[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Molecular Size Distribution in Three Dimensional Polymers. VI. Branched Polymers Containing $A\text{-}R\text{-}B_{f-1}$ Type Units

BY PAUL J. FLORY

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Highly branched polymer molecules may be synthesized without incidence of gelation through the use of a monomer having one functional group (A) of one kind and two or more of another (B) capable of reacting with the former. More extended structures conforming to a similar branched pattern should be obtainable by condensing a mixture of bifunctional monomers of the A–B type and the branching monomer $A\text{-}R\text{-}B_{f-1}$. Molecular size distributions in these systems are derived using a comparatively simple procedure involving direct enumeration of configurations. Such polymerizations offer unique advantages for the preparation of highly branched polymers suitable for investigations on the influence of non-linearity on physical properties. The present treatment is easily extended to the more common non-linear condensations involving monomers of the type $R\text{-}A_f$. The method appears to be applicable also to polymerizations involving two or more polyfunctional monomers differing in functionality f.

Introduction

Intermolecular condensation of monomer molecules each of which possesses a single functional group A of one type and two or more of another B, the condensation being restricted to reactions between an A and a B group, offers interesting possibilities for the preparation of polymers unique in their combination of structural and molecular weight distribution features. Although highly branched, they should resemble linear polymers in their elusion of infinite network (*i.e.*, gelation) formation, which cannot occur except by intervention of other interlinking reactions. The situation may be illustrated by the condensation of a trifunctional ($f = 3$) monomer, which may for convenience be represented by $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{B}}$. Structures such as that indicated in Fig. 1 will be formed. Each molecule may contain at most one unreacted A group; it will contain exactly one unless an intramolecular condensation has occurred involving one of the B's on the same molecule as the A. As in previous publications of this series,[1-3] we introduce as an approximation the assumption that intramolecular condensations do not occur. Then every molecule must possess exactly one unreacted A group and, if the monomer is trifunctional, there will be $x + 1$ unreacted B groups in a molecule comprised of x units. In the more general case of an f-functional monomer of the type considered, each polymer molecule will retain a single unreacted A and $fx - 2x + 1$ unreacted B's. It is easy to show that infinite structures will not be generated short of complete intermolecular condensation of all A groups in such a system, regardless of the value of f.

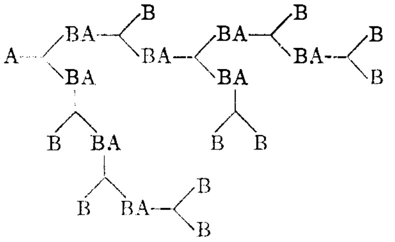
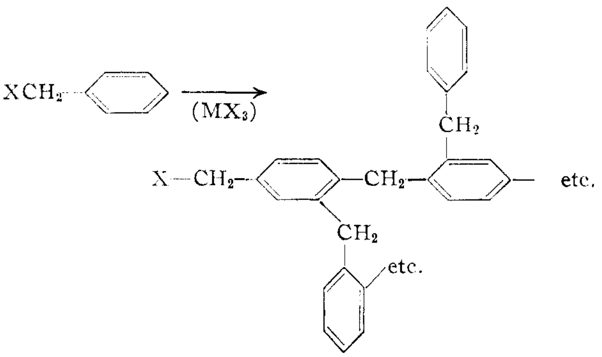
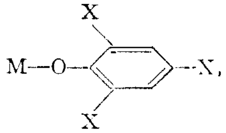


Fig. 1.

Polymers conforming to the above scheme are comparatively rare, and none of the known examples appears to have been investigated from the point of view of molecular constitution. Among examples which may be cited are the polymers obtained by Friedel–Crafts condensation of benzyl halides.[4]



The halomethyl group corresponds here to the A and the several nuclear positions to the B's. The polymers generally are amorphous, indicating an irregular structure, and they remain soluble and fusible provided that reaction conditions are sufficiently mild to avoid excessive rearrangement in the presence of the catalyst used. Polymers formed by elimination of metal halide from alkali metal salts of trihalophenols,  display similar properties in accordance with expectation.[5]

Copolymers of bifunctional monomers of the type A–B with the f-functional monomer $A\text{-}R\text{-}B_{f-1}$ retain the essential features of the polymers prepared from the latter monomer alone. The structural plan indicated in Fig. 1 for the trifunctional case is altered merely by inserting sequences (As B)$_y$ of the bifunctional units between the junction of B with A groups of the f-functional monomers. These sequences will vary in length at random, y

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

(2) P. J. Flory, *ibid.*, **63**, 3091 (1941).

(3) P. J. Flory, *ibid.*, **63**, 3096 (1941); **69**, 30 (1947); *J. Phys. Chem.*, **46**, 132 (1942).

(4) T. Zincke, *Ber.*, **2**, 737 (1869); *Ann. Chem. Pharm.*, **159**, 367 (1871); C. Friedel and J. M. Crafts, *Bull. soc. chim.*, **43**, 53 (1885); C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2258 (1928); R. A. Jacobson, THIS JOURNAL, **54**, 1513 (1932); S. Bezzi, *Gazz. chim. ital.*, **66**, 491 (1936).

(5) W. H. Hunter and G. H. Woollett, THIS JOURNAL, **43**, 135 (1921).

being permitted to assume all values zero and greater. The resulting structure is a prototype of the amylopectin fraction of starch and of glycogen.[6] The single reducing end group of the former corresponds to the unreacted A group. The bifunctional units consist of 1,4-α-anhydroglucose, the trifunctional of 1,4,6-α-anhydroglucose.

The recently reported[7] synthetic polyglucoses prepared by acid-catalyzed condensation of glucose afford a particularly interesting case. Chemical evidence indicates that the hydroxyl in position 1 of one unit may condense with various of the 2-, 3-, 4- and 6-hydroxyls of the other, but that the 6-position may be favored under certain conditions, at least. That the polymer must be highly branched is shown by the presence in the polymer of an abundance of glucose units condensed only at the 1-position. Branching is easily accounted for by assuming that two or more of the 2-, 3-, 4- and 6-hydroxyls of some of the units condense.[8]

The molecular weight distributions in polymers formed by random condensation of A–R–B_{f-1} monomers alone, or with A–B monomers also, are derived in the present paper by direct enumeration of molecular configurations, and unique features of these distributions are pointed out. The extension of the relatively simple method to the more commonly occurring condensations involving a polyfunctional monomer of the type R–B_f, with $f > 2$, is demonstrated.

Condensation of A–R–B_{f-1} Units Alone

Assumptions.—All of the functional groups of a given type (A or B) are assumed to be equally reactive at any given stage of the condensation. Thus, all of the B groups of a monomer molecule are assumed equally reactive initially, and the reactivity of any one of them (or of the A group) is assumed to be unaffected by reaction of one or more of the other functional groups in the same molecule. Furthermore, according to the basic assumption, the reactivity of a group is considered to be independent of the size of the molecule involved.

Whether the assumption of equal reactivity is required to apply in the kinetic or equilibrium sense will depend on the circumstances attending the condensation. If, for example, it is conducted with ample opportunity for interchange processes to occur, then the equal reactivity assumption reduces to the stipulation that the standard state free energy change for the formation of an AB linkage shall be independent of structure elsewhere in the molecule.

Intramolecular condensations are neglected out of despair at the difficulty of treating the problem otherwise. The same approximation has been employed in treatments of other non-linear polymers, without seriously impairing the significance of the results obtained. This approximation becomes more serious the greater the size of the species, or, more accurately, the greater the "density" of f-functional units in the molecule.

Primary Derivations.—As in previous treatments of polyfunctional condensations,[1,2,9] the branching coefficient α is defined as the probability that a given functional group of a branch unit is connected to another branch unit. When A–R–B_{f-1} units alone are present in the polymer, α is simply the probability that an arbitrarily selected B group has reacted. Under the assumption that all B groups are equally reactive, $\alpha = p_B$, where p_B is the fraction of the B groups which have condensed. Since the numbers of A and of B groups which react must be equal, $p_B(f-1) = p_A$, where p_A represents the extent of reaction, or fraction of the A groups reacted. Replacing p_A with p

$$\alpha = p/(f-1) \tag{1}$$

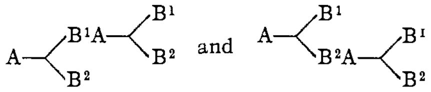
The maximum value which α may approach (but never reach) is $1/(f-1)$, therefore. But in an f-functional system the critical condition for incipient formation of infinite structures[1] is $\alpha_c = 1/(f-1)$. It follows that the generation of infinite structures is impossible in the present system.

We note also that the total number of molecules will be $N_0(1-p)$ where N_0 is the number of units. Consequently, the number average degree of polymerization given by

$$\bar{x}_n = 1/(1-p) = 1/[1-\alpha(f-1)] \tag{2}$$

remains finite for extents of reaction short of $p = 1$.

For convenience in enumerating configurations, the $f - 1$ B groups of a unit are assumed to be distinguishable, although identical in reactivity. Whether or not an actual basis for differentiation is afforded by the asymmetry of the monomer is immaterial. This assumption is introduced merely as a device to simplify the enumeration of configurations, hence it has no effect on the final result. A particular structure, or configuration, may then be specified by designating which of the B's of each successive unit, starting with the one bearing the free A-group, have reacted. Thus, the simple dimeric structures



will be regarded as different from one another for purposes of enumeration, the possibility that B^1 and B^2 may be physically indistinguishable notwithstanding. The probability that an unreacted A group belongs to an x-mer having a specific structure defined in this manner equals the probability that the particular sequence of $x - 1$ B groups have reacted while the remaining $fx - 2x + 1$ B's have not. This specific probability

$$\alpha^{x-1}(1-\alpha)^{fx-2x+1}$$

is the same for each x-meric configuration. Hence, the probability that any given unreacted A group is attached to an x-mer molecule of any structural configuration whatever is

$$N_x = \omega_x \alpha^{x-1}(1-\alpha)^{fx-2x+1} \tag{3}$$

where ω_x is the total number of configurations. Since, according to the assumption that intramolecular condensation may be neglected, each

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(6) K. H. Meyer, "Natural and Synthetic High Polymers," Second Edition, Interscience Publishers, Inc., New York, N. Y., 1950, p. 456 *et seq.*

(7) E. Pacsu and P. T. Mora, THIS JOURNAL, **72**, 1045 (1950).

(8) The writer is indebted to Dr. Mora with whom he has had the opportunity to discuss the structure of polyglucose.

(9) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).

molecule bears a single unreacted A group, N_x is also the mole fraction of x-mer.

In order to evaluate ω_x, it will be assumed tentatively that the individual monomer molecules are distinguishable from one another. Since the B's within a monomer must be considered distinguishable (in order to validate the procedure adopted above for enumerating configurations), then every B is distinguishable from every other in the system. Having chosen the x-monomers from which an x-mer is to be constructed, an arbitrary set of $x - 1$ B groups are selected for reaction out of the total of $(f - 1)x$ B's. The total number of sets which may be selected is simply the number of combinations of $fx - x$ things taken $x - 1$ at a time, or

$$(fx - x)!/(fx - 2x + 1)!(x - 1)!$$

Identical polymer configurations cannot be constructed using different sets of B's, but many configurations may be had from each set by combining them with the A's in different ways. The number of different ways in which the $x - 1$ B's may be paired with $x - 1$ A's, avoiding always a combination between a B and the A of the same molecule, is $(x - 1)!$ Hence, the total number of arrangements under the assumption that the individual monomers are distinguishable is

$$(fx - x)!/(fx - 2x + 1)!$$

This physically unrealistic assumption may be abolished by dividing by $x!$, the number of permutations of the monomer units for a given configuration as originally defined. Hence

$$\omega_x = (fx - x)!/(fx - 2x + 1)!x! \qquad (4)^{10}$$

Equation (3) may be written

$$N_x = [(1 - \alpha)/\alpha]\, \omega_x \beta^x \qquad (5)$$

where

$$\beta = \alpha(1 - \alpha)^{f-2} \qquad (6)$$

The similarity between these expressions and those derived in the treatment of ordinary branched polymers becomes apparent on comparison.[2,9] The β used here, for example, corresponds exactly with the parameter introduced by the author[2] and with greater generality by Stockmayer.[9] The most important distinction between the presently considered distribution and the one previously treated occurs in the fact that there exists here only one physically significant root α for each permissible value of β. Thus, β reaches a maximum at $\alpha = 1/(f - 1)$, which corresponds to the value of α for complete reaction in the present problem. All larger values of α are physically unattainable in the system being considered.

Evaluation of Summations.—For the purpose of obtaining the weight distribution and higher average degrees of polymerization it is necessary to evaluate summations of the type

$$S_m = [\alpha/(1 - \alpha)] \sum_1^\infty x^m N_x$$

or

$$S_m = \sum_1^\infty (fx - x)!x^m\beta^x/(fx - 2x + 1)!x! \qquad (7)$$

These resemble those encountered by Stockmayer[9] and may be evaluated similarly, as follows. Differentiating S_m as given by equation (7)

$$S_m = \beta(dS_{m-1}/d\beta) = \beta(dS_{m-1}/d\alpha)(d\alpha/d\beta) \qquad (8)$$

Since $\sum_1^\infty N_x = 1$

$$S_0 = \alpha/(1 - \alpha) \qquad (9)$$

Substituting $d\alpha/d\beta$ from equation (6) and $dS_0/d\alpha$ from (9) into equation (8) with $m = 1$

$$S_1 = \alpha/(1 - \alpha)[1 - \alpha(f - 1)] \qquad (10)$$

Repeating the process

$$S_2 = [\alpha/(1 - \alpha)][1 - \alpha^2(f - 1)]/[1 - \alpha(f - 1)]^3 \qquad (11)$$

etc.

Weight Distribution.—The weight fraction of x-mer is given by

$$\begin{aligned} w_x &= xN_x/\sum xN_x = [\alpha/(1 - \alpha)]xN_x/S_1 \\ &= [(1 - \alpha)/\alpha][1 - \alpha(f - 1)]x\omega_x\beta^x \qquad (12) \end{aligned}$$

Weight Average Degrees of Polymerization $\bar{x}_w$.—This average is defined by

$$\begin{aligned} \bar{x}_w &= \sum x^2N_x/\sum xN_x \\ &= S_2/S_1 \end{aligned}$$

Substituting

$$\bar{x}_w = [1 - \alpha^2(f - 1)]/[1 - \alpha(f - 1)]^2 \qquad (13)$$

The ratio of weight to number average is

$$\bar{x}_w/\bar{x}_n = [1 - \alpha^2(f - 1)]/[1 - \alpha(f - 1)] \qquad (14)$$

Discussion

The mole and weight fraction distributions calculated from equations (5) and (12), respectively, are shown in Figs. 2 and 3 for $f = 3$ and several values of α. Broadening of the distribution with increase in α is particularly evident in the weight fraction distribution. As α proceeds to $\alpha_c = 1/2$, the weight fraction distribution degenerates to a line coinciding with the x-axis, *i.e.*, the weight fraction of each species falls to zero. Since the area under the curve is unity for all α's, it is apparent that in this limit the weight distribution becomes infinitely wide while infinitesimally high.

The mole fractions (equation (5) and Fig. 2) remain finite throughout the range $0 < \alpha \leqq \alpha_c$. This is not inconsistent with the above at $\alpha = \alpha_c$. While the number of molecules of a given size falls to zero at $\alpha = \alpha_c$, the total number of molecules also reaches zero. Their ratio, the mole fraction, is finite.

Broadening of the distribution is best indicated by comparison of the different average degrees of polymerization. As α approaches α_c, the total number of molecules decreases toward zero. Obviously both $\bar{x}_n$ and $\bar{x}_w$ must approach infinity as $\alpha \rightarrow \alpha_c$. Equation (14) shows further that the ratio of $\bar{x}_w$ to $\bar{x}_n$ also becomes infinite at $\alpha = \alpha_c$, which is indicative of "infinite" heterogeneity.

Condensation of A–B with A–R–B_{f-1}

The polymers formed in this case will have structures as indicated in Fig. 4 for a trifunctional

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[10] The above derivation of ω_x resembles to some extent Stockmayer's[9] evaluation of the combinatory factor for ordinary polyfunctional condensation, although it is simpler than the latter. The nature of the present problem is such as to avoid the necessity of introducing an artificial analog such as he was obliged to use. As will be shown, the combinatory factor for the ordinary polyfunctional problem is easily obtained from ω_x.

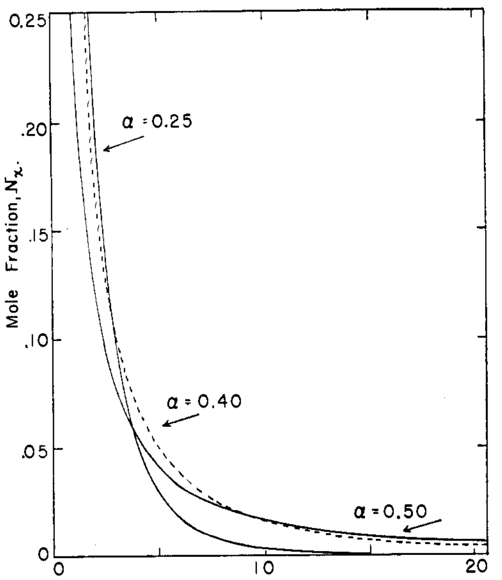

Fig. 2.

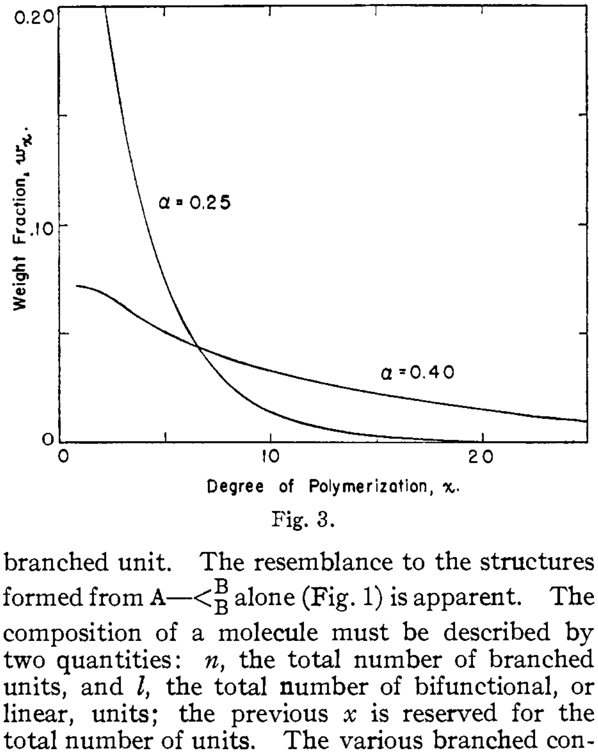

Fig. 3.

branched unit. The resemblance to the structures formed from A—$<^{\mathrm{B}}_{\mathrm{B}}$ alone (Fig. 1) is apparent. The composition of a molecule must be described by two quantities: n, the total number of branched units, and l, the total number of bifunctional, or linear, units; the previous x is reserved for the total number of units. The various branched configurations for a given n obviously correspond exactly to those for the same number (x) of units in the simpler case discussed above. Each branched configuration possesses $fn - n + 1$ "chains" of bifunctional units, a chain being defined as that portion of the structure extending from one branch unit to another, from a branch to an unreacted functional group, or, in the case of an unbranched molecule ($n = 0$), between two unreacted groups. Each chain may contain zero or more bifunctional units, except, of course, the single chain of the linear $n = 0$ species which must contain a minimum of one bifunctional unit.

We consider first the complete statistical distribution which takes account of both n and l. The more tractable complexity distribution expressed in terms of the number of branched units alone will then be discussed.

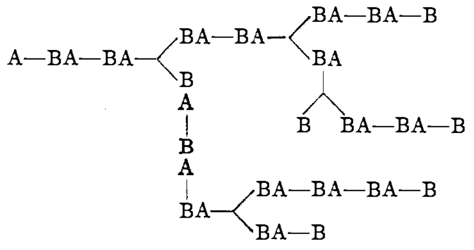

Fig. 4.

Derivation of the Complete Statistical Distribution.—Let ρ be the ratio of A groups belonging to branched units to total A's; ρ is then the mole fraction of branched units. It follows that

$$p_{\mathrm{B}} = p/[1 - \rho + (f - 1)\rho] \qquad (15)$$

where p is written for p_{A} as above. A specific configuration is defined as previously with the further stipulation of the number of bifunctional units occurring in each chain. The probability that an arbitrarily selected unreacted A group is connected with a particular configuration comprised of a total of n branched and l bifunctional units is readily found to be

$$\rho(p_{\mathrm{B}}\rho)^{n-1}(1 - p_{\mathrm{B}})^{fn - 2n + 1}[(1 - \rho)p_{\mathrm{B}}]^{l}$$

and the same probability applies to each configuration comprised of the same numbers (n and l) of units. The number of branching arrangements, irrespective of the disposition of the l bifunctional units, is again ω_n as given by equation (4) with n replacing x. The l bifunctional units may be partitioned among the $fn - n + 1$ chains, each of which may contain zero or more of them, in

$$(l + fn - n)!/l!(fn - n)!$$

different ways. The total number of configurations, consisting of the product of ω_n and this factor, is therefore

$$\omega_{n,l} = (l + fn - n)!/l!n!(fn - 2n + 1)! \qquad (16)$$

Hence, the probability, or mole fraction, of an n, l-mer is given by

$$\mathrm{N}_{n,l} = [(1 - p_{\mathrm{B}})/p_{\mathrm{B}}]\zeta^{n}\eta^{l}\omega_{n,l} \qquad (17)$$

where

$$\left.\begin{aligned} \zeta &= p_{\mathrm{B}}\rho(1 - p_{\mathrm{B}})^{f-2} \\ \eta &= (1 - \rho)p_{\mathrm{B}} \end{aligned}\right\} \qquad (18)$$

In order to derive the weight fraction distributions, summations of the following form are required

$$\Sigma_{\mathrm{m}} = \sum_{n=0}^{\infty}\sum_{l=0}^{\infty}(n + l)^{m}\zeta^{n}\eta^{l}\omega_{n,l} \qquad (19)$$

Now the summation for $m = 0$, which on substituting from equation (17) may be written

$$\Sigma_0 = [p_{\mathrm{B}}/(1 - p_{\mathrm{B}})]\sum_{n=0}^{\infty}\sum_{l=0}^{\infty}\mathrm{N}_{n,l}$$

includes the fictitious term $\mathrm{N}_{0,0}$. The summation over all $\mathrm{N}_{n,l}$ exclusive of this term is, of course, equal to unity, and, according to equations (16) and (17), $\mathrm{N}_{0,0} = (1 - p_{\mathrm{B}})/p_{\mathrm{B}}$. It follows that

$$\Sigma_0 = 1/(1 - p_{\mathrm{B}}) \qquad (20)$$

Through the use of the relationship

$$\Sigma_1 = \eta(\partial\Sigma_0/\partial\eta)_\zeta + \zeta(\partial\Sigma_0/\partial\zeta)_\eta$$

there is obtained

$$\Sigma_1 = p_B/[(1 - p_B)^2 - (f - 2)\rho p_B(1 - p_B)] \quad (21)$$

For the purpose of simplification, equal weights will be assumed for the two monomer units. Then, the weight fraction of n,l-mers is

$$\begin{aligned}\omega_{n,l} &= (n + l)\,\mathrm{N}_{n,l}\Big/\sum_{n=0}^{\infty}\sum_{l=0}^{\infty}(n + l)\mathrm{N}_{n,l}\\ &= (n + l)\mathrm{N}_{n,l}/[(1 - p_B)/p_B]\Sigma_1\\ &= [(1 - p_B)^2/p_B - (f - 2)(1 - p_B)\,\rho\,](n + l)\zeta^n\eta^l\omega_{n,l}\end{aligned} \quad (22)$$

The Complexity Distribution.—Expressions such as equations (17) and (22) are too cumbersome to be of much practical use. As a more tractable approach, we consider the "complexity distribution," or distribution of molecules according to the number n of branch units, ignoring the variable number of bifunctional units.[2] This distribution may, of course, be obtained by summing equation (17) over all l. We shall obtain the same result by a more intuitive consideration of the probability α that a B group of a branch unit leads *via* a series of zero or more A–B units to another branch, *i.e.*

$$\begin{aligned}\alpha &= \sum_{i=0}^{\infty}[p_B(1 - \rho)]^i p_B\rho\\ &= p_B\rho/[1 - p_B(1 - \rho)]\end{aligned} \quad (23)$$

The probability α' that the unreacted A group of the molecule leads to a branch unit (*i.e.*, the probability that the molecule is not linear) unfortunately is not the same as α. Application of the above method yields

$$\alpha' = \alpha/p_B \quad (24)$$

Equipped with these branching probabilities it is now an easy matter to ascertain the probability that the molecule in question contains n branch units. Starting with the unreacted A group, the probability of reaching a branched unit is α'. Thenceforth the problem is identical with that involved in the derivation of equation (5). Hence, we have at once for the complexity distribution

$$\left.\begin{aligned}\mathrm{N}_n &= (\alpha'/\alpha)(1 - \alpha)\,\omega_n\beta^n \quad (n > 0)\\ \mathrm{N}_0 &= 1 - \alpha'\end{aligned}\right\} \quad (25)$$

where β is defined as in equation (6). The expected molecular weight of a chain should be independent of the complexity (n) of the molecule as a whole, and of its location in the molecule. Consequently, the average weight of a molecule of complexity n will be proportional to the number of chains, hence their weight fraction is

$$w_n = (fn - n + 1)\mathrm{N}_n/\sum_{n=0}^{\infty}(fn - n + 1)\mathrm{N}_n$$

Substituting from equation (25) and recalling the definition of S_m given by the previous equation (7)

$$w_n = \frac{(\alpha'/\alpha)(1 - \alpha)(fn - n + 1)\beta^n\omega_n}{(\alpha'/\alpha)(1 - \alpha)(f - 1)\,S_1 + 1}\ (n > 0) \quad (26)$$

Substituting for S_1 from equation (10)

$$w_n = \left\{\frac{(\alpha'/\alpha)(1 - \alpha)[1 - \alpha\,(f - 1)]}{1 + (\alpha' - \alpha)(f - 1)}\right\} \times (fn - n + 1)\beta^n\omega_n\ (n > 0) \quad (27)$$

Similarly

$$w_0 = (1 - \alpha')[1 - \alpha(f - 1)]/[1 + (\alpha' - \alpha)(f - 1)] \quad (27')$$

The complexity distribution as represented by equations (25) and (27) and (27′) differs little from the size distribution, equations (5) and (12), for the simple f-functional case. The correspondence is especially evident if $\alpha' \cong \alpha$, which will hold if ρ is small and the extent of reaction p is near unity (see equations (23), (24) and (15)). Equation (27), for example, simplifies to

$$w_n \cong (1 - \alpha)[1 - \alpha(f - 1)](fn - n + 1)\omega_n\beta^n \quad (27'')$$

which differs from equation (12) (with x replaced by n) by a factor $\alpha(fn - n + 1)/n$ which for large n approaches $\alpha(f - 1)$. But in the range of interest α is not much less than its limiting value $(f - 1)^{-1}$, hence the factor under consideration approaches unity and the correspondence is established. It may be noted further that for small degrees of branching (ρ) such that $\alpha' \cong \alpha$, the w_0 given by equation (27′) converges with the w_0 which would be calculated from equation (27), thus permitting the entire distribution to be expressed by this equation alone.

The mole fraction N_0 of linear species remains large under all conditions. Substituting equations (15), (23) and (24) in (25), the mole fraction of linear species at completion of the condensation ($p = 1$), for example, is

$$\mathrm{N}_0 = (1 - \rho)(f - 2)/(f - 1) \quad (28)$$

For small degrees of branching this approaches $(f - 2)/(f - 1)$, which equals one-half for $f = 3$. The *weight* fraction of linear polymer, given by equation (27′), falls to zero as the reaction approaches completion. Thus, whereas the mole fraction of linear polymer tends to be large (except for larger values of ρ), their proportion by weight may be made extremely small by forcing the condensation toward completion.

If the extent of reaction is sufficient to make $1 - p$ much smaller than ρ, the preponderant part by weight of the polymer will consist of multiply branched species. The degree of polymerization of a species of given complexity n is subject to variation, of course, as it depends also on the total number (l) of bifunctional units in its $fn - n + 1$ chains. Among those species for which this number is large, *i.e.*, where n exceeds two or three, this variation will be small. The degree of polymerization of a species of complexity $n > 2$ may, therefore, be approximated by

$$n + (fn - n + 1)\bar{l}$$

where $\bar{l}$ is the average number of bifunctional units per chain, with small likelihood that the error committed will be serious. Thus, for all but the lowest values of n, the complexity distribution is a generally satisfactory substitute for the actual size distribution.

Branched polymerizations of the above type, and especially the copolymers with A–B units in large excess, offer unique advantages for the preparation of highly branched polymer molecules. Polymerizations involving branched units of the R–A$_f$ type inevitably lead to formation of infinite network structures before the average degree of branching reaches about one per primary polymer molecule. The same holds for cross-linked polymers. Large deviations from linearity in soluble polymer molecules consequently are virtually unattainable by these more common procedures. Conceivably, one might separate a small fraction of very high molecular weight from such a polymer and thereby secure a sample which is highly branched, or cross-linked. The breadth of the distribution coupled with the impossibility of selectively fractionating "branching" and "molecular weight" separately make this approach impractical. Attempts to investigate "branching" by such means consequently have been notably fruitless. The extent of branching per molecule obtainable through the use of an A–R–B_{f-1} monomer, on the other hand, is subject to no theoretical limit. Furthermore, the extent of branching, expressed as the fraction ρ of units which are branched, should be very nearly uniform at all molecular weights, except within the lowermost portion of the distribution. It should be possible, therefore, to separate such a polymer into a series of fractions in which the number of branches per molecule in successive fractions increases as the molecular weight of the fraction, and to investigate the influence of branching on properties under properly controlled conditions through their use.

According to Zimm and Stockmayer's[11] treatment of average dimensions of branched polymer molecules, the effective volume $\sim(\overline{R^2})^{3/2}$ where $\overline{R}^2$ represents the average of the distances of the units from the center of gravity of the molecule, should be asymptotically proportional to $x^{3/2}/n^{3/4}$ for very large n, where x is the total number of units and n the number of branch units. For the homologous series of fractions considered above, n is proportional to x, hence the effective molecular volume for successive fractions should increase as $x^{3/4}$. To the extent that the dimensions of the molecule in dilute solution are unaffected by polymer–solvent interactions, the hydrodynamically effective volume should vary also as $x^{3/4}$ and the intrinsic viscosity,[12] being proportional to the ratio of this volume to the molecular weight, should decrease slightly with increase in molecular weight as $M^{-1/4}$ (or as $x^{-1/4}$). This would apply only in the limit of very large molecules having in excess of a hundred branches. Further examination of Zimm and Stockmayer's calculations shows that over the molecular weight range in which n increases from four to fifty (at fixed ρ) the effective volume increases approximately as x, hence the intrinsic viscosities of the homologous fractions over this rather broad range should be approximately independent of M.

Extension to Ordinary Polyfunctional Condensations

Monomers of the type R–A_f condense to structures which correspond to those obtainable from an A–R–B_{f-1} monomer. The principal difference lies in the fact that α, which for simple condensation of R–A_f alone is equal to the extent of reaction p, is not restricted to the range below α_c, hence networks may be generated. The pattern of Fig. 1 for $f = 3$ may be employed here also merely by stipulating that A and B are identical.

If one of the $fx - 2x + 2$ identical unreacted functional groups of an x-mer is selected arbitrarily, the various configurations extending from this group may be enumerated in precisely the same way as previously. It follows that the probability that an unreacted A group selected at random belongs to an x-mer is given by

$$P_x = \alpha^{x-1}(1-\alpha)^{fx-2x+1}\omega_x \qquad (29)$$

the previous definition of ω_x according to equation (4) being retained. However, this expression is not a mole fraction, since there are $fx - 2x + 2$ eligible functional groups in the molecule, any one of which might have been selected. P_x should be equated instead to the ratio of the number of unreacted A's on x-mer molecules to the total number of unreacted A's in the system. Thus

$$P_x = (fx - 2x + 2)N_x/N_0f(1 - \alpha) \qquad (30)$$

where N_x is the number of x-mers and N_0 is the total number of units. Eliminating P_x from equations (29) and (30)

$$N_x = N_0[(1-\alpha)^2/\alpha]\omega_x'\beta^x \qquad (31)$$

where β is defined by equation (6) and

$$\omega_x' = f(fx - x)!/(fx - 2x + 2)!x! \qquad (32)$$

The total number of molecules, assuming no intramolecular reaction, is

$$N = N_0(1 - \alpha f/2) \qquad (33)$$

Hence, the mole fraction of x-mer is

$$\mathrm{N}_x = [(1-\alpha)^2/\alpha(1 - \alpha f/2)]\omega_x'\beta^x \qquad (34)$$

The weight fraction distribution, $w_x = xN_x/N_0$, is given by

$$w_x = [(1-\alpha)^2/\alpha]x\omega_x'\beta^x \qquad (35)$$

These distributions were derived previously by Stockmayer[9], who used a lengthier method involving maximization of the expression for the probability of any distribution, and evaluation of ω_x' through the use of an artificial analog. The writer[2] obtained the distribution for the trifunctional case using a method appropriate for this case only. The present procedure is both more direct and simpler than either of these earlier methods, without sacrifice of rigor or generality.

The distributions in copolymers of R–A_f monomers with bifunctional monomers, also obtained previously by Stockmayer, may be derived by an extension of the above procedure paralleling that applied in the preceding section to systems containing A–R–B_{f-1} branch units. The present method may be applied also to non-linear polymers prepared by condensing two or more polyfunctional units having different functionalities.

The adaptation of the above distribution expressions for description of the constitution of the sol fraction beyond the gel point has been discussed previously.[13]

ITHACA, N. Y.

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[11] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949). See especially their equation (40b) and Table I.

[12] P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[13] P. J. Flory, *Chem. Revs.*, **39**, 137 (1946).