

STATISTICAL PARAMETERS
OF A NETWORK FORMED BY RANDOM COPOLYCONDENSATION
OF A BIFUNCTIONAL AND A TETRAFUNCTIONAL MONOMER
AND NETWORKS FORMED BY RANDOM CROSSLINKING

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The theory of branching processes was applied to the determination of the number and length of the active chains and free ends of a network formed by random copolycondensation of a bifunctional and a tetrafunctional monomer. The number and length thus determined were then compared with the parameters of a network formed by crosslinking of macromolecules having a random distribution. It follows from the results that the networks formed are identical as expected, whereas the statistical parameters differ in the course of formation of the network. The length of primary molecules, active chains and free ends is lower in the case of the network prepared by copolycondensation over almost the whole process of formation, compared with the network formed by crosslinking of macromolecules.

Besides the usual method of preparation of a network by crosslinking of macromolecules it is also possible to prepare a network by copolymerization of a bifunctional and tetrafunctional monomer. It has been shown¹ that the crosslinking of molecules having a random distribution is equivalent to the random copolycondensation of a bifunctional and a tetrafunctional monomer, if the reactivities of the functionalities present in both monomers are identical. This equivalency concerns only the structure of the resulting network; the course of its formation is different to such an extent that it may be a cause of changes in the topology of the network, as is shown by some experimental data².

In the present work, relationships have been derived describing the course of concentration of the active chains and free ends and of their lengths as a function of the gel content for both systems on the assumption that the distribution of the primary molecular weights is in both cases a random one. The basic difference between both networks is given by the fact that in the network obtained by crosslinking of macromolecules the number of the crosslinked units increases, but the degree of conversion of the primary molecules and the corresponding average molecular weight do not

change in the course of reaction. On the contrary, in the case of the network prepared by copolycondensation there is an increase in conversion and the corresponding primary molecular weight, whereas the number of crosslinked units defined by the ratio of the bifunctional and tetrafunctional monomers remains unchanged during the reaction.

To derive relationships describing the concentration and length of active chains and free ends we used the theory of branching processes³⁻⁵, which had already been applied in the calculations of concentration of the active network chains prepared by crosslinking of macromolecules having different length distribution⁶. It has been our objective to extend these calculations to further statistical parameters, and in the first place to determine these parameters in the networks formed by copolycondensation of bifunctional and tetrafunctional monomeric units.

THEORETICAL

Network Formed by Crosslinking of Macromolecules

This case has been examined by Gordon for various molecular weight distributions⁶. He considered the original macromolecules to be the starting units which form the "tree" (cf.³⁻⁵). The probability generating function for the number of ties radiating from a randomly selected chain is given by the relationship⁶

$$T(\theta) = \sum_y n_y [r + (1-r)\theta]^y = \sum_i t_i \theta^i, \quad (1)$$

where n_y is number distribution of molecular weight, y , number of structure units in a macromolecule, t_i is the probability that i ties radiate from a randomly selected chain; $r = 1 - \rho + \rho v$, where ρ is the fraction of crosslinked monomeric units from all the monomeric units present in the system, and v is the extinction probability. It holds for a random distribution¹ that $n_y = (1-p)p^{y-1}$, where p is the degree of conversion of the monomer in the formation of the starting molecules. It can be demonstrated that it holds for the extinction probability, v (cf.⁶),

$$v^{1/2} = -1/2 + (4K + 1)^{1/2}/2, \quad (2)$$

$$K = (1-p)/p\rho. \quad (3)$$

The gel point of this system is defined by the well-known relationship¹

$$\rho = 1/(\bar{y}_w - 1) = (1-p)/2p, \quad (4)$$

where \bar{y}_w is the weight average polymerization degree of the primary molecules.

The weight fraction of the sol is given by the relationship

$$S = \{2(1 - p) + (2 - p)[\varrho p - (\varrho^2 p^2 - 4\varrho p^2 + 4\varrho p)^{1/2}]\}/2\varrho p^2 = \\ = [v - v^{1/2}(1 - p)]/p = \varrho v^2 + (1 - \varrho)v. \quad (5)$$

The weight fraction of the gel can easily be determined from the relationship

$$G = 1 - S = (1 - v^{1/2})(p + v^{1/2})/p = (1 - v)(1 + \varrho v). \quad (6)$$

According to Gordon, the concentration of the active chains will be⁶

$$N_e = \varrho \bar{y}_n (1 - v^{1/2})^3 (1 + 2v^{1/2}), \quad (7)$$

where \bar{y}_n is the number average degree of polymerization of the primary molecules.

The length of the active chain represented by the number of the monomeric units, L_e , and if each unit is counted once only, can be described by the relationship

$$L_e = (\chi \bar{y}_n - \sum_2^{\infty} t_i)/N_e, \quad (8)$$

where χ is the fraction of the monomeric units which form a part of the active chains. The second term in brackets is necessary because in each primary chain there are two monomeric units, forming a part of both the active chain and the free end. Gordon has shown that χ is defined by the relationship⁶

$$\chi = 1 + v - 2\varrho v(1 - v) - 2(1 - \varrho + \varrho v)^{1/2}. \quad (9)$$

The second term is with respect to Eq. (1) defined as follows:

$$\sum_2^{\infty} t_i = 1 - T'(0) - T(0) = \varrho \bar{y}_n (1 - v^{1/2})^2 (v + v^{1/2}). \quad (10)$$

By substituting (7), (9), and (10) into (8) we finally obtain

$$L_e = [1 + \varrho v^{1/2}(1 + v^{1/2})]/\varrho(1 - v^{1/2})(1 + 2v^{1/2}). \quad (11)$$

The number of free ends, N_f , is given by double the number of primary molecules present in the network, *i.e.* for $i \geq 1$

$$N_f = 2 \sum_1^{\infty} t_i = 2[T(1) - T(0)] = 2\varrho \bar{y}_n (1 - v) v^{1/2}. \quad (12)$$

Their length, L_f , is expressed in a way similar to the active chains as a fraction of the

total number of monomeric units present in the free ends and the number of free ends, N_f ,

$$L_f = [G - N_e L_e / \bar{y}_n] / (N_f \bar{y}_n) = \\ = [2 + \varrho(1 + v^{1/2})(2v^{1/2} - 1)] / 2\varrho(1 + v^{1/2}). \quad (13)$$

So far, the calculated values have been related to an average molecule of the whole system, *i.e.* of both sol and gel. If they are related to the molecules in the gel alone, we obtain for the number of the active chains in the gel, $N_{e,g}$, and the number of the free ends in the gel, $N_{f,g}$, the following relationships:

$$N_{e,g} / \bar{y}_{n,g} = N_e / G \bar{y}_n, \quad (14)$$

$$N_{f,g} / \bar{y}_{n,g} = N_f / G \bar{y}_n, \quad (15)$$

where $\bar{y}_{n,g}$ is the number average polymerization degree of the primary molecules present in the gel. Owing to the fact that each primary molecule has two free ends, it holds, on substituting $N_{f,g} = 2$ into (15) and an appropriate treatment,

$$\bar{y}_{n,g} = (1 + \varrho v) / \varrho v^{1/2}. \quad (16)$$

For an average size of the primary molecules in the sol, the relationship is valid

$$1 / \bar{y}_n = (S / \bar{y}_{n,s}) + (G / \bar{y}_{n,g}) \quad (17)$$

so that we have after substitution

$$\bar{y}_{n,s} = [1 + \varrho v^{1/2}(1 + v^{1/2})] / \varrho(1 + v^{1/2}). \quad (18)$$

Network Formed by Copolycondensation of a Bifunctional and a Tetrafunctional Monomer

The "tree" characterizing this network will correspond to the "tree" for the polycondensation of the f -functional units with the difference that the units of which it is compounded will be of two types. We have therefore to employ in this case the vector generating functions⁷, for which it holds

$$\mathbf{F}_0(\Theta) = [F_{01}(\Theta), F_{02}(\Theta), \dots, F_{0s}(\Theta)], \quad (19)$$

where $\Theta = [\Theta_1, \Theta_2, \dots, \Theta_s]$ is also a vector quantity. In the case under study, concerning a random copolycondensation of the bifunctional (type 1) and tetrafunctional

(type 2) units, the probability generating functions for the number of off-springs borne by members of the zeroth or first generations ($F_{01}(\Theta)$ and $F_{02}(\Theta)$, or $F_{11}(\Theta)$ and $F_{12}(\Theta)$) are described by relationships⁷.

$$F_{01}(\Theta) = [1 - p + p(1 - \varrho) \Theta_1 + p\varrho\Theta_2]^2, \quad (20)$$

$$F_{02}(\Theta) = [1 - p + p(1 - \varrho) \Theta_1 + p\varrho\Theta_2]^4, \quad (21)$$

$$F_{11}(\Theta) = [1 - p + p(1 - \varrho) \Theta_1 + p\varrho\Theta_2], \quad (22)$$

$$F_{12}(\Theta) = [1 - p + p(1 - \varrho) \Theta_1 + p\varrho\Theta_2]^3, \quad (23)$$

where p is the fraction of all the reacted functionalities, *i.e.* the total degree of conversion, and ϱ is the fraction of functionalities which have reacted with the units of the second type. For a random polymerization, ϱ is also identical with the ratio of functionalities on the units of the second type, which corresponds to the definition of ϱ given for the preceding type of the network.

The extinction probabilities, v_1 and v_2 are expressed as follows:

$$v_1 = 1 - p + p(1 - \varrho) v_1 + p\varrho v_2, \quad (24)$$

$$v_2 = [1 - p + p(1 - \varrho) v_1 + p\varrho v_2]^3 = v_1^3. \quad (25)$$

On substituting (24) into (25) and treatment we obtain

$$v_1^3 - v_1(K + 1) + K = 0, \quad (26)$$

where $K = (1 - p)/p\varrho$. Owing to the fact that one root of Eq. (26) is $v = 1$, it can also be written in the form

$$v_1^2 + v_1 - K = 0 \quad (27)$$

the solution of which yields v_1 in the form

$$v_1 = -1/2 + (4K + 1)^{1/2}/2. \quad (28)$$

The values r_1 and r_2 are defined by identical expressions

$$r_1 = r_2 = r = 1 - p + p(1 - \varrho) v_1 + p\varrho v_2. \quad (29)$$

The probability generation function for the number of ties radiating from a random

unit is

$$\mathbf{T}(\theta) = [\mathbf{T}_1(\theta), \mathbf{T}_2(\theta)], \quad (30)$$

where

$$\mathbf{T}_1(\theta) = [r + (1 - r)\theta]^2 = \sum_0^2 t_{1i}\theta^i, \quad (31)$$

$$\mathbf{T}_2(\theta) = [r + (1 - r)\theta]^4 = \sum_0^4 t_{2i}\theta^i. \quad (32)$$

It holds for the gel point in a multicomponent system that the determinant

$$|\delta_j^i - (\partial F_{1i}/\partial \theta_j)_{\theta=1}| = 0 \quad (33)$$

where δ_j^i is Kronecker's delta. On substituting from (22) and (23) we obtain for the gel point

$$p = 1/(1 + 2\varrho). \quad (34)$$

In the sol only those units will be present from which no ties radiate; their number is $t_{10}(1 - \varrho)$ for the units of the first type, and $t_{20}\varrho/2$ for the units of the second type. With respect to the fact that the weight of the units of the second type is two fold in comparison with the units of the first type, the weight content of the sol is defined by relationship

$$S = [2t_{20}\varrho/2 + (1 - \varrho)t_{10}] = \varrho t_{20} + (1 - \varrho)t_{10}. \quad (35)$$

After substitution from (31) and (32) we obtain

$$S = \varrho v_1^4 + (1 - \varrho)v_1^2 = [v_1^2 - (1 - p)]/p. \quad (36)$$

The number of the active chains can be derived from the fact that each monomeric unit from which more than two ties radiate contributes by a number of $i/2$ of the active chains. In the case under investigation, only units of type 2 come into consideration. It holds, therefore,

$$N_e = (\varrho \sum_3^4 t_{2i}i)/4 = \varrho[\mathbf{T}_2'(1) - \mathbf{T}_2'(0) - \mathbf{T}_2''(0)]/4. \quad (37)$$

On substituting from (31) and (32) into (37) we obtain

$$N_e = \varrho(1 - v_1)^3(1 + 2v_1). \quad (38)$$

The average length of an active chain can be determined by dividing the total number of monomeric units present in the active chains with the number of the active chains.

It holds

$$L_c = [(1 - \varrho) t_{12} + \varrho(\sum_2^4 t_{2i} i/2)/2]/N_c. \quad (39)$$

By calculations using (31) and (32) we obtain

$$L_c = [1 + \varrho v_1(1 + v_1)]/\varrho(1 - v_1)(1 + 2v_1). \quad (40)$$

The number of the free ends is given by the number of untied chains radiating from a unit of type 2. An exception is presented by the units with three untied chains radiating from them, which contribute solely to the formation of two new free ends. It holds

$$N_f = \varrho(t_{23} + 2t_{22} + 2t_{21})/2, \quad (41)$$

which after substitution from (31) and (32) will yield

$$N_f = 2\varrho(1 - v_1^2) v_1. \quad (42)$$

To determine their length the same relationship will be used as in the determination of the length of active chains

$$L_f = [(1 - \varrho) t_{11} + \varrho(2t_{21} + t_{22} + t_{23}/2)/2]/N_f \quad (43)$$

and on substituting

$$L_f = [2 - \varrho(1 + v_1)(1 - 2v_1)]/2\varrho(1 + v_1). \quad (44)$$

Also in this case the number average of degree polymerization the primary molecules present in both gel and sol can be determined by using the same reasoning as in the case of networks prepared by crosslinking. It holds

$$\bar{y}_{n,g} = (1 + \varrho v_1^2)/\varrho v_1, \quad (45)$$

$$\bar{y}_{n,s} = [1 + \varrho v_1(1 + v_1)]/\varrho(1 + v_1). \quad (46)$$

DISCUSSION

We can see from the comparison of Eqs (2) and (28) that $v_1 = v^{1/2}$; it follows therefrom that relationships derived for G , S , L_c , L_f are identical for both network types, whereas those for N_c and N_f are \bar{y}_n times higher for the network prepared by crosslinking. This finding, however, is in accord with the assumption that N_c and N_f are

in the network formed by crosslinking related to the original macromolecule, whereas in the other case they are related to the monomeric unit. Thus, all the statistical parameters for both network types are identical as expected at the same values of p and q .

On the other hand, if we compare the course of all the three parameters in the network formation, we arrive at some differences due to the fact that the crosslinking takes place at a constant value of $p = P$ and increasing q , whereas the copolycondensation occurs at a constant value of $q = R$ and increasing value of p , and therefore also at an increasing value of the "primary" polymerization degree, \bar{y}_n . At a constant content of the sol S in both networks the following relationships are valid for the values v :

$$v_1^2 = -(1 - R)/2R + \{[(1 + R)/2R]^2 - (1 - S)/R\}^{1/2}, \quad (47)$$

$$v = (1 - P)/2 + \{[(1 - P)/2]^2 + PS\}^{1/2}, \quad (48)$$

which for $R \rightarrow 0$ and $P \rightarrow 1$ take on a simplified form

$$v_1 = v^{1/2} = S^{1/2}. \quad (49)$$

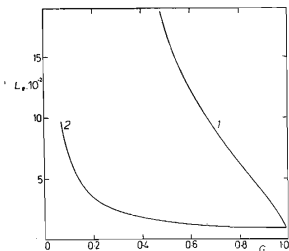


FIG. 1

Dependence of the Length of Active Chains, L_e , on the Gel Content G for Both Network Types

1 Network prepared by crosslinking of macromolecules with random primary distribution; 2 network prepared by copolymerization of a bifunctional and tetrafunctional monomer; $P = 0.999$; $R = 0.01$.

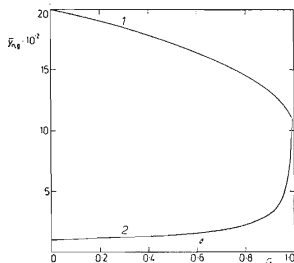


FIG. 2

Dependence of the Average Length of Primary Molecules in the Gel, $\bar{y}_{n,g}$, on the Gel Content G for Both Network Types

Designation of curves and conditions of network formation are the same as in Fig. 1.

Figs 1–3 show the dependences of L_e , $\bar{y}_{n,g}$ and $\bar{y}_{n,s}$ on the gel content G calculated by use of Eq. (49) for $R = 0.01$ and $P = 0.999$. It follows from the comparison of both networks that all calculated parameters are lower for the networks formed by copolymerization over almost the whole course of the network formation than for the network formed by crosslinking. They are identical for the resulting network only, *i.e.* for $p = P$ in the case of the network formed by copolymerization and for $q = R$ in the case of the network formed by crosslinking. The differences in the course of crosslinking increase with increasing content of the crosslinking agent. This fact will probably influence the topology of the network formed, *i.e.* it can, along with

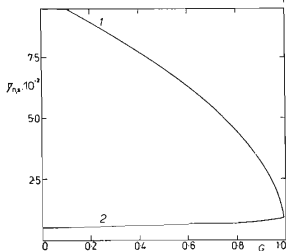


FIG. 3

Dependence of the Average Length of a Primary Molecule in the Sol, $\bar{y}_{n,s}$, on the Gel Content for Both Network Types

Designation of the curves and conditions of network formation are the same as in Fig. 1.

other factors, participate in the lower content of entanglements in the network formed by copolycondensation².

The above procedure represents the simplest treatment of the problems under investigation. It proves that the branching process method can be used successfully also in the calculations of the statistical parameters of the network formed by random copolycondensation. In real systems, however, the situation is more complicated, since the reactivities of the copolymerization components are usually different, and the distribution of the primary molecular weights also differs from the most probable distribution. These problems, however, can be solved in principle by introducing different values of p and q for individual components and by including real distributions of molecular weights of the crosslinked macromolecules.

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