Statistics of Degradation and Cross-Linking of Polymer Chains with the Use of the Theory of Branching Processes

Miloš Demjanenko[+] **and Karel Dušek***

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received December 31, 1979*

ABSTRACT: The theory of branching processes based on the graph (tree) model and employing cascade substitution and probability generating functions has been modified so as to include, in addition to cross-linking, also degradation of the existing or newly formed bonds. In the treatment, primary chains are rooted by their repeat units, and the probability of existence of the bond is determined by the degree of degradation and cross-linking. The random degradation of both the discrete and continuous degree of polymerization distribution of initial primary chains and random degradation and cross-linking have been treated. The method has been extended to include more complicated mechanisms, viz., bond scission in systems arising by linking of reactive ends of primary chains through a polyfunctional cross-linking agent and cross-linking associated with degradation, in which the reactive ends produced by scission may be joined to any repeat unit. Relations for the degree of polymerization averages and conditions for attainment of the gel point have been derived. Similarly to existing theories (especially the kinetic theory), the treatment is based on the neglect of cyclization, but unlike earlier theories, it is not restricted by the condition of a high degree of polymerization of primary chains and of a very low degree of cross-linking and degradation.

The statistical treatment of processes of cross-linking and gelation dates back as far as the early forties, when Flory (cf., e.g., ref 1–3) and Stockmayer[4,5] formulated the laws of the formation of cross-linked structures by a random addition reaction of polyfunctional monomers. This approach, based on the tree-like model, is still used. It was soon noticed, however, that the cross-linking and degradation of macromolecular compounds frequently occurred simultaneously or consecutively. A typical example can be seen in the effects of high-energy radiation on polymers or in the cross-linking with compounds which on splitting yield free radicals. Also, the thermal, photooxidative or mechanochemical degradation is usually accompanied by branching, and gel formation may take place despite the generally decreasing number of bonds in the system.

Stochastic treatments of these processes summarized in several monographs (cf., e.g., ref 6–9) were based either on the statistical or on the kinetic approach and the independence of the scission and cross-linking process was assumed, so that the solutions were independent of the succession of the processes. In a kinetically controlled process, this assumption holds for random reactions and in the absence of cyclization, i.e., for structures which are in principle tree-like. Under these conditions, both statistical and kinetic approaches should give identical results, and observed deviations should follow from the approximations used (cf., e.g., ref 10 for cross-linking or the comparison of two variants of the kinetic approach to degradation[11–13]). The simultaneous formation and splitting of rings is a complicating factor, because the ring formation is determined by long-range correlations in the structure and because these correlations determine the distribution of positional probabilities of the reactive sites in a given molecule. No adequate stochastic solution to this case has been offered yet.

Generally, not only bonds formed in the cross-linking but also those existing in the initial system can undergo splitting. Therefore, the procedure usually employed in the stochastic treatment consists of the degradation of the initial system and subsequent cross-linking of degraded molecules. There are several methods for calculating changes in the degree of polymerization distribution and averages occurring in the degradation (based, e.g., on combinatorial statistics,[11,14–16] recurrent equations,[17] the theory of numbers,[18,19] kinetic differential equations for the change of the x-mer distribution,[12,20] or the distribution moments[6]), of which Simha's[12] approach is obviously the most general one.

Charlesby[6] was the first who did some intensive research into the treatment of cross-linking and degradation, but it was the kinetic theory as presented by Saito and coworkers[13,20–24] which has become the approach most widely used in the treatment of the degradation and cross-linking of primary chains in a ring-free case and under conditions of randomness. The theory is suited for continuous distributions of the degrees of polymerization of primary chains. A change in the distribution of the degrees of polymerization due to degradation to the degree β is given by integrodifferential eq 1, while the cross-linking of the degraded polymer to the degree α is given by integrodifferential eq 2, where $c(x,\beta)$ and $c(x,\beta,\alpha)$ are number concentrations of an x-mer degraded to the degree β or degraded to the degree β and cross-linked to the degree α. The concentrations are normalized with respect to the constant number of monomer units, i.e.,

$$\partial c(x,\beta)/\partial\beta = -xc(x,\beta) + 2\int_x^\infty c(s,\beta)\,\mathrm{d}s \qquad (1)$$

$$\partial c(x,\beta,\alpha)/\partial\alpha = -xc(x,\beta,\alpha) + \tfrac{1}{2}\int_0^\infty i(x-i)c(i,\beta,\alpha)c(x-i,\beta,\alpha)\,\mathrm{d}i \qquad (2)$$

$$\int_0^\infty xc(x,\beta)\,\mathrm{d}x = \int_0^\infty xc(x,\beta,\alpha)\,\mathrm{d}x = 1$$

Both equations are based on the assumption of chemical kinetics that scission is a first-order reaction and cross-linking a second-order reaction and employ the approximations $\mathrm{d}\beta = k_\beta\,\mathrm{d}t$ or $\mathrm{d}\alpha = k_\alpha\,\mathrm{d}t$ (k_α and k_β being constants), which restricts their validity to low β or α values. It is also assumed that the rate of scission or cross-linking of an x-mer is proportional to x, while in fact the scission is proportional to $x - 1$ and the rate of cross-linking is proportional to the number of repeat units so far uncross-linked. These approximations and the utilization of continuous distribution are suitable for $\alpha \ll 1$ and $\beta \ll 1$, but they may affect the results in an uncontrollable way in those cases where we have systems with short chains or more complicated scission and cross-linking mechanisms.

[+] G. V. Akimov State Research Institute of Materials Protection, 170 04 Prague 7, Czechoslovakia.

0024-9297/80/2213-0571$01.00/0

The theory of branching processes (TBP) based on the graph (tree-like) model and utilizing the probability generating functions and cascade substitution for the generation of a forest of rooted trees (cf., e.g., ref 25–29) was formulated by Gordon et al. (cf. ref 25–28) and at present is the most elaborated statistical method of description of the growth of molecules involving polyfunctional compounds. It offers not only distributions or statistical averages of the degrees of polymerization before the gel point and in the sol, but with a certain approximation also provides statistical averages related to the gel structure (cf. ref 29). The introduction of the path-weighting generating function into TBP yielded a powerful tool permitting calculation of the configuration- and conformation-dependent averages,[29–34] such as, e.g., the radii of gyration or scattering functions.[35,36]

We show in this paper that the TBP approach can be adapted so as to take account of degradation which may accompany the cross-linking. The modification is demonstrated especially on an example of the random degradation of primary chains and of combined cross-linking and degradation, but also on some more complex mechanisms, viz., cross-linking by end-linking of primary chains and cross-linking due to degradation.

Degradation of Linear Molecules

Discrete Distribution. Let it be assumed that at the beginning of degradation there is a set of linear molecules with a discrete weight distribution v_x. If bonds joining monomer units are randomly split to the degree β, then $\beta = 1 - \gamma$ at the same time gives the probability of splitting of a randomly chosen bond. The generating function $W(\theta)$ for the resulting weight distribution w_x is given by

$$W(\theta) \equiv \sum_x w_x \theta^x = \sum_x v_x W_x(\theta) \tag{3}$$

where θ is the dummy variable and $W_x(\theta)$ is the generating function for weight distribution after the degradation of a monodisperse x-mer system. In the calculation of the generating function $W_x(\theta)$, we shall consider an x-mer chain rooted by an arbitrary ith repeat unit (cf. also ref 34 for the construction of the path weighting generating function). Then, the adjoining repeat units form the first and higher generations, and both branches issuing from the root, are not statistically equivalent. If these branches are indicated by p and q, the generating function $W_{xi}(\theta)$ obtained by cascade substitution (cf. ref 25 and 34) for the chain position shown in Figure 1 is given by

$$W_{xi}(\theta) = \theta(1 - \gamma + \gamma u_{\mathrm{q}1})(1 - \gamma + \gamma u_{\mathrm{p}1}) = \theta a_{xi} b_{xi}$$

$$\begin{aligned} u_{\mathrm{q}1} &= \theta(1 - \gamma + \gamma u_{\mathrm{q}2}) \\ u_{\mathrm{q}2} &= \theta(1 - \gamma + \gamma u_{\mathrm{q}3}) \\ &\;\;\vdots \\ u_{\mathrm{q},i-2} &= \theta(1 - \gamma + \gamma u_{\mathrm{q},i-1}) \\ u_{\mathrm{q},i-1} &= \theta \\ u_{\mathrm{p}1} &= \theta(1 - \gamma + \gamma u_{\mathrm{p}2}) \\ u_{\mathrm{p}2} &= \theta(1 - \gamma + \gamma u_{\mathrm{p}3}) \\ &\;\;\vdots \\ u_{\mathrm{p},x-i-1} &= \theta(1 - \gamma + \gamma u_{\mathrm{p},x-i}) \\ u_{\mathrm{p},x-i} &= \theta \end{aligned} \tag{4}$$

The functions a_{xi} and b_{xi} are the generating functions of the left and right branches of the tree. After the cascade substitution mentioned above we obtain

$$a_{xi} = 1 - \gamma + \gamma\theta\{1 - \gamma + \gamma\theta[\ldots + \gamma\theta(1 - \gamma + \gamma\theta)]\} = (1 - \gamma)\sum_{j=0}^{i-2}(\gamma\theta)^j + (\gamma\theta)^{i-1} = [1 - \gamma + (\gamma\theta)^{i-1}(1 - \theta)\gamma]/(1 - \gamma\theta) \tag{5}$$

The procedure employed in the calculation of b_{xi} is completely analogous, i.e., we start with cascade substitution and sum the geometric series thus obtained:

$$b_{xi} = [1 - \gamma + (\gamma\theta)^{x-i}(1 - \theta)\gamma]/(1 - \gamma\theta) \tag{6}$$

The probability of finding the ith monomer unit in the root ($i = 1, 2, \ldots, x$) is x^{-1}, and therefore the resulting generating function $W_x(\theta)$ for the distribution of the degraded x-mer is the average over all possible ways of rooting the x-mer,

$$W_x(\theta) = \sum_{i=1}^{x} x^{-1} W_{xi}(\theta) \tag{7}$$

$$W_x(\theta) = \frac{\theta}{x(1 - \gamma\theta)^2}\{x(1 - \gamma)^2 + x\gamma^2(1 - \theta)^2(\gamma\theta)^{x-1} + 2(1 - \gamma)(1 - \theta)\gamma[1 - (\gamma\theta)^x]/(1 - \gamma\theta)\} \tag{8}$$

The resulting weight distribution $w_{xk} = [d^k W_x(\theta)/\mathrm{d}\theta^k]_{\theta=0}/k!$ is given by

$$\begin{aligned} w_{xk} &= 0 && \text{for } k \geq x + 1 \\ w_{xk} &= (1 - \beta)^{k-1} && \text{for } k = x \end{aligned} \tag{9}$$

$$w_{xk} = (k/x)\beta(1 - \beta)^{k-1}[2 + \beta(x - k - 1)] \qquad \text{for } k = 1, 2, \ldots, x - 1 \tag{10}$$

Relations 9 and 10 are identical with the results obtained by employing other procedures.[11,12,14–19] If at the beginning of degradation the system contained a polydisperse set of chains with the weight distribution v_x, the generating function for the resulting weight distribution is given by eq 3 after substitution for $W_x(\theta)$ from eq 8.

Continuous Distribution. The case where the initial set of molecules is described by a continuous distribution has so far been solved only by means of integrodifferential eq 1 and therefore holds only for low degrees of degradation.

The method of cascade substitution may be successfully employed also for cases of the degradation of continuous distribution to a higher degree. The resulting generation function is obtained by a procedure similar to discrete distributions, only summation is replaced by an integral:

$$W(\theta) = \int_0^\infty w(x)\theta^x \,\mathrm{d}x = \int_0^\infty v(x) W_x(\theta)\,\mathrm{d}x \tag{11}$$

where $w(x)$ and $v(x)$ are the resulting and initial weight distributions, respectively. The generating function $W_x(\theta)$ is given by eq 8.

Moments of the resulting continuous distribution are calculated in the same way as for the discrete distribution; a quite different situation arises with the resulting distribution, $w(k)$. At present, the only exact method for the calculation of distribution from the generating function is based on the Laplace transform. The generating function is first rearranged to

$$W(p) \equiv W(\theta) = \int_0^\infty w(k)\theta^k \,\mathrm{d}k = \int_0^\infty w(k)e^{-(-\ln\theta)k}\,\mathrm{d}k = \int_0^\infty w(k)e^{-pk}\,\mathrm{d}k \tag{12}$$

where p represents a constant in the integration. From tables in ref 37, we then find a function $w(k)$ to the known function $W(p)$. As an example, let us consider a general case for the continuous initial weight distribution v_k. The generating function $W(\theta)$ for the resulting weight distribution $W(k)$ is calculated by using eq 11:

$$W(\theta) = \int_0^{\infty} v(x) \frac{\theta}{x(1-\gamma\theta)^2} \{x(1-\gamma)^2 + x\gamma^2(1-\theta)^2(\gamma\theta)^{x-1} + 2(1-\gamma)(1-\theta)\gamma[1-(\gamma\theta)^x]/(1-\gamma\theta)\}\, \mathrm{d}x \quad (13)$$

The relation is split into the four summands

$$W(\theta) = W_1 + W_2 + W_3 + W_4 = \int_0^{\infty} w(k)\theta^k\, \mathrm{d}k \quad (14)$$

where

$$W_1 = \int_0^{\infty} v(x)\, \mathrm{d}x\, \theta(1-\gamma)^2/(1-\gamma\theta)^2 = \int_0^{\infty} w_1(k)\theta^k\, \mathrm{d}k$$

$$W_2 = \int_0^{\infty} v(x)x^{-1}\, \mathrm{d}x\, 2\gamma(1-\gamma)(1-\theta)/(1-\gamma\theta)^3 = \int_0^{\infty} w_2(k)\theta^k\, \mathrm{d}k$$

$$W_3 = \int_0^{\infty} v(x)(\gamma\theta)^x\, \mathrm{d}x\, \gamma(1-\theta)^2/(1-\gamma\theta)^2 = \int_0^{\infty} w_3(k)\theta^k\, \mathrm{d}k$$

$$W_4 = -\int_0^{\infty} v(x)x^{-1}(\gamma\theta)^x\, \mathrm{d}x\, 2\gamma(1-\gamma)\theta(1-\theta)/(1-\gamma\theta)^3 = \int_0^{\infty} w_4(k)\theta^k\, \mathrm{d}k \quad (15)$$

Obviously, $w(k) = w_1(k) + w_2(k) + w_3(k) + w_4(k)$. Assuming that the initial distribution $v(x)$ is normalized, we obtain after the Laplace transform

$$w_1(k) = (1-\gamma)^2 \sum_{i=0}^{\infty} (i+1)\gamma^i \delta(k-i-1)$$

$$w_2(k) = [\gamma(1-\gamma)/P_{\mathrm{n}}^{\,0}] \sum_{i=0}^{\infty} (i+1)(i+2)\gamma^i \times [\delta(k-i-1) - \delta(k-i-2)]$$

$$w_3(k) = \sum_{i=0}^{i=|k|-3} (i+1)\gamma^k[\gamma v(k-i) - 2v(k-i-1) + v(k-i-2)\gamma^{-1}] + (|k|-1)\gamma^k[\gamma v(k-|k|+2) - 2v(k-|k|+1)] + |k|\gamma^{k+1}v(k-|k|+1)$$

$$w_4(k) = -(1-\gamma)\{\sum_{i=0}^{|k|-3} (i+1)(i+2)\gamma^k[v(k-i-1)/(k-i-1) - v(k-i-2)\gamma^{-1}/(k-i-2)] + |k|(|k|-1)\gamma^k v(k-|k|+1)\} \quad (16)$$

where $P_{\mathrm{n}}^{\,0}$ is the number average degree of polymerization of initial chains, and $\delta(x)$ is a δ function, i.e.,

$$\delta(k-i) = 0 \qquad \text{for } k \neq i$$

$$\delta(k-i) = \infty \qquad \text{for } k = i$$

and

$$\int_0^{+\infty} \delta(k-i)\, \mathrm{d}i = 1$$

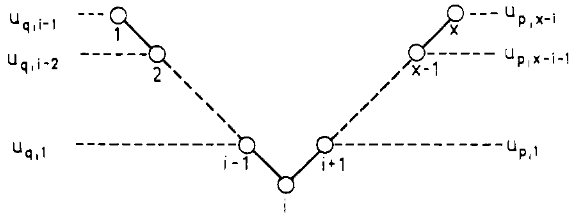

Figure 1. The linear x-mer arranged to form a stochastic tree, if rooted by its ith monomer unit.

The symbol $|k|$ is the smallest integer equal to or higher than k. For k which is $|k| - 3 < 0$, the summations in relations 16 are zero (as follows from the inverse Laplace transform). After rearrangement we obtain

$$w(k) = (1-\gamma)\sum_{i=0}^{\infty}(i+1)\gamma^i\{(1-\gamma)\delta(k-i-1) + [\gamma(i+2)\delta(k-i-1)]/P_{\mathrm{n}}^{\,0} - [\gamma(i+2)\delta(k-i-2)]/P_{\mathrm{n}}^{\,0}\} + \gamma^{k-1}\{\sum_{i=1}^{|k|-1} v(k-i)(1-\gamma) \times [i(1-\gamma) - 1 - \gamma]k/(k-i) + \gamma^2 v(k)\} \quad (17)$$

Let us now examine extreme cases. For the degree of degradation $\beta = 0$, i.e., $\gamma = 1$, we obtain $w(k) = v(k)$. The initial distribution remains unchanged. The second extreme case occurs when degradation reaches the highest degree, $\beta = 1$, i.e., $\gamma = 0$. Then $w(k) = \delta(k-1)$, which means that, after the splitting of all bonds, the system contains only monomer units.

Hence, an important conclusion follows from the theory of cascade substitution for continuous distributions: At the beginning of degradation let the system contain a continuous distribution $v(k)$ with averages $P_i^{\,0}$ ($i = 1, 2, \ldots$; $P_1^{\,0} \equiv P_{\mathrm{n}}^{\,0}$, $P_2^{\,0} \equiv P_{\mathrm{w}}^{\,0}, \ldots$), and after degradation the system contains a set of molecules with averages P_i ($i = 1, 2, \ldots$; $P_1 \equiv P_{\mathrm{n}}$, $P_2 \equiv P_{\mathrm{w}}, \ldots$). If the ith average of the distribution $w(k)$ is defined by

$$P_i = \int_0^{\infty} x^{i-1}w(x)\, \mathrm{d}x \Big/ \int_0^{\infty} x^{i-2}w(x)\, \mathrm{d}x \qquad \text{for } i = 1, 2, \ldots \quad (18)$$

the only weight distribution that gives correct resulting moments is given by eq 17.

Degradation and Cross-Linking without Cyclization

The basic assumptions are: (1) cross-linking proceeds randomly and without cyclization, (2) cross-linking involves linear molecules having one cross-linkable functionality on each repeat unit, and (3) scission of cross-links and links joining repeat units in the primary chains is mutually independent and completely random. Hence, it is possible to carry out cross-linking to the degree α, followed by degradation main chain bonds to the degree β and cross-links to the degree β_1, or degradation of chains to degree β and then cross-linking to degree $\alpha' = \alpha(1 - \beta_1)$, or simultaneously cross-linking and degradation.

Monodisperse System. Let us have an infinite number of x-mer chains, where each repeat unit contains one of the cross-linkable functionalities which react to the degree α, and where bonds linking units are degraded to the degree β. The resulting system is then described by the generating function W_x for trees rooted with an arbitrary ith repeat unit. The probability that a bond issues from the root to the left or to the right is $\gamma = 1 - \beta$ (cf. Figure 1), and the probability that a unit in the root issues a cross-link is equal to the degree of cross-linking α. In this case, the generating function is given by the product of the following three generating functions

$$W_{xi}(\theta) = \theta(1 - \gamma + \gamma u_{\mathrm{p}1})(1 - \gamma + \gamma u_{\mathrm{q}1})(1 - \alpha + \alpha u) = \theta a_{xi} b_{xi} c_{xi} \quad (19)$$

$$\begin{aligned} u_{\mathrm{p}1} &= \theta(1 - \gamma + \gamma u_{\mathrm{p}2})(1 - \alpha + \alpha u) \\ &\cdot \\ &\cdot \\ &\cdot \\ u_{\mathrm{p},i-2} &= \theta(1 - \gamma + \gamma u_{\mathrm{p},i-1})(1 - \alpha + \alpha u) \\ u_{\mathrm{p},i-1} &= \theta(1 - \alpha + \alpha u) \\ u_{\mathrm{q}1} &= \theta(1 - \gamma + \gamma u_{\mathrm{q}2})(1 - \alpha + \alpha u) \\ &\cdot \\ &\cdot \\ &\cdot \\ u_{\mathrm{q},x-i-1} &= \theta(1 - \gamma + \gamma u_{\mathrm{q},x-i})(1 - \alpha + \alpha u) \\ u_{\mathrm{q},x-i} &= \theta(1 - \alpha + \alpha u) \end{aligned} \quad (20)$$

$$u = x^{-1}\sum_{i=1}^{x}\theta(1 - \gamma + \gamma u_{\mathrm{p}1})(1 - \gamma + \gamma u_{\mathrm{q}1}) = x^{-1}\sum_{i=1}^{x}\theta a_{xi} b_{xi} \quad (21)$$

The resulting generating function is then given by

$$W_x(\theta) = \sum_{i=1}^{x} x^{-1} W_{xi}(\theta) \quad (22)$$

where x^{-1} is again the probability of choosing just the ith monomer unit as a root (cf. eq 7). After substitution into eq 22 and summation we obtain

$$W_x(\theta) = \frac{\omega}{x(1 - \gamma\omega)^2}\{x(1 - \gamma)^2 + x\gamma^2(1 - \omega)^2(\gamma\omega)^{x-1} + 2\gamma(1 - \gamma)(1 - \omega)[1 - (\gamma\omega)^x]/(1 - \gamma\omega)\} \quad (23)$$

where $\omega = \theta(1 - \alpha + \alpha u)$. It is obvious that eq 23 is identical with eq 8, only the original variable θ is replaced by the expression $\theta(1 - \alpha + \alpha u)$.

Polydisperse System. The generating function for the resulting weight distribution after cross-linking and degradation is given by

$$W(\theta) = \sum_{i=1} v_i W_i(\theta) \quad (24)$$

where $W_i(\theta)$ is given by eq 23 and the variable u is given by $W(\theta) = u(1 - \alpha + \alpha u)$. If the initial set of molecules is described by the continuous weight distribution $v(i)$, the procedure is similar to that of the degradation alone, i.e.,

$$W(\theta) = \int_0^\infty v(i) W_i(\theta)\,\mathrm{d}i = u(1 - \alpha + \alpha u) \quad (25)$$

where $W_i(\theta)$ is given by eq 23. The relations which hold for the most probable distribution, the Poisson distribution, the distribution arising in radical polymerization when termination occurs by recombination of macroradicals, and the continuous Schulz–Zimm distribution are the same as those valid for the degradation (Appendix), only the variable θ is replaced by the variable $\theta(1 - \alpha + \alpha u)$.

Number Average Degree of Polymerization. The resulting number average may be calculated by using the equation $P_{\mathrm{n}} = 1/\int_0^\infty[W(\theta)/\theta]\,\mathrm{d}\theta$, or by employing a simpler procedure from the mass balance (bond splitting or formation means an increase or loss, respectively, of the number of molecules in the system by one):

$$P_{\mathrm{n}} = P_{\mathrm{n}}^0/[1 + \beta(P_{\mathrm{n}}^0 - 1) - \alpha P_{\mathrm{n}}^0/2] \quad (26)$$

where P_{n}^0 is the number average of the initial chains.

Weight Average Degree of Polymerization P_{w}. The resulting weight average is given by

$$P_{\mathrm{w}} = [\mathrm{d}W(\theta)/\mathrm{d}\theta]_{\theta=1} = [\mathrm{d}W(\omega)/\mathrm{d}\omega]_{\omega=1}\,[\mathrm{d}(1 - \alpha + \alpha u)\theta/\mathrm{d}\theta]_{\theta=1}$$

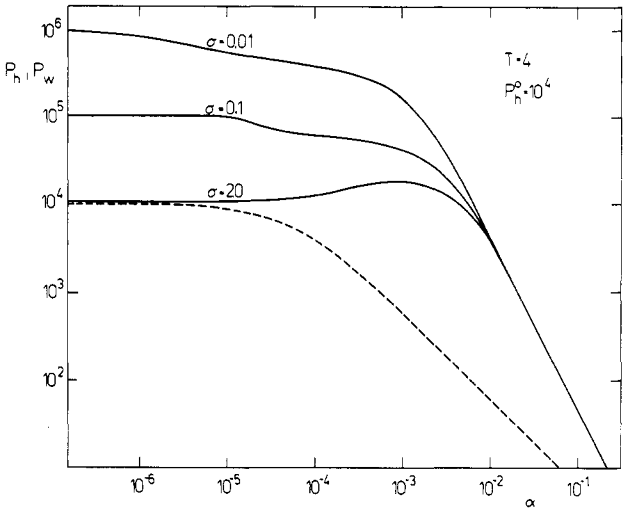

Figure 2. The dependence of the weight P_{w} and number P_{n} averages of the degree of polymerization in the cross-linking and degradation process, if the initial distribution is of the Schulz–Zimm type.

because for $\theta = 1$, $\omega = 1$. The value of $[\mathrm{d}u/\mathrm{d}\theta]_{\theta=1}$ may be calculated from $W(\theta) = u(1 - \alpha + \alpha u)$. After rearrangement, we have

$$P_{\mathrm{w}} = [\mathrm{d}W(\omega)/\mathrm{d}\omega]_{\omega=1}\,(1 + \alpha)/[1 - \alpha(P_{\mathrm{w}}' - 1)] = P_{\mathrm{w}}'(1 + \alpha)/[1 - \alpha(P_{\mathrm{w}}' - 1)] \quad (27)$$

where P_{w}' is the weight average degree of polymerization of a distribution which would arise from the initial distribution by degradation without cross-linking. As long as the cross-links are also split to the degree β_1 during degradation, the resulting weight average is given by

$$P_{\mathrm{w}} = P_{\mathrm{w}}'[1 + \alpha(1 - \beta_1)]/[1 - \alpha(1 - \beta_1)(P_{\mathrm{w}}' - 1)] \quad (28)$$

The weight averages for concrete cases are given in the Appendix.

Gel Point. Gel formation occurs under certain conditions during simultaneous cross-linking and degradation. At the gel point it holds that $P_{\mathrm{w}} \to \infty$, and therefore according to eq 28 we obtain the condition for network formation:

$$\alpha_{\mathrm{g}} = [(1 - \beta_1)(P_{\mathrm{w}}' - 1)]^{-1} \quad (29)$$

At the same time, eq 29 represents the condition for the degree of degradation of the main chains at the overall degree of cross-linking α. Thus, e.g., for the most probable initial distribution, we obtain

$$\beta_{\mathrm{g}} = 1 - \gamma_{\mathrm{g}} = [q(1 + 2\alpha) - 1]/[q(1 + 2\alpha)] \quad (30)$$

where $q = (P_{\mathrm{n}}^0 - 1)/P_{\mathrm{n}}^0$. Thus, if the cross-linking of linear molecules with the most probable initial distribution proceeds to the degree α and if during this process gel formation is to occur, it is necessary that the degree of degradation of the initial chains should not exceed β_{g}. With increasing degree of degradation the critical value of α_{g} increases, and at a certain β it becomes $\alpha_{\mathrm{g}} = 1$. Hence, for the most probable distribution we obtain from eq 30 the highest possible value of the degree of degradation for gel formation, $\beta_{\mathrm{g,max}} = (2P_{\mathrm{n}}^0 - 3)/[3(P_{\mathrm{n}}^0 - 1)]$. For higher values of the initial number average P_{n}^0, $\beta_{\mathrm{g,max}}$ is independent of P_{n}^0, and it holds approximately that $\beta_{\mathrm{g,max}} \approx {}^2/_3$. In practice, the process of cross-linking and degradation occurs so that cross-linking and degradation take place simultaneously; i.e., with increasing α, β also increases.

Let us take as an example the case of the proportionality of the intensity of cross-linking and degradation for the

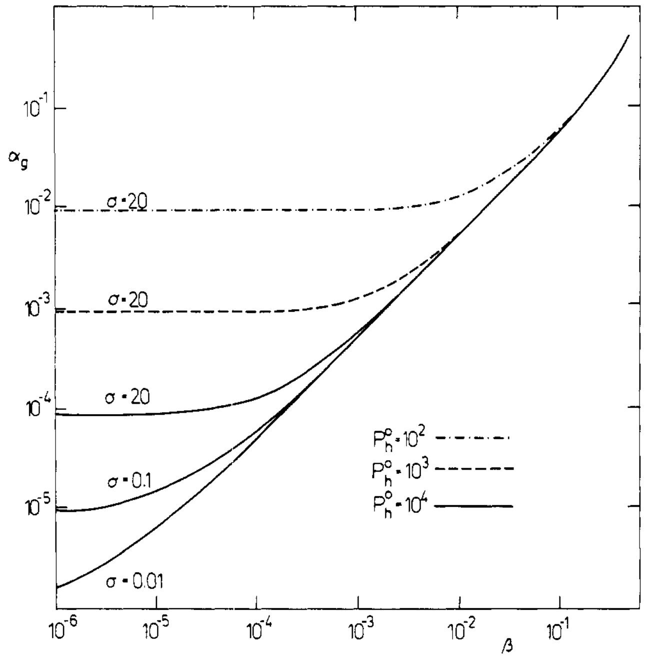

Figure 3. The dependence of the degree of cross-linking α_g at the gel point on the degree of the degradation β in the cross-linking and degradation of linear molecules with the initial Schulz–Zimm distribution.

initial Schulz–Zimm distribution, when $\beta = \alpha T/2$, where T is a constant (cf. eq 26 and the relation given for P_w in the Schulz–Zimm distribution in the Appendix). While for $T < 1$ both P_w and P_n increase and at a certain α network is formed, for $T = 1$ network is also formed, but P_n remains constant. Even at $T = 3$ for $P_n^0 = 10^4$ cross-linking and degradation may be accompanied by network formation, but the resulting number average decreases. As shown in Figure 2, under certain conditions (e.g., $T = 4$, $P_n^0 = 10^4$, and $\sigma = 20$ with $\sigma = 1/(1 - P_w^0/P_n^0)$), the dependence $P_w(\alpha)$ may be rather complicated. At the beginning, the cross-linking effect is operative (P_w increases), but at a certain stage of the process degradation becomes increasingly important, and P_w begins to decrease. It can be seen, therefore, that the rise or decrease in the number average in the degradation-cross-linking process cannot decide whether the process tends to network formation or not.

Figure 3 shows the dependence of the gel point α_g on the degree of degradation β for $P_n^0 = 10^2$, 10^3, and 10^4 and for $\sigma = 10^{-2}$, 10^{-1}, and 20. It can be seen that for narrow distributions or for a monodisperse system at low degrees of degradation, α_g is almost independent of the degree of degradation β. Here, a compensating effect following from the decrease in the average degree of polymerization and from the broadening of distribution is operative. The results for $\sigma = 0.1$ and $P_n^0 = 10^2$ are similar to those for $\sigma = 20$ and $P_n^0 = 10^3$; also, the results for $\sigma = 20$ and $P_n^0 = 10^4$ are similar to those at $\sigma = 0.1$ and $P_n^0 = 10^3$ and at $\sigma = 0.01$ and $P_n^0 = 10^2$; this is why the respective curves are not presented in Figure 3.

As mentioned before, the cross-linking and degradation have also been treated by employing the method of the integrodifferential equation.[20] Figures 4 and 5 show a comparison between the weight averages P_w and the gel points α_g of Saito's theory and of the theory of branching processes. P represents a deviation (in percent) from the result of the theory of branching processes. It is evident that the deviation is larger the higher the degree of degradation β and the lower P_n^0. Large differences in P_w are also near the gel point. It is of interest, moreover, that Saito's theory gives lower P_w and the gel point conversion α_g, but higher P_w if only degradation occurs ($\alpha = 0$).

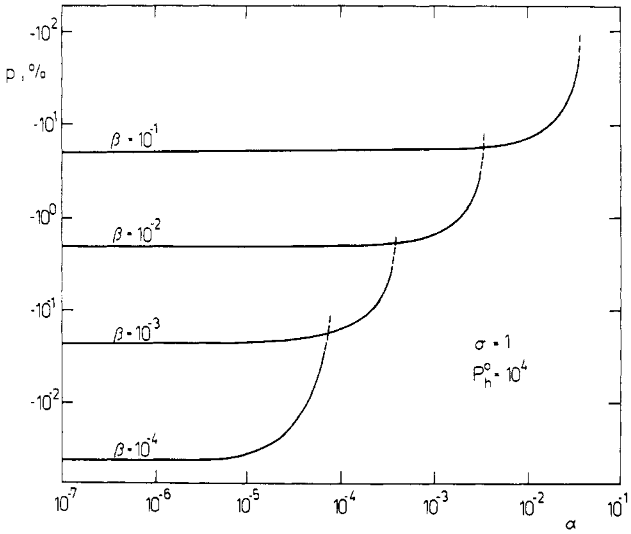

Figure 4. The deviation in percent, P, of P_w according to Saito from the P_w obtained by the theory of branching processes for random cross-linking and degradation of linear chains with the initial Schulz–Zimm distribution.

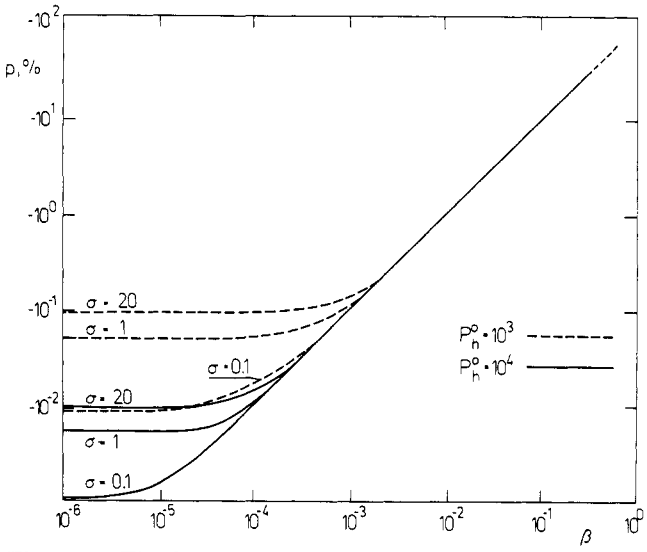

Figure 5. The deviation in percent, P, of critical α_g according to Saito from α_g obtained by the theory of branching processes for random cross-linking and degradation of linear chains with initial Schulz–Zimm distribution.

More Complicated Processes of Degradation and Cross-Linking

Cross-Linking by End-Linking and Degradation. A more complex situation arises in the case of end-linking of initial chains, having functional groups only at their ends, with an f-functional cross-linking agent and simultaneous degradation of the initial chains. We assume that (1) the cross-linking and degradation processes are independent of eath other, (2) at the beginning of the process, the system contains chains consisting of monomer units of type 1, having the number or weight distribution n_i or v_i, respectively, and (3) the cross-linking f-functional units are referred to as units of type 2.

The fraction of monomer units in the whole system of type 1 is φ_1 and that of monomer units of type 2 is $\varphi_2 = 1 - \varphi_1$. Let P_n^0 be the number average degree of polymerization of the initial chain distribution, α_1 be the conversion of chain ends, and α_2 be the conversion of functionalities in f-functional molecules. It follows from the stoichiometry of the reaction that

$$\alpha_2 = 2\alpha_1\varphi_1/[f\varphi_2P_n^0] \qquad (31)$$

The procedure employed in the formulation of the generating function for the resulting weight distribution is similar to that used in the process of degradation, or of degradation and cross-linking. Individual monomer units differing in their type (1 or 2) or in their position in the initial chains of various length are taken as roots of the probability trees. The resulting generating function $W(\theta_1,\theta_2)$ for the distribution w_{ij} of an $(i + j)$-mer consisting of i units of type 1 and j units of type 2 may be written as

$$W(\theta_1,\theta_2) = \varphi_1W_1 + \varphi_2W_2 \qquad (32)$$

where $W_1 \equiv W_1(\theta_1,\theta_2)$ or $W_2 \equiv W_2(\theta_1,\theta_2)$ represents the generating functions for the distribution $v_{ij}^{(1)}$ or $v_{ij}^{(2)}$, respectively, when units of type 1 or 2, respectively, were used as roots. The meaning of the generating functions is similar to that of homopolymers. If at the end of the process there are N_{ij} molecules, each of which has i units of type 1 and j units of type 2, then

$$W_1 = \sum_{i=1}^{\infty}\sum_{j=0}^{\infty}v_{ij}^{(1)}\theta_1^{\,i}\theta_2^{\,j}$$

$$W_2 = \sum_{i=0}^{\infty}\sum_{j=1}^{\infty}v_{ij}^{(2)}\theta_1^{\,i}\theta_2^{\,j} \qquad (33)$$

where

$$v_{ij}^{(1)} = \frac{iN_{ij}}{\sum\limits_{i=1}\sum\limits_{j=0}iN_{ij}}$$

$$v_{ij}^{(2)} = \frac{jN_{ij}}{\sum\limits_{i=0}\sum\limits_{j=1}jN_{ij}} \qquad (34)$$

Since

$$\varphi_1 = \frac{\sum\limits_{i=1}\sum\limits_{j=0}iN_{ij}}{\sum\limits_{i=0}\sum\limits_{j=0}(i + j)N_{ij}} \qquad (35)$$

eq 32 may be written as

$$W(\theta_1,\theta_2) = \sum_{i=0}\sum_{j=0}w_{ij}\theta_1^{\,i}\theta_2^{\,j}$$

where

$$w_{ij} = \frac{(i + j)N_{ij}}{\sum\limits_{i=0}\sum\limits_{j=0}(i + j)N_{ij}} \qquad (36)$$

Similarly to eq 22, we obtain

$$W_1 = \sum_{i=1}^{\infty}v_ii^{-1}\sum_{j=1}^{i}\theta_1a_jb_j \qquad (37)$$

where

$$a_j = (1 - \gamma)[1 - (\gamma\theta_1)^{j-1}]/(1 - \gamma\theta_1) + (\gamma\theta_1)^{j-1}(1 - \alpha_1 + \alpha_1u) \qquad (38)$$

$$b_j = a_{i-j+1}$$

where $\beta = 1 - \gamma$ is the total degree of degradation of initial chains.

We obtain, after rearrangement

$$W_1 = (\theta_1/P_n^0)\sum_{i=1}^{\infty}n_i\{i[(1 - \gamma)/(1 - \gamma\theta_1)]^2 + 2(1 - \gamma) \times [1 - \alpha_1 + \alpha_1u(1 - \gamma)/(1 - \gamma\theta_1)][1 - (\gamma\theta_1)^i]/(1 - \gamma\theta_1)^2 + i(\gamma\theta_1)^{i-1}[1 - \alpha_1 + \alpha_1u - (1 - \gamma)/(1 - \gamma\theta_1)]^2\} \qquad (39)$$

where $(1 - \alpha_1 + \alpha_1u)$ is the generating function adequately expressing the possibility of an f-functional molecule being attached to the chain end; hence,

$$u = \theta_2[1 - \alpha_2 + \alpha_2\theta_1\sum_{i=1}^{\infty}n_ia_i]^f = \theta_2A^{f-1} \qquad (40)$$

The generating function W_2 is given by

$$W_2 = \theta_2A^f \qquad (41)$$

and the weight average degree of polymerization P_w by

$$P_w = [\mathrm{d}W/\mathrm{d}\theta_1]_{\theta_1=\theta_2=1} + [\mathrm{d}W/\mathrm{d}\theta_2]_{\theta_1=\theta_2=1} \qquad (42)$$

If $[\mathrm{d}W_i/\mathrm{d}\theta_j]_{\theta_1=\theta_2=1} = W_i^{\,j}$, then eq 39, 40, and 41 yield

$$W_1^{\,1} = \{P_n^0(1 - \gamma)^2[1 - \alpha_1\alpha_2(f - 1)S] + 2(1 - \gamma S) \times [\alpha_1\alpha_2(f - 1) - \gamma]\}/\{P_n^0(1 - \gamma)^2[1 - \alpha_1\alpha_2(f - 1)S]\}$$

$$W_1^{\,2} = 2\alpha_1(1 - \gamma S)/\{P_n^0(1 - \gamma)[1 - \alpha_1\alpha_2(f - 1)S]\}$$

$$W_2^{\,1} = \alpha_2f(1 - \gamma S)/\{(1 - \gamma)[1 - \alpha_1\alpha_2(f - 1)S]\}$$

$$W_2^{\,2} = (1 + \alpha_1\alpha_2S)/[1 - \alpha_1\alpha_2(f - 1)S] \qquad (43)$$

where

$$S = \sum_{i=1}^{\infty}n_i\gamma^{i-1}$$

The resulting weight average degree of polymerization P_w is

$$P_w = \varphi_1(W_1^{\,1} + W_1^{\,2}) + \varphi_2(W_2^{\,1} + W_2^{\,2}) \qquad (44)$$

Since by the splitting of one bond the number of molecules in the system increases by one and by reacting one end functionality the number of molecules also decreases by one, the resulting number average degree of polymerization P_n is given by

$$P_n = \frac{P_n^0 + \varphi_2P_n^0/\varphi_1}{1 + \beta(P_n^0 - 1) - 2\alpha_1 + \varphi_2P_n^0/\varphi_1} \qquad (45)$$

At the gel point, the P_w assumes an infinite value; therefore, the gel point condition is given by

$$\alpha_1\alpha_2(f - 1)S = 1 \qquad (46)$$

From eq 31 and 46 one obtains

$$\alpha_{1g} = (f\varphi_2P_n^0/[2(f - 1)\varphi_1S])^{1/2} \qquad (47)$$

If network formation is to take place in the course of the process, it is necessary that the conversion of reactive chain ends reach at least α_{1g}.

As a special case, let us consider the most probable initial distribution $n_i = (1 - q)q^{i-1}$, where $q = (P_n^0 - 1)/P_n^0$. According to eq 43 and 44 we obtain

$$P_w = \varphi_1\frac{P_n^0(1 + \gamma) - \gamma + \alpha_1\alpha_2(f - 1) + 2\alpha_1}{P_n^0(1 - \gamma) + \gamma - \alpha_1\alpha_2(f - 1)} + \varphi_2\frac{P_n^0(1 - \gamma) + \gamma + \alpha_1\alpha_2 + \alpha_2fP_n^0}{P_n^0(1 - \gamma) + \gamma - \alpha_1\alpha_2(f - 1)} \qquad (48)$$

The condition for the gel point is

$$\alpha_{1g} = \{f\varphi_2P_n^0[P_n^0(1 - \gamma) + \gamma]/[2(f - 1)\varphi_1]\}^{1/2} \qquad (49)$$

or

$$\beta_g = 1 - \gamma_g = [2\alpha_1^{\,2}\varphi_1(f - 1) - f\varphi_2P_n^0]/[f\varphi_2P_n^0(P_n^0 - 1)] \qquad (50)$$

If the network is to be formed during the cross-linking to

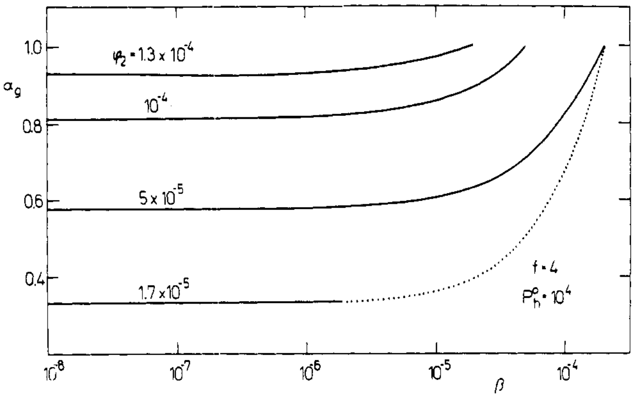

Figure 6. Cross-linking of chains carrying reactive end groups with a tetrafunctional cross-linking agent and chain degradation. Dependence of the conversion of end groups α_g at the gel point on the degree of degradation.

the degree α_1, it is necessary that the degree of degradation should not exceed β_g.

Let us have a closer look at the possibilities of network formation for the most probable initial distribution. Two cases may be distinguished with respect to mass balance, namely, (1) for $f\varphi_2P_n^0/2\varphi_1 \geq 1$ we have $\alpha_1 \in \langle 0.1\rangle$ (stoichiometrically equivalent ratio or an excess of component 2), and (2) for $f\varphi_2P_n^0/2\varphi_1 < 1$ we have $\alpha_1 \in \langle 0, f\varphi_2P_n^0/2\varphi_1\rangle$ (excess of component 1).

According to eq 49, it may hold at the gel point that

$$\varphi_2P_n^0f/2\varphi_1 \leq (f-1)/[P_n^0(1-\gamma)+\gamma]$$

Thus in the former case gelation also takes place at the stoichiometrically equivalent ratio ($2\varphi_1/P_n^0 = f\varphi_2$) and at a 100% conversion ($\alpha_1 = \alpha_2 = 1$) only if

$$\beta \leq (f-2)/(P_n^0-1)$$

In the latter case, network formation could occur only if

$$\beta \leq [(f-1)f\varphi_2P_n^0/(2\varphi_1) - 1]/(P_n^0-1)$$

Figure 6 shows the dependence of the gel point conversion α_{1g} on the degree of degradation β for various initial compositions. It is obvious that if network formation is to occur, the initial composition cannot be arbitrary. Equation 31 with the condition $\alpha_2 \leq 1$ and eq 49 determine the lowest possible φ_2, if gelation is to take place. The highest φ_2 follows from eq 49 and from the condition $\alpha_1 \leq 1$,

$$\varphi_{2,\max} = \{1 + fP_n^0(P_n^0\beta+\gamma)/[2(f-1)]\}^{-1}$$

$$\varphi_{2,\min} = \{1 + f(f-1)P_n^0/[2(P_n^0\beta+\gamma)]\}^{-1} \qquad (51)$$

As demonstrated by Figure 7, $\varphi_{2,\max}$ decreases with increasing degree of degradation β, while $\varphi_{2,\min}$ increases. In this way, the interval of the possible φ_2 values becomes narrower, and at $\beta = (f-2)/(P_n^0-1)$, $\varphi_2 = \varphi_{2,\min} = \varphi_{2,\max}$.

Cross-Linking Due to Degradation

Already Charlesby[6] has investigated a case when, in the degradation of chains, reactive ends are formed which may become attached to another unit in another chain. At the same time, the moments of distribution of molecules in the system also change, and under certain circumstances, network formation may take place. Saito[20] investigated the same problem by means of an integrodifferential equation. Both authors assumed, however, that the initial distribution has a sufficiently large number average.

The theory of branching processes allows us to solve the problem in a general and exact manner. Let the number or weight distribution of primary linear molecules be n_i or v_i, respectively. After the splitting of one bond, two reactive ends are formed, which may become attached to the monomer unit of another chain. Only one reactive end may become attached to the monomer unit. Degradation occurs to the degree $\beta = 1 - \gamma$, and only the fraction α_1 of the newly formed reactive ends react. Let α_2 be the fraction of monomeric units to which reactive ends have been attached; mass balance gives

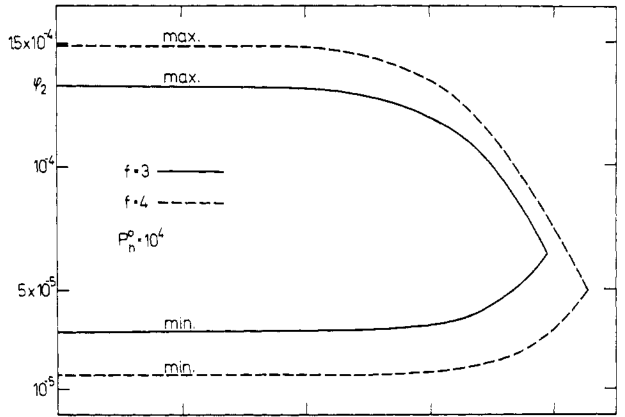

Figure 7. Cross-linking of chains carrying reactive end groups with a tetrafunctional cross-linking agent and chain degradation. The highest and lowest allowed φ_2 value for infinite network formation to occur as a function of the degree of degradation.

$$\alpha_2 = 2\alpha_1\beta(P_n^0-1)/P_n^0$$

therefore

$$0 \leq \alpha_1 \leq P_n^0/[2\beta(P_n^0-1)] \qquad (52)$$

By employing a procedure similar to that used for degradation, or degradation and cross-linking (cf. eq 7 and 22), we obtain the generating function $W(\theta)$ for the resulting weight distribution

$$W(\theta) = \sum_{i=1}^{\infty}(v_i/i)\sum_{j=1}^{i}\theta F a_j b_j \qquad (53)$$

where

$$a_j = (1-\gamma)(1-\alpha_1+\alpha_1G)[1-(\gamma\theta F)^{j-1}]/(1-\gamma\theta F) + (\gamma\theta F)^{j-1}$$

$$b_j = a_{i-j+1} \qquad (54)$$

and the generating function $G_1(\theta) \equiv G_1 = 1 - \alpha_1 + \alpha_1G(\theta)$ describes the possibility that the reactive end is involved in the formation of a link to another chain with the probability α_1. Of each monomeric unit, randomly chosen as the root, as many as three branches may lead to higher generations. Two of them are related to the original chain, while the third one is given by the possibility of attaching a randomly chosen reactive end to the given monomer unit. This third branch is characterized by the generating function $F \equiv F(\theta)$. It holds that

$$W(\theta) = G(\theta)F(\theta) \qquad (55)$$

After substitution of eq 54 into eq 53 and summation over j and rearrangement, we obtain

$$W(\theta) = \theta F\{P_n^0(1-\gamma)^2G_1 + [1-\gamma\theta F-(1-\gamma)G_1]^2\sum_{i=1}^{\infty}in_i(\gamma\theta F)^{i-1} + 2(1-\gamma)G_1[1-\gamma\theta F-(1-\gamma)G_1][1-\sum_{i=1}^{\infty}n_i(\gamma\theta F)^i]/(1-\gamma\theta F)\}[P_n^0(1-\gamma\theta F)^2]^{-1} \qquad (56)$$

The probability that a randomly chosen radical (reactive end) of all radicals formed in the reaction originally belonged to the initial i-mer is p_i

$$p_i = n_i(i - 1)/(P_n{}^0 - 1) \tag{57}$$

The probability that this radical belongs to a monomer unit which occupies a predetermined position in the initial i-mer is

$$t = 1/(i - 1) \tag{58}$$

This probability is obviously the same for all positions. Hence, for F we obtain

$$F = 1 - \alpha_2 + \alpha_2 \sum_{i=2}^{\infty} p_i \sum_{j=1}^{i-1} t\theta F a_j \tag{59}$$

After substitution of eq 54, 57, and 58,

$$F = 1 - \alpha_2 + \alpha_2\theta F/(1 - \gamma\theta F)\{(1 - \gamma)G_1 + [1 - \sum_{i=1}^{\infty} n_i(\gamma\theta F)^{i-1}][1 - \gamma\theta F - (1 - \gamma)G_1]/[(1 - \gamma\theta F)(P_n{}^0 - 1)]\} \tag{60}$$

It is possible to calculate the moments of the resulting distribution by using eq 55, 56, and 59.

Weight Average Degree of Polymerization P_w. If $[dF/d\theta)_{\theta=1} \equiv F'$ and $[dG/d\theta]_{\theta=1} \equiv G'$, then the resulting weight average P_w is then given by

$$P_w = G' + F' = \{[P_n{}^0(1 - \gamma)^2 + 2\gamma A][P_n{}^0 + 2\alpha_1{}^2K] - 4\alpha_1{}^2A^2\}\{[P_n{}^0(1 - \gamma) - 2\alpha_1 A]^2 - 4\alpha_1{}^2\gamma AK\}^{-1} \tag{61}$$

where $A = P_n{}^0(1 - \gamma) - 1 + \gamma S$, $K = (P_n{}^0 - 1)(1 - \gamma) - 1 + S$, and $S = \sum_{i=1}{}^\infty n_i\gamma^{i-1}$. Under certain conditions, network formation may take place. From eq 61 we obtain for the gel point

$$\alpha_{1g} = P_n{}^0(1 - \gamma)/[2\{A + (AK\gamma)^{1/2}\}] \tag{62}$$

The Resulting Number Average Degree of Polymerization P_n. Since with the formation or scission of one bond the number of molecules in the system is reduced or raised by one, the resulting number average is

$$P_n = P_n{}^0/[1 + \beta(1 - 2\alpha_1)(P_n{}^0 - 1)] \tag{63}$$

As a special case, we consider the initial most probable distribution $n_i = (1 - q)q^{i-1}$, where $q = (P_n{}^0 - 1)/P_n{}^0$. From eq 61 we obtain

$$P_w = \frac{(P_n{}^0)^2 + \gamma P_n{}^0(P_n{}^0 - 1) - 2\alpha_1{}^2(P_n{}^0 - 1)^2(1 - \gamma)^2}{[P_n{}^0 - 2\alpha_1(P_n{}^0 - 1)(1 - \gamma)]^2 - \gamma P_n{}^0(P_n{}^0 - 1)} \tag{64}$$

Infinite network formation occurs when

$$\alpha_{1g} = [P_n{}^0 - \{\gamma P_n{}^0(P_n{}^0 - 1)\}^{1/2}]/[2(P_n{}^0 - 1)(1 - \gamma)] \tag{65}$$

under the condition that $1 - \gamma = \beta \geq [3P_n{}^0 - \{9(P_n{}^0)^2 - 16P_n{}^0\}^{1/2}]/[8(P_n{}^0 - 1)]$ or

$$\beta_g = [P_n{}^0(4\alpha_1 - 1) \mp \{(P_n{}^0)^2(4\alpha_1 - 1)^2 - 16\alpha_1{}^2P_n{}^0\}^{1/2}]/[8\alpha_1{}^2(P_n{}^0 - 1)] \tag{66}$$

under the condition that $\alpha_1 \geq (P_n{}^0)^{1/2}/[4\{(P_n{}^0)^{1/2} - 1\}]$. Conditions 65 and 66 follow from the requirement $\alpha_1 \leq 1$ and $\beta \leq 1$. If during the given process degradation reaches the degree β and if infinite network is to be formed, it is necessary that $\alpha_1 \geq \alpha_{1g}$. If only the fraction α_1 of the newly formed reactive ends reacts, degradation must attain the degree β_g for gelation to occur. The relations given above are exact for any β, α_1, and $P_n{}^0$ values. Charlesby[6] and Saito[20] assumed that the given system may be described with sufficient accuracy by using continuous distribution. An analysis shows that our results for the most probable distribution are approximately identical with those obtained by Saito only for a high $P_n{}^0$ and low degrees of degradation β. For the sake of comparison, Figure 8 shows the deviation of the critical α_g obtained by Saito with respect to that obtained by the theory of branching processes.

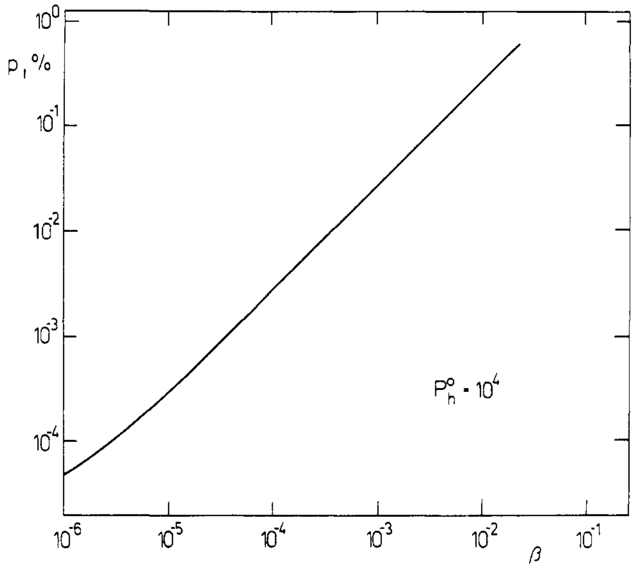

Figure 8. Cross-linking due to degradation. The deviation (in percent) of the critical degree of cross-linking according to Saito with respect to the value obtained by the theory of branching processes for the most probable initial distribution ($P_n{}^0 = 10^4$).

Conclusion

The methods of probability generation functions and cascade substitution may be utilized also for other, more complicated mechanisms of polymer network formation involving cross-linking and scission processes, such as, e.g., the unlike types of bonds or functional groups appearing in homopolymers and especially in copolymers. The procedure may also be extended to include the postgel stage, especially for the description of the sol fraction. Introduction of the formalism of the path-weighting generating function would provide an access to conformation averages. The results are free from approximations following in particular from assumptions of a high degree of polymerization of the initial system and of a low degree of cross-linking and degradation on which the existing theories (especially the most widely used kinetic theory of Saito et al.) are based. Similarly to the other theories, this approach also neglects cyclization. Nevertheless, a comparatively good agreement between high-energy radiation experiments and theory, when assumptions concerning the magnitude of $P_n{}^0$, α, β, and the distribution type are met and with a relative dose being used, indicates that rescaling with respect to the gel point allows us to reduce the effect of cyclization to a considerable extent. In this connection one may recall the efficiency of the rescaling method in the treatment of the pre- and postgelation cyclization in the cross-linking of primary chains by vulcanization[38] and end-linking.[39]

Appendix. The Resulting Generating Function, $W(\theta)$, for the Weight Distribution, Weight Average Degree of Polymerization P_w, Number Degree of Polymerization Average P_n, and Critical Degree of Cross-Linking α_g in the Degradation and Cross-Linking for Special Initial Distributions v_x

Monodisperse System.

$$\upsilon_x = \delta_x{}^i \qquad P_w{}^0 = P_n{}^0 = x$$

where $\delta_x{}^i$ is Kronecker's δ, i.e., $\delta_x{}^i = 0$ for $i \neq x$ and 1 for $i = x$.

$$W(\omega) = \frac{\omega}{x(1-\gamma\omega)^2}\{x(1-\gamma)^2 + x\gamma^2(1-\omega)^2(\gamma\omega)^{x-1} + 2\gamma(1-\gamma)(1-\omega)[1-(\gamma\omega)^x]/(1-\gamma\omega)\}$$

$$P_w = \frac{[(1-\gamma^2)x - 2\gamma + 2\gamma^{x+1}][1+\alpha(1-\beta_1)]}{x(1-\gamma)^2 - 2\alpha(1-\beta_1)\gamma[x(1-\gamma) - 1 + \gamma^x]}$$

$$\alpha_g = \frac{x(1-\gamma)^2}{2\gamma[x(1-\gamma) - 1 + \gamma^x](1-\beta_1)}$$

The Most Probable Distribution.

$$\upsilon_x = (1-q)^2 i q^{i-1}$$

$$P_n{}^0 = (1-q)^{-1}$$

$$P_w{}^0 = (1+q)/(1-q)$$

$$W(\omega) = (1-\gamma q)^2\omega/(1-\gamma\omega q)^2$$

$$P_w = 2\gamma q\frac{1+\alpha(1-\beta_1)}{1-\gamma q - 2\gamma q\alpha(1-\beta_1)}$$

$$\alpha_g = (1-\gamma q)/[2\gamma q(1-\beta_1)]$$

The Poisson Distribution.

$$\upsilon_x = e^{-\nu}\nu^{x-1}x/[(\nu+1)(x-1)!]$$

$$P_n{}^0 = \nu + 1$$

$$P_w{}^0 = (\nu^2 + 3\nu + 1)/(\nu + 1)$$

$$W(\omega) = \omega\{(1-\gamma)^2(1-\gamma\omega)(1+\nu) + 2(1-\gamma)\gamma(1-\omega) + e^{-\nu(1-\gamma\omega)}[\gamma^2(1-\omega)^2(1-\gamma\omega)(1+\nu\gamma\omega) - 2\gamma^2(1-\gamma) \times (1-\omega)\omega]\}(\nu+1)^{-1}(1-\gamma\omega)^{-3}$$

$$P_w = \{[(\nu+1)(1-\gamma^2) - 2\gamma + 2\gamma^2 e^{-\nu(1-\gamma)}] \times [1+\alpha(1-\beta_1)]\}/\{(\nu+1)(1-\gamma)^2 - 2\alpha(1-\beta_1)\gamma[(\nu+1)(1-\gamma) - 1 + 2\gamma e^{-\nu(1-\gamma)}]\}$$

$$\alpha_g = (\nu+1)(1-\gamma)^2/\{2\gamma(1-\beta_1)[(\nu+1) \times (1-\gamma) - 1 + \gamma e^{-\nu(1-\gamma)}]\}$$

Distribution in Radical Polymerization When Termination Occurs by Recombination of Macroradicals.

$$\upsilon_x = (1-a)^3 x(x-1)a^{x-2}/2$$

$$P_n{}^0 = 2/(1-a)$$

$$P_w{}^0 = (2+a)/(1-a)$$

$$W(\omega) = \frac{\omega}{(1-\gamma\omega)^3}\{(1-\gamma)^2(1-\gamma\omega) + \gamma(1-\gamma)(1-a) \times (1-\omega) + \gamma^3(1-a)^3(1-\omega)^2(1-\gamma\omega)\omega(1-a\gamma\omega)^{-3} - \gamma^3(1-\gamma)(1-a)^3\omega^2(1-\omega)(1-a\gamma\omega)^{-2}\}$$

$$P_w = \{[(1-\gamma)^2 - \gamma(1-a) + \gamma^3(1-a)^3/(1-\gamma a)^2] \times [1+\alpha(1-\beta_1)]\}/\{(1-\gamma)^2 - \alpha(1-\beta_1)[2\gamma(1-\gamma) - \gamma(1-a) + \gamma^3(1-a)^3/(1-\gamma a)^2]\}$$

$$\alpha_g = (1-\gamma)^2/\{(1-\beta_1)[\gamma(1-2\gamma+a) + \gamma^3(1-a)^3(1-\gamma a)^{-2}]\}$$

The Schulz–Zimm Distribution.

$$\upsilon(x) = [\sigma^\sigma/(P_n{}^0\Gamma(\sigma))](x/P_n{}^0)^\sigma e^{-\sigma x/P_n{}^0}$$

$$P_w{}^0 = P_n{}^0(\sigma+1)/\sigma$$

$$W(\omega) = (\omega/P_n{}^0)(1-\gamma\omega)^{-2}\{P_n{}^0(1-\gamma)^2 + (P_n{}^0/\omega)\gamma(1-\omega)^2[\sigma/(\sigma - P_n{}^0 \ln \gamma\omega)]^{\sigma+1} + 2\gamma(1-\gamma)(1-\omega)(1-\gamma\omega)^{-1}[1-(\sigma/[\sigma - P_n{}^0 \ln \gamma\omega])^\sigma]\}$$

$$P_w = \{(P_n{}^0(1-\gamma^2) - 2\gamma + 2\gamma[\sigma/(\sigma - P_n{}^0 \ln \gamma)]^\sigma) \times [1+\alpha(1-\beta_1)]\}/\{P_n{}^0(1-\gamma)^2 - 2\alpha(1-\beta_1)\gamma[P_n{}^0(1-\gamma) - 1 + [\sigma/(\sigma - P_n{}^0 \ln \gamma)]^\sigma]\}$$

$$\alpha_g = P_n{}^0(1-\gamma)^2/\{2\gamma(1-\beta_1) \times [P_n{}^0(1-\gamma) - 1 + [\sigma/(\sigma - P_n{}^0 \ln \gamma)]^\sigma]\}$$

In all relations it holds that $\omega = \theta(1 - \alpha + \alpha u)$ and $W(\theta) = u\,(1 - \alpha + \alpha u)$. The resulting number average P_n is independent of the type of distribution and is determined only by the degree of cross-linking α and degradation β and by the initial number average $P_n{}^0$ (cf. eq 26).

References and Notes

(1) P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083 (1941).
(2) P. J. Flory, *Chem. Rev.*, **39**, 137 (1946).
(3) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, 1953.
(4) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).
(5) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).
(6) A. Charlesby, "Atomic Radiation and Polymers", Pergamon Press, Oxford, 1960.
(7) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Interscience, New York, 1962.
(8) "The Radiation Chemistry of Macromolecules", M. Dole, Ed., Academic Press, New York, 1972.
(9) C. H. Bamford and C. F. H. Tipper, Eds., "Degradation of Polymers", Elsevier, Amsterdam, 1975.
(10) K. Dušek, *Polym. Bull.*, **1**, 523 (1979).
(11) E. W. Montroll and R. Simha, *J. Chem. Phys.*, **8**, 721 (1940).
(12) R. Simha, *J. Appl. Phys.*, **12**, 569 (1941).
(13) O. Saito, *J. Phys. Soc. Jpn.*, **13**, 198, 1451 (1958).
(14) S. W. Lee, *J. Polym. Sci., Part A-2*, 77 (1969).
(15) B. J. Coyne, *J. Polym. Sci., Part A-2*, 633 (1967).
(16) H. H. G. Jellinek, "Degradation of Vinyl Polymers", Academic Press, New York, 1955.
(17) D. Mejzler, J. Schmorak, and M. Lewin, *J. Polym. Sci.*, **46**, 289 (1960).
(18) V. S. Nanda and R. K. Pathria, *J. Chem. Phys.*, **30**, 27–36, 1322 (1959).
(19) V. S. Nanda and R. K. Pathria, *Proc. R. Soc. London, Ser. A*, **270**, 14 (1962).
(20) O. Saito in "The Radiation Chemistry of Macromolecules", Vol. I, M. Dole, Ed., Academic Press, New York, 1972, Chapter 11.
(21) O. Saito, *Polym. Eng. Sci.*, **19**, 234 (1979).
(22) M. Inokuti, *J. Chem. Phys.*, **38**, 1174, 2999 (1963).
(23) T. Kimura, *J. Phys. Soc. Jpn.*, **17**, 1884 (1962).
(24) T. Kimura, *J. Phys. Soc. Jpn.*, **19**, 777 (1964).
(25) M. Gordon, *Proc. R. Soc. London, Ser. A*, **268**, 240 (1962).
(26) M. Gordon and G. N. Malcolm, *Proc. R. Soc. London, Ser. A*, **295**, 29 (1966).
(27) M. Gordon and S. B. Ross-Murphy, *Pure Appl. Chem.*, **43**, 1 (1975).
(28) M. Gordon and W. B. Temple in "Chemical Application of Graph Theory", A. T. Balaban, Ed., Academic Press, New York, 1976.
(29) K. Dušek, *Makromol. Chem., Suppl. 2*, **180**, 35 (1979).
(30) K. Kajiwara, W. Burchard, and M. Gordon, *Br. Polym. J.*, **2**, 110 (1970).
(31) K. Kajiwara, *J. Chem. Phys.*, **54**, 296 (1971).
(32) K. Kajiwara and M. Gordon, *J. Chem. Phys.*, **59**, 3623 (1973).
(33) K. Kajiwara and C. A. M. Ribeiro, *Macromolecules*, **7**, 121 (1974).
(34) I. Franken and W. Burchard, *Macromolecules*, **6**, 848 (1973).
(35) W. Burchard, *Macromolecules*, **10**, 919 (1977).
(36) W. Burchard, *Macromolecules*, **11**, 455 (1978).
(37) F. Oberhettinger, "Tables of Laplace Transforms", Springer-Verlag, New York, 1973.
(38) K. Dušek, M. Gordon, and S. B. Ross-Murphy, *Macromolecules*, **11**, 236 (1978).
(39) K. Dušek and V. Vojta, *Br. Polym. J.*, **9**, 164 (1977).