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A Theory of the Gel-forming Polymerization of Polyvinyl Compounds

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A theory of the molecular-size distribution of the cross-linked polymers to be formed from a mixture of vinyl monomers with a distribution of functionalities by radical polymerization is presented. It is assumed that all the unconverted vinyl groups are equireactive to the propagation, which proceeds without 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. The general theory is applied to three practical cases; the curing reaction of unsaturated polyesters, the polymerization of polyvinyl compounds, and the copolymerization of vinyl and divinyl compounds.

A theory of gel formation by the radical copolymerization of divinyl compounds with monovinyl compounds was originally presented by Flory[1] and subsequently by Stockmayer[2] under principal assumptions which will be presented at the outset of the next section. In the first place, Flory[1] tried to explain the gel point of the polymerization. In his theory, he regarded every doubly-converted divinyl monomer as a single tetrafunctional monomer, each functional group of which was able to react independently with the vinyl groups of other monomers. According to this concept, a polymerization of this type is equivalent to the condensation reaction of tetrafunctional and bifunctional monomers.

Then he applied the results obtained in the case of the condensation to the case of this polymerization only in order to obtain the gel point. This interpretation, however, disregards the fact that the mechanism differs essentially from the condensation reaction in that polymerization and cross-linking are concomitant rather than consecutive. (This type of polymerization is usually called "cross-polymerization.") Hence, he hesitated to adopt, in the case of cross-polymerization, the molecular-size distribution of the copolymers obtained by the condensation. Subsequently, Stockmayer[2] treated this case with the following concept: every cross-link of the copolymers is equivalent to the cross-link between chains which would be obtained by cutting the middle of every doubly-reacted divinyl monomer of the copolymers. Thus he also reduced the polymerization to the cross-linking of primary-chain molecules, in any arbitrary size distribution, where the gel point was as presented by Eq. (1). Then he concluded that Eq. (1) was also valid in this case if another assumption was made.*1

$$\rho_c = \frac{1}{w_2 (P_w - 1)} \tag{1}$$

where ρ_c is the fraction of converted vinyl groups at the gel point, where P_w is the weight-average size of the cross-linking chains, and where w_2 is the weight fraction of the divinyl monomers. In the same paper, he demonstrated that, according to the same interpretation, the distribution for the cross-linking of primary chains might be also employed in the present case. Stockmayer's concept is, however, not only based on the unnatural interpretation mentioned above, but is also quite invalid for such simple cases as the cross-polymerization of trivinyl compounds.

By the use of another method, not by statistical methods, but by solving kinetic equations, Ohiwa[3] first obtained a reasonable size distribution of polymers obtained by the cross-polymerization of f-vinyl monomers. In his theory, the critical value is presented by Eq. (2) under the same assumptions as ours:

$$\rho_c = \frac{1}{(f-1)(P_w - 1)} \tag{2}$$

Thus, in the cross-polymerization or copolymerization of primary polyvinyl compounds, the gel

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

[2] W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

*1 This assumption was that, at any instant, the fraction of material involved in active growing chains is negligible compared to the amounts of stable polymers and residual monomers.

[3] M. Ohiwa, *Nippoin Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **76**, 508, 684 (1955).

point can at any rate be predicted by the Flory method[1] of the expectation value or by the other methods described above. However, the molecular-size distribution of the polymers and the post-gelation relationships have not been presented except for a few special cases treated by Ohiwa.[3]

On the other hand, a number of experiments[4] have qualitatively supported these theories with respect only to the critical value, ρ_c. Some remarkable quantitative deviations from the theoretical value which had been attributed to the effect of cyclization reactions were fairly well explained by modified theories including this effect.[4,5]

The present paper will present an exact and reasonable size distribution and the post-gelation relationships in the cross-polymerization of polyvinyl compounds, in any arbitrary distribution of their vinyl groups. Help was not sought from unnatural explanations nor by solving complicated kinetic equations. Only the statistical theory of gel formation with multifunctional interunit junctions developed by the present authors[6] was applied to the case. The basic concept is that a cross-linking chain is to be regarded as an interunit junction. This general theory is employed in three practical cases; the curing reaction of unsaturated polyesters, the polymerization of polyvinyl compounds, and the copolymerization of vinyl and divinyl compounds.

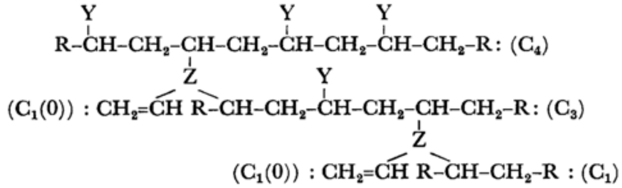
The Size Distribution and the Gel Point

The present treatment is based on the following usual assumptions in the first approximation: (1) all of the vinyl groups in polymers and primary molecules are equally reactive, and (2) no kind of intramolecular reaction leading to a cyclic structure occurs. Also, it is assumed that: (3) the distribution of cross-linking chains follows the Flory distribution[1] during the entire course of the polymerization. The last assumption is, however, not essential. Other distributions are also applicalbe, if desired.

The initial system treated here is generally composed of primary molecules with any arbitrary distribution of their vinyl groups, say, N_1 mono-, N_2 di-,$\cdots$, N_s s-vinyl compounds. The weight fraction, w_s, of the s-vinyl compounds is, then:

$$w_s=\frac{sN_s}{F},\quad F=\sum_s sN_s$$

Now, to speak of a single polymeric molecule, it is constructed of chains (called "cross-linking chains" in this paper) formed by the polymerization of some vinyl groups, each in different primary molecules. A simple case can be visualized thus:



$$\{n_1=4,\ n_3=2\}\ \{j_1=j_3=j_4=1,\ j_1(0)=2\}$$

$$\nu=\sum_k j_k=3$$

The cross-polymerization of vinyl compounds (CH_2=CHY) and trivinyl compounds ($[CH_2{=}CH]_3Z$) is illustrated in the above scheme, where C_k represents a cross-linking chain formed by the polymerization of k vinyl groups, where $C_1(0)$ is an unconverted vinyl group, and where R stands for one of the terminators or initiators produced from, for example, the catalysts. The description of any single polymer requires, therefore, the specification of the number of primary molecules of each kind and the number of crosslinking chains of each size. We denote the numbers of primary molecules by n_1, n_2, n_3,$\cdots$, n_s, and the numbers of cross-linking chains by j_1, j_2, j_3,$\cdots$, j_k, *etc.* For brevity, any particular set of these numbers is represented by the symbols $\{n_s\}$ and $\{j_k\}$. The number of unconverted vinyl groups, $j_1(0)$, can be obtained from the $\{n_s\}$ and $\{j_k\}$ as presented by Eq. (7). The symbol $m(\{n_s\};\{j_k\})$ will be used for the mole fraction of polymers described by a particular set $\{n_s\}$ and $\{j_k\}$.

In this paper, the results obtained by the use of our previous general theory[6] are directly employed to derive the distribution of the molecular size. The essential point of the present paper is based on the reasonable concept that any cross-linking chain is to be regarded as a kind of interunit junc-

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4) T. Holt and W. Simpson, *Proc. Roy. Soc.*, **A238**, 154 (1954); M. Gordon and R-J. Roe, *J. Polymer Sci.*, **21**, 27, 39, 57, 75 (1956); L. Minnema and A. J. Stavermann, *ibid.*, **29**, 281 (1958); B. T. Storey, *ibid.*, **A3**, 265 (1965).

5) M. Gordon, *J. Chem. Phys.*, **22**, 610 (1954); R. N. Haward, *J. Polymer Sci.*, **14**, 535 (1954); C. A. J. Hoeve, *ibid.*, **21**, 1, 11 (1956).

6) K. Fukui and T. Yamabe, This Bulletin, **40**, 2052 (1967).

tion as defined in the previous paper.[6] Therefore, a C_k-chain corresponds to a k-functional interunit junction. Unconverted vinyl groups should be distinguished from C_1-chains, although, according to the definitions, both are monofunctional interunit junctions; they are treated here as different monofunctional interunit junctions.

According to the third assumption, the total number of C_k-chains, J_k, in the system is presented as follows:

$$J_k = F\rho\alpha^{k-1}(1-\alpha)^2$$

where ρ is the fraction of converted vinyl groups and where α is the probability of chain propagation. The probability of the formation of a C_k-chain, p_k, is then given from the definition of Eq. (8) in Ref. 6 as follows:

$$p_k = \frac{kJ_k}{F} = k\alpha^{k-1}(1-\alpha)^2\rho \quad (k = 1, 2, 3, \cdots) \tag{3}$$

Hence, ρ can be rewritten as:

$$\rho = \sum_k p_k$$

The fraction of unconverted vinyl groups, $p_1(0)$, can then be simply expressed as:

$$p_1(0) = 1 - \sum_k p_k = 1 - \rho \tag{4}$$

From Eq. (48) in Ref. 6 and Eqs. (3) and (4), the distribution of the molecular size of the polymeric species can readily be obtained as follows:

$$\begin{aligned} m(\{n_s\};\{j_k\}) &= \frac{(\sum_s (s-1)n_s)!\,(\sum_s n_s-1)!}{(\sum_s (s-1)n_s - \sum_k j_k+1)!} \\ &\quad\times \rho^{\sum_k j_k}(1-\rho)^{\sum_s (s-1)_s - \sum_k j_k+1} \\ &\quad\times \alpha^{\sum_s n_s-1}(1-\alpha)^{2\sum_k j_k} \prod_k \frac{k^{j_k}}{j_k!} \prod_s \frac{w_s{}^{n_s}}{n_s!} \end{aligned} \tag{5}$$

where $\{j_k\}$, $j_1(0)$, and $\{n_s\}$ satisfy the following relations:

$$\sum_k (k-1)j_k = \sum_s n_s - 1 \tag{6}$$

$$j_1(0) = \sum_s (s-1)n_s - \sum_k j_k + 1 \tag{7}$$

From this distribution, we can easily obtain the mol fraction, $m(\{n_s\};\nu)$, of polymers containing $\sum_k j_k = \nu$ cross-linking chains;

$$\begin{aligned} m(\{n_s\};\nu) &= \sum_{\sum_k j_k=\nu} m(\{n_s\};\{j_k\}) \\ &= \frac{(\sum_s (s-1)n_s)!\,(\sum_s n_s+2\nu-1)!}{(\sum_s (s-1)n_s-\nu+1)!\,(2\nu-1)!\,\nu!} \\ &\quad\times \rho^{\nu}(1-\rho)^{\sum_s (s-1)n_s-\nu+1} \\ &\quad\times \alpha^{\sum_s n_s-1}(1-\alpha)^{2\nu} \prod_s \frac{w_s{}^{n_s}}{n_s!} \end{aligned} \tag{8}$$

The gel point is characterized by the following equation (see Eq. (19) in Ref. 6):

$$1 = (\lambda_w - 1)(\mu_w - 1)$$

where:

$$\lambda_w = \sum_s s w_s$$

$$\mu_w - 1 = \sum_k (k-1)p_k$$

or by the use of the weight-average chain length, P_w:

$$\mu_w - 1 = \rho(P_w - 1)$$

Hence, the fraction, ρ_c, of converted vinyl groups at the gel point is represented by:

$$\rho_c = \frac{1}{(\lambda_w - 1)(P_w - 1)} \tag{9}$$

This expression can be used for any arbitrary distributions of chain length and includes the previous results (Eqs. (2) and (3)) in their most simple case. In the present case, P_w is equal to $(1+\alpha)/(1-\alpha)$; hence, Eq. (9) is reduced to:

$$\rho_c = \frac{1-\alpha}{2\alpha(\lambda_w - 1)} \tag{9'}$$

The number- and weight-average molecular sizes can immediately be obtained from the results of the previous paper as follows respectively:

$$\langle \sum_s sn_s \rangle = \frac{\sum (\sum_s sn_s)\, m(\{n_s\};\nu)}{\sum m(\{n_s\};\nu)} = \frac{\lambda_n}{1-\alpha\rho\lambda_n} \tag{10}$$

$$\langle (\sum_s sn_s)^2 \rangle = \frac{\sum (\sum_s sn_s)^2 m(\{n_s\};\nu)}{\sum (\sum_s sn_s)\, m(\{n_s\};\nu)} = \frac{(1-\alpha+2\alpha\rho)\lambda_w}{1-\alpha-2\alpha\rho(\lambda_w-1)} \tag{11}$$

or, more generally:

$$\langle (\sum_s sn_s)^2 \rangle = \frac{\lambda_w[1+\rho(P_w-1)]}{1-\rho(\lambda_w-1)(P_w-1)} \tag{11'}$$

where $\lambda_n = 1/\sum_s (w_s/s)$

Likewise, the number- and weight-average degrees of polymerization are, respectively:

$$\langle (\sum_s n_s) \rangle = \frac{1}{1-\alpha\rho\lambda_n} = \frac{\langle (\sum_s sn_s) \rangle}{\lambda_n} \tag{12}$$

and:

$$\langle (\sum_s n_s)^2 \rangle = \frac{1-\alpha+2\alpha\rho}{1-\alpha-2\alpha\rho(\lambda_w-1)} = \frac{\langle (\sum_s sn_s)^2 \rangle}{\lambda_w} \tag{13}$$

These average numbers are, of course, only valid until the gel point is reached.

Relationships after the Gel Point

The relative abundances of cross-linking chains and of various primary species in the sol and in the gel fractions may be easily determined by applying our previous general theory[6] to the present case. The results of the previous theory will be used here after without further remark. The characteristic equation defined by Eq. (26′) in Ref. 6 is presented in this case as:

$$x = \sum_s w_s u^{s-1} \tag{14}$$

$$u(x) = p_1(0) + \sum_k p_k x^{k-1} \tag{15}$$

which, on substituting the expression given by Eq. (3) for p_k, reduces to:

$$u(x) = 1 - \rho + \rho\left(\frac{1-\alpha}{1-\alpha x}\right)^2 \tag{15′}$$

where ρ is the over-all fraction of polymerized vinyl groups beyond the gel point. It is proved that the lowest real positive root, x_1, of this equation is equal to unity before the gel point, and less than unity after that point. With x_1 or $u_1 = u(x_1)$, the sol fraction $w_s^{(\mathrm{sol})}$ of s-vinyl compounds is given by:

$$w_s^{(\mathrm{sol})} = w_s u_1^s \quad (s = 1, 2, \cdots) \tag{16}$$

Hence, the total fraction, W_{sol}, of the sol is:

$$W_{\mathrm{sol}} = \sum_s w_s u_1^s \tag{17}$$

which, by the use of Eq. (14), reduces to:

$$W_{\mathrm{sol}} = x_1 u_1 \tag{17′}$$

Finally,

$$W_{\mathrm{sol}} = x_1\left[1 - \rho\left(1 - \left(\frac{1-\alpha}{1-\alpha x_1}\right)^2\right)\right] \tag{17″}$$

The weight fraction, $w_s'^{(\mathrm{sol})}$, of the sol consisting of s-vinyl primary compounds is:

$$w_s'^{(\mathrm{sol})} = w_s^{(\mathrm{sol})}/W_{\mathrm{sol}} = w_s u_1^s/W_{\mathrm{sol}} \tag{18}$$

The number- and weight-average values of s in the sol fraction are then, respectively:

$$\lambda_n' = 1/\sum_s (w_s'^{(\mathrm{sol})}/s) \tag{19}$$

and:

$$\lambda_w' = \sum_s s w_s'^{(\mathrm{sol})} \tag{20}$$

Similarly, the fraction of C_k-chains in the sol is given by:

$$p_k^{(\mathrm{sol})} = p_k x_1^k \tag{21}$$

Hence, the fraction of the sol consisting of C_k-chains, $p_k'^{(\mathrm{sol})}$ is expressed by:

$$p_k'^{(\mathrm{sol})} = p_k^{(\mathrm{sol})}/W_{\mathrm{sol}} = p_k x_1^k/W_{\mathrm{sol}} \tag{22}$$

The number- and weight-average lengths of the chains in the sol are, then, respectively:

$$\langle k_n \rangle^{(\mathrm{sol})} = 1/(\sum p_k'^{(\mathrm{sol})}/k) = \frac{1}{1-\alpha x_1} \tag{23}$$

and:

$$\langle k_w \rangle^{(\mathrm{sol})} = \sum_k k p_k'^{(\mathrm{sol})} = \frac{1+\alpha x_1}{1-\alpha x_1} \tag{24}$$

The fraction of polymerized vinyl groups in the sol, ρ', is obtained from the definition as follows:

$$\rho' = \sum_k p_k'^{(\mathrm{sol})} = 1 - \frac{(1-\rho)}{1-\rho+\rho\left(\frac{1-\alpha}{1-\alpha x_1}\right)^2} \tag{25}$$

or:

$$\rho' = 1 - \frac{(1-\rho)}{u_1} \tag{25′}$$

which shows, on the contrary, the fraction of unconverted vinyl groups of the sol $p'^{(\mathrm{sol})}_{1(0)}$ to be $1-\rho'$.

Furthermore, from these equations, the number- and weight-average molecular sizes in the sol are, respectively:

$$\langle(\sum_s s n_s)\rangle^{(\mathrm{sol})} = \frac{\lambda'_n}{1-\alpha\rho'\lambda'_n} \tag{26}$$

and:

$$\langle(\sum_s s n_s)^2\rangle^{(\mathrm{sol})} = \frac{(1-\alpha+2\alpha\rho')\lambda'_w}{1-\alpha-2\alpha\rho'(\lambda'_w-1)} \tag{27}$$

Likewise, the number- and weight-average degrees of polymerization are, respectively:

$$\langle(\sum_s n_s)\rangle = \frac{1}{1-\alpha\rho'\lambda'_n} \tag{28}$$

and:

$$\langle(\sum_s n_s)^2\rangle = \frac{1-\alpha+2\alpha\rho'}{1-\alpha-2\alpha\rho'(\lambda'_w-1)} \tag{29}$$

It is noteworthy that these equations (Eqs. (26) and (29)) possess the same forms as Eqs. (10) and (12) after the replacement of λ_n, λ_w, and ρ in Eqs. (10) and (13) by λ'_n, λ'_w, and ρ' respectively.

The weight fraction of s-vinyl compounds in the gel, $w_s^{(\mathrm{gel})}$, is then obtained by the difference:

$$w_s^{(\mathrm{gel})} = w_s - w_s^{(\mathrm{sol})} = w_s(1-u^s) \tag{30}$$

Hence,

$$W_{\mathrm{gel}} = 1 - W_{\mathrm{sol}} \tag{31}$$

Likewise, the weight fraction, $p_k^{(\mathrm{gel})}$, of C_k-chains in the gel is:

$$p_k^{(\mathrm{gel})} = p_k - p_k^{(\mathrm{sol})} = p_k(1-x_1^k) \tag{32}$$

The fraction of vinyl groups in the gel which have polymerized, ρ'', is:

$$\rho'' = \frac{\sum_k p_k^{(\mathrm{gel})}}{W_{\mathrm{gel}}} = \frac{1-\left(\frac{1-\alpha}{1-\alpha x_1}\right)^2}{1-x_1\left[1-\rho+\rho\left(\frac{1-\alpha}{1-\alpha x_1}\right)^2\right]}\cdot\rho \tag{33}$$

Namely,

$$\rho'' = \frac{2\alpha-(1+x_1)\alpha^2}{(1-\rho)\alpha^2 x_1^{\,2}+\alpha(2-2\rho+\alpha\rho)x_1+1}\cdot\rho \tag{33′}$$

Similarly, the number- and weight-average lengths of the cross-linking chains with which the gel is constructed are, respectively:

$$\langle k_n\rangle^{(\mathrm{gel})} = \frac{\sum_k p_k^{(\mathrm{gel})}}{(\sum_k p_k^{(\mathrm{gel})}/k)} = \frac{1-\alpha^2 x_1}{(1-\alpha)(1-\alpha x_1)} \tag{34}$$

$$\begin{aligned}\langle k_w\rangle^{(\mathrm{gel})} &= \frac{\sum_k k p_k^{(\mathrm{gel})}}{\sum_k p_k^{(\mathrm{gel})}} \\ &= \frac{1+(1+x_1)\alpha-6x_1\alpha^2+x_1(1+x_1)\alpha^3+x_1{}^2\alpha^4}{(1-\alpha)(1-\alpha x_1)(1-\alpha^2 x_1)}\end{aligned} \tag{35}$$

These relationships for the gel may afford some information to make clear the structure of the gelled network polymers, which we will discuss in detail elsewhere. It should be noticed here however that, before the gel point, the number-average length of the cross-linking chains maintains a constant value:

$$\langle k_n\rangle = \frac{1}{1-\alpha}$$

and that even beyond the gel point the same value remains as an average over the whole system containing the sol and the gel, while the average length in the sol and in the gel are different from each other, as Eqs. (23) and (34), respectively, indicate. This is a consequence of the preferential acquisition of larger molecules by the gel.

Near the gel point, both x_1 and u_1 may be slightly smaller than unity; these can then be written as:

$$x_1 = 1-\varepsilon \qquad 1 \gg \varepsilon > 0 \tag{36}$$

$$u_1 = 1-\delta \qquad 1 \gg \delta > 0 \tag{37}$$

By substituting the x_1 of Eq. (36) into Eqs. (14) and (15) and by neglecting the terms of a higher order than ε and δ, these factors may be approximated by:

$$\varepsilon \cong \frac{[2\alpha\rho(\lambda_w-1)+\alpha-1](1-\alpha)}{\alpha^2\rho[2\rho\lambda_z+3(\lambda_w-1)]} \tag{38}$$

$$\delta \cong \frac{[2\alpha\rho(\lambda_w-1)+\alpha-1](1-\alpha)}{\alpha\rho[(1-\alpha)\lambda_z+3\alpha(\lambda_w-1)^2]} \tag{39}$$

where $\lambda_z = \sum_s (s-1)(s-2)w_s$. Furthermore, if ρ is expressed by the following equation, which may be employed to define Δ,

$$\rho = \rho_c(1+\Delta) \qquad 1 \gg \Delta > 0 \tag{40}$$

ε and δ can then be rewritten in other expressions:

$$\varepsilon \cong \frac{2(1-\alpha)(\lambda_w-1)^2}{(1-\alpha)\lambda_z+3\alpha(\lambda_w-1)^2}\cdot\Delta \tag{38'}$$

$$\delta \cong \frac{2(1-\alpha)(\lambda_w-1)}{(1-\alpha)\lambda_z+3\alpha(\lambda_w-1)^2}\cdot\Delta \tag{39'}$$

By the use of ε and δ, we can obtain the relationships available near the gel point as follows:

$$\rho' \cong \rho_c[1-\frac{\alpha(\lambda_w-1)^2-(1-\alpha)[2(\lambda_w-1)+\lambda_z}{(1-\alpha)\lambda_z+3\alpha(\lambda_w-1)^2}\cdot\Delta] \tag{41}$$

$$\rho'' \cong \frac{1}{\lambda_w} + \frac{\lambda_w-1}{\lambda_w{}^2}\left\{1-\frac{(\lambda_w-1)(3\alpha\lambda_w-\alpha-2)}{(1-\alpha)(\lambda_z+3\alpha(\lambda_w-1)^2}\right\}\Delta \tag{42}$$

$$\lambda_n{}' = \lambda_n[1-(\lambda_w-\lambda_n)\delta] \tag{43}$$

$$\lambda_w{}' = \lambda_w\left[1-\left(\lambda_w-\frac{\lambda_z}{\lambda_w}\right)\delta\right] \tag{44}$$

$$W_{\mathrm{sol}} = 1-\lambda_w\delta \tag{45}$$

$$\langle k_n\rangle^{(\mathrm{sol})} = \frac{1}{1-\alpha}\left(1-\frac{\alpha}{1-\alpha}\varepsilon\right) \tag{46}$$

$$\langle k_w\rangle^{(\mathrm{sol})} = \frac{1+\alpha}{1-\alpha} - \frac{2\alpha}{(1-\alpha)^2}\varepsilon \tag{47}$$

$$\langle k_n\rangle^{(\mathrm{gel})} = \frac{1+\alpha}{1-\alpha} - \frac{\alpha}{(1-\alpha)^2}\varepsilon \tag{48}$$

At incipient gelation, it holds that $\rho''=1/\lambda_w$ and $\rho'=\rho_c$; that is, the converted fraction of the vinyl groups of the first increment of gel is $[(\lambda_w-1)/\lambda_w]\cdot(P_w-1)$ times as large as that of the sol. Similarly, $\langle k_n\rangle^{(\mathrm{sol})}=P_n$, $\langle k_n\rangle^{(\mathrm{gel})}=\langle k_w\rangle^{(\mathrm{sol})}=P_w$, and, in addition:

$$\langle k_w\rangle^{(\mathrm{gel})} = P_z \tag{49}$$

where $P_n=1/(1-\alpha)$, and $P_z=(1+4\alpha+\alpha^2)/(1-\alpha)^2$.

It is noticeable that, at incipient gelation, the number-average chain length of the gel is equal to the weight-average chain length of the sol.

These general relationships has thus been obtained for the partitioning of the components between the sol and the gel obtained by the cross-polymerization of primary molecules with any arbitrary distribution. Tractable expressions are also, of course, obtained for certain specified primary distributions. Three special cases will be discussed below.

Curing Reaction of Unsaturated Polyesters

As the first example of the specified distribution of the vinyl groups of primary molecules, let us consider the curing reaction of unsaturated polyesters. In this case we may employ the Flory distribution for the distribution of primary chains (linear unsaturated polyesters):

$$w_s = s(1-\gamma)^2\gamma^{s-1} \tag{50}$$

where γ is the fraction of converted functional groups in condensation reaction, such as, for instance, between glycol and maleic anhydride. Once the distribution has been determined thus, all the relationships obtained in the previous section can be expressed with observable quantities, such as α, γ, and ρ.

In the first place, we will try to obtain the mole fraction $m(n, p;\nu)$ of polymers constructed by ν

cross-linking chains connecting the n primary chians which had p vinyl groups at all in the initial state. From the definition,

$$m(n, p; \nu) = \sum m(\{n_s\}; \nu) \tag{51}$$

where the summation should cover all non-negative integers, $\{n_s\}$, satisfying the conditions; $\sum_s n_s = n$ and $\sum_s sn_s = p$. Simple manipulations lead to the following distribution:

$$m(n,p;\nu) = \frac{1}{(p+n-\nu)} \binom{n+\nu-1}{n} \binom{p+n-1}{\nu} \binom{p+n-\nu}{2n-1} \times \rho^{\nu}(1-\rho)^{p-n-\nu+1}\alpha^{n-1}(1-\alpha)^2(1-\gamma)^{2n}\gamma^{p-n} \tag{51'}$$

If the number of converted vinyl groups, $i=\nu+n-1$, and the number of cross-links in the polymer, $j=n-1$, are employed instead in the above distribution, it is consistent with the distribution obtained by Ohiwa[3] with the aid of the kinetic method. He demonstrated that it is different from that of the case of cross-linking by the condensation reactions of primary chins.

By substituting the relationships available for the present case into Eqs. (9′) and (13),

$$\lambda_n = \frac{1}{1-\gamma}, \quad \lambda_w = \frac{1+\gamma}{1-\gamma} \tag{52}$$

we obtain:

$$\rho_c = \frac{(1-\alpha)(1-\gamma)}{4\alpha\gamma} \tag{53}$$

$$\langle p \rangle = \frac{1}{1-\gamma-\alpha\rho} \tag{54}$$

$$\langle p^2 \rangle = \frac{(1+\gamma)(1-\alpha+2\alpha\rho)}{(1-\alpha)(1-\gamma)-4\alpha\gamma\rho} \tag{55}$$

$$\langle n \rangle = \frac{1-\gamma}{1-\gamma-\alpha\rho} \tag{56}$$

$$\langle n^2 \rangle = \frac{(1-\gamma)(1-\alpha+2\alpha\rho)}{[(1-\alpha)(1-\gamma)-4\alpha\gamma\rho](1+\gamma)} \tag{57}$$

which are, of course, valid only before the gel point.

The characteristic equation (Eq. (14)) is now simply:

$$x = \left(\frac{1-\gamma}{1-\gamma u}\right)^2 \tag{58}$$

or, alternatively:

$$u = \frac{1}{\gamma}\left[1 - \frac{(1-\gamma)}{\sqrt{x}}\right] \tag{58'}$$

From Eqs. (15′) and (58), it follows that:

$$\rho = \frac{1-\gamma}{\alpha\gamma} \frac{(1-\alpha x_1)^2}{(x_1+\sqrt{x_1})(2-\alpha-\alpha x_1)} \qquad (\rho \geqq \rho_c) \tag{59}$$

from which x_1 or u_1 can be obtained for a given value of ρ as well as α and γ, even if numerically. To get the sol fraction or other fractions presented in the previous section one need, then, do nothing but do the numerical calculations using this x_1.

The sol fraction is now simply:

$$W_{\text{sol}} = \frac{x_1-(1-\gamma)\sqrt{x_1}}{\gamma} \tag{60}$$

In this case, the number- and weight-average sizes of the primary chains in the sol decrease as the reaction proceeds beyond the gel point, following the relations:

$$\lambda_n' = \frac{1}{1-\gamma u_1}, \quad \lambda_w' = \frac{1+\gamma u_1}{1-\gamma u_1} \tag{61}$$

These are, however, constant until the gel point, as is shown in Eq. (52). From Eqs. (28) and (29), the number- and weight-average degrees of polymerization are presented with $\gamma'=\gamma u_1$ and ρ', or, equivalently, u_1 and ρ (since, from Eq. (25′),

$$\langle n \rangle^{(\text{sol})} = \frac{1-\gamma'}{1-\gamma'-\alpha\rho'} \tag{62}$$

and

$$\langle n^2 \rangle^{(\text{sol})} = \frac{(1-\alpha+2\alpha\rho')(1-\gamma')}{[(1-\alpha)(1-\gamma')-4\alpha\gamma'\rho'](1+\gamma')} \tag{63}$$

At incipient gelation, ε and δ can now be obtained from Eq. (28′) and Eq. (39′) respectively:

$$\varepsilon \cong \frac{2(1-\alpha)}{6(1-\alpha)(\gamma/[1+\gamma]^2+3\alpha} \cdot \Delta \tag{64}$$

and:

$$\delta \cong \frac{(1-\alpha)}{6(1-\alpha)(\gamma/[1+\gamma])^2+3\alpha} \cdot \frac{(1-\gamma)}{\gamma} \cdot \Delta \tag{65}$$

Hence, from Eq. (45):

$$W_{\text{sol}} \cong 1 - \frac{(1-\alpha)}{6(1-\alpha(\gamma/[1+\gamma])^2+3\alpha} \cdot \frac{1+\gamma}{\gamma} \cdot \Delta \tag{66}$$

The approximation used in deriving these equations is, of course, based on the condition that the Δ defined by Eq. (40) is sufficiently small compared to unity and, hence, valid only very near the gel point. In curing reactions, however, ρ is usually small since ρ_c is sufficiently small; the primary chain length is, therefore, great (*cf.* Eq. (9)). This situation leads Eq. (66) to another approximation:

$$x_1 \cong W_{\text{sol}} \tag{67}$$

When we apply this approximation to Eq. (25), ρ' nearly becomes:

$$\rho' \cong \rho\left(\frac{1-\alpha}{1-\alpha W_{\text{sol}}}\right)^2 \tag{68}$$

which is useful apart from the gel point as long as ρ is small.

Similarly, from Eq. (33), ρ'' is:

$$\rho'' \cong \rho \frac{\alpha[2-\alpha(1+W_{\text{sol}})]}{(1-\alpha W_{\text{sol}})^2} \tag{69}$$

At incipient gelation $\rho'' \cong (P_w - 1)\rho'$, as has been pointed out at the end of the preceding section.

Polymerization of Polyvinyl Compounds

In this section, the case of the polymerization of f-vinyl monomers will be treated as the second example of the general case. Polyallyl compounds as well as polyvinyl compounds are also valid for the monomer, since allyl groups polymerize much like vinyl groups. In fact, some kinds of diallyl or triallyl esters are used to produce some thermosetting resins.

Now, from Eq. (8), the mole fraction $m(n;\nu)$ of polymers composed of n monomers connected by ν cross-linking chains can be immediately presented by:

$$m(n;\nu)=\frac{(fn-n)!\,(n+2\nu-1)!}{(fn-n-\nu+1)!\,(2\nu-1)!\,\nu!\,n!}\times\rho^{\nu}(1-\rho)^{fn-n-\nu+1}\alpha^{n-1}(1-\alpha)^{2\nu} \tag{70}$$

The gel point is simply:

$$\rho_c=\frac{(1-\alpha)}{2\alpha(f-1)} \tag{71}$$

The number-average degree of polymerization is given by:

$$\langle n\rangle=\frac{1}{1-f\alpha\rho} \tag{72}$$

Its weight-average degree of polymerization is:

$$\langle n^2\rangle=\frac{1-\alpha+2\alpha\rho}{1-\alpha-2(f-1)\alpha\rho} \tag{73}$$

These equations (Eqs. (70) and (73)) agree with that obtained by the kinetical method.[3] Formulas derived in quite a different manner have proved to be a special case of the present general theory.

The sol fraction or the composition of the gel can be calculated by means of the root of the characteristic equation, x_1, which, for this case, is presented by:

$$x=\left[1-\rho+\rho\left(\frac{1-\alpha}{1-\alpha x}\right)^2\right]^{f-1} \tag{74}$$

This root, x_1, is usually obtained by numerical calculations. For the simplest case ($f=2$), it is obtained explicitly as follows:

$$x_1=\frac{(2-\alpha\rho)-\sqrt{[\alpha\rho+4(1-\alpha)]\alpha\rho}}{2\alpha}\quad(\rho\geqq\rho_c) \tag{75}$$

The relation between x_1 and ρ is shown in Fig. 1 for the cases of $f=2$ and 3, and $\alpha=0.8$.

The sol fraction, W_{sol}, is simply:

$$W_{sol}=x_1^{\frac{f}{f-1}} \tag{76}$$

which is shown in Fig. 2 for the case of $f=2$ and 3.

Likewise, the relationships of the number-average lengths of the cross-linking chains in the sol and in the gel are drawn in Fig. 3 according to Eqs. (23) and (34). This figure may afford information about the structure of the gel and about the difference between the sol and the gel.

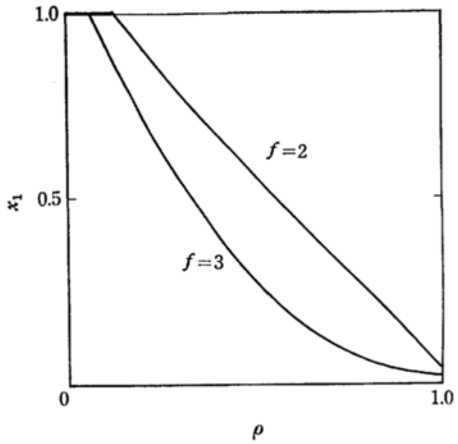

Fig. 1. The relationships between x_1 and ρ ($\alpha=0.8$).

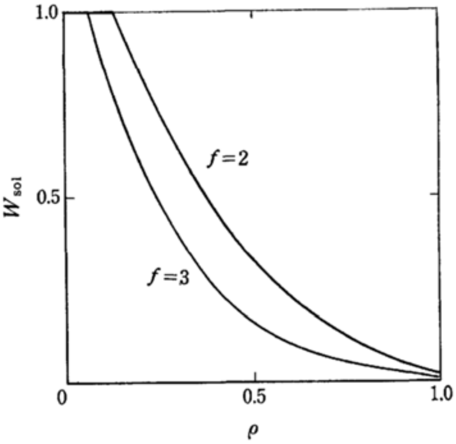

Fig. 2. The sol fraction W_{sol} ($\alpha=0.8$).

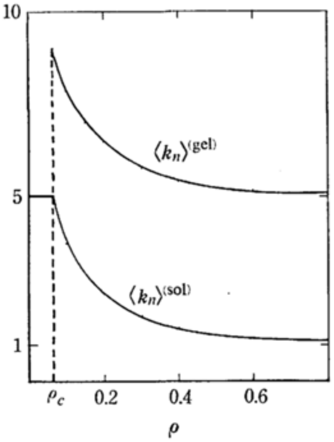

Fig. 3. The number average lengths of crosslinking chains in the sol and in the gel.

Copolymerization of Vinyl and Divinyl Monomers

Lastly, let us treat the case of the copolymerization of vinyl and divinyl monomers, which we discussed in the introduction of this article. The general relationships for calculating the distribution obtained by cross-polymerizing primary molecules of any arbitrary distribution have been derived in the first section. Then, in the present case, the molecularsize distribution of Eq. (8) reduces to:

$$m(n_1,n_2;\nu)=\frac{(n_1+n_2+2\nu-1)!}{n_1!(n_2-\nu+1)!(2\nu-1)!\nu!}\times\rho^{\nu}\cdot(1-\rho)^{n_2-\nu+1}\alpha^{n_1+n_2-1}(1-\alpha)^{2\nu}\times w_1^{n_1}\cdot w_2^{n_2} \tag{77}$$

This is, therefore, the exact and reasonable distribution first obtained by the present authors.

The number- and weight-average molecular sizes are, respectively:

$$\langle(n_1+2n_2)\rangle=\frac{2}{2-w_2-2\alpha\rho} \tag{78}$$

and:

$$\langle(n_1+2n_2)^2\rangle=\frac{(1-\alpha+2\alpha\rho)(1+w_2)}{1-\alpha-2\alpha\rho\cdot w_2} \tag{79}$$

The gel point is now given from Eq.(9′) by:

$$\rho_c=\frac{1-\alpha}{2\alpha w_2}=\frac{1}{w_2(P_w-1)} \tag{80}$$

which coincides with Eq. (1) obtained by Flory[1)] and by Stockmayer.[2)] It is of interest to see that this Eq. (1) derived from quite different considerations, is also obtained as a special case of the more general theory. This equation shows that, since $\rho_c\leqq 1$, w_2 should be larger than $(1-\alpha)/2\alpha=1/(P_w-1)$ for the attainment of the gel point (even if intramolecular reactions are excluded); otherwise the gelation does not occur at any extent of polymerization reaction. Such a situation is fully discussed in another paper.[*]

The polymer conversion, W_p, is given by:

$$W_p=1-[w_1(1-\rho)+w_2(1-\rho)^2] \tag{81}$$

since the monomers should be excluded from the polymers. Hence, the fraction of the unconverted vinyl groups in polymers, $R_{u.s.}$, is:

$$R_{u.s.}=\frac{W_p-\rho}{W_p}=\frac{w_2(1-\rho)}{1+w_2(1-\rho)} \tag{82}$$

At the initial stage of the reaction, Eq. (81) reduces to:

$$R_{u.s.}\cong\frac{w_2}{1+w_2} \tag{83}$$

The charactristic equation can now be rewritten in the following form:

$$x=w_1+w_2\left[1-\rho+\rho\left(\frac{1-\alpha}{1-\alpha x}\right)^2\right] \tag{84}$$

which, after simple manipulation, gives:

$$x_1=\frac{(2-\alpha w_2\rho)-\sqrt{[4(1-\alpha)+\alpha w_2\rho]\alpha w_2\rho}}{2\alpha} \tag{85}$$

Hence:

$$u_1=\frac{(2-\alpha w_2\rho)-\sqrt{[4(1-\alpha)+\alpha w_2\rho]\alpha w_2\rho}}{2\alpha w_2} \tag{86}$$

where the relation $(1-x_1)=w_2(1-u_1)$ is used to obtain the u_1 from the x_1.

At incipient gelation, from Eqs. (38′) and (29′):

$$x_1=1-\frac{2(1-\alpha)}{3\alpha}\cdot\Delta \tag{85′}$$

$$u_1=1-\frac{2(1-\alpha)}{3\alpha w_2}\cdot\Delta \tag{86′}$$

On the other hand, near complete conversion ($\rho\cong 1$), these may be approximated as follows:

$$x_1=1-w_2\rho+\frac{(1-\alpha)^2}{w_2\rho} \tag{85″}$$

$$u_1=1-\rho+\frac{(1-\alpha)^2}{w_2{}^2\rho} \tag{86″}$$

where it is supposed that $w_2\gg(1-\alpha)$. It should be remarked that, in Eqs. (85″) and (86″) near the full conversion, $x_1\cong 1-w_2=w_1$, whereas $u_1\cong 0$. The latter value means that both monomers are almost entirely changed into gel near the full conversion since $W_{sol}=w_1u_1+w_2u_1{}^2$. On the other hand, the former indicate that in the gel the monovinyl monomers do not take part in the unit of branches extending to infinity as it ought to. These situa-

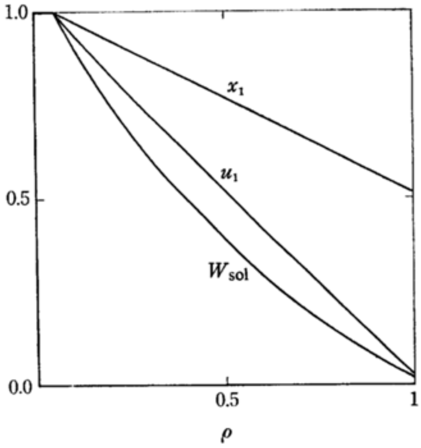

Fig. 4. The relationships between x_1, u_1, W_{sol} and ρ ($W_2=0.5$, $\alpha=0.95$).

[*2] T. Yamabe and K. Fukui, This Bulletin, to be submitted.

tions, visualized in Fig. 4, may reflect the difference between the meanings of x_1 and u_1, as will be discussed in the Appendix.

Appendix

Recently, Dobson and Gordon[7] presented a theory of branching processes and of the statistics of rubber elasticity by adopting the stochastic theory of cascade processes. As an example, they treated vulcanization by cross polymerization and obtained the same equation (see Eq. (4) in Ref. 7) as Eq. (14) in this paper:

$$x = \sum_s w_s u^{s-1} \tag{A-1}$$

where u was as presented by the following equation (translated into our notations (see Eq. (43) in Ref. 7):

$$u = 1 - \rho + \rho\,(1 - \alpha + \alpha x)^2 \tag{A-2}$$

This is, however, in disagreement with the corresponding equation (Eq. (15)) of the present paper; namely,

$$u = 1 - \rho + \rho\left(\frac{1-\alpha}{1-\alpha x}\right)^2 \tag{A–3}$$

Apparently, Eq. (A-2) was derived on the basis of the same concept as Flory's with regard to the cross-linking chain; hence, as has been discussed above, it is not reasonable and does not represent the characteristic features of the polymerization. Figure A-1 indicates the remarkable difference between $1-\alpha+\alpha x$ and $(1-\alpha)/(1-\alpha x)$, a difference equivalent to the difference between Eq. (A-2) and Eq. (A-3).

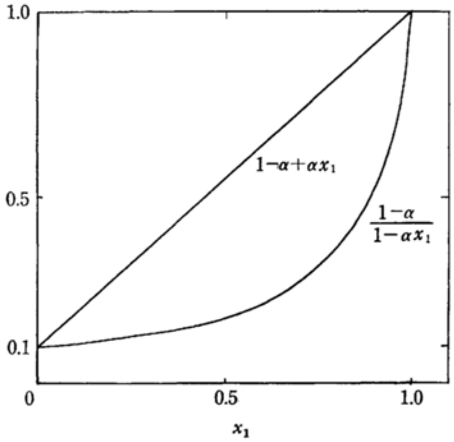

Fig. A-1. Functions $1-\alpha+\alpha x_1$ and $(1-\alpha)/(1-\alpha x_1)$ ($\alpha=0.9$).

Equation (A-2) is, however, approximated by Eq. (A-1) for $\alpha x \ll 1$, since:

$$\frac{1-\alpha}{1-\alpha x} \approx 1 - \alpha + \alpha x$$

Such an approximation is valid only for $x \ll 1$. The other case, that $\alpha \ll 1$, is almost meaningless since no polymer is obtained in this case. Therefore, the theory presented by Dobson and Gordon should be reformulated by our treatment. A paper on this subject will be presented elsewhere.

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[7] G. R. Dobson and M. Gordon, *J. Chem. Phys.*, **43**, 705 (1965).