 1164 (1934).

[3] H. Staudinger and W. Heuer, *ibid.*, **68**, 1618 (1935); *Trans. Faraday Soc.*, **32**, 323 (1936).

[4] K. G. Blaikie and R. N. Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936); R. G. W. Norrish and E. F. Brookman, *Proc. Roy. Soc.* (London), **A163**, 205 (1937).

[5] W. G. Myers and W. G. France, *J. Phys. Chem.*, **44**, 1113 (1940).

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

mer chain is tetrafunctional, or is cross-linked, is considered to be independent of the proximity of other tetrafunctional units, or cross-linkages. The restriction of the treatment to chains of uniform length renders the quantitative aspects of the results inapplicable to all of the examples mentioned above, except the proteins.

As in the preceding papers[6,7] it is assumed that no intramolecular reactions occur in species of finite size.

Theoretical

Let ρ represent the probability that any unit selected at random is cross-linked, *i. e.*, is part of a tetrafunctional unit. Thus, in a styrene–divinylbenzene copolymer ρ is given by

$$\rho = \frac{2(\text{divinylbenzene})}{(\text{styrene}) + 2(\text{divinylbenzene})}$$

the factor, 2, being included since each divinylbenzene furnishes two chain units. Of course, only those divinylbenzenes both vinyl groups of which have polymerized are to be counted as tetrafunctional. Similarly, for a vulcanized rubber ρ is twice the ratio of sulfur cross linkages to the total number of isoprene units.

Derivation of the Distribution Function.—The probability that a chain selected at random has i cross linkages is given by

$$P_i = \frac{(\nu + 1)!}{(\nu + 1 - i)!i!}\,\rho^i(1 - \rho)^{\nu+1-i} \qquad (1)$$

where $\nu + 1$ is the number of units in one chain. These i cross linkages lead to i additional chains, each of which possesses ν units in addition to the unit which is cross-linked to the original chain. The probability that these i chains possess a total of j additional cross linkages is

$$P_{ij} = \frac{(i\nu)!\rho^j}{(i\nu - j)!j!}\,(1 - \rho)^{i\nu-j} \qquad (2)$$

The probability that a chain selected at random possesses i cross linkages, the i neighboring chains possess j additional cross linkages, the next tier of j chains possess k additional cross linkages, etc., and finally zero cross linkages in the s-th tier is

$$R_{i.j.\,\ldots\,r.0} = P_i\,P_{ij}\,P_{jk}\,\ldots\,P_{r.0}$$

Substituting from (1) and (2)

$$R_{i.j.\,\ldots\,r,0} = \frac{[(\nu + 1)!(i\nu)!(j\nu)!\,\ldots\,(r\nu)!]\rho^{z-1}(1 - \rho)^{z(\nu-1)+2}}{[(\nu + 1 - i)!(i\nu - j)!(j\nu - k)!\,\ldots\,(r\nu)!][i!j!\,\ldots\,r!]}$$

where the total number of chains in the molecule is given by $z = 1 + i + j + \ldots r$. Since ν is large, it is permissible to let

$$(m\nu)!/(m\nu - n)! = (m\mu)^n$$

where $\nu - 1 < \mu < \nu$. Then[8]

$$R_{i.j.\,\ldots\,r,0} = \left[\frac{i^ij^k\,\ldots\,r^0}{i!\,j!\,\ldots\,r!}\right](\mu\rho)^{z-1}\,(1 - \rho)^{z(\nu-1)+2} \qquad (3)$$

The probability that the chain selected at random is connected to $z - 1$ other chains by any possible configuration is

$$W_z = (\mu\rho)^{z-1}\,(1 - \rho)^{z(\nu-1)+2}\sum\frac{i^j\,j^k\,\ldots\,r^0}{i!j\,!\ldots\,r!} \qquad (4)$$

where the summation is over all combinations of i, j, k, etc., consistent with the conditions $i + j + k \ldots + r = z - 1$

$$i > 0 \qquad j > 0, \text{ etc.}$$

The additional requirements that

$$i < \nu + 1 \qquad j < \nu \qquad k < \nu, \text{ etc.}$$

can be overlooked since ν is large and in all situations of interest here the probability of an i, j or k, etc., greater than ν would be negligibly small.

The author has found by numerical evaluations that the summation in (4) is exactly equal to $z^{z-1}/z!$ for values of z from 0 to 9. Salkover[9] has shown that the validity of this simple expression for all values of z can be established by induction. Substitution in (4) gives for the weight fraction of the species composed of z chains the comparatively simple expression

$$W_z = \frac{(1 - \rho)^2}{\mu\rho}\,\frac{z^{z-1}}{z!}\left(\frac{\beta}{e}\right)^z \qquad (5)$$

where

$$\beta/e = \mu\rho(1 - \rho)^{\nu-1} \qquad (6)$$

The distribution function (5) is subject to the approximations introduced in the preceding paragraphs. It will be shown below that certain further approximations, appropriate when ν is large, are necessary in order to give (5) the proper limiting characteristics.

Substituting

$$(1 - \rho)^\nu = e^{-\nu\rho}\,[1 - \nu\rho^2/2 + (\nu\rho/4 - 2/3)\nu\rho^3/3! + \ldots\ldots]$$

in (6) and letting[8] $\mu = \nu - {}^1/_2$

$$\beta/e \cong e^{-\nu\rho}\,[1 - \nu\rho^2/2 + \ldots](\nu - 1/2)\rho/(1 - \rho)$$

or

$$\beta/e \cong \gamma e^{-\gamma}[1 - (1 - \gamma)^2/2\nu + \ldots] \qquad (7)$$

where $\gamma = \nu\rho$. When the number $\nu + 1$ of units per chain is large, the *cross linking index* γ is ap-

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(7) P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).

(8) It is evident from the nature of the approximations involved that the best value which can be chosen for μ must lie between ν and $\nu - 1$. It will be assumed below that $\mu = \nu - {}^1/_2$.

(9) The author is indebted to Professor M. L. Salkover of the University of Cincinnati for contributing this proof, which has not been reproduced here.

proximately equal to the number of cross-linked units per chain, or twice the number of cross-linkages per chain. Situations of most interest are those for which γ is of the order of unity, where higher terms of the series in (7) are negligible. In any case the magnitude of the error introduced by setting $\mu = \nu - 1/2$ probably justifies omission of all terms above the first, giving

$$\beta \cong \gamma e^{1-\gamma} \qquad (7.1)$$

Regardless of whether (7) or (7.1) is used, β reaches a maximum value of unity when $\gamma = 1$, and decreases for higher values of γ. The function $\beta(\gamma)$ is analogous to $\beta(\alpha)$ of the preceding paper.[6] For every value of β (except $\beta = 1$) there are two solutions γ of (7.1), one of them less than unity and the other greater than unity (see Fig. 1).

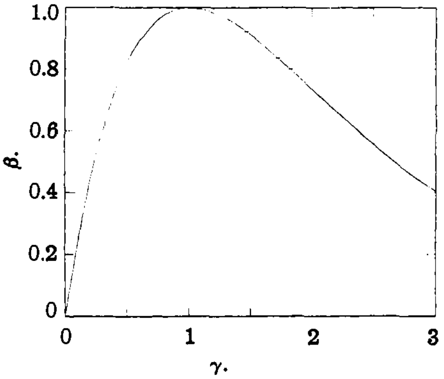

Fig. 1.—β *vs.* the cross-linking index γ.

Substituting (7.1) in (5) and replacing $(1 - \rho)^2/\mu\rho$ with $1/\gamma$, an approximation which is of the same order as that introduced in the derivation of (5)

$$W_z = \frac{z^{z-1}}{\gamma z!}(\gamma e^{-\gamma})^z = \frac{z^{z-1}}{\gamma z!}\left(\frac{\beta}{e}\right)^z \qquad (8)$$

Introducing Stirling's approximation $z! \cong \sqrt{2\pi z}(z/e)^z$

$$W_z \cong (1/\gamma\sqrt{2\pi})\beta^z/z^{5/2} \qquad (8.1)$$

These distribution functions are similar to those of the preceding paper.[10] Throughout the physically accessible range $\beta = 0$ to 1, W_z is finite for all values of z and $\sum_{z=1}^{\infty} W_z$ is convergent.

The Sol–Gel Ratio.—It has been found that

$$\sum_{z=1}^{\infty} (z^{z-1}/z!)(\beta/e)^z = \gamma'$$

where γ' is the lower of the two roots of (7.1) for the particular value of β (see Fig. 1). Hence, when $\gamma \leqq 1$

$$\sum_{z=1}^{\infty} W_z = 1 \qquad (9)$$

and when $\gamma > 1$

$$\sum_{z=1}^{\infty} W_z = \gamma'/\gamma \qquad (10)$$

where γ' is the lower root of (7.1) for the value of β corresponding to γ.

In complete analogy with the results for trifunctionally branched polymers, the summation of the weight fractions of all finite species is unity until the critical value of the cross linking index γ is exceeded. Thereafter, the summation decreases continuously as γ increases. This decrease in $\sum W_z$ below unity is attributed to the formation of infinite networks, which are not accounted for in the distribution function. Hence, $\gamma = 1$ represents the critical value for incipient gelation, and, when γ is greater than unity, weight fractions of sol and gel are, respectively

$$W_s = \gamma'/\gamma \qquad (10)$$

and

$$W_g = 1 - \gamma'/\gamma \qquad (11)$$

where γ and γ' are roots of (7.1) for the same value of β.

The approximation introduced in the derivation of equation (8) by the substitution of $1/\gamma$ for $(1 - \rho)^2/\mu\rho$ proves to have been particularly appropriate. Otherwise, $\sum W_z$ when $\gamma < 1$ would have been a function of ρ not exactly equal to unity. Equation (5) has been converted to (8), which fulfills the necessary limiting conditions for an acceptable distribution function, through the introduction of approximations which are small under the conditions assumed, namely, ν large and $\gamma \sim 1$. None of the approximations are beyond the order of those introduced in the original derivation of (5). It is not improbable that a completely rigorous treatment of this problem would show that (8) is exact, or, at least, more nearly so than (5).

Number Average and Weight Average Molecular Weights.—By a procedure analogous to that presented in the preceding paper,[11] the number average number of chains per molecule can be shown to be

$$\bar{z}_n = 1/(1 - \gamma/2) \qquad (12)$$

assuming that no intramolecular cross-linking

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[10] Compare equation (8.1) with (5.2) of ref. 6.

[11] See p. 3093 of ref. 6.

occurs. The weight average number of chains is

$$\bar{z}_w = \sum_{z=1}^{\infty} \frac{(\beta z/e)^z}{\gamma z!} \tag{13}$$

$$\cong (1/\gamma\sqrt{2\pi}) \sum \beta^z/z^{1/2} \tag{13.1}$$

The number and weight average molecular weights are proportional to $\bar{z}_n$ and $\bar{z}_w$, respectively, since the chains are assumed to be of uniform length. As was found in the preceding paper,[6] $\bar{z}_w$ reaches infinity at the critical point, $\beta = 1$, $\gamma = 1$. On the other hand, $\bar{z}_n$ is only equal to 2 at the critical point.

Discussion

Weight fraction distributions are plotted in Fig. 2 for several values of the cross-linking index γ. The curves have been calculated from eq. (8). Only integral values of z are significant. Since all chains are assumed to be of the same length, the curves represent weight fraction distributions according to actual molecular size. It follows from the form of (8) that the $\gamma = 0.40$ and 0.80 curves in Fig. 2 are also applicable to the sol fractions in gelled polymers for which γ has the values 2.02 and 1.23, respectively (see Fig. 1).

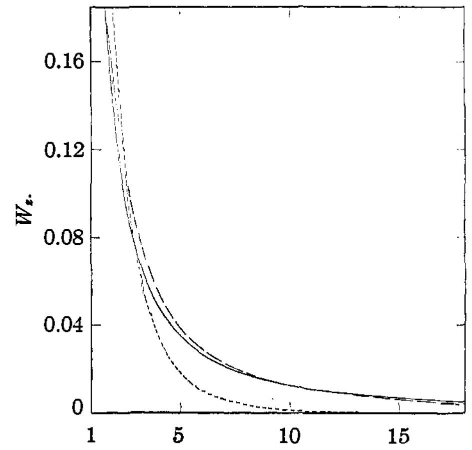

Fig. 2.—Weight fractions *vs.* number of chains per molecule for $\gamma = 0.40$, -----, $\gamma = 0.80$; — — —, $\gamma = 1.00$, ———.

Weight fractions of single chains ($z = 1$) for each of the three curves are 0.67, 0.45 and 0.37, respectively. The quantities of successively larger species decrease rapidly; this rate of decrease becomes less as γ approaches unity. Although the distribution broadens rapidly as gelation is closely approached, there is always a preponderance of smaller species. The similarity of these distributions to the complexity distribution curves shown for trifunctionally branched polymers in Fig. 1 of the preceding paper obviates further comment.

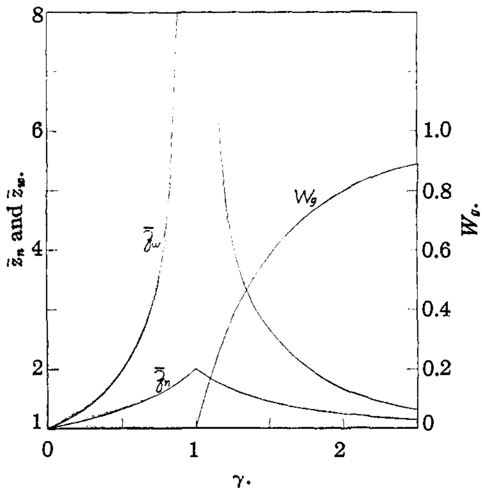

Fig. 3.—Weight fraction of gel (W_g), and number average ($\bar{z}_n$) and weight average ($\bar{z}_w$) number of chains per molecule as functions of γ. Beyond $\gamma = 1$ the curves for $\bar{z}_n$ and $\bar{z}_w$ refer to the sol fraction only.

The weight fraction of gel, plotted in Fig. 3, has been evaluated from the curve in Fig. 1, according to the relationship (11). The curve for $\bar{z}_n$, the number average number of chains per molecule, which is proportional to the number average molecular weight, has been calculated from (12). The corresponding weight average ($\bar{z}_w$) curve has been drawn through points computed by direct summation according to (13) as far as $z = 10$, supplemented with an evaluation of the integral corresponding to (13.1) from $z = 11$ to ∞.[12] Curves for $\bar{z}_n$ and $\bar{z}_w$ beyond the gel point apply to the sol fraction of the polymer.

The rapid separation of the $\bar{z}_n$ and $\bar{z}_w$ curves as the gel point is approached is even more pronounced than in the trifunctional case.[13] Whereas $\bar{z}_w$ is infinite when $\gamma = 1$, $\bar{z}_n$ is only equal to two. That is, at the gel point cross-linking has merely doubled the number average molecular weight; this is the average which one would obtain by cryoscopic or osmotic methods. The comments presented in the preceding paper[6] concerning the bearing of analogous results on the progress of the viscosity as the gel point is approached are equally applicable here.

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(12) See footnote (11) of the preceding paper.[6]

(13) In comparing Fig. 3 above with Fig. 2 of the preceding paper,[6] it should be observed that although γ plays a role analogous to that of α of the preceding paper, the two quantities are not equivalent. α cannot exceed unity, but γ must reach a very large value before substantially all sol has disappeared.

For tetrafunctionally branched polymers composed of long chains randomly distributed in length,[14] the critical condition, according to results of a preceding paper,[7,15] is given by

$$\alpha_c = \frac{4\ (\text{no. of cross links})}{4(\text{no. of cross links}) + (\text{unreacted terminal groups})} = 1/3$$

Since there are two unreacted terminal groups per chain, the number of cross linkages at the gel point is *one-fourth* of the number of chains. This result is one-half of the critical degree of cross-linking derived above for chains of uniform length. The number average molecular weight of the polymer at the gel point, therefore, is only three-halves the number average molecular weight of the non-uniform chains.

In principle, the theory presented here should be applicable to vinyl–divinyl copolymers,[2,3,4] *e. g.*, styrene–divinylbenzene copolymers. However, it is necessary to know the ratio in which the two co-reactants enter the polymer chains (on the average) and not merely their ratio in the initial mixture. Staudinger and co-workers[2,3] have shown that divinylbenzene is more reactive than styrene. Until the ratio of divinylbenzene to styrene in the polymer chains is known, quantitative application of statistical theory to these co-polymers would be futile.

Although the principles which have been deduced from statistical consideration should be of widespread assistance toward an understanding of the composition and behavior of three dimensional polymers and high polymer gels, few experimental data suitable for a quantitative test of the theory are available. Application of the theory to rubber and to protein gels will be discussed in another paper.

The author desires to acknowledge his indebtedness to Professor William C. Taylor, of the Mathematics Department of the University of Cincinnati, with whom he had the opportunity to discuss various phases of the theory presented in the three papers of this series.

Summary

The distribution of species in three dimensional polymers composed of randomly cross-linked chains of uniform length has been discussed. The results parallel those of the preceding paper for trifunctionally branched polymers. Gelation occurs when the cross-linking index γ (equal to the number of structural units which are cross-linked per chain) is equal to unity, and the number average molecular weight is twice that of the chains.

The effect of non-uniformity in the lengths of the chains has been discussed. When the chains are randomly distributed in length, $\gamma = 1/2$ at the gel point.

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(14) The distribution given by eq. (1) of ref. (7) is referred to here as the "random" distribution; it seems to prevail frequently in linear polymers.

(15) See in particular equations (2) and (8) of ref. (7).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Structure–Property Relationships in Some Isomeric Octanols

BY G. L. DOROUGH,[1] H. B. GLASS,[1] THOS. L. GRESHAM,[1] G. B. MALONE[1] AND E. EMMET REID

Introduction

In most previous studies of the relations between structures and properties of isomeric organic compounds, the number of isomers has been small or only a few properties have been measured. The work of Edgar and co-workers[2] on the isomeric heptanes stands out for its completeness. Clarke's summary for the octanes[3] includes a larger number of compounds but fewer properties. Other outstanding studies are represented by the work of Sherrill and Errera[4] on the straight chain heptanols and certain of their derivatives, and by the work of Hovorka, Lankelma, and co-workers[5] on the isomeric hexanols. It does not appear, however, that any comprehensive study of a large number of properties of a large number of isomers ever has been made. We have accordingly undertaken an investigation of this type.

The following considerations governed the selection of the compounds to be studied and the manner of study: a large but not excessive number of isomers; a functional variant to give wide

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(1) Taken in part from Dissertations submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1929 and 1930.

(2) Edgar and co-workers, THIS JOURNAL, **51**, 1483 (1929).

(3) Clarke, *ibid.*, **33**, 520 (1911).

(4) Sherrill and Errera, *ibid.*, **52**, 1982, 1993 (1930).

(5) Hovorka, Lankelma, *et al.*, *ibid.*, **62**, 2372 (1940), and earlier papers there referred to.