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Theory of the Gel-forming Polymerization of Polyepoxy and Related Compounds

Tokio YAMABE and Kenichi FUKUI

Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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A theory of the molecular-size distribution of cross-linked polymers to be formed from a mixture of polyfunctional monomers and mono-functional monomers through step-by-step polymerizations by certain initiators is presented on the assumption that all unconverted functional groups are equireactive for both initiations and propagations, which proceed without termination, transfer, or cyclization. The distribution is obtained by applying the statistical theory of gel formation with multifunctional interunit junctions, which are, in this case, equivalent to cross-linking chains. Some noticeable theoretical results are obtained: (1) the distribution obtained is quite different from that obtained for branched-chain polymers by condensation polymerization; (2) the fraction of converted functional groups at the gel point is independent of the initial concentration of the monofunctional monomer, while it is in proportion to the ratio of the initial concentration of the initiator to that of polyfunctional monomers; (3) there is a certain condition under which the gelation will never take place, even at complete conversion, and (4) the state to be reached after the gel point is quite different from the results obtained previously. The case of a mixture of monomers with any distribution of functionalities is also briefly presented. An explanation of the validity of the distribution beyond the gel point is discussed in the Appendix.

It happens that, in certain step-by-step polymerizations, the chain-initiation and the subsequent addition proceed with comparable velocities, without either termination or transfer. Such is the case in some ring-opening polymerizations of cyclic compounds, such as epoxy, cyclic imino, amide, or anhydride compounds, or in some anionic polymerizations of vinyl compounds.[*1]

The molecular-size distribution of linear polymers obtained from a monofunctional monomer such as ethylene oxide through the step-by-step polymerization was first given by Flory,[1] while the distribution of cross-linked polymers formed from f-functional monomers ($f \geqq 1$) was reported in our own previous paper.[2] Both were obtained by solving kinetic equations describing the polymerization processes.

In the present paper, a theory of the molecular-size distribution of cross-linked polymers to be formed from a mixture of polyfunctional and monofunctional monomers is presented. By this theory, one can sufficiently explain the characteristic features of such a polymerization process without any loss of generality. The condition for the gelation and the property of the sol fraction after the gel point are also investigated. In the last portion of this text, the case of a mixture of polyfunctional monomers with any distribution of their functionality is treated.

The distribution was obtained, not by solving the kinetic equations as in the previous paper, but by applying the statistical theory of polymerization with multifunctional interunit junctions.[3] A chain to be cross-linked may reasonably be regarded as a kind of interunit junction, as was treated previously.[3] With this idea, which is the essential point of the present paper, we are able to obtain the exact product distribution for the step-by-step polymerization process.

Let us treat first a mixture of f-functional monomers and monofunctional monomers, and then a mixture of monomers of various functionalities. The former and the latter are referred to as Case I and Case II respectively.

Case I. A System Composed of f-Functional and Monofunctional Monomers

Molecular-size Distribution. It should be remarked at the outset that the treatment presented below is applicable to all polymerization processes of this kind which fulfill the following assumptions, already set up in the previous paper:[2] (1) Each polyfunctional monomer possesses f identical

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[*1] For instance, see F. W. Billmeyer, Jr., "Textbook of Polymer Science," Interscience, New York (1962).

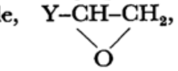
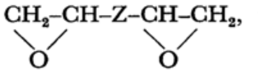
[1] P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York (1953).

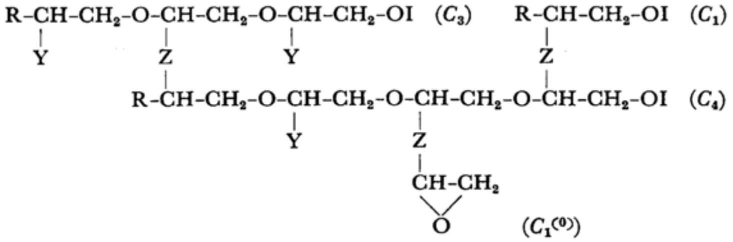
[2] K. Fukui and T. Yamabe, *J. Polymer Sci.*, **A2**, 3743 (1964).

[3] K. Fukui and T. Yamabe, This Bulletin, **40,** 2052 (1967).

functional groups, and all unconverted functional groups on the monomers or polymers are equivalent and of the same reactivity. (2) Any unconverted functional group can react with the initiator to be changed into a growing chain, and the rate of the initiating step is equal to that of the subsequent addition step. (3) Moreover, reactions proceed without either termination or transfer. Therefore, the number of growing chains is equal to the number of initiators consumed. (4) No formation of rings, not even of the small ones formed by intra-inter polymerization, occurs through the process of polymerization.

Suitable examples may be supplied from the polymerizations of polyepoxides initiated by some hydroxy compounds or secondary amines, or catalyzed by some tertiary amines or boron trifluoride complexes.[4,5] Another ideal case may be realized in the anionic polymerization of some polyvinyl compounds by sodium.[6]

Under these assumptions, a polymeric molecule is composed of various lengths of growing chains. This may be visualized by the following scheme, in which the example taken is the ring-opening copolymerization of monoepoxide,  $Y\text{-}CH\text{-}CH_2$, and diepoxide,  $CH_2\text{-}CH\text{-}Z\text{-}CH\text{-}CH_2$, where RI is the initiator and where Y and Z designate the residues of monoepoxide and diepoxide respectively:



In this schematic presentation, C_k and $C_1^{(0)}$ stand for a growing chain containing k functional groups and an unconverted functional group respectively. The polymeric molecule can be described, therefore, by specifying the length of each growing chain, that is, the number of functional groups involved in it, if any further difference in the structure of the polymeric molecule is disregarded.

On the other hand, a previous paper[3] has treated, in general, the case where the polymerization proceeds with various kinds of interunit junctions being concurrently formed in a system. Here the term "interunit junction" indicates a junction connecting several functional groups, each in different monomeric units, irrespective of the order of combination. According to the number of functional groups involved in one interunit junction formed, they are named as mono-, bi-, ter-, …, and, more generally, multifunctional interunit junctions. Following this definition, a growing chain composed of k functional units is a k-functional interunit junction.

Moreover, it should be noted here that there are two kinds of monofunctional interunit junctions. The one is apparently a growing chain produced from a functional group indicated by C_1, and the other is that of an unconverted functional group indicated by $C_1^{(0)}$ in the sense of the scheme mentioned above. In this fashion the molecular-size distribution of the polymerization of polyfunctional epoxy or vinyl compounds can be obtained exactly, as long as the polymerization satisfies the conditions already assumed.

Now, let I_0, N_1, and N_f be the numbers of initially-existing initiators, monofunctional monomers, and f-functional monomers respectively, in a system and let $M(n_1, n_f;\ \nu)$ be the number of polymeric molecules containing ν growing chains, n_1 monofunctional monomers, and n_f f-functional monomers.

Then, as the polymeric molecule has ν growing chains, it contains $(n_1+n_f+\nu-1)$ units of converted functional groups and, hence, $\{(f-1)n_f-\nu+1\}$ unconverted functional groups, since intramolecular reactions are excluded. According to this definition, $M(0, 0;\ 1)$, $M(1, 0;\ 0)$, and $M(0, 1;\ 0)$ represent the instantaneous values of the numbers of initiators, monofunctional monomers, and f-functional monomers respectively.

From the above definitions, we obtain:

$$I_0 = \sum M(n_1, n_f;\ \nu) \qquad (1)$$

$$N_1 = \sum n_1 M(n_1,\ n_f;\ \nu) \qquad (2)$$

$$N_f = \sum n_f M(n_1,\ n_f;\ \nu) \qquad (3)$$

where the summation should cover all the integers of n_1, n_f, and ν satisfying $(f-1)n_f+1 \geqq \nu \geqq 0$.

Moreover, if we denote the total number of molecules at the initial state and at a given instant by M_0 and M, respectively, these can be obtained

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[4] H. Lee and K. Neville, "Epoxy Resin," McGraw Hill Book Co., New York (1957).

[5] I. Skeist, "Epoxy Resins," Reinhold Publishing Co., New York (1958).

[6] M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956); R. Waack, A. Rembaum, J. D. Coombes and M. Szwarc, *ibid.*, **79**, 2026 (1957).

as follows:

$$M = \sum M(n_1,\ n_f;\ \nu) \tag{4}$$

$$M_0 = I_0 + N_1 + N_f = \sum(\nu + n_1 + n_f)M(n_1,\ n_f;\ \nu) \tag{5}$$

In order to formulate the molecular-size distribution, it is convenient to introduce two variables, α and ρ, in such a way as:

$$\alpha = F/I_0 \tag{6}$$

$$\begin{aligned}\rho &= (1/F)\sum(n_1+n_f+\nu-1)M(n_1,\ n_f;\ \nu)\\ &= (M_0-M)/F\end{aligned} \tag{7}$$

where α stands for the initial number of functional groups per initiator, where ρ is the fraction of converted functional groups, and where $F = N_1 + fN_f$ is the total number of functional groups in the system.

Now let us attempt to obtain the distribution by the use of the statistical theory of polymerization with multifunctional interunit junctions previously proposed by the present authors.[3]

Let $m(n_1, n_f;\ \{j_k\})$ be the number of polymeric molecules which are composed of n_1 monofunctional monomeric units and n_f f-functional monomereric units and are also constructed by j_1 monofunctional, j_2 bifunctional, $\cdots$, j_k k-functional chains. The set of these numbers is designated as $\{j_k\}$. In particular, the number of unconverted functional groups is written as $j_1^{(0)}$. Also, we designate the probabilities that a functional group is involved in the growing chain composed of k functional chains ($k \geqq 1$) and in that of unconverted ones as P_k and $P_1^{(0)}$ respectively. It obviously follows that:

$$P_1^{(0)} + \sum_{k=1} P_k = 1 \tag{8}$$

According to Eq. (48) in Ref. 3, the most probable distribution of $m(n_1,\ n_f;\ \{j_k\})$ in equilibrium is given by:

$$m(n_1,\ n_f; \{j_k\}) = (N_1+fN_f)((f-1)n_f)!(n_1+n_f-1)!\frac{w_1^{n_1}}{n_1!}\cdot\frac{w_f^{n_f}}{n_f!}\cdot\frac{P^{j_1^{(0)}}}{j_1^{(0)}}\cdot\prod_{k\geqq 1}\frac{P_k^{j_k}}{j_k!} \tag{9}$$

with these conditions:

$$j_1^{(0)} + \sum_k j_k - 1 = (f-1)n_f \tag{10}$$

and:

$$n_1 + n_f - 1 = \sum_k (k-1)j_k \tag{11}$$

where w_1 and $w_f(=1-w_1)$ are the weight fractions of monofunctional monomers and f-functional monomers respectively; namely,

$$w_1 = N_1/(N_1+fN_f), \qquad w_f = fN_f/(N_1+fN_f) \tag{12}$$

In the step-by-step polymerization, the number of growing chains composed of k functional groups, which is denoted hereafter by J_k, was given by Flory[7] as follows:

$$J_k = \frac{\lambda^k e^{-\lambda}}{k!}I_0 \qquad (k \geqq 1) \tag{13}$$

$$J_1^{(0)} = I_0 e^{-\lambda}$$

The probability of the formation of a k-functional interunit junction, P_k, is then given, according to the definition, by:

$$P_k = \frac{kJ_k}{F} = \frac{I_0}{F}\cdot\frac{\lambda^{k-1}e^{-\lambda}}{(k-1)!} \tag{14}$$

Therefore, the fraction of converted functional groups, ρ, is represented by the following relation:

$$\rho = \sum_{k\geqq 1} P_k = \frac{\lambda I_0}{F}\sum_{k\geqq 1}\frac{\lambda^{k-1}e^{-\lambda}}{(k-1)!} = \frac{\lambda I_0}{F} = \frac{\lambda}{\alpha}$$

which endows the $\lambda(=\alpha\rho)$ of Eq. (13) with the physical meaning as the mean length of a growing chain (see Eq. (25)). Then, the fraction of unconverted functional groups, $P_1^{(0)}$, is given by:

$$P_1^{(0)} = 1 - \sum_{k\geqq 1} P_k = 1 - \rho \tag{16}$$

By the use of these equations, the distribution, $m(n_1,\ n_f;\ \{j_k\})$, may be rewritten as follows:

$$\begin{aligned} m(n_1,\ n_f;\ \{j_k\}) = F\cdot\frac{(fn_f-n_f)!(n_1+n_f-1)!}{(fn_f-n_f+1-\sum\limits_{k\geqq 1} j_k)!}\cdot\frac{w_1^{n_1}}{n_1!}\cdot\frac{w_f^{n_f}}{n_f!}\cdot\prod_k\frac{1}{j_k!((k-1)!)^{j_k}}\\ \times(1-\rho)^{fn_f-n_f+1-\sum_k j_k}\cdot\rho^{\sum_k j_k+n_1+n_f-1}\cdot e^{-(\sum_k j_k)\alpha\rho}\end{aligned} \tag{9'}$$

According to the definition of $M(n_1,\ n_f;\ \nu)$ it is obvious that;

$$M(n_1,\ n_f;\ \nu) = \sum_{\sum_k j_k=\nu} m(n_1,\ n_f;\ \{j_k\}) \tag{17}$$

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[7] P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).

where summation should cover all sets of positive integers (zero included), j_k, which satisfy the condition: $\sum\limits_k j_k=\nu$.

On the other hand, the following mathematical relation is necessary in calculating the summation in Eq. (17):

$$\sum_{\sum\limits_k j_k=\nu}\frac{(\sum\limits_k j_k)!}{\prod\limits_k j_k![(k-1)!]^{j_k}}=\left[\text{the coefficient of } Z^{\sum\limits_k(k-1)j_k} \text{ in the expantion of } \left(\sum_{k\geqq 1}^{\infty}\frac{Z^{k-1}}{(k-1)!}\right)^{\sum\limits_k j_k}\right]$$

$$=\frac{\nu^{\sum\limits_k(k-1)j_k}}{(\sum\limits_k(k-1)j_k)!}=\frac{\nu^{n_1+n_f-1}}{(n_1+n_f-1)!} \tag{18}$$

Using this relation, we finally obtain the size distribution as follows:

$$M(n_1,\ n_f;\ \nu)=(N_1+fN_f)\frac{(fn_f-n_f)!\,\nu^{n_1+n_f-1}}{(fn_f-n_f+1-\nu)!\,\nu!}\cdot\frac{w_1{}^{n_1}}{n_1!}\cdot\frac{w_f{}^{n_f}}{n_f!}\rho^{\nu}(1-\rho)^{(f-1)n_f+1-\nu}(\alpha\rho)^{n_1+n_f-1}\cdot \mathrm{e}^{-\nu\alpha\rho} \tag{17'}$$

The resulting distribution is, however, by no means restricted to the case of equilibrium system; it should be equally applicable to unidirectionally changing systems, as long as the assumptions mentioned above are fulfilled. This point is supported by the fact that the distribution given by Eq. (17′) can equally be derived from differential equations describing the polymerization kinetics, although they are too complex. Also, the following fact helps the present discussion. The distribution for the special case in which only *f*-functional monomers are contained is reduced to the equation:

$$M(0,\ n_f;\ \nu)=\frac{(fN_f)(fn_f-n_f)!\,\nu^{n_f-1}}{\nu!\,(fn_f-n_f+1-\nu)!\,n_f!}\rho^{\nu}(1-\rho)^{(f-1)n_f+1-\nu}(\alpha\rho)^{n_f-1}\mathrm{e}^{-\nu\alpha\rho}$$

which agrees with the distribution function of our previous paper[2] derived from the kinetic method.

The instantaneous values of the initiators, the monofunctional monomers, and the *f*-functional monomers may be presented, respectively, as:

$$M(0,\ 0;\ 1)=I=I_0\mathrm{e}^{-\alpha} \tag{19}$$

$$M(1,\ 0;\ 0)=N_1(1-\rho) \tag{20}$$

$$M(0,\ 1;\ 0)=N_f(1-\rho)^f \tag{21}$$

The number and weight-average molecular sizes can readily be obtained as:

$$\langle P_n\rangle=1+\frac{f\rho}{1-f\rho-(1-\rho)^f+f/\alpha} \tag{22}$$

$$\langle P_w\rangle=1+\frac{(f/\alpha)[(\alpha\rho)^2+2\alpha\rho+(f-1)\alpha\rho^2]}{[1-(1-\rho)^f+f/\alpha][1-(f-1)\alpha\rho^2]} \tag{23}$$

Both the unconverted monomers and the initiators are excluded in these averages.

The number- and the weight-average chain lengths, $\langle k_n\rangle$, $\langle k_w\rangle$, of cross-linked polymers are easily obtained from Eq. (14) as:

$$\langle k_n\rangle=\sum_{k=1}^{\infty}P_k\Big/\sum_{k=1}^{\infty}(P_k/k)=\lambda/(1-\mathrm{e}^{-\lambda}) \tag{24}$$

$$\langle k_w\rangle=\sum_{k=1}^{\infty}kP_k\Big/\sum_{k=1}^{\infty}P_k=1+\lambda \tag{25}$$

where the unconverted functional groups and the initiators are not taken into account.

The Condition for Gelation. The critical condition determining the gel point can be characterized by the following equation, derived from Eqs. (6) and (23):

$$\rho_c=\left[\frac{I_0}{f(f-1)N_f}\right]^{1/2} \tag{26}$$

where ρ_c is the extent of reaction at the gel point. It is remarkable that ρ_c is dependent on the amount of initiators as well as on that of *f*-functional monomers, while it is independent of the amount of monofunctional monomers.

It should be noted here, however, that there exists a restriction for the attainment of the gel point. This comes from the condition $\rho\leqq 1$, which implies that the fraction of converted functional groups should be less than unity. Therefore, it is necessary, on the basis of Eq. (26), that:

$$f(f-1)N_f\geqq I_0 \tag{27}$$

for the attainment of the gel point. If the system is initially prepared, irrespective of the amount of the monofunctional monomer, in such a way that

$$I_0>f(f-1)N_f\geqq 0 \tag{28}$$

the critical conversion, ρ_c, can never be reached at any extent of reaction. Such an amount of *f*-functional monomers compared with that of initiators is too small for the gelation to occur, so such a system will remain as a sol phase. The circumstance mentioned above may be clarified by information as to the number and the weight averages of chains in a mixture of polymeric molecules. Using Eq. (17′), we obtain the number-average number of chains, $\langle\nu_n\rangle$, which is usually called by the crosslinking index, γ:

$$\langle\nu_n\rangle=\frac{\sum\nu M(n_1,n_f;\nu)}{\sum M(n_1,n_f;\nu)}$$

$$=\left[1-\frac{N_f}{I_0}\left(\frac{(1-\rho)^f-(1-f\rho)}{1-\mathrm{e}^{-\alpha\rho}}\right)\right]^{-1} \tag{29}$$

while the weight-average number of chains, $\langle\nu_w\rangle$, is written:

$$\langle\nu_w\rangle=\frac{\sum\nu(n_1+fn_f)M(n_1,n_f;\nu)}{\sum(n_1+fn_f)M(n_1,n_f;\nu)}$$
$$=\frac{1+(f-1)w_f}{(1-w_f(f-1)\alpha\rho^2)(1-w_f(1-\rho)-w_f(1-\rho)^f)} \tag{30}$$

Therefore, the number-average number of chains at the gel point, $\langle\nu_n\rangle_c$, can be represented by:

$$\langle\nu_n\rangle_c\cong\left[\frac{1}{2}+\frac{(f-2)}{3!}\rho_c-\frac{(f-2)(f-3)}{4!}\rho_c{}^2+\cdots\right]^{-1} \tag{31}$$

where the term of $e^{-\alpha\rho}$ is neglected.

If the initial condition, namely, the N_f/I_0, ratio is varied within the range indicated by Eq. (27) within which the gelation occurs, ρ_c will change from zero to unity. Then we have:

$$2\geqq\langle\nu_n\rangle\geqq\frac{f}{f-1} \tag{32}$$

which shows that in the N_1 - N_f system the cross-linking index at the gel point keeps the value between two and $f/(f-1)$ as long as the gelation takes place. On the other hand, $\langle\nu_w\rangle$ tends to become infinite as ρ nears ρ_c, irrespective of the functionality, f, of the polyfunctional monomer.

At complete conversion ($\rho=1$) without gelation, which is attained by means of Eq. (28), the number-average number of branches is:

$$\langle\nu_n\rangle_{\rho=1}=\frac{I_0}{I_0-N_f(f-1)} \tag{33}$$

while the weight-average number is:

$$\langle\nu_w\rangle_{\rho=1}=\frac{N_1+f^2N_f}{N_1+fN_f}\cdot\frac{I_0}{I_0-f(f-1)N_f} \tag{34}$$

The weight-average molecular size is a finite value, as is given by:

$$\langle P_w\rangle_{\rho=1}=\frac{N_1+f^2N_f}{N_1+fN_f}\cdot\frac{I_0+N_1+fN_f}{I_0-f(f-1)N_f} \tag{35}$$

Likewise, according to the variation in the initial ratio, N_f/I_0, in the range of Eq. (28), $\langle\nu_n\rangle_{\rho=1}$ and $\langle\nu_w\rangle_{\rho=1}$ vary in the ranges:

$$\frac{f}{f-1}>\langle\nu_n\rangle_{\rho=1}\geqq1 \tag{36}$$

and

$$\infty>\langle\nu_w\rangle_{\rho=1}\geqq1 \tag{37}$$

respectively.

The small average number of branches indicated by Eq. (36) implies that a small amount of the functional groups of the f-functional monomers specified by the condition of Eq. (28) is consumed by the reaction with the initiator, thus preventing the branching. The chains in polymeric monomers can grow longer and longer by means of the reaction with monofunctional monomers, without any branching in the polymeric molecules. In this way, the average length of a chain, given by Eq. (24), in polymeric molecules finally reaches $\alpha=F/I_0$ at complete conversion.

Furthermore, at a given value of F for a fixed value of I_0, the range of N_1, where the gelation does not occur at any extent of reaction, can be rewritten from Eq. (28) as:

$$F\geqq N_1\geqq F-\frac{I_0}{f-1} \tag{28'}$$

This equation presents the amount of monofunctional monomers which may be present without causing gelation; it may have practical significance since this equation gives the experimental condition under which the polymerization of polyfunctional monomers might be carried out without gelation. The equation determining the gel point reported in a previous paper[2)] is completely consistent with Eq. (26).

The situation is different in the corresponding case of the selfcondensation between f-functional and bi-functional monomers. The fraction of converted functional groups at the gel point, ρ_c in our notation, expressed by Flory[7)] and Stockmayer[8)] as:

$$\rho_c=\frac{1}{1+(f-2)w_f}$$

can never exceed unity, so the gelation always takes place at a certain conversion. Compared with this result, one can recognize that the present treatment indicates the importance of the amount of initiator for the condition of gelation.

Relationships after the Gel Point. This section will be devoted to a discussion of the sol fraction after the gel point has been reached. Our general theory, presented previously,[3)] will be used here.

In the present case, the generating function, $f(x)$, defined by Eq. (15) in Ref. 3 is expressed as follows:

$$f(x)=w_1+w_fu^{f-1} \tag{38}$$

where:

$$u(x)=P_1{}^{(0)}+\sum_{k=1}P_kx^{k-1} \tag{39}$$

or, by the use of Eq. (14):

$$u(x)=1-\rho+\rho e^{-(1-x)\lambda} \tag{39'}$$

The characteristic equation defined by Eq. (26) in Ref. 3 can be readily obtained from Eqs. (38) and (39') as:

$$x=f(x)=w_1+w_f\{1-\rho+\rho e^{-(1-x)\lambda}\}^{f-1} \tag{40}$$

It was proved also in Ref. 3 that, besides the trivial solution $x=1$, there exists another real positive root, $x_1<1$, of Eq. (38) beyond the gel point ($(f-1)\alpha^2>1$). In general, the root is obtained only by numerical methods except in a few special cases.

With this root, x_1, the sol fractions of the mono- and the f-functional monomers, $w_1{}^{(s)}$ and $w_f{}^{(s)}$,

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

are obtained as, respectively (see Eq. (25) in Ref. 3):

$$w_1^{(s)} = w_1 u_1 \tag{41}$$

$$w_f^{(s)} = w_f u_1^f \tag{42}$$

where $u_1 = u(x_1)$.

The total sol fraction, W_{sol}, is then given by:

$$W_{sol} = w_1^{(s)} + w_f^{(s)} = x_1\{1 - \rho + \rho e^{-(1-x_1)\lambda}\} \tag{43}$$

The soluble part, $P_k^{(s)}$, of the weight fraction of C_k-chains is given by:

$$P_k^{(s)} = P_k x_1^k \tag{44}$$

$$^{(s)}P_1^{(0)} = P_1^{(0)} x_1 \tag{45}$$ [*2]

By the use of Eqs. (42) and (43), the probability, $P_k'^{(s)}$, of forming a C_k-chain in the sol phase is obtained as:

$$P_k'^{(s)} = P_k^{(s)}/W_{sol} = P_k x_1^k / W_{sol} \tag{46}$$

The number- and the weight-average lengths of the chains in the sol phase are expressed as follows:

$$\langle k_n \rangle^{(sol)} = \sum_{k=1}^{\infty} P_k'^{(s)} \Big/ \sum_{k=1}^{\infty} (P_k'^{(s)}/k) = \frac{x_1 \lambda}{e^{-\lambda}(e^{x_1 \lambda} - 1)} \tag{47}$$

$$\langle k_w \rangle^{(sol)} = \sum_{k=1}^{\infty} k P_k'^{(s)} \Big/ \sum_{k=1}^{\infty} P_k'^{(s)} = (1 + \lambda x_1) e^{-(1-x_1)\lambda} \tag{48}$$

Equations (47) and (48) show that the average chain length varies with the progress of the reaction after the gel point.

Likewise, the fraction, ρ', of converted functional groups in the sol phase is:

$$\rho' = \sum_{k=1}^{\infty} P_k'^{(s)} = \frac{\rho e^{-(1-x_1)\lambda}}{1 - \rho + \rho e^{-(1-x_1)\lambda}} \tag{49}$$

The quantities of the gel phase are then obtained by their differences from the totals, namely:

$$\left.\begin{aligned} w_f^{(g)} &= w_f - w_f^{(s)} = w_f(1 - u_1^f) \\ w_1^{(g)} &= w_1 - w_1^{(s)} = w_1(1 - u_1) \\ W_{gel} &= 1 - W_{sol} = w_1^{(g)} + w_f^{(g)} \end{aligned}\right\} \tag{50}$$

Similarly, we get:

$$\left.\begin{aligned} P_k^{(g)} &= P_k - P_k^{(s)} = P_k(1 - x_1^k) \\ ^{(g)}P_1^{(0)} &= P_1^{(0)} - {}^{(s)}P_1^{(0)} = P_1^{(0)}(1 - x_1) \end{aligned}\right\} \tag{51}$$

and, hence:

$$\left.\begin{aligned} P_k'^{(g)} &= P_k^{(g)}/W_{gel} \\ ^{(g)}P_1'^{(0)} &= {}^{(g)}P_1^{(0)}/W_{gel} \end{aligned}\right\} \tag{52}$$

The fraction, ρ'', of converted functional groups in the gel phase is obtained from Eq. (52) as follows:

$$\rho'' = \sum_{k=1}^{\infty} P_k'^{(g)} = \frac{\rho(1 - x_1 e^{-(1-x_1)\lambda})}{(1 - x_1) + \rho x_1 (1 - e^{-(1-x_1)\lambda})} \tag{53}$$

The weight-average chain length $\langle k_w \rangle^{(gel)}$ forming the gel phase is presented from Eq. (52):

$$\langle k_w \rangle^{(gel)} = \frac{\sum_{k=1}^{\infty} k P_k^{(g)}}{\sum_{k=1}^{\infty} P_k^{(g)}} = \frac{(1+\lambda) - x_1(1 + x_1\lambda) e^{-(1-x_1)\lambda}}{1 - x_1 e} \tag{54}$$

Especially, at the instant immediately after the gel point, *i. e.*, at the point where:

$$\rho = \rho_c + \Delta\rho \tag{55}$$

x_1 and u_1 are approximated to the first order of $\Delta\rho$ as follows:

$$x_1 \cong 1 - \frac{4(f-1)w_f}{1 + (f-2)\rho_c} \Delta\rho \tag{56}$$

$$u_1 \cong 1 - \frac{4}{1 + (f-2)\rho_c} \Delta\rho \tag{57}$$

With these values of x_1 and u_1, all the quantities expressed in Eqs. (41) to (54) may be approximated in explicit forms as functions of $\Delta\rho$. For example,

$$W_{gel} \cong \frac{4(w_1 + f w_f)}{1 + (f-2)\rho_c} \Delta\rho \tag{50'}$$

$$\rho'' \cong \frac{1 + (f-1) w_f \rho_c}{1 + (f-1) w_f} + \frac{(f-1) w_f \{2 - (2f-5)\rho_c + (f-6)\rho_c^2\}}{(1 - (f-1) w_f)(1 + (f-2)\rho_c)} \Delta\rho \tag{53'}$$

$$\langle k_w \rangle^{(gel)} \cong 1 + \alpha\rho_c + \frac{\alpha\rho_c}{1 + \alpha\rho_c} - \frac{\alpha}{2}(\alpha\rho_c + 2)(\alpha\rho_c - 1)\Delta\rho \tag{54'}$$

At the gel point, $\Delta\rho \to 0$, both ρ'' and $\langle k_w \rangle^{(gel)}$ have finite values, indicated by the first terms of Eqs (53′) and (54′).

Case II. A Mixture of Monomers of Various Functionalities

Molecular-size Distribution. Here let us consider briefly the system of a mixture of polyfunctional monomers with different numbers of equivalent functional groups; say, N_1 monofunctional, N_2 bifunctional, ⋯, and N_s s-functional monomers.

With the same treatment as in Case I, we can obtain the molecular size distribution of the copolymers formed under the same assumptions:

$$M(n_1, n_2, \cdots, n_s; \nu) = (\textstyle\sum sN_s) \dfrac{(\sum_s (s-1) n_s)!\, \nu^{\sum_s n_s - 1}}{\nu!\, (\sum_s (s-1) n_s + 1 - \nu)!} \cdot \Pi \dfrac{w_s^{n_s}}{n_s!} \times \rho^{\nu} (1-\rho)^{\sum_s (s-1) n_s + 1 - \nu} \cdot (\alpha\rho)^{\sum_s n_s - 1} \cdot e^{-\nu\alpha\rho} \tag{58}$$

where:

[*2] Only for $P_1^{(0)}$, the suffixes (s) and (g), indicating the soluble part and the gel respectively, are hereafter replaced by $^{(s)}P_1^{(0)}$ to avoid confusion.

$$w_s = \frac{sN_s}{\sum\limits_s sN_s}, \quad \text{and} \quad \alpha = \frac{\sum\limits_s sN_s}{I_0}$$

The fraction of converted functional groups at the gel point, ρ_c, is given by:

$$\rho_c = \sqrt{\frac{I_0}{\sum\limits_s s(s-1)N_s}} \tag{59}$$

The sol fraction, W_{sol}, is represented by:

$$W_{sol} = \sum_{f=1}^{s} w_f u_1{}^f \tag{60}$$

where x_1 in Eq (39′) defining u_1 is, instead, the lowest positive root of the following equation:

$$x = \sum_{f=1}^{s} w_f u^{f-1} \tag{61}$$

The other relationships after the gel point may be obtained in a similar fashion.

Discussion

First let us discuss the noticeable theoretical finding of Eq. (26), the finding that the fraction of converted functional groups at the gel point depends on the concentration of the initiator or the catalyst.

In the case of the polycondensation of polyfunctional monomers (and, hence, in the case of the radical polymerization of divinyl compounds, which has been considered by Flory and Stockmayer to be equivalent to the case of the self-condensation of tetrafunctional monomers), such a dependency on the initiator has been out of question from the theoretical point of view. Some experimental results show, however, in a few polymerizations of divinyl compounds[9] or diepoxy compounds,[10] a dependency of ρ_c on the initiator concentration which has been confirmed by a careful reinvestigation. For example, Kakurai and Noguchi[10] reported on the curing process of diepoxide (Epon 828) with tertiary amine, where the assumptions set up in the present theoretical treatment seemed to be roughly fulfilled. In their case, they found that $\rho_c=0.5$, independent of the amount of the catalyst employed, using a complicated treatment based on Flory's expectation method; they concluded, from Fig. 1, that this value agreed with the actual observations. Figure 1 seems to show, however, that in fact ρ_c depends upon the amount of the catalyst. If so, it may be of interest to reanalyze these results by means of the present theory, which requires that $\rho_c=1/\sqrt{\alpha}$. The theoretical gel points indicated in Fig. 1 appear to explain the observed gel point satisfactorily.

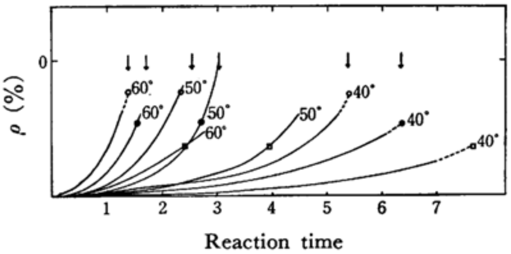

Fig. 1. The comparison between the total gel point (ρ_c) and the experimental ones obtained by Kakurai and Noguchi (from Fig. 4 in Ref. 10).
Theoretical gel points: ○ ($\alpha=7$, $\rho_c=0.37$), ● ($\alpha=14$, $\rho_c=0.28$), □ ($\alpha=28$, $\rho_c=0.18$)
Observed gelation time: ↓ (dotted lines are extrapolated by present authors)

The same paper also reports some experimental information on the sol fraction after the gel point, as is shown in Fig. 2. The theoretical value for the sol fraction of this case ($f=2$, $w_1=0$, $w_f=1$) given by Eq. (42) is presented in the same figure. The relationship between ρ and the reaction time, t, was obtained from Eq. (7a) of Ref. 2, *i. e.*, $\rho=1-\exp(-2kN_2t/\alpha)$ with $2kN_2=2.3$ ¹/hr.[*3] The agreement of the theory with the experimental results is satisfactory.

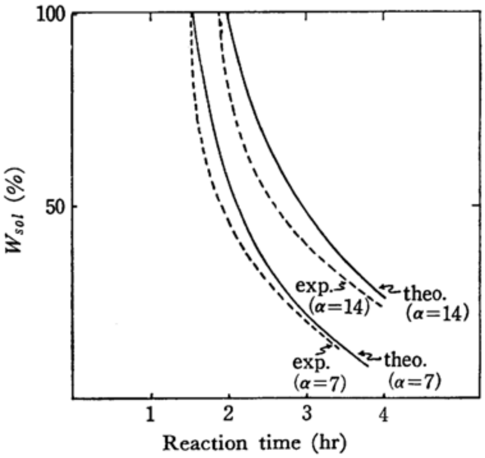

Fig. 2. The comparison between the theoretical sol fraction and the experimental ones obtained by Kakurai and Noguchi (Fig. 5 in Ref. 10).

Usually, the amount of catalysts directly affects the physical properties of the cured epoxy resins. For various kinds of catalysts, the favorable ratio of $\alpha=F/I_0$, *i. e.*, the number of epoxy groups per initiator, is determined through experiments; for instance, Bruin[11] observed that one amine

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[9] M. Gordon and R-J. Roe, *J. Polymer Sci.*, **21**, 27, 39, 57, 75 (1956); C. Walling, *J. Am. Chem. Soc.*, **67**, 441 (1945); L. Minnema and A. J. Staverman, *J. Polymer Sci.*, **29**, 281 (1958); B. T. Storey, *ibid.*, **A3**, 215 (1965).

[10] T. Kakurai and T. Noguchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 827 (1962).

[*3] This value was determined from the observed value of the gelation time.

[11] P. Bruin, *Chem. & Ind.*, **1957**, 616.

nitrogen atom in the catalyst is sufficient for from six to eight epoxide groups (namely, $\alpha=6$—8). It may be reasonable to attribute some physical properties of the gel to the average chain length (Eq. (54)) and the average number of active network chains, which can be calculated by the present theory.

In commercial practice, the epoxy resins are usually modified by reactive diluents, which are usually monoepoxides,[4] such as allylglycidyl ether and phenylglycidyl ether. To the extent that these diluents are incorporated, they lower the epoxide functionality of the resin, *i. e.*, the average number of epoxides per monomeric molecule. Since it is only the excess over one epoxide per molecule that can result in cross-linking, too large an amount of a reactive diluent ruins some physical properties of the cured resin.[12] In fact, it has been demonstrated that, in concentrations above 15 per cent, they much reduce the strength and solvent resistance of the cured resin.[5] The present theory can provide a basis for a quantitative discussion of this important diluent effect; such a detailed discussion will be undertaken elsewhere.

Appendix

It is well known that, in commenting on the earlier theory of Flory regarding gel formation, Stockmayer, in 1943,[8] threw doubt upon the validity of the application of the distribution equation beyond the gel point. Stockmayer pointed out the contradiction that the fraction of converted functional groups in the gel phase exceeds a limit which could not be surpassed if intramolecular reaction were forbidden (for instance, in the case of the self-condensation of f-functional monomers, the value of this limit is $2/f$). Notwithstanding Flory's protest,[1,13] it seems that no unequivocal explanation of this problem has yet been given. Therefore, we will present here a simple explanation of Stockmayer's paradox. For the convenience of explanation, let us consider the following "hypothetical" gel to be formed by the self-condensation of f-functional monomers ($f\geqq 3$). All the functional groups are converted to form a single gel molecule in which *any* functional group is converted and is connected to paths to infinity without cyclization. Such a gel would have a structure of an infinite number of monomeric units with an infinite number of branches without end. In this gel, ρ'' is considered to be unity.

Therefore, according to our opinion, it may be considered that, from a purely theoretical point of view, there is no such limit of ρ''. However, physically, it is quite imperfect, since the number of units and the number of branches of the "physical" gel are finite after all. In conclusion, the validity of the distribution beyond the gel point in the present theory may have been verified only from a theoretical point of view. In this way, the Stockmayer paradox may be attributed to the fact that the "facsimile" of nature treated in physical theory is not nature itself.

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[12] P. Bruin, *Kunststoffe*, **45**, 383 (1955).

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