A Theory of Gel Formation with a Multifunctional Interunit Junction

By Tokio YAMABE and Kenichi FUKUI

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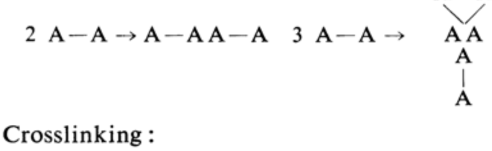
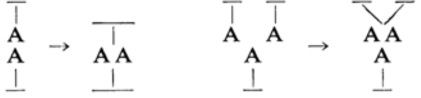
The ways in which high polymer substances are formed from monomeric units or by the crosslinking of polymer chains may be classified according to the number of functional groups involved in the formation of an interunit junction. Each case may be referred to as polymerization by a bi-, a ter-, a quadri-, a ⋯, or a multifunctional interunit junction. A schematic representation follows:

Polymerization:



$2\ \mathrm{A{-}A} \rightarrow \mathrm{A{-}AA{-}A} \quad 3\ \mathrm{A{-}A} \rightarrow$

Crosslinking:



bifunctional interunit junction

terfunctional interunit junction

In the polymerization by a bifunctional interunit junction, the theory of molecular size distribution and gel formation has been studied by Flory,[1] Stockmayer[2] and many other

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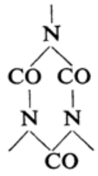
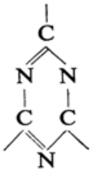
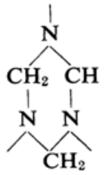
[1] P. J. Flory, "Principles of Polymer Chemisty," Cornell University Press, Ithaca, New York (1953), Chaps. 8 and 9.

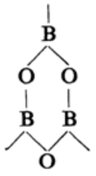
[2] W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).

researchers.[3] The theory of gel formation with a terfunctional interunit junction has been developed by the present authors[4] for the case in which any monomer possesses equivalent f functional groups. Recently such a type of polycondensation by a terfunctional interunit junction has come to our attention as we attempted to prepare thermosetting resins. For example:









where the interunit junctions are the isocyanuric ring, the s-trizine ring, the hexahydro-s-triazine ring, and the boroxin ring respectively. These interunit junctions are applicable to the crosslinking of polymer chains, as was realized in the crosslinking of polyacrylonitrile[5] or of polyacrylhydroxanic acid.[6] In the present paper, the theory is extended to a more general case than those previously considered, namely, the case of the formation of a multifunctional interunit junction (say, j functional: $j=2, 3, 4, \cdots$) not only in the polycondensations of a monomer with f equivalent functional groups ($f \geqq 2$), but also in the cross linking of a system of chains with an arbitrary initial size distribution. Of course, the $j=2$ case is equivalent to that of the bifunctional interunit junction, while $j=3$ is equivalent to that of a terfunctional interunit junction. Here the methods developed by Stockmayer are employed to derive the distribution of molecular sizes up to the gel point, and as was done in his papers, we also neglect the formation of macrorings, namely, rings which contain two or more endocyclic interunit junctions, for the first approximation.

f-Functional Monomer

In this part, each monomer possesses f equivalent functional groups, and those monomers are combined as polymer by a j-functional interunit junction, where j is the number of functional groups composing an interunit junction. If ν is the number of interunit junctions in an n-mer, and if the symbol ${}_jM_\nu^{(f)}$, is used for the number of n-mers $(n=(j-1)\nu+1)$, the total number of units, N, and the total number of molecules, M, can be expressed as follows:

$$\sum_{\nu\geqq0}((j-1)\nu+1)\,{}_jM_\nu^{(f)}=N \tag{1}$$

$$\sum_{\nu\geqq0}{}_jM_\nu^{(f)}=M \tag{2}$$

Therefore, the most probable molecular size distribution may be written as:

$${}_jM_\nu^{(f)}=A\frac{{}_jW_\nu^{(f)}}{N!}B^n \tag{3}$$

where ${}_jW_\nu^{(f)}$ is the number of different ways in which a polymeric molecules can be formed from n monomeric units (therefore, with ν interunit junctions) and is equal to:

$${}_jW_\nu^{(f)}=\frac{f^{(j-1)\nu+1}((f-1)(j-1)\nu+f-1)!\,(j-1)\nu)!}{\nu!\,((fi-f-j)\nu+f)!\,\{(j-1)!\}^\nu} \tag{4}$$

A and B are Lagrangian multipliers to be determined from Eqs. 1 and 2. Those summations can easily be evaluated by introducing Eq. 3 into Eqs. 1 and 2; the results are:

$$N=\frac{AB}{(1-\alpha)^f} \tag{5}$$

$$M=B\left(1-\frac{j-1}{j}f\alpha\right) \tag{6}$$

where

$$\frac{(fB)^{j-1}}{(j-1)!}=\alpha(1-\alpha)^{(f-1)(j-1)-1} \tag{7}$$

The molecular size distribution may then be rewritten:

$$\begin{aligned}{}_jM_\nu^{(f)}&=f\cdot N\\&\times\frac{((f-1)(j-1)\nu+f-1)!\,((j-1)\nu)!}{\nu!\,((j-1)\nu+1)!\,((f-1)\nu-\nu+f)!}\\&\times\alpha^\nu(1-\alpha)^{(f-1)(j-1)\nu-\nu+f}\end{aligned} \tag{8}$$

The fraction of reacted functional groups is obtained from Eqs. 5 and 6:

$$p=\frac{\sum_{\nu\geqq0}j\nu\,{}_jM_\nu^{(f)}}{fN}=\frac{j(N-M)}{(j-1)N}=\alpha \tag{9}$$

which means that α is equal to the fraction of reacted functional groups. The number and weight-average molecular size can easily be calculated from Eq. 6 and by direct summation:

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[3] M. Gordon *J. Chem. Phys.*, **22**, 610 (1954); F. E. Harris, ibid., **23**, 1518 (1955); L. C. Case, *J. Polymer Soc.*, **26**, 333 (1957).

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

[5] K. Takemoto, *Chemistry* (*Kagaku*), **17**, 124 (1962).

[6] W. Kern and R. C. Schulz, *Angew. Chem.*, **69**, 153 (1957).

$$\langle W\rangle_{\text{av.}}=\frac{\sum\limits_{\nu\geqq 0}(j-1)\nu+1)^{2}{}_{j}M_{\nu}^{(f)}}{\sum\limits_{\nu\geqq 0}((j-1)\nu+1)_{j}M_{\nu}^{(f)}}$$

$$=\frac{1+(j-1)\alpha}{1-(f-1)(j-1)\alpha} \qquad (10)$$

$$\langle N\rangle_{\text{av.}}=\frac{\sum\limits_{\nu\geqq 0}((j-1)\nu+1)_{j}M_{\nu}^{(f)}}{\sum\limits_{\nu\geqq 0}{}_{j}M_{\nu}^{(f)}}$$

$$=\frac{N}{M}=\frac{1}{1-(j-1)f\alpha/j} \qquad (11)$$

Therefore, the gel point is characterized by the following equation:

$$\alpha_{\text{gel}}=\frac{1}{(f-1)(j-1)} \qquad (12)$$

For the special case of $j=2$, Eqs. 10 and 11 become:

$$\langle n\rangle_{\text{av.}}=\frac{1}{1-f\alpha/2}, \qquad \langle w\rangle_{\text{av.}}=\frac{1+\alpha}{1-(f-1)\alpha}$$

which agree with Stockmayer's results,(2) For yet another case, $j=3$, these equations are:

$$\langle n\rangle_{\text{av.}}=\frac{1}{1-2f\alpha/3}, \quad \langle w\rangle_{\text{av.}}=\frac{1+2\alpha}{1-2(f-1)\alpha}$$

which are in accord with our previous results.(4)

The Crosslinking of Polymer Chains

In this section, the theory of the crosslinking of polymer chains by a j function interunit junction will be treated. For the sake of simplicity, the treatment is restricted to cases in which all units in the chains carry a functional group, all of which are assumed to be equivalent and of the same reactivity. Let the system contain N_1 monomeric chains, N_2 dimeric chains,⋯, N_s s-meric chains,⋯, etc. The number-average size of the chain that initially exist is thus:

$$\lambda_n=\frac{\sum\limits_{s}sN_s}{\sum\limits_{s}N_s}=\frac{1}{\sum\limits_{s}W_s/s} \qquad (13)$$

and the weight-average size is:

$$\lambda_w=\frac{\sum\limits_{s}s^2N_s}{\sum\limits_{s}sN_s}=\sum_{s}sW_s \qquad (14)$$

where W_s, the weight fraction of s-meric chains, is given by:

$$W_s=\frac{sN_s}{\sum\limits_{s}sN_s} \qquad (15)$$

and where, therefore,

$$\sum_{s}W_s=1 \qquad (16)$$

The description of any crosslinked molecules requires the specification of the number of chains of each size which it coniains. We denote by n_1, n_2, n_3,⋯, n_s, etc., these numbers of chains and represent any particular set of these numbers by the symbol $\{n_s\}$. The symbole $m\{n_s\}$ will be used for the number of molecules described by a particular set $\{n_s\}$ (which is joined with ν j-functional interunit juctions). The most probable molecular size distribution is, therefore, written as:

$$m\{n_s\}=A\cdot{}_{j}W_{\nu}\{n_s\}\prod_{s}\xi_s n_s/n_s\,! \qquad (17)$$

where A and ξ_s are Lagrangian multipliers which must be so chosen that

$$N_t=\sum_{\text{all}\{n_s\}}n_t m\{n_s\} \qquad (18)$$

$$M=\sum_{\text{all}\{n_s\}}m\{n_s\} \qquad (19)$$

and ${}_{j}W_{\nu}\{n_s\}$ is the number of different ways in which a molecule described by $\{n_s\}$ can be constructed from its constituent chains by ν interunit junctions. The use of the Stockmayer method for calculating this number gives the result:

$${}_{f}W_{\nu}\{n_s\}=$$

$$\frac{(\sum\limits_{s}(s-1)n_s)!((j-1)\nu)!}{(\sum\limits_{s}(s-1)n_s-(\nu-1))!\,\nu\,!\,((j-1)!)\nu}\prod_{s}sn_s \qquad (20)$$

where

$$\sum_{s}n_s=(j-1)\nu+1 \qquad (21)$$

Using Eq. 20, Eq. 17 may be rewritten as follows:

$$m\{n_s\}=(\sum_{s}sN_s)$$

$$\frac{(\sum\limits_{s}(s-1)n_s)!((j-1)\nu)!}{\nu!(\sum\limits_{s}(s-1)n_s-(\nu-1))!}$$

$$\times\alpha^{\nu}(1-\alpha)^{\sum\limits_{s}(s-1)n_s-(\nu-1)}$$

$$\times\prod_{s}\frac{W_s n_s}{n_s\,!} \qquad (22)$$

where

$$s\xi_s=\{(j-1)!\,\alpha(1-\alpha)^{-j}\}^{1/(j-1)}W_s(1-\alpha)^s$$

$$A=(\sum_{s}sN_s)\{(j-1)!\,\alpha(1-\alpha)^{-j}\}^{-1/(j-1)}$$

which satisfies the conditions of Eqs. 18 and 19, as is shown in the Appendix. After the evaluation of the necessary sums, the number- and weight-average molecular sizes are obtained as follows:

$$\overline{P}_n=\frac{\sum(\sum\limits_{s}sn_s)m\{n_s\}}{\sum m\{n_s\}}=\frac{1}{1-(j-1)\alpha\lambda_n/j} \qquad (23)$$

$$\overline{P}_w=\frac{\sum(\sum_s sn_s)^2 m\{n_s\}}{\sum(\sum_s sn_s)m\{n_s\}}=\frac{1+(j-1)\alpha\lambda_w}{1-(j-1)(\lambda_w-1)\alpha} \tag{24}$$

Therefore, the gel-point is given by

$$\alpha_{\text{gel}}=\frac{1}{(j-1)(\lambda_w-1)} \tag{25}$$

Of course, for the special case of $j=2$, these results are consistent with those of Stockmayers.

In the above formulations, the size distribution of the chains which initially exist is arbitrary, but the distribution of almost all the synthesized polymer chains is the most probable distribution. In this case, the molecular size distribution and the average sizes in the course of cross linking are found to be as follows. It is well known that the most probable molecular size distribution of chain polymers is given by $W_s=s\rho^{s-1}(1-\rho)^2$, where s is the number of units in a chain, and ρ is the probability that the reactive group in the unit has reacted. Let $m_{p,\nu}$ be the number of crosslinked polymeric molecules composed of p units and jointed with functional interunit junctions. This $m_{p,\nu}$ can be expressed:

$$m_{p,\nu}=\sum m\{n_s\} \tag{26}$$

where the summation should cover all possible sets, $\{n_r\}$, with the conditions:

$$\sum_s n_s=(j-1)\nu+1,\ \sum_s sn_s=p \tag{27}$$

Equation 26 easily be evaluated, with the result that

$$m_{p,\nu}=\frac{((j-1)\nu)\,!\,(p+(j-1)\nu)\,!}{\nu\,!((j-1)\nu+1)\,!\,(p-j\nu)\,!\,(2(j-1)\nu+1)!}$$
$$\times\alpha^{\nu}(1-\alpha)^{p-j\nu}\rho^{-(j-1)\nu-1}(1-\rho)^{2(j-1)\nu+2} \tag{28}$$

Form Eqs. 23 and 24, the number- and weight-average size are found to be;

$$\overline{P}_n=\frac{1}{1-\rho-(j-1)\alpha/j} \tag{29}$$

$$\overline{P}_w=\frac{(1+\rho)(1+(j-1)\alpha)}{1-\rho-2(j-1)\alpha\rho} \tag{30}$$

$$\alpha_{\text{gel}}=\frac{1-\rho}{2(j-1)\rho} \tag{31}$$

since $\lambda_n=1/(1-\rho)$, and $\lambda_w=(1+\rho)/(1-\rho)$ for the case of chains with the most probable distribution. When $j=2$, the result is consistent with that of Ohiwa derived by the kinetical method.[7]

Department of Fuel Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

Appendix

We wish to show that the distribution law:

$$m\{n_s\}=\{\sum_s sN_s\}\,\frac{(\sum_s(s-1)n_s\,!\,((j-1)\nu)\,!}{(\sum_s(s-1)n_s-(\nu-1))\,!\,\nu\,!}$$
$$\times\alpha^{\nu}(1-\alpha)^{\sum_s(s-1)n_s-(\nu-1)}\quad\prod_s\frac{W_s{}^{n_s}}{n_s\,!}$$

satisfies the conditions:

$$N_t=\sum n_t m\{n_s\} \tag{A-1}$$

$$M=\sum m\{n_s\} \tag{A-1}$$

Putting $\nu_t=n_t-1$ and $\nu_s=n_s(s\neq t)$, and expanding the power of $(1-\alpha)$ in Eq. A-1, we have;

$$\sum n_t m\{n_s\}=(\sum_s SN_s)\,W_t\sum_{q=0}\frac{(-\alpha)^q}{q\,!}\ \sum_{\nu=0}^{q}\binom{q}{\nu}(-1)^{\nu}$$
$$\times\sum\frac{(\sum_s(s-1)\nu_s+(t-1))\,!\,(\sum_s\nu_s)!}{(\sum_s(s-1)\nu_s+(t-1)-(q-1))}\quad\times\prod_s\frac{W_s{}^{\nu_s}}{\nu_s\,!} \tag{A-3}$$

where $\sum_s\nu_s=(j-1)\nu$

Consider now the function:

$$\mathscr{X}(x)=(1-(\sum_s W_s x^{s-1})^{j-1})^q x^{t-1}$$
$$=\sum_{\nu=0}^{q}\binom{p}{\nu}(-1)^{\nu}\sum(\sum_s\nu_s)\,!\ \prod_s\frac{W_s{}^{\nu s}}{\nu_s\,!}$$
$$\times x^{\sum_s(s-1)\nu_s+t-1}$$

where q is an integer greater than one.

Repeated differentiations give:

$$\left[\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{q-1}\mathcal{X}(x)\right]_{x=1}=\sum_{\nu=0}^{q}\binom{p}{\nu}(-1)^{\nu}$$
$$\times\sum\frac{(\sum_s(s-1)\nu_s+t-1)\,!\,(\sum_s\nu_s)!}{(\sum_s(s-1)\nu_s+t-1-(q-1))!}\ \prod_s\frac{W_s{}^{\nu_s}}{\nu_s\,!}$$

which is recognized as the sum required in Eq. A-3. However, since this derivative necessarily contains the $(1-(\sum_s W_s)^{j-1})$ factor, its value is zero, and the sum of Eq. A-3 is reduced to the term of $q=0$. Evaluating these, we obtain

$$\sum n_s m\{n_s\}=\frac{W_t}{t}\,(\sum_s sN_s)=N_t$$

Since the procedure for the summation of Eq. 18 resembles that used above, it may be omitted.

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[7] M. Ohiwa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 1244 (1954).