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A General Theory of Gel Formation with Multifunctional Interunit Junctions

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A theory is presented for a general treatment of the molecular size distribution, the gel point, and the post-gelation phenomena with respect to polymerization with formations of various kinds of interunit junctions, assuming (1) that all functional groups are equally reactive, and (2) that no kind of intramolecular interunit junction occurs. These interunit junctions appear concurrently in a system composed of a mixture of monomeric molecules and with a distributions of functionalities. Two cases are treated: (1) when the interunit junction is characterized only by the number of functional groups involved in its formation, and (2) when the interunit junction is characterized not only by the number of groups, but also by the magnitude of the free energy of its formation. The former is illustrated by the polycondensation with bi- or terfunctional interunit junctions or with both. The latter is illustrated by the polycondensation between A and B groups in a mixture of A-monomers with equireactive A groups and B-monomers with equireactive B groups, where a B-monomer is regarded as a kind of interunit junction.

The way in which high polymeric substances are formed from monomeric units may be classified according to the number of functional groups involved in the formation of an interunit junction (hereafter we will call this the order of the interunit junction). Each case may be referred to as polymerization by bi-, ter-, quadri-, …or, in general, multifunctional interunit junctions. The simplest kind, polymerization by bifunctional interunit junctions, is most familiar; almost all polycondensations so far established belong to this group. For this group, the theory of molecular size distribution and gel formation has been studied comprehensively by Flory,⁽¹⁾ Stockmayer⁽³⁾ and many other researchers.⁽²⁾ The theory of gel formation with the terfunctional interunit junction has been developed by the present authors,⁽⁴⁾ and the theory was extended to the case of the formation of multifunctional interunit junctions (say, j-functional: $j=2, 3, 4, \cdots$) in the preceding paper.⁽⁵⁾

The case treated in these papers were, however, limited to those which contain only one kind of interunit junction. It is, therefore, the purpose of the present paper to extend the theory to more generally, to cases in which the monomeric molecules are combined with one another to form polymeric molecules by means of various kinds of interunit junctions appearing concurrently in the system. The interunit junction presented here is characterized not only by the order of the interunit junction, but also by the magnitude of the free energy of its formation. Therefore, two interunit junctions with the same order but with different free energies of formation are not regarded as equivalent. Moreover, the present theory affords relationships after the gel point by which to judge success.

Flory first employed the statistical method to find the distribution of molecular species in a polymer system. In the present paper the distribution of various molecular species will be studied by a mathematical method essentially similar to that one which has been introduced into the theory of the condensation of real gas by Mayer⁽⁶⁾ and by others and which has been applied to the theory of molecular size distribution and gel formation in branched chain polymers by Stockmayer, who generalized Flory's theory employing the same basic assumptions. The present work makes the same two assumptions as Flory and Stockmayer. One is that an intraaggregate reaction yielding two or more endo-cyclical structures (interunit junctions) cannot occur; the other is that any unreacted functional group is as reactive as any other functional group, regardless of the size or shape of the molecule to which it is attached. Besides, it is also assumed that the functional

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1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York (1953), Chapter 9.

2) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); *ibid.*, **12**, 125 (1944).

3) M. Gordon, *ibid.*, **22**, 610 (1954); F. E. Harris, *ibid.*, **23**, 1518 (1955); L. C. Case, *J. Polymer Sci.*, **26**, 333 (1960).

4) K. Fukui and T. Yamabe, *J. Polymer Sci.*, **45**, 305 (1960).

5) T. Yamabe and K. Fukui, This Bulletin, **37**, 1061 (1964).

6) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York (1940), Chapters 13 and 14.

groups forming an interunit junction are combined together simultaneously. This assumption implies that the order of their combination is not taken into account.

The present treatment covers, to give some simple examples of its application, cases when the polycondensation reaction proceeds with the formation of either bi- or trifunctional interunit junctions, or with both, as the preceding papers,⁷⁾ have already described, and cases when the polycondensation proceeds between the A group and the B group.

The present treatment is distinctive in having other successful applications. Several of the results will be given below as examples. The molecular size distirbution and the gel point of the polymerizations of polyfunctional vinyl compounds or epoxy compounds can be explained reasonably on the basis of the conception that a chain composed of k functional units is to be regarded as a k-functional interunit junction, although some special cases (the copolymerization of vinyl and divinyl compounds) were treated by Flory and Stockmayer. These authors, however, considered a vinyl group to be two functional groups which react independently with each other as in a polycondensation reaction, ignoring the fact that such a functional group can react only as a pair; consequently, they obtained the same most probable distribution as in the case of polycondensation reactions. Also, we expect to apply the present theory in explaining vairous kinds of association phenomena, the solubility of polar compounds in nonpolar solvents, antigen-antibody interactions, and so on. These items will be discussed in succeeding papers.

The Size Distribution and the Gel Point (I)

The first case to be considered is the simplest, that of a system where the interunit jucntions are characterized only by their order or, in other words, where all of the same order of interunit junctions have the same given energy of formation. In this case the simplest interunit jucntion, namely, the monofunctional interunit junction, may be regarded as the unreacted functional group. An extension to the general case can easily be made, as will be shown in a later section.

Now let us consider a system composed of various kinds of monomeric molecules, *i. e.*, N_1 monofunctional, N_2 bifunctional,⋯, N_f f-functional,⋯, *etc.*, and in which these molecules are combined to make a mixture composed of some larger molecules, with, in total, J_1 monofunctional, J_2 bifunctional,⋯, J_k k-functional,⋯, interunit junctions. Let us represent such a system by $\boldsymbol{S}(\boldsymbol{N};\boldsymbol{J})$, where $\boldsymbol{N}$ and $\boldsymbol{J}$ are denoted, like vectors, as:

$$\boldsymbol{N} = (N_1,\ N_2,\ \cdots,\ N_f,\ \cdots)$$
$$\boldsymbol{J} = (J_1,\ J_2,\ \cdots,\ J_k,\ \cdots).$$

From these definitions, the following equation is immediately obtained:

$$\sum_f fN_f = \sum_k kJ_k\,. \tag{1}$$

It is convenient for subsequent calculations to introduce several averaged quantities:

$$\lambda_n = \sum_f fN_f/\sum_f Nf = 1/\sum_f (w_f/f) \tag{2}$$

$$\lambda_w = \sum_f f^2N_f/\sum_f fN_f = \sum_f fw_f \tag{3}$$

where:

$$w_f = fN_f/\sum_f fN_f \tag{4}$$

which represents the fraction of the functional groups on the f-functional monomers, and where, therefore:

$$\sum_f w_f = 1\,. \tag{5}$$

Likewise, we define:

$$\mu_n = \sum_k kJ_k/\sum_k J_k = 1/\sum_k (p_k/k) \tag{6}$$

$$\mu_w = \sum_k k^2J_k/\sum_k kJ_k = \sum_k kp_k \tag{7}$$

$$p_k = kJ_k/\sum_k kJ_k \tag{8}$$

which stands for the probability that a functional group is involved in the formation of k-functional interunit junctions: accordingly,

$$\sum_k p_k = 1\,. \tag{9}$$

In order to describe any polymeric molecular species, it is necessary to specify the numbers of monomeric constituents and the interunit junctions of each order. Therefore, let as denote by n_f the number of f-functional monomeric constituents, and by j_k, the number of interunit junctions of the order k, and let us represent any particular set of these numbers, n_1, n_2, …, n_f,… or j_1, j_2,…, j_k,⋯, by the symbols $\boldsymbol{n}\equiv\{n_f\}$ and $\boldsymbol{j}\equiv\{j_k\}$ respectively.

When $m(\boldsymbol{j};\boldsymbol{n})$ is used for the number of such a kind of polymeric molecule, $M(\boldsymbol{j};\boldsymbol{n})$, as specified by two particular sets, $\{j_k\}$ and $\{n_f\}$, the following relationships are obtained:

$$\sum j_k m(\boldsymbol{j};\boldsymbol{n}) = J_k. \tag{10}$$

$$\sum n_f m(\boldsymbol{j};\boldsymbol{n}) = N_f \tag{11}$$

where the summation $\sum$ should cover any set of nonnegative integers, j_k, n_f and $m(\boldsymbol{j};\boldsymbol{n})$, which satisfy Eqs. (1), (10) and (11).

For a given particular system, $\boldsymbol{S}(\boldsymbol{N};\boldsymbol{J})$, we will discuss the most probable distribution of polymeric molecules, which corresponds to a configuration of maximum occurrence, namely, the maximum entropy. After the usual procedures[2,5,6] we find the most probable distribution to be:

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7) T. Yamabe and K. Fukui, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 686 (1963).

$$m(\boldsymbol{j}\,;\boldsymbol{n}) = \frac{\omega(\boldsymbol{j}\,;\boldsymbol{n})}{\prod\limits_f n_f!} \prod_f \xi_f{}^{n_f} \prod_k \eta_k{}^{j_k}$$

where $\omega(\boldsymbol{j}\,;\boldsymbol{n})$ is the number of ways to construct a single polymeric molecular species, $M(\boldsymbol{j}\,;\boldsymbol{n})$, containing no endocyclic structure and is easily found by the use of the Mayer[6]—Stockmayer[2] method to be:

$$\omega(\boldsymbol{j}\,;\boldsymbol{n}) = \frac{(\sum\limits_k j_k - 1)!(\sum\limits_f n_f - 1)!}{\prod\limits_k j_k!((k-1)!)^{j_k}} \prod f^{n_f}$$

with the following conditions:

$$\sum_f f n_f = \sum_k k j_k = \sum_f n_f + \sum_k j_k - 1 \tag{12}$$

where ξ_f and η_k are Lagrangian multipliers which can be determined from Eqs. (10) and (11). If the variables, ξ_f and η_k, are transformed into previous variables, w_f and p_k, by the equations:

$$f\xi_f = w_f \text{ and } \eta_k/(k-1)! = p_k$$

the most probable distribution may be rewritten as:

$$m(\boldsymbol{j}\,;\boldsymbol{n}) = (\sum_f f N_f) \frac{(\sum\limits_k j_k)!(\sum\limits_f n_f)!}{(\sum\limits_k j_k)(\sum\limits_f n_f)} \prod_k \frac{p_k{}^{j_k}}{j_k!} \prod_f \frac{w_f{}^{n_f}}{n_f!} \tag{13}$$

which satisfies the conditions of Eqs. (10) and (11) provided that $1 \geqq (\lambda_w - 1)(\mu_w - 1) \geqq 0$, as is shown in Appendix A.

The total number of polymeric molecules composed of l monomeric molecules (l-mer), m_l, is, then:

$$m_l = \sum_{\sum\limits_f n_f = l} m(\{j_k\}\,;\{n_f\})$$

summed over all the sets of nonnegative values, $\{j_k\}$, $\{n_f\}$, subject to:

$$\begin{aligned} \sum_f n_f &= \sum_k (k-1) j_k + 1 = l \\ \sum_k j_k &= \sum_f (f-1) n_f + 1\,. \end{aligned} \tag{14}$$

We have here to form the generating function:

$$f(x) = \sum_f w_f u^{f-1} \tag{15}$$

where:

$$u = \sum_k p_k x^{k-1}\,.$$

It then follows from the multinomial theorem that:

$$m_l = \text{the coefficient of } x^l \text{ in } \frac{(\sum\limits_k (k-1) p_k x^k)}{l(l-1)} [f(x)]^l$$

and that hence, by Cauchy's theorem:

$$m_l = \frac{1}{2\pi i} \oint \frac{x(\mathrm{d}u/\mathrm{d}x)}{l(l-1)} \frac{[f(x)]^l}{x^l} \mathrm{d}x\,.$$

We can use the method of steepest descents in evaluating the contour integral. Then the integration is carried out along the circle of a radius, x_0, around the point of origin, where x_0 is the one, and only one, positive real root of the equation:

$$g(x) = f(x) - x f'(x) = 0 \tag{16}$$

as is shown in Appendix B.

Calculation yields the asymptotic value of the distribution available for the mole fraction of l-mers:

$$m_l \cong \frac{x_0 u'(x_0)}{[2\pi f''(x_0)/f(x_0)]^{1/2}} \frac{[f(x_0)/x_0]}{l^{5/2}} \tag{17}$$

for a large l value.

Since a series of the $\sum\limits_{n=1}^{\infty} z^n n^{-k}$ form converges for $z \leqq 1$ if $k > 1$ and converges for $z < 1$ if $0 < k \leqq 1$, it is apparent that all the sums, $\sum m_l$, $\sum l m_l$, and $\sum l^2 m_l$, have a radius of convergence, x_0, satisfying an additional condition:

$$\frac{f(x_0)}{x_0} = 1 \tag{18}$$

and that at this value of x_0, $\sum m_l$ and $\sum l m_l$ converge, while $\sum l^2 m_l$ diverges.

As has been stated in Stockmayer's paper,[2] such a point may be called the gel-point, which is characterized from Eqs. (16) and (18) as:

$$1 = (\lambda_w - 1)(\mu_w - 1) \tag{19}$$

where, $x_0 = 1$, as is shown in Appendix B.

Therefore, $0 \leqq (\lambda_w - 1)(\mu_w - 1) \leqq 1$ should hold as long as the reaction does not proceed beyond the gel point. It is also shown in Appendix B that, in this range, x_0 is larger than unity. Therefore, near the gel point, x_0 will be so slightly larger than unity that we may put:

$$x_0 = 1 + \varepsilon \qquad (0 < \varepsilon < 1)\,. \tag{20}$$

Substituting Eq. (20) into Eq. (16) and neglecting the terms of order higher than ε in the expansion in the power series of ε, we obtain:

$$\varepsilon \cong \frac{1 - (\lambda_w - 1)(\mu_w - 1)}{\mu_z'(\lambda_w - 1) + \lambda_z'(\mu_w - 1)^2} \tag{21}$$

where:

$$\lambda_z' = \sum_f (f-1)(f-2) w_f \tag{22}$$

$$\mu_z' = \sum_k (k-1)(k-2) p_k\,. \tag{23}$$

Therefore,

$$\begin{aligned} \frac{f(x_0)}{x_0} &\cong 1 - [1 - (\mu_w - 1)(\lambda_w - 1)]\varepsilon \\ &\cong 1 - \frac{[1 - (\lambda_w - 1)(\mu_w - 1)]^2}{\mu_z'(\lambda_w - 1) + \lambda_z'(\mu_w - 1)^2} \end{aligned} \tag{24}$$

which indicates that this value of x_0 is in the range of convergence. Using Equation (24) we can obtain an explicit presentation of m_l in terms of the measurable parameters, $\{w_s\}$ and $\{p_k\}$, near the gel point. Equation (24) is, however, also valid after the gel point, as will be discussed in the next section.

Relationships after the Gel Point

In this section, we will discuss the relationships after the gel point.

We find in Appendix A that the weight fraction of f-functional monomers is given as:

$$\sum f n_f m(\boldsymbol{j}\,;\boldsymbol{n})/\sum_f f N_f = w_f u_1{}^f \equiv w_f{}^{(s)} \qquad (25)$$

$$u_1 = u(x_1)$$

as long as the molecular size distribution is presented by Eq. (13), where x_1 is the lower of the two positive real roots of the characteristic equation:

$$G(x) = x - f(x) = 0\,. \qquad (26)$$

Equation (26) may be rewritten in the following reciprocal forms:

$$x = \sum_f w_f u^{f-1} \qquad (26'\text{-}1)$$

$$u = \sum_k p_k x^{k-1}\,. \qquad (26'\text{-}2)$$

It is proved in Appendix B that Eq. (26) has two real positive roots; one is equal to 1, while in the other $x_G > 1$ if $1 > f'(1) > 0$ or $x_G < 1$ if $f'(1) > 1$.

Before the gel point $(1 > f'(1) = (\lambda_w - 1)(\mu_w - 1) \geqq 0)$, $u_1 = 1$, since $x_1 = 1$; therefore, $w_f{}^{(s)} = w_f$, just for its definition, whereas, after the gel point $((\lambda_w - 1)(\mu_w - 1) > 1)$, $u_1 < 1$, since $x_1 = x_G (< 1)$; therefore,

$$w_f > w_f{}^{(s)} \qquad (27)$$

$w_f{}^{(s)}$ may, therefore, represent the soluble part of the weight fraction of f-functional monomers after the gel point, and, hence, u_1 may represent the probability that a functional group selected at random is a part of the sol fraction. Equation (25) also shows that the gel is liable to acquire preferentially the larger molecules.

The sol fraction, W_{sol}, is, therefore, given by:

$$W_{\text{sol}} = \sum_f w_f{}^{(s)} = \sum_f w_f u_1{}^f \left(= \sum_k p_k x_1{}^k\right)$$
$$= x_1 u_1\,. \qquad (28)$$

The weight fraction of f-functional monomers in the sol phase is, then:

$$w'_f{}^{(s)} = w_f{}^{(s)}/\sum_f w_f{}^{(s)} = w_f{}^{(s)}/W_{\text{sol}}\,. \qquad (29)$$

The gel part of the weight fraction of the f-functional monomer, $w_f{}^{(g)}$, is, therefore, defined by their difference; *i. e.*,

$$w_f{}^{(g)} = w_f - w_f{}^{(s)} = w_f(1 - u_1{}^f)\,. \qquad (30)$$

Hence, the gel fraction, $W_{\text{gel}} = 1 - W_{\text{sol}}$.

The soluble part of the weight fraction of functional groups forming k-functional interunit junctions after the gel point is similarly obtained as:

$$p_k{}^{(s)} = p_k x_1{}^k\,. \qquad (31)$$

Therefore, x_1 may be considered to be the probability that an unreacted functional group selected at random belongs to the sol fraction in a polymeric molecule. The two probabilities, x_1 and u_1, are neither equivalent to nor independent of each other, as Eqs. (26′-1) and (26′-2) show.

The probability of forming of a k-functional interunit junction in the sol phase, $p_k{}'^{(s)}$, is given by:

$$p_k{}'^{(s)} = p_k{}^{(s)}/W_{\text{sol}}\,. \qquad (32)$$

Likewise, the gel part of the weight fraction of functional groups composed of k-functional interunit junctions, $p_k{}^{(g)}$ is obtained from the difference:

$$p_k{}^{(g)} = p_k(1 - x_1{}^k)\,. \qquad (33)$$

Hence, the probability of a k-functional interunit junction in the gel, $p_k{}'^{(g)}$, is:

$$p_k{}'^{(g)} = p_k{}^{(g)}/W_g\,. \qquad (34)$$

The molecular size distribution of the sol phase after the gel point is also presented by Eq. (13), which should, however, be rewritten with parameters of the sol phase as follows:

$$m^{(\text{sol})}(\boldsymbol{j}\,;\boldsymbol{n}) = \left(\sum_f f N_f\right) \frac{\left(\sum_k j_k\right)!}{\left(\sum_k j_k\right)} \cdot \frac{\left(\sum_f n_f\right)!}{\left(\sum_f n_f\right)}$$
$$\times \prod_k \frac{p_k{}'^{(s)}}{j_k!} \prod_f \frac{w_f{}'^{(s)}}{n_f!} \cdot (W_{\text{sol}})^{\sum_f f n_f} \qquad (35)$$

which shows that $m^{(\text{sol})}(\boldsymbol{j}\,;\boldsymbol{n})$ is proportional to $(W_{\text{sol}})^{\sum_f f n_f}$. This again is a consequence of the preferential acquisition of larger molecules by the gel.

A few special, but fundamental, cases of these representations were discussed first by Flory(1) and subsequently by Charlesby(8) with regard to the problem of gel formation by the radiation of R-ray to linear polymers. Recently Gordon(9) has investigated the situation more generally, including the cases mentioned above, with another method, *i. e.*, with the help of the cascade or branching theory of stochastic processes; his method is, however, very closely related to our treatment. In fact, we can obtain W_{sol} from Eq. (11) of Gordon's paper by the substitution of $f(x)$ into Gordon's $F_1(x)$. The other results in this section have not been, however, obtained by Gordon.

Average Numbers

After the evaluation of the necessary sums found in Appendix A, various kinds of averaged quantities, which will appear in practical problems, were obtained:

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8) A. Charlesby, *Proc. Roy. Soc.*, **A222**, 542 (1954).

9) M. Gordon, *ibid.*, **A268**, 240 (1962).

$$\bar{p}_{<fn_f>} = \frac{\sum(\sum_f fn_f)m(\boldsymbol{j}\,;\,\boldsymbol{n})}{\sum m(\boldsymbol{j}\,;\,\boldsymbol{n})} = \frac{1}{\dfrac{1}{\lambda_n}+\dfrac{1}{\mu_n}-1} \tag{36}$$

$$\bar{p}_{<fn_f>^2} = \frac{\sum(\sum_f fn_f)^2 m(\boldsymbol{j}\,;\,\boldsymbol{n})}{\sum(\sum_f fn_f)m(\boldsymbol{j}\,;\,\boldsymbol{n})} = \frac{1}{\dfrac{1}{\lambda_w}+\dfrac{1}{\mu_w}-1}\,. \tag{37}$$

The $\bar{p}_{<fn_f>}$ and $\bar{p}_{<fn_f>^2}$ quantities are the number and the weight-average molecular size before the gel point respectively. Considering the Schwarz inequality,

$$\frac{\lambda_w}{\lambda_n} = \left(\sum_f \frac{w_f}{f}\right)\left(\sum_f fw_f\right) \geqq 1$$

and the consequent relations $\lambda_w \geqq \lambda_n$ and $\mu_w \geqq \mu_n$, we get:

$$\bar{p}_{<fn_f>^2} \geqq \bar{p}_{<fn_f>}\,.$$

From Eq. (37), the gel point may also be characterized by the fact that $\bar{p}_{<fn_f>^2}$ tends to be infinite, as has been pointed out by Stockmayer. Similarly, we obtain the number and the weight-average degree of polymerization as follows:

$$\bar{p}_{<n_f>}(\equiv\bar{p}_l) = \frac{\sum lm_l}{\sum m_l} = \frac{\mu_n}{\mu_n+\lambda_n-\lambda_n\mu_n} \tag{38}$$

$$\bar{p}_{<n_f>^2}(\equiv\bar{p}_{l^2}) = \frac{\sum l^2 m_l}{\sum lm_l} = 1 + \frac{\lambda_n(\mu_w-1)}{\lambda_w+\mu_w-\lambda_w\mu_w}\,. \tag{39}$$

The relationships of the above quantities in the sol phase after the gel point are simiarly obtained as follows:

$$\bar{p}^{(\mathrm{sol})}_{<fn_f>} = \frac{1}{\dfrac{1}{\lambda_n^{(s)}}+\dfrac{1}{\mu_n^{(s)}}-1} \tag{40}$$

$$\bar{p}^{(\mathrm{sol})}_{<fn_f>^2} = \frac{1}{\dfrac{1}{\lambda_w^{(s)}}+\dfrac{1}{\mu_w^{(s)}}-1} \tag{41}$$

$$\bar{p}_l^{(\mathrm{sol})} = \frac{\mu_n^{(s)}}{\mu_n^{(s)}+\lambda_n^{(s)}-\lambda_n^{(s)}\mu_n^{(s)}} \tag{42}$$

$$\bar{p}_{l^2}^{(\mathrm{sol})} = \frac{\lambda_n^{(s)}(\mu^{(s)}-1)}{\lambda_w^{(s)}+\mu_w^{(s)}-\lambda_w^{(s)}\mu_w^{(s)}} + 1 \tag{43}$$

where:

$$\begin{aligned} &\lambda_n^{(s)} = 1/\sum_f (w_f'^{(s)}/f),\ \lambda_w^{(s)} = \sum_f fw_f'^{(s)} \\ &\mu_n^{(s)} = 1/\sum_k (p_k'^{(s)}/k),\ \mu_w^{(s)} = \sum_k kp_k'^{(s)}\,. \end{aligned} \tag{44}$$

These equations will be employed for practical problems in succeeding papers.

Size Distribution (II)

In this section we will discuss briefly the case in which the interunit junctions are characterized not only by their order, but also by the energy of their formation.

Let us refer to $J_k^{(i_k)}$ as the number of interunit junctions, of which the order is k and the energy is specified as the i_kth different value, and $j_k^{(i_k)}$ as the number of such interunit junctions in one polymeric molecule. Then, the probability, $p_k^{(i_k)}$, at which a functional group is involved in the formation of the interunit junction described above may be written as:

$$\bar{p}_k^{(i_k)} = \frac{kJ_k^{(i_k)}}{\sum_k kJ_k} \tag{45}$$

where:

$$J_k = \sum_{i_k} J_k^{(i_k)} \tag{46}$$

and, therefore, $p_k = \sum_{i_k} p_k^{(i_k)}$. (47)

With $p_k^{(i_k)}$ defined as above, the most probable distribution may similarly be obtained as;

$$m(\boldsymbol{j}^{(i)}\,;\,\boldsymbol{n}) = (\sum_f fN_f)\frac{(\sum_k j_k)!}{(\sum_k j_k)}\cdot\frac{(\sum_f n_f)!}{(\sum_f n_f)} \times \prod_{k,i_k}\frac{{p_k^{(i_k)}}^{j_k^{(i_k)}}}{j_k^{(i_k)}!}\prod_f \frac{w_f^{n_f}}{n_f!} \tag{48}$$

where:

$$j_k = \sum_{i_k} j_k^{(i_k)}\,. \tag{49}$$

Since, from the definition by Eq. (47), the μ_n, μ_w and μ_z' symbols can be used with the same meanings as the definitions by Eqs. (6), (7) and (23), any of results presented by μ and λ in previous sections are also valid in this case.

The distribution presented here is very useful in solving practical problems.

Applications to Polycondensation

Condensation of a Distribution of Functionalities with a Bifunctional Interunit Junctions. First let us take a sample calculation from the field of the most familiar and well known condensation between monomers or the cross-linking of primary chains with a distribution of functionalities, where a reacted site corresponds to a bifunctional interunit junction and an unreacted site, to a monofunctional one.

When we denote the probabilities of forming these interunit junctions as $p_2=\alpha$ and $p_1=1-\alpha$ respectively, the molecular size distribution is easily reduced from Eq. (13) to:

$$m(\{j_1,\ j_2\}\ ;\ \{n_f\}) = (\sum_f fN_f)\frac{(\sum(f-1)n_f)!}{(\sum(f-2)n_f+2)!}$$
$$\times\alpha^{\sum_f n_f-1}\ (1-\alpha)^{\sum_f (f-1)n_f+2}\ \Pi\frac{w_f{}^{n_f}}{n_f!} \qquad (50)$$

where, from Eq. (12):

$$j_1 = \sum_f(f-2)n_f + 2, \quad j_2 = \sum_f n_f - 1.$$

The weight-average molecular size is, from Eq. (37):

$$\bar{p}_{<fn_f>^2} = \frac{(1+\alpha)\lambda_w}{1-\alpha(\lambda_w-1)} \qquad (51)$$

since $\mu_w = 1+\alpha$ in Eq. (37). Equations (50) and (51) are completely consistent with Stockmayer's results.[2)]

Post-gelation relationships are expressed below with the lower real positive root, x_1, of the characteristic equation, Eq. (26′-1), where u is reduced to:

$$u = 1 - \alpha + \alpha x. \qquad (51)$$

The sol fraction, W_{sol}, is, from Eq. (28):

$$W_{\text{sol}} = x_1u_1 = x_1(1 - \alpha + \alpha x_1) \qquad (52)$$

and is also:

$$= \sum_f w_f{}^{(s)} = \sum_f w_f u_1{}^f \qquad (53)$$

since $w_f{}^{(s)}$ is given by:

$$w_f{}^{(s)} = w_f u_1{}^f. \qquad (54)$$

Hence, $u_1{}^f$ represents the probability that an f-functional monomer selected at random is a part of the sol fraction. The fraction of reacted functional groups (or the cross-linking density) in the sol and that of unreacted are, from Eqs. (31) and (32) respectively:

$$p_2{}'^{(s)} = \alpha x_1{}^2/W_{\text{sol}} \qquad (55)$$

and

$$p_1{}'^{(s)} = (1 - \alpha)x_1/W_{\text{sol}}\,. \qquad (56)$$

Similarly, these fractions in the gel are, respectively:

$$p_2{}'^{(g)} = \alpha(1 - x_1{}^2)/W_{\text{gel}} \qquad (57)$$

and:

$$p_1{}'^{(g)} = (1 - \alpha)(1 - x_1)/W_{\text{gel}}\,. \qquad (58)$$

These results (Eqs. (26′-1), (51)—(58)) are consistent with Flory's[1)] derivation, although that was derived with quite a different method, *i. e.*, with a help of the probability theory. Gordon[9)] had also derived the same results as Flory's (and hence ours) by yet another method, *i. e.*, by an adaption of Good's stochastic theory of branching processes, where a generating function corresponding to Eq. (26) was used in quite a general form; he obtained an exact sol fraction equation for the vulcanization of chains obeying the Flory distribution.

When the α is small (and the functionality, f, is, therefore, great), Flory showed that x_1 and u_1 may be approximated as $x_1 \cong W_{\text{sol}}$ and $u_1 \cong 1-\alpha(1-W_{\text{sol}})$ respectively; hence, from Eq. (53):

$$W_{\text{sol}} \cong \sum_f w_f[1 - \alpha(1 - W_{\text{sol}})]^f \qquad (54')$$

Eq. (54′) may be further approximated as:

$$W_{\text{sol}} \cong \sum_f w_f e^{-\alpha f(1-W_{\text{sol}})} \qquad (59)$$

or:

$$\cong 1 - \frac{2(\lambda_w\alpha-1)}{\lambda_z\alpha^2} \qquad (60)$$

where $\lambda_z = \sum_f f^2 w_f$. For the self-condensation of f-functional monomers, or for the vulcanization of long chains of equal length ($w_f = 1$), Eq. (59) leads to a formula quoted by Flory[1)] and Charlesby[8)]. Furthermore, for the vulcanization of chains obeying the Flory distribution, $w_f = f(1-p)^2\cdot p^{f-1}$, where p is the fractional conversion of the functionalities used in the precondensation of the chains or the probability that a chain had propagated.

$$W_{\text{sol}} = 1 - 2\frac{(1-p)[(1+p)\alpha-(1-p)]}{(1+4p+p^2)\alpha^2} \qquad (61)$$

since $\lambda_w = (1+p)/(1-p)$ and $\lambda_z = (1+4p+p^2)/(1-p)^2$ in this case.

When we denote the fraction of reacted functional groups in the sol as $p_2{}'^{(s)} = \alpha'$ (and hence $p_1{}'^{(s)} = 1-\alpha$), simple algebra gives these other expressions of the same results:

$$x_1 = \frac{\alpha'(1-\alpha)}{\alpha(1-\alpha')} \qquad (62)$$

$$u_1 = \frac{\alpha-1}{1-\alpha'} \qquad (63)$$

$$w_f{}^{(s)} = w_f\left(\frac{1-\alpha}{1-\alpha'}\right)^f \qquad (64)$$

$$W_{\text{sol}} = \frac{\alpha'(1-\alpha)^2}{\alpha(1-\alpha')^2} = \sum_f w_f\left(\frac{1-\alpha}{1-\alpha'}\right)^f \qquad (65)$$

$$p_2{}'^{(g)} = \frac{\alpha+\alpha'-2\alpha\alpha'}{1-\alpha\alpha'} \qquad (66)$$

$$p_1{}'^{(g)} = \frac{(1-\alpha)(1-\alpha')}{1-\alpha\alpha'} \qquad (67)$$

$$p^{(\text{sol})}_{<fn_f>} = \frac{2}{2-\alpha'\lambda_n{}^{(s)}} \qquad (68)$$

$$p^{(\text{sol})}_{<fn_f>^2} = \frac{(1+\alpha')\lambda_w{}^{(s)}}{1-(\lambda_w{}^{(s)}-1)\alpha'} \qquad (69)$$

where $\lambda_n{}^{(s)}$ and $\lambda_w{}^{(s)}$ are the number and the weight-average values of the functionality in the sol fraction defined by Eqs. (44). Equation (65) may be employed to obtain α' at a given α. For the self-condensation of f-functional monomers ($w_f = 1$),

$$W_{\text{sol}} = w_f{}^{(s)} = \left(\frac{1-\alpha}{1-\alpha'}\right)^f = \frac{\alpha'(1-\alpha)^2}{\alpha(1-\alpha')^2}\,. \qquad (70)$$

Good[10)] has given a more detailed discussion of

[10)] I. J. Good, *Proc. Roy. Soc.*, **A272**, 54 (1963).

this case, especially for the case when $f=4$.

For the condensation of the bifunctional with f-functional monomers, Eq. (64) can be reduced to:

$$w_2^{(s)} = w_2\left(\frac{1-\alpha}{1-\alpha'}\right)^2$$

$$w_f^{(s)} = w_f\left(\frac{1-\alpha}{1-\alpha'}\right)^f$$

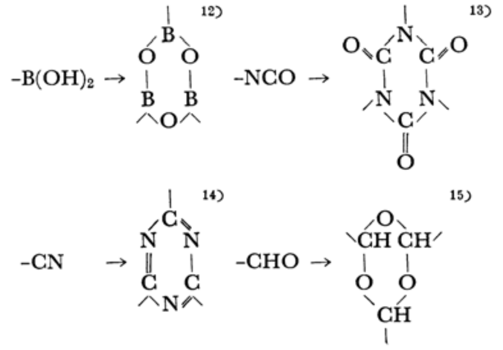
where $w_2+w_f=1$, and where, if the proportion of f-functional monomers is small ($w_f \ll 1$):

$$W_{\mathrm{sol}} \cong w_2^{(s)} = \left(\frac{1-\alpha}{1-\alpha'}\right)^2 \qquad (71)$$

Eqs. (70) and (71) are nothing but the results derived by Flory.[1]

Here we may point out that Eqs. (62) and (63) were also derived by Case[11] in his discussion of the branching in polymers formed from the self-condensation of f-functional monomers, where u_1 was interpreted to be the fraction of chains leading to a finite assembly of chains, and that Eq. (66) was first proposed by Stockmayer,[2] who said, however, that Eq. (66) was not physically rigorous.

Condensation of a Distribution of Functionalities with a Terfunctional Interunit Junction. Another example will be given, that of a terfunctional interunit junction which is formed, for instance, by the following reactions:



When we denote the fraction of reacted functional groups, *i. e.*, the probability of forming of a terfunctional interunit junction, as $p_3=\alpha$ (hence $p_1=1-\alpha$), the molecular size distribution is reduced as well to:

$$m(\{j_1, j_3\} ; \{n_f\}) =$$

$$(\sum_f fN_f)\frac{(\sum_f(f-1)n_f)!(\sum_f n_f-1)!}{(\sum_f fn_f-j_3)!\,j_3!}$$

$$\times\ \alpha^{j_3}(1-\alpha)^{\sum_f n_f-j_3}\prod_f\frac{w_f^{n_f}}{n_f!} \qquad (72)$$

where $2j_3=\sum_f n_f-1$, $j_1=\sum_f fn_f-j_3$.

The number and weight-average molecular sizes are, from Eqs. (36) and (37) respectively:

$$\bar{p}_{<fn_f>} = \frac{3\lambda_n}{3-2\alpha\lambda_n}$$

$$\bar{p}_{<fn_f>^2} = \frac{(1+2\alpha)\lambda_w}{1-2\alpha(\lambda_w-1)}$$

since $\mu_n=3/(3-2\alpha)$ and $\mu_w=1+2\alpha$ in Eqs. (36) and (37). The gel point may be characterized as:

$$2\alpha(\lambda_w-1)=1\,. \qquad (74)$$

Eqs. (72), (73), and (74) are consistent with the results of our previous papers.[5]

Similarly, we can obtain post-gelation relationships with the lower positive real root, x_1, of the characteristic equation, here written as:

$$x = \sum_f w_f u^{f-1}, \quad u = 1-\alpha+\alpha x^2\,. \qquad (75)$$

The sol fraction, W_{sol}, is, from Eq. (28):

$$W_{\mathrm{sol}} = x_1(1-\alpha+\alpha x_1^2) = \sum_f w_f u_1^f\,. \qquad (76)$$

The fraction, $p_3'^{(s)}$, of reacted functional groups in the sol phase is:

$$p_3'^{(s)} = \alpha x_1^3/W_{\mathrm{sol}}\,. \qquad (77)$$

When the functionality, f, is large, x_1 and u_1 may be approximated, respectively, as $x_1 \cong W_{\mathrm{sol}}$ and $u_1 \cong 1-\alpha(1-W_{\mathrm{sol}}^2)$ as before; consequently, from Eq. (76):

$$W_{\mathrm{sol}} \cong \sum_f w_f[1-\alpha(1-W_{\mathrm{sol}}^2)]^f\,. \qquad (78)$$

Similarly, this may be further approximated as:

$$\cong \sum_f w_f e^{-\alpha f(1-W_{\mathrm{sol}}^2)} \qquad (79)$$

or:

$$\cong \sqrt{1-\frac{2\ \alpha\lambda_w-1}{\alpha^2(\lambda_w+\lambda_z)}} \qquad (80)$$

or to a further approximation:

$$W_{\mathrm{sol}} \cong 1-\frac{2\alpha\lambda_w-1}{2\alpha^2(\lambda_w+\lambda_z)}\,. \qquad (81)$$

When we denote $p_3'^{(s)}=\alpha'$, we can obtain other expressions of the same results, namely:

$$x_1 = \sqrt{\frac{\alpha'(1-\alpha)}{\alpha(1-\alpha')}} \qquad (82)$$

$$u_1 = \frac{1-\alpha}{1-\alpha'} \qquad (83)$$

$$w_f^{(s)} = w_f\left(\frac{1-\alpha}{1-\alpha'}\right)^f \qquad (84)$$

$$W_{\mathrm{sol}} = \sqrt{\frac{\alpha'}{\alpha}\left(\frac{1-\alpha}{1-\alpha'}\right)^3} \qquad (85)$$

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11) L. C. Case, *J, Polymer Sci.*, **45**, 397 (1960).
12) O. C. Musgrave, *Chem.* & *Ind.*, **1957**, 1151.
13) T. Yamabe and K. Fukui, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 690 (1963).
14) M. S. Smolin and L. Rapoport, "The Chemistry of Heterocyclic Compounds, *s*-Triazines and Derivatives," Interscience Pub. Inc., N. Y. (1959).
15) F. L. Ramp, E. T. Dewitt and L. E. Trapasse, *J. Polymer Sci.*, **A1-4**, 2267 (1966).

$$\bar{p}^{(\mathrm{sol})}_{<fn_f>} = \frac{3\lambda_n{}^{(s)}}{3-2\alpha'\lambda_n{}^{(s)}} \tag{86}$$

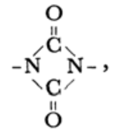
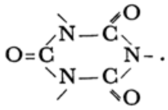
$$\bar{p}^{(\mathrm{sol})}_{<fn_f>^2} = \frac{(1+2\alpha')\lambda_w{}^{(s)}}{1-2\alpha'(\lambda_w{}^{(s)}-1)}\,. \tag{87}$$

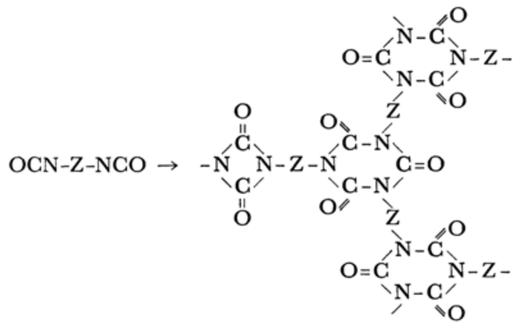
It is impossible, however, for us to obtain the root in a simple explicit form except in a special case, *i. e.*, $f=2$, where:

$$x_1 = u_1 = \frac{1-\alpha}{\alpha} \tag{88}$$

since, from Eq. (75), $\alpha'=1-\alpha$. With this root, we can rewrite, for example, the sol fraction as:

$$W_{\mathrm{sol}} = \left(\frac{1-\alpha}{\alpha}\right)^2. \tag{89}$$

Condensation of Bifunctional Monomers (f=2) with the Formation of both Bi- and Terfunctional Interunit Junctions. As a characteristic example of the present theory, we will treat the case in which the polycondensation of bifunctional monomers proceeds with the formation of both bi- and terfunctional interunit junctions, as, for example, in the polymerization of isocyanate compounds,[13,16] where a bifunctional interunit junction corresponds to an uretidinedione group,  and a terfunctional junction, to a isocyanuric ring, .



Here we will try to obtain the post-gelation relationships because we have already reported about the pre-gelation period.[7] In this case, the root, x_1, of the characteristic equation:

$$x(=u) = p_1 + p_2x + p_3x^2 \tag{90}$$

is obtained as:

$$x_1(=u_1) = p_1/p_3 \tag{91}$$

where $p_1+p_2+p_3=1$ and $p_3>p_1$ after the gel point. Then, the sol fraction, W_{sol}, is:

$$W_{\mathrm{sol}} = (p_1/p_3)^2 \tag{92}$$

Likewise, the other quantities after the gel point are given as follows:

$$\begin{aligned}
&p_1'^{(s)} = p_3; \quad p_2'^{(s)} = p_2; \quad p_3'^{(s)} = p_1;\\
&p_1'^{(g)} = p_1/(1+p_1); \quad p_2'^{(g)} = p_2;\\
&p_3'^{(g)} = (p_1^2+p_1p_3+p_3^2)/(p_1+p_3)\\
&\bar{p}^{(\mathrm{sol})}_{<2n>} = 6/(3p_3-p_1);\\
&\bar{p}^{(\mathrm{sol})}_{<2n>^2} = 2(2+p_1-p_3)/(p_3-p_1).
\end{aligned} \tag{93}$$

It is noticeable that the probability of forming a bifunctional interunit junction possesses the same value in both the sol and gel phases after the gel point.

Polycondensation between A and B Functional Groups. Let us treat here the case of polycondensation between A and B groups in a mixture of $N_1{}^{\mathrm{A}}$ mono-, $N_2{}^{\mathrm{A}}$ di-,..., $N_f{}^{\mathrm{A}}$ f-functional A monomers with all equireactive A groups, and $N_1{}^{\mathrm{B}}$ mono-, $N_2{}^{\mathrm{B}}$ di-,..., $N_g{}^{\mathrm{B}}$: g-functional B monomers with all equireactive B groups, where polymers with structures such as the one shown in Fig. 1 will be formed:

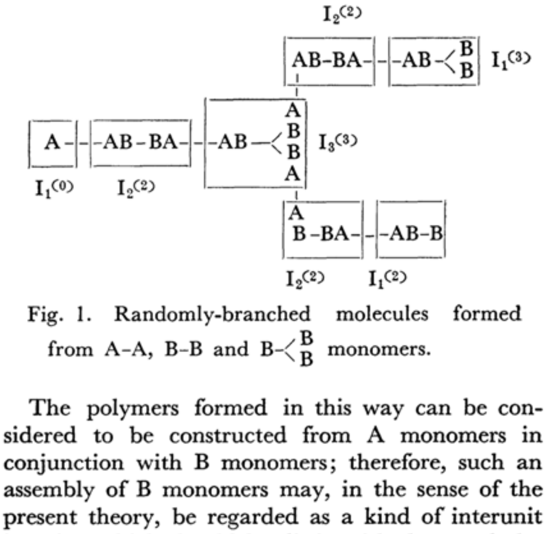


Fig. 1. Randomly-branched molecules formed from A-A, B-B and B-<$\substack{\mathrm{B}\\ \mathrm{B}}$ monomers.

The polymers formed in this way can be considered to be constructed from A monomers in conjunction with B monomers; therefore, such an assembly of B monomers may, in the sense of the present theory, be regarded as a kind of interunit junction which should be distinguished not only by the order of the interunit junction, but also by the functionality of the B monomer. This case, therefore, corresponds to one of examples of the part II in the present paper.

When we represent the unreacted A group by $\mathrm{I}_1(0)$ and the g-functional B monomer, the k of which have reacted with A groups ($g\geqq k\geqq 1$), by $\mathrm{I}_k(g)$, the probabilities of forming of these interunit junctions may readily be given as:

$$p_1(0) = 1-p \tag{94}$$

$$p_k{}^{(g)} = p_{g-1}C_{k-1}q^{k-1}(1-q)^{g-k}w_g. \tag{95}$$

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16) T. Yamabe, A. Nagasawa, H. Kitano and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 821 (1963).

Hence, from Eq. (47):

$$p_k = \sum_{g \geqq k \geqq 1} p_k^{(g)} \tag{96}$$

where p is the fraction of reacted A groups and q is that of B groups, and

$$w_f = \frac{fN_f^{\mathrm{A}}}{\sum\limits_f fN_f^{\mathrm{A}}} \qquad w_g = \frac{gN_g^{\mathrm{B}}}{\sum\limits_g gN_g^{\mathrm{B}}}\,.$$

In order to check our calculations, let us now obtain the relation at the gel point. In the present case $u(x)$ is:

$$\begin{aligned} u(x) &= \sum_k p_k x^{k-1} \\ &= 1 - p + p\sum_g w_g(1-q+qx)^{g-1}\,. \end{aligned} \tag{97}$$

Hence:

$$u'(1) = pq\sum_g (g-1)w_g\,. \tag{98}$$

From Eq. (19) the relation at the gel point is found to be:

$$\begin{aligned} 1 &= (\lambda_w{}^{(f)} - 1)(\mu_w - 1) = (\lambda_w{}^{(f)} - 1)u'(1) \\ &= pq(\lambda_w{}^{(f)} - 1)(\lambda_w{}^{(g)} - 1) \end{aligned} \tag{99}$$

where:

$$\lambda_w{}^{(g)} = \sum_g g w_g, \qquad \lambda_w{}^{(f)} = \sum_f f w_f$$

which agrees with the results of Stockmayer's calculations.[17)]

Moreover, we can obtain post-gelation relationships using the solution, x_1, of the characteristic equation:

$$x = \sum_f w_f u^{f-1}\,. \tag{100}$$

The soluble parts of the weight fractions of f-functional A monomers and g-functional B monomers are given easily by:

$$w_f{}^{(s)} = w_f u_1{}^f \tag{101}$$

$$w_g{}^{(s)} = w_g x_1{}'^g \tag{102}$$

where:

$$x_1{}' = 1 - q + qx_1. \tag{103}$$

For a simple case of A-A + B-B + $\mathrm{B}\text{-}\!<^{\mathrm{B}}_{\mathrm{B}}$, Eq. (100) can easily be solved, obtaining the results:

$$x_1 = u_1 = \frac{1-\alpha(2-q)}{\alpha q} \tag{104}$$

$$x_1{}' = \frac{1-\alpha}{\alpha} \tag{105}$$

where:

$$\alpha = \frac{pqw_3}{1-pqw_2} \tag{106}$$

which is the so-called expected number of branching, a term first introduced by Flory.

With these results, the weight fraction of A monomers in the sol phase, $W_{\mathrm{sol}}{}^{\mathrm{A}}$, is:

$$W_{\mathrm{sol}}{}^{\mathrm{A}} = \left[\frac{1-\alpha(2-q)}{\alpha q}\right]^2 \tag{107}$$

and the weight fractions of B monomers in the sol phase, $w_2{}^{\mathrm{B}(s)}$ and $w_3{}^{\mathrm{B}(s)}$, are given, respectively, by:

$$w_2{}^{\mathrm{B}(s)} = w_2{}^{\mathrm{B}}\left(\frac{1-\alpha}{\alpha}\right)^2 \tag{108}$$

and

$$w_3{}^{\mathrm{B}(s)} = w_3{}^{\mathrm{B}}\left(\frac{1-\alpha}{\alpha}\right)^3. \tag{109}$$

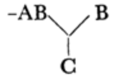
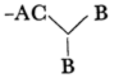
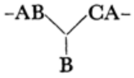
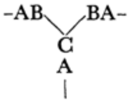
$W_{\mathrm{sol}}{}^{\mathrm{B}}$ is, accordingly, the weight fraction of B monomers in the sol phase:

$$\begin{aligned} W_{\mathrm{sol}}{}^{\mathrm{B}} &= w_2{}^{\mathrm{B}(s)} + w_3{}^{\mathrm{B}(s)} \\ &= \frac{(1-\alpha)^2}{\alpha^2}\left(w_2{}^{\mathrm{B}} + w_3{}^{\mathrm{B}}\left(\frac{1-\alpha}{\alpha}\right)\right). \end{aligned} \tag{110}$$

Further discussions will be undertaken elsewhere.

Polycondensation between A-A and $\mathrm{C}\text{-}\!<^{\mathrm{B}}_{\mathrm{B}}$ Monomers. As the last sample calculation, let us treat the case of polycondensation between A-A (or A_2) and $\mathrm{C}\text{-}\!<^{\mathrm{B}}_{\mathrm{B}}$ (or B_2C) monomers, where the AB and AC reactions are possible. The glycerol/adipic acid system may be used as practical example.

Here, the interunit junctions to be considered and their probabilities may be given as follows:

Interunit junctions		Probabilities
-A	$\equiv \mathrm{I}_1{}^{(0)}$	$p_1{}^{(0)} = 1-p$
	$\equiv \mathrm{I}_1{}^{(\mathrm{B})}$	$p_1{}^{(\mathrm{B})} = 2q(1-q)(1-r)\beta$
	$\equiv \mathrm{I}_1{}^{(\mathrm{C})}$	$p_1{}^{(\mathrm{C})} = r(1-q)^2\beta$
	$\equiv \mathrm{I}_2{}^{(\mathrm{B}_2)}$	$p_2{}^{(\mathrm{B}_2)} = 2q^2(1-r)\beta$
	$\equiv \mathrm{I}_2{}^{(\mathrm{BC})}$	$p_2{}^{(\mathrm{BC})} = 4qr(1-q)\beta$
	$\equiv \mathrm{I}_3{}^{(\mathrm{B}_2\mathrm{C})}$	$p_3{}^{(\mathrm{B}_2\mathrm{C})} = 3q^2r\beta$

where p, q, and r are the fractions of reacted A, B, and C groups respectively, and where $\beta = 2p/(2q+r)$ or, from stoichiometrie considerations, where $\beta = M/N$, where N and M are the total numbers of A_2 and B_2C monomers respectively.

The molecular size distribution is given from Eq. (48) as:

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17) W. H. Stockmayer, *J. Polymer Sci.*, **9**, 69 (1952).

$$m(\{j_1^{(0)},\ j_1^{(\mathrm{B})},\cdots\}\ ;\ 2n_\mathrm{A}) = 2N\frac{(n_\mathrm{A}-1)!}{(n_\mathrm{A}-n_\mathrm{B}+1)!}(1-p)^{n_\mathrm{A}-n_\mathrm{B}+1}$$
$$\times\frac{p_1{}^{(\mathrm{B})j_1{}^{(\mathrm{B})}}\cdot p_1{}^{(\mathrm{C})j_1{}^{(\mathrm{C})}}\cdot p_2{}^{(\mathrm{BC})j_2{}^{(\mathrm{BC})}}\cdot p_2{}^{(\mathrm{B_2})j_2{}^{(\mathrm{B_2})}}\cdot p_3{}^{(\mathrm{B_2C})j_3{}^{(\mathrm{B_2C})}}}{j_1{}^{(\mathrm{B})}!\ j^{(\mathrm{C})}!\ j_2{}^{(\mathrm{BC})}!\ j_2{}^{(\mathrm{B_2})}!\ j_3{}^{(\mathrm{B_2C})}!} \tag{111}$$

where $J_1{}^{(0)}$, $j_1{}^{(\mathrm{B})}$,... are the numbers of each interunit junction in a polymeric molecule, while n_A and n_B are those of A_2 and B_2C monomers respectively, and where, from Eqs. (14) and (49):

$$\begin{aligned} &j_1{}^{(0)} = n_\mathrm{A} - n_\mathrm{B} + 1, \\ &j_1{}^{(\mathrm{B})} + j_1{}^{(\mathrm{C})} = n_\mathrm{B} - n_\mathrm{A} + j_3 + 1 = j_1 \\ &j_2{}^{(\mathrm{B_2})} + j_2{}^{(\mathrm{BC})} = n_\mathrm{A} - 2j_3 - 1 = j_2 \\ &j_3{}^{(\mathrm{B_2C})} = j_3\,. \end{aligned} \tag{112}$$

Therefore, the fraction of a polymeric molecule composed of n_A A_2 monomers and n_B B_2C monomers is:

$$m(n_\mathrm{A},\ n_\mathrm{B}) = \frac{(n_\mathrm{A}-1)!\ (1-p)^{n_\mathrm{A}-n_\mathrm{B}+1}(r+2q-3gr)^{j_1}(2[q+2r-3qr])^{j_2}(3q^2r)^{j_3}\beta^{n_\mathrm{B}}}{(n_\mathrm{A}-n_\mathrm{B}+1)!\ j_1!\ j_2!\ j_3!} \tag{113}$$

To represent the sol fraction after the gel point, we must find the solution, x_1, of the characteristic equation, which is here written as:

$$\begin{aligned} x = u = 1 - p + \beta\{&2q(1-q)(1-r) + \\ &r(1-q)^2 + [2q^2(1-r) + 4qr(1-q)]x + \\ &3q^2rx^2\} \end{aligned} \tag{114}$$

or:

$$x = 1 - p + \beta\frac{\mathrm{d}v(x)}{\mathrm{d}x} \tag{114'}$$

where $v=(1-q+qx)^2(1-r+rx)$, giving:

$$x_1 = 2q + r + pq(3rq - 2q - 4r)/3pq^2r \tag{115}$$

With this root, the sol fractions of these monomers are found to be, respectively:

$$W_\mathrm{sol}(A_2) = x_1{}^2 \tag{116}$$

and

$$\begin{aligned} W_\mathrm{sol}(B_2C) &= v(x_1) \\ &= (1-q+qx_1)^2(1-r+rx_1) \end{aligned} \tag{117}$$

These equations are in agreement with Gordon's derivations[9] *via* other methods.

Appendix A

First let us consider the sum:

$$S_2{}^{(k)} = \sum j_k(\sum_f n_f)m(\boldsymbol{j};\,\boldsymbol{n}) = \sum_{l=1}^{\infty} m_l{}'^{(k)} \tag{A-1}$$

where:

$$m_l{}'^{(k)} = \sum_{\substack{\sum_f n_f = l \\ \sum_k (k-1)j_k = l-1}} j_k(\sum_f n_f)m(\boldsymbol{j};\,\boldsymbol{n}) \tag{A-2}$$

The summation covers all the terms subject to the conditions:

$$\sum_f n_f = \sum_k (k-1)j_k + 1 = l \tag{A-3}$$

By applying the generating function, $f(x)$, we obtain:

$$m_l{}'^{(k)} = kJ_k \times \left[\begin{matrix}\text{the coefficient of } x^{l-k} \\ \text{in the expansion of } [f(x)]^l\end{matrix}\right].$$

Hence, from Cauchy's therorem:

$$= \frac{kJ_k}{2\pi i}\oint\frac{[f(x)]^l}{x^{l-k+1}}\,\mathrm{d}x \tag{A-4}$$

where the path of integration must be a circle enclosing the point of origin. Now let us define the following function, $H_0{}^k(z)$, as:

$$H_0{}^{(k)}(z) = \sum_{l=0}^{\infty} m_l{}'^{(k)}z^l \tag{A-5}$$

where $m_0{}'^{(k)}(=0)$, which makes no contribution to $H_0{}^{(k)}(z)$, is added for the sake of convienience.

Substituting (A-4) into (A-5), we obtain:

$$H_0{}^{(k)}(z) = \frac{kJ_k}{2\pi i}\sum_{l=0}^{\infty} x^{k-1}\left[\frac{f(x)}{x}\,z\right]^l\mathrm{d}x \tag{A-6}$$

For small enough absolute values of z, it follows that the inequality holds on the path of integration.

$$\left|\frac{f(x)}{x}\,z\right| < 1$$

The summation in (A-6) can, then, be performed before integration; we thus get:

$$H_0{}^{(k)}(z) = \frac{kJ_k}{2\pi i}\oint\frac{x^k}{x - zf(x)}\,\mathrm{d}x \tag{A-7}$$

$$= \frac{kJ_kx_1{}'^k}{1 - zf'(x_1{}')} \tag{A-8}$$

namely:

$$H_0{}^{(k)}(z) = \frac{kJ_kx_1{}'^k}{1 - z(\sum_f(f-1)w_fu_1{}'^{f-2})(\sum_k k-1)p_kx_1{}'^{k-2})}$$

where $x_1{}'$ is defined as the minimum real positive root of the characteristic equation:

$$z = \frac{x}{f(x)} \tag{A-9}$$

for a given real positive z, if we choose the path of integration in such a way that it encloses $x_1{}'$ as the only singularity, which is possible with sufficiently small values of $|z|$.

Although (A-8) is derived for small values of z, it is valid in general through the procedure of analytic continuation. The sum, (A-1), is nothing but (A-5) for $z=1$; accordingly, x_1' is the lower real positive root, x_1 of the characteristic equation:

$$G(x) = x - f(x) = 0 \tag{A-9$'$}$$

As will be shown in Appendix B, x_1 is equal to unity provided that $1 \geqq (\lambda_w - 1)(\mu_w - 1) \geqq 0$ whereas it is less than unity, varying the change of μ_w and λ_w, provided that $(\lambda_w - 1)(\mu_w - 1) > 1$. Therefore, from (A-8), we obtain:

$$S_2^{(k)} = H_0^{(k)}(1) = \frac{kJ_k x_1^k}{1 - f'(x_1)} \tag{A-1$'$}$$

Here let us introduce a function defined as:

$$H_1^{(k)}(z) = \sum_{l=0}^{\infty} \frac{m_l'^{(k)}}{l} z^l \tag{A-10}$$

which is connected to $H_0^{(k)}(z)$ by:

$$H_1^{(k)}(z) = \int_0^z H_0^{(k)}(z') \frac{\mathrm{d}z'}{z'} \tag{A-11}$$

Using the following relation obtained from (A-9):

$$\frac{\mathrm{d}z}{z} = \frac{\mathrm{d}x}{x}(1 - zf'(x)) \tag{A-12}$$

we obtain:

$$H_1^{(k)}(z) = kJ_k \int_0^{x_1'} x^{k-1} \mathrm{d}x = J_k x_1'^k \tag{A-13}$$

which, from the definition (A-10), leads to:

$$S_1^{(k)} = \sum j_k m(\boldsymbol{j}; \boldsymbol{n}) = H_1^{(k)}(z=1) = J_k x_1^k \tag{A-14}$$

By replacing w by p in the generating function, $f(x)$, we can easily obtain:

$$S_2^{(f)} = \sum n_f (\sum_k j_k) m(\boldsymbol{j}; \boldsymbol{n}) = \frac{fN_f u_1^f}{1 - f'(x_1)} \tag{A-15}$$

and, likewise:

$$S_1^{(f)} = \sum n_f m(\boldsymbol{j}; \boldsymbol{n}) = N_f u_1^f \tag{A-16}$$

Eqs. (A-11) and (A-15) show that Eqs. (10) and (11) hold before the gel point, since, then, $x_1 = u_1 = 1$.

Furthermore, from Eqs. (A-1$'$), (A-14), (A-15) and (A-16):

$$\sum(\sum_k j_k) m(\boldsymbol{j}; \boldsymbol{n}) = \sum_k J_k x_1^k \tag{A-17}$$

$$\sum(\sum_f n_f) m(\boldsymbol{j}; \boldsymbol{n}) = \sum_f N_f u_1 \tag{A-18}$$

$$\sum(\sum_k kJ_k)(\sum_f n_f)\, m(\boldsymbol{j}; \boldsymbol{n}) = \frac{\sum_k k^2 J_k x_1^k}{1 - f'(x_1)} \tag{A-19}$$

$$\sum(\sum_f fn_f)(\sum_k j_k)\, m(\boldsymbol{j}; \boldsymbol{n}) = \frac{\sum_f f^2 N_f u_1^f}{1 - f'(x_1)}. \tag{A-20}$$

Using these results, several useful equations may be obtained:

$$\begin{aligned} \sum m(\boldsymbol{j}; \boldsymbol{n}) &= \sum(\sum_f n_f + \sum_k j_k - \sum_f fn_f) m(\boldsymbol{j}; \boldsymbol{n}) \\ &= \sum_k J_k x_1^k + \sum_f N_f u_1^f - (\sum_f fN_f) x_1 u_1 \end{aligned} \tag{A-21}$$

$$\begin{aligned} \sum(\sum_f fn_f) m(\boldsymbol{j}; \boldsymbol{n}) &= \sum_f fN_f u_1^f \\ &= (\sum_f fN_f)(\sum_f w_f u_1^f) \end{aligned} \tag{A-22}$$

$$\sum(\sum_f fn_f)^2 m(\boldsymbol{j}; \boldsymbol{n}) = (\sum_f fN_f)\left(\frac{\sum_k kp_k x_1^k + \sum_f fw_f u_1^f}{1 - f'(x_1)} - x_1 u_1\right) \tag{A-23}$$

$$\sum(\sum_f n_f)^2 m(\boldsymbol{j}; \boldsymbol{n}) = (\sum_f fN_f)\left(\frac{\sum_k (k-1) p_k x_1^k}{1 - f'(x_1)} + \sum_f \frac{w_f}{f} u_1^f\right) \tag{A-24}$$

$$\sum(\sum_k j_k)^2 m(\boldsymbol{j}; \boldsymbol{n}) = (\sum_f fN_f)\left(\frac{\sum_f (f-1) w_f u_1^f}{1 - f'(x_1)} + \sum_k \frac{p_k}{k} x_1^k\right). \tag{A-25}$$

Appendix B

Let us hope consider the functions defined by Eqs. (16) and (26), *i. e.*,

$$g(x) = f(x) - xf'(x) \text{ and } G(x) = x - f(x)$$

and its derivative,

$$G'(x) = 1 - f'(x)$$

Here, from the nature of $G''(x)$ and $g'(x)$, $G'(x)$ and $g(x)$ are known to be monotonously decreasing functions, with the boundary conditions of $g(0) > 0$, $G(0) < 0$, $G'(0) > 0$, and $G(1) = 0$, because $f(x)$ as defined by Eq. (15) is a monotonously increasing positive function with $f(1) = 1$; accordingly, $f'(x)$ and $f''(x)$ are also

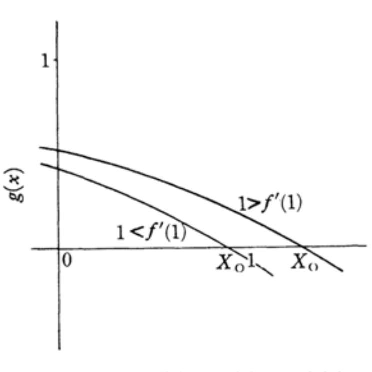

Fig. A-1. $g(x) = f(x) - xf'(x)$.

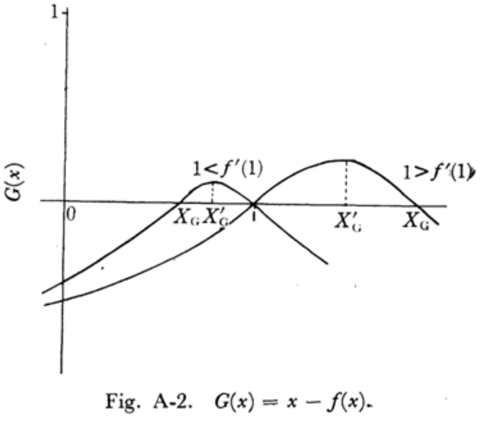

Fig. A-2. $G(x) = x - f(x)$.

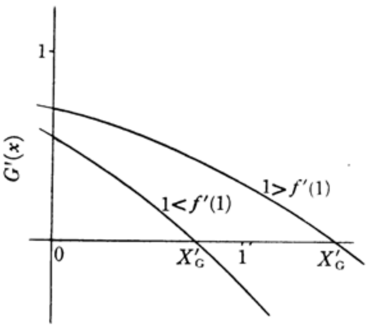

Fig. A-3. $G'(x) = 1 - f'(x)$

monotonously increasing positive functions for $x \geqq 0$.

Therefore, there exists one, and only one, positive real root, x_0 and x_G', for each of the equations, $g(x)=0$ and $G'(x)=0$ respectively, while there exist two positive real roots of the equation, $G(x)=0$, one of which is unity from $G(1)=0$, while the other is denoted by x_G.

Moreover, it is found that if $1>f'(1)$, *i. e.*, if $1>(\lambda_w-1)(\mu_w-1)$, both x_0 and x_G' are larger than unity and x_G is larger than the x_0' derived from Rolle's theory, and that $G(x)>0$ is in the $1<x<x_G$ range, so that $g(x_G')=f(x_G')-x_G'=-G(x_G')<0$, which shows $x_0<x_G'$. The discussion above indicates that $1<x_0<x_G'<x_G$ and, hence, that:

$$\frac{f(x_0)}{x_0} < 1, \ \frac{f(x_0')}{x_0'} < 1$$

satisfying the condition of convergence of the series. On the other hand, if $(\lambda_w-1)(\mu_w-1)>1$, these are in an inverse relationship, namely, $0<x_G<x_G'<x_0<1$. It is only when $x_0 = x_G' = x_G = 1$ that the $1=(\lambda_w-1)(\mu_w-1)$ relation holds.

Moreover, we can prove by Rouche's theorem that $G(x)$ has exactly one root in the interior of C, even if x is a complex variable, where C is a circle of a given radius, γ, between 1 and x_G, with its center at the point of origin.

The circumstances are visualized by Figs. (A-1), (A-2), and (A-3).