Russian Chemical Reviews **73** (3) 251 – 265 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n03ABEH000881

Methods of calculation of the critical conversion in the formation of network polymers

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Abstract. Mathematical methods of calculation of the critical conversion (gel point) in the formation of cross-linked polymers by polycondensation, cross-linking of macromolecules and three-dimensional polymerisation are considered. The results obtained using the statistical approach ('ideal' polycondensation), the concept of bond blocks (the 'non-ideal' or 'non-statistical' polycondensation) and kinetic calculations that allowed the determination of the gel point in three-dimensional polymerisation processes are discussed. The bibliography includes 105 references.

I. Introduction

The value of critical conversion in the formation of cross-linked polymers, the so-called gel point, characterises the transition of a system from a fluid state to a state with an equilibrium elastic modulus. It is a parameter of great importance both in applied and theoretical studies. At conversions smaller than the critical conversion, a polymer is characterised by a finite molecular mass. At higher conversions, the molecular mass becomes formally infinite, or, in mathematical terms, higher moments of molecular-mass distribution, starting from the second one, become infinite. The formation of an insoluble gel can result in complications in technological processes of polymer synthesis and, *vice versa*, finding the relationship between the critical conversion, on the one hand, and the structural and kinetic parameters of the process, on the other hand, makes it possible to state the conditions for forming a cross-linked polymer with required physico-mechanical characteristics.

The gel point determines the flow threshold in a polymeric system being formed, and finding the dependence of this value on kinetic and structural parameters is an important problem. For example, polymer properties in the critical point have recently become a subject of scientists' attention.[1] The relaxation properties of polymeric systems on transition from a sol to a gel have a distinctive feature due to the fact that macromolecules in this point are characterised by a specific structure shaped as fractal trees with an extraordinarily broad size distribution. The relaxation modulus has a power-law rather than exponential time dependence;[1–4] this is characteristic of pre-gel rather than post-gel regions. It follows that the real and imaginary components of the relaxation modulus are congruent and that the loss tangent is independent of frequency. Obviously, correct assessment of the critical conversion region in the formation of a three-dimensional polymeric system occurring by any mechanism can make it possible to determine conditions required to obtain a material with predefined properties.

The problem of determining the critical conversion for the polycondensation of *f*-functional monomers was solved by Flory [5] and Stockmayer [6] by statistical methods using combinatory analysis. The formulas they obtained were confirmed by kinetic calculations [7,8] and by experimental data.[5,8] They are applicable provided that intramolecular reactions (reactions between groups belonging to a single macromolecule) do not occur. It was later shown that probabilistic approaches are applicable only to those systems where the so-called substitution effect is absent, *i.e.*, where kinetic constants do not change during the process.[7,9,10] Otherwise, a strict kinetic calculation is required.

Three-dimensional polymerisation is usually described according to Flory [5] and Stockmayer [11] using the probabilistic approach,[12] which is of quite limited use for polymerisation processes. Monte Carlo computer simulation, which is also based on the probabilistic approach, was found to be more efficient.[13–15] Other approaches were also proposed, based on the analysis of infinite systems of differential equations describing different kinetic schemes of the polymerisation process: a method based on the calculation of the instantaneous value of molecular mass distribution;[11,16–20] approximation of a system of ordinary differential-difference equations by a continuous system of partial differential equations;[21–28] the method of moments;[29–35] the method of generating functions;[7,36,37] numeric inversion of *z*-[38] and Fourier transformations;[39] methods of discrete weighed residues;[40–42] numeric fractionation [43–45] and discrete population balance.[46,47] These methods were mainly used to evaluate the molecular mass distribution parameters in the formation of linear and branched polymers, and it is only in restricted cases (see, *e.g.*, Refs 7 and 48) that they were used to find critical conversion values.

The formulas obtained by any of these methods were not confirmed by experimental data. However, their validity was not disputed, because it is well known that intramolecular cyclisation occurs rather intensely under ordinary three-dimensional polymerisation conditions due to the fast chain growth in the case of

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Received 4 November 2003
Uspekhi Khimii **73** (3) 275 – 291 (2004); translated by S S Veselyi

the radical mechanism and the low concentration of chains at early process stages.[8] Repeated cross-linking between a single pair of chains (formation of multiplet nodes and 'staircase' macromolecular structures) is also believed to be a factor that decreases the effective concentration of inter-chain cross-links and thus increases the critical conversion.[49] Because of this, radical polymerisation is a typical microheterogeneous process.[50] The combination of all these reasons makes it difficult to expect that any theoretical dependencies would be obeyed.

In this review, we intend to determine the applicability ranges of the statistic and kinetic approaches. Based on this, well-founded results on the calculation of critical conversion values with different mechanisms of formation of cross-linked polymers will be presented. The author has previously developed the bond blocks (BB) concept.[9, 51] This approach, which combines kinetic and probabilistic methods, makes it possible to simplify considerably the solution of problems that cannot be solved using the purely statistical method. In this review we consider the results of critical conversion calculations obtained by this method.

Thus, the review consists of three parts. The first part presents the results of statistical calculations ('ideal' polycondensation); the second part, the results obtained using the BB concept ('non-ideal' or 'nonstatistical' polycondensation); the third part, the kinetic calculations that allowed the determination of the gel point in three-dimensional polymerisation processes to be carried out.

II. Methods for the description of the kinetics of formation of cross-linked polymers

Unlike low-molecular compounds (not bodies!) that are defined almost unambiguously by their chemical formulas, the structures of polymers, and hence their properties, are not exhausted by their chemistry. Polymer structure is a multilevel characteristic, and the topological level is the most important.[8] In fact, the properties of linear polymers cannot be described if their molecular mass distribution is neglected. For cross-linked polymers, the concentration of nodes and the length distribution of internode chains are the most important structural parameters. Branched and star polymers and dendrimers differ principally both from each other and from linear polymers due to differences in their topological structures. Therefore, consideration of the polymer formation kinetics should not be limited to chemical reactions; it is also necessary to analyse how the polymeric chain is formed.

Taking the above considerations into account, we should discriminate at least two reaction types: polymerisation type and, tentatively speaking, polycondensation type (called 'Addition Polymerisation' and 'Stepwise Polymerisation' in English-language literature). Turning aside from chemistry, the reagents involved in these reactions can be described by vectors; in the former case, as R(m,n,p), where R is a macromolecule comprising m units, n functional groups (for vinyl polymers, n is the number of double bonds) and p active centres; m, n, p = 0, 1, 2, 3, ... *etc*., to infinity; in the latter case, as R(m,n).

This is certainly the easiest description method, which does not take certain details of the topological structure into account, but these characteristics suffice for the solution of the problem of interest, *viz*., determination of the gel point.

The former reaction type is described by the following scheme:

$$\mathrm{I} \xrightarrow{k_\mathrm{i}} f\mathrm{R}(0,0,1)$$

$$\mathrm{R}(i,j,l) + \mathrm{R}(m,n,p) \longrightarrow \begin{cases} \xrightarrow{k_\mathrm{p}} \mathrm{R}(i+m, j+n-l, l+p) \\ \xrightarrow{k_\mathrm{tr}} \mathrm{R}(i+m, j+n, l+p-2), \\ \xrightarrow{k_\mathrm{td}} \mathrm{R}(i,j,l-1) + \mathrm{R}(m,n,p-1) \end{cases} \quad (1)$$

$$\mathrm{R}(i,j,l) + \mathrm{X} \xrightarrow{k_\mathrm{X}} \mathrm{R}(i,j,l-1) + \mathrm{R}(0,0,1),$$

$$\mathrm{R}(i,j,l) + \mathrm{Y} \xrightarrow{k_\mathrm{Y}} \mathrm{R}(i,j,l-1).$$

where I is the initiator; f is the initiation efficiency (number of active centres formed in one initiation act); R(0,0,1) is a primary active centre; k_i, k_p, k_tr, k_td, k_X and k_Y are the rate constants of initiation, growth, square-law termination by recombination and disproportionation, chain transfer on transfer agent X and linear inhibition-type termination on agent Y.

For simplicity, it was assumed when developing this scheme that initiation occurs by monomolecular decomposition of initiator I and that the reactivity of functional groups does not depend on the complexity and size of the macromolecule that carries them (Flory's principle [5]). The reactivity of active centres in the chain growth, transfer and termination is also independent of this factor.

The second reaction type is described by the scheme (also with the use of Flory's principle)

$$\mathrm{R}(i,j) + \mathrm{R}(m,n) \xrightarrow{k} \mathrm{R}(i+m, j+n-2). \quad (2)$$

This is a simplified version where it is assumed that the reacting functional groups belong to a single type.

Schemes (1) and (2) result in infinite systems of differential equations. For scheme (1):

$$\frac{\mathrm{d}\mathrm{I}}{\mathrm{d}t} = -k_\mathrm{i}\mathrm{I},$$

$$\frac{\mathrm{d}\mathrm{R}(0,0,1)}{\mathrm{d}t} = fk_\mathrm{i}\mathrm{I} - \mathrm{R}(0,0,1)\,(k_\mathrm{p}\mathrm{F} + k_\mathrm{X}\mathrm{X} + k_\mathrm{t}\mathrm{R} + k_\mathrm{Y}\mathrm{Y}) + k_\mathrm{X}\mathrm{X}\mathrm{R},$$

$$\frac{\mathrm{d}\mathrm{R}(i,j,l)}{\mathrm{d}t} = -\mathrm{R}(i,j,l)\,[k_\mathrm{p}(l\mathrm{F} + j\mathrm{R}) + l(k_\mathrm{X}\mathrm{X} + k_\mathrm{t}\mathrm{R})] + \mathrm{R}(i,j,l+1) \times$$

$$\times (k_\mathrm{Y}\mathrm{Y} + k_\mathrm{X}\mathrm{X} + k_\mathrm{td}\mathrm{R}) + k_\mathrm{p} \sum_{m,n,p}^{i,j,l} \{[n(k-p)\mathrm{R}(i-m, j-n+1, l-p) +$$

$$+ p(j-n+1)\,\mathrm{R}(i-m, j-n+1, l-p)]\mathrm{R}(m,n,p)\} + \quad (3)$$

$$+ \frac{1}{2}k_\mathrm{tr} \sum_{m,n,p}^{i,j,l} [(l-p+1)\mathrm{R}(i-m, j-n+1, l-p+1)\,(p+1) \times$$

$$\times \mathrm{R}(m,n,p+1)].$$

In the above equations, I is the initiator concentration, $\mathrm{R} = \sum_{i,j,l}^{\infty} l\,\mathrm{R}(i,j,l)$ is the total concentration of active centres, X is the concentration of the chain transfer agent, Y is the concentration of the linear termination agent, F is the total concentration of reactive functional groups, and $k_\mathrm{t} = k_\mathrm{tr} + k_\mathrm{td}$ is the overall square-law termination constant.

For scheme (2)

$$\frac{\mathrm{d}\mathrm{R}(i,j)}{\mathrm{d}t} = -kj\mathrm{R}(i,j) \sum_{m,n=1}^{\infty} n\mathrm{R}(m,n) +$$

$$+ \frac{1}{2}k \sum_{m,n=1}^{i-1,j-1} (j-n)\mathrm{R}(i-m, j-n)\, n\mathrm{R}(m,n). \quad (4)$$

Infinite systems of differential equations can be solved only in convolute form. The simplest method involves the use of generating functions [7, 36, 37]

$$\Phi(q_1, q_2, q_3) = \sum_{i,j,l}^{\infty} q_1^i q_2^j q_3^l R(i,j,l), \quad (5)$$

where q_1, q_2, q_3 are arbitrary variables.

This procedure results in relatively simple partial equations that are principally soluble (in simplest cases, they can even be solved analytically).[52]

In generating function terms, system (3) gives a partial equation (its development can be found, *e.g*., in Refs 7 and 52) of the form:

$$\frac{\partial\Phi(\boldsymbol{q})}{\partial t} = fk_{\mathrm{i}}q_3\mathrm{I} + k_{\mathrm{p}}\left[q_3\frac{\partial\Phi(\boldsymbol{q})}{\partial q_2}\frac{\partial\Phi(\boldsymbol{q})}{\partial q_3} - q_3F\frac{\partial\Phi(\boldsymbol{q})}{\partial q_3} - q_2\mathrm{R}\frac{\partial\Phi(\boldsymbol{q})}{\partial q_2}\right] + (k_{\mathrm{Y}}\mathrm{Y} + k_{\mathrm{X}}\mathrm{X})(1-q_3)\frac{\partial\Phi(\boldsymbol{q})}{\partial q_3} + \frac{1}{2}k_{\mathrm{tr}}\left[\frac{\partial\Phi(\boldsymbol{q})}{\partial q_3}\right]^2 + (k_{\mathrm{td}} - q_3k_{\mathrm{t}})\frac{\partial\Phi(\boldsymbol{q})}{\partial q_3}\mathrm{R}, \quad (6)$$

where $\boldsymbol{q} \equiv (q_1,q_2,q_3)$.

A similar equation describing polycondensation has the form

$$\frac{\partial\Phi(\boldsymbol{q})}{\partial t} = -kq_2\frac{\partial\Phi(\boldsymbol{q})}{\partial q_2}\mathrm{F} + \frac{1}{2}k\left[\frac{\partial\Phi(\boldsymbol{q})}{\partial q_2}\right]^2, \quad (7)$$

where

$$\mathrm{F} = \sum_{i,j,l}^{\infty} j\,\mathrm{R}(i,j).$$

Equation (6) cannot be solved analytically even in its simplest version. Numeric solution encounters the problem of finding a general expression for critical conversion (for arbitrary values of kinetic constants). We shall try to answer this question below.

In the version presented above, Eqn (7) is much more simple than Eqn (6) and has an analytical solution. In any case, as shown in Ref. 53, the solution of Eqns (6) and (7) branches in some instant of time t_{c}, which corresponds to the gel point, and finding this point solves the problem. However, it is not possible to obtain such a simple analytical or even numerical solution in more complex cases, for example, if the reaction involves several types of functional group with different reactivity. Therefore, a method to solve the problem based on a statistical approach was suggested.[5,6]

III. Statistical methods

Flory was probably the first to suggest the use of the statistical approach to describe the polycondensation kinetics and the structure of polymers obtained by this method.[5,54] The molecular-mass distribution upon *f*-functional polycondensation was calculated using combinatorial analysis and the critical conversion condition was obtained. Later calculations were based on the use of a formalised and therefore simpler and more elegant method,[55,56] which is based on the theory of branching processes.[57]

Assuming that cyclisation reactions are excluded, the structure of a macromolecule is represented [8] as a branching tree; any chain unit or a whole fragment can be considered as the root. Reagent molecules are chosen as such fragments in order to link the macromolecule structure with the process of its formation. After that, the probabilities of transitions from generation to generation are considered (the root is taken as the zeroth generation). Probabilities are analysed in terms of generating functions. The kinetic parameters of the process, the depth of conversion by functional groups and their concentrations determine the probabilities of transitions.

The key point of the theory of branching processes [57] is that the generating functions for probabilities of transitions from generation to generation do not depend on the generation number (except the zeroth one), and their calculation requires that algebraic rather than differential (!) equations be solved.

Let us consider the principle of finding the critical conversion in a simple example, *viz*., *f*-functional polycondensation.

In each generation except the zeroth generation, an *f*-functional unit can derive a maximum of $f-1$ units; the probability of the event that each functional group reacts, *i.e*., derives a new unit, equals the conversion value (α). Thus, the generating function of probabilities is

$$Z(q) = \sum_{i=0}^{f-1} q^i\frac{(f-1)!}{i!(f-i-1)}\alpha^i(1-\alpha)^{f-i-1} = (1-\alpha+\alpha q)^{f-1}. \quad (8)$$

The gel formation condition is determined from the solution of the equation

$$u(q) = qZ[u(q)] = q[1-\alpha+\alpha u(q)]^{f-1}. \quad (9)$$

The generating function $u(q)$ characterises the molecular mass distribution of a polymer. The moments of this function correspond to distribution moments. For example, $u(1)$ is the first moment of distribution, and the first derivative on q at $q = 1$ is the second moment of molecular mass distribution.

The critical conversion equals the value α where the derivative $\partial u(1)/\partial q$ turns to infinity

$$\frac{\partial u(q)}{\partial q} = [1-\alpha+\alpha u(q)]^{f-1} + q(f-1)[1-\alpha+\alpha u(q)]^{f-2}\frac{\partial u(q)}{\partial q}. \quad (10)$$

At $q = 1$, we have $u(1) = 1$ and

$$\frac{\partial u(1)}{\partial q} = \frac{1}{1-\alpha(f-1)}. \quad (11)$$

Hence we obtain the gel formation condition (critical conversion):

$$\alpha_{\mathrm{c}}(f-1) = 1. \quad (12)$$

The equation for the first distribution moment $u(1)$ has only one root $u(1) = 1$ below the gel point. Starting from the time instant corresponding to critical conversion, the second root $u(1) < 1$ appears, which characterises the fraction of the soluble polymer (the sol fraction),

$$u(1) = \{1-\alpha[1-u(1)]\}^{f-1}, \quad (13)$$

$$1-u(1) = \alpha(f-1)[1-u(1)]\{1 - \frac{f-2}{2!}\alpha[1-u(1)] + \frac{(f-2)(f-3)}{3!}\alpha^2[1-u(1)]^2 - \ldots\}. \quad (13a)$$

Dividing both parts of this equation by $[1-u(1)]$ and equating the equation root to unity (gel point), we obtain the same expression (12) for critical conversion.

The conversion value is found by solving the differential equation for functional groups

$$\frac{\mathrm{dF}}{\mathrm{d}t} = -k\mathrm{F}^2,$$

$$\alpha = 1 - \frac{\mathrm{F}}{\mathrm{F}(0)}. \quad (14)$$

We present below formulas for determining the critical conversion for different cases of polycondensation.

1. Monomers with different functionality and single-type functional groups with equal reactivity (reactions between any groups are possible):

$$\alpha_{\mathrm{c}}(\langle f\rangle_{\mathrm{w}} - 1) = 1, \quad (15)$$

$$\langle f\rangle_{\mathrm{w}} = \sum_i in_i,$$

$$n_i = \frac{im_i}{\sum_j jm_j},$$

where m_i is the molar concentration of a monomer containing i functional groups. Thus, $\langle f\rangle_{\mathrm{w}}$ is the weight-average functionality.

2. Monomers with different functionality and different-type functional groups (A and B), in which single-type groups cannot

react with each other and the rate constant of the reaction between different-type groups is the same.

$$\alpha_{c\,A}\alpha_{c\,B}(\langle f_A\rangle_w - 1)(\langle f_B\rangle_w - 1) = 1. \quad (16)$$

Since

$$F_{A0} - F_A = F_{B0} - F_B,$$

hence

$$\alpha_A = \frac{F_{B0}}{F_{A0}}\alpha_B,$$

where F_{A0} and F_{B0} are the initial concentrations of the corresponding functional groups.

If the reactivities of functional groups are initially different, it is acceptable to use the statistical approach. For example, the secondary and primary hydroxy groups are non-equal in reactivity in the reaction of glycerol (B) with diisocyanate (A). Therefore, the formula for critical conversion will have the form

$$\frac{2}{3}\alpha_{c\,A}(2\alpha_{c\,B1} + \alpha_{c\,B2}) = 1, \quad (16a)$$

where the indices 1 and 2 correspond to the primary and secondary hydroxy groups of glycerol, respectively. The conversions of functional groups α_{B1} and α_{B2} are determined by solving the corresponding kinetic equations. If the reactivities are equal, *i.e.*, $\alpha_{c\,B1} = \alpha_{c\,B2}$, we obtain the formula (16).

In the case that the functional groups of reagents differ in reactivity, it is also necessary to modify formula (16). Assume that in the reaction

$$A_f + \sum_i B_i \rightarrow \text{products}$$

(the subscript indicates the number of reactive functional groups in a monomer molecule), the functional groups of each monomer B_i have different rate constants of the reaction with A. Therefore, each of them will have its own value of conversion α_i at any given instant in time. Hence, one can write:

$$(f-1)\alpha_{c\,A}\sum_i (i-1)n_i\alpha_{c\,i} = 1. \quad (16b)$$

It is obvious that we obtain Eqn (16) at $\alpha_i = \alpha$.

3. Cross-linking of polymeric chains with a bifunctional reagent. If each polymeric chain unit carries a functional group, then this is essentially the case described above, with the difference that the weight-average functionality of the polymeric reagent equals the weight-average degree of polymerisation ($\langle P\rangle_w$), which is generally much greater than unity. Furthermore, the concentration of the cross-linking agent m_A is usually much lower than the concentration of polymer functional groups. It hence follows that $\alpha_{c\,A} \approx 1$; therefore, Eqn (16) is transformed to the form

$$\alpha_{c\,B}\langle P\rangle_w = 1. \quad (16c)$$

Equations (16c) and (15) coincide formally.

If reactive functional groups are not contained in each unit and their molar fraction is $\rho < 1$, then $\langle f\rangle_w = \rho\langle P\rangle_w$, and, accordingly,

$$\alpha_{c\,B}\rho\langle P\rangle_w = 1. \quad (16d)$$

Simple relationships obtained by the statistical method are widely used in the analysis of various polycondensation processes. However, the so-called substitution effect is usual for polyfunctional reagents: the reactivity of functional groups changes after one group has reacted. In fact, the reaction rate constants for the primary (k_1) and secondary amino group (k_2), which appears as a result of the first reaction, are different in the reaction of epoxy compounds with an amine (Table 1).

The results of calculating the molecular mass distribution in linear polycondensation with the substitution effect depend on the calculation method.[7] Hence, the statistical approach is not suitable in this case. It has been shown[48,59] that a statistical calculation gives wrong results for critical conversion if the formation of a cross-linked polymer involves the substitution effect.

Table 1. Relative rate constants (k_2/k_1) of addition of the second epoxy group to the amine.[58]

T/°C	DDS [a]	MDA [b]	MDEA [c]	MCDA [d]
80	0.46	0.65	–	0.67
135	0.42	–	0.66	0.64
160	0.51	–	–	0.70

[a] DDS is 4,4′-diaminodiphenylsulfone, [b] MDA is 4,4′-methylenediamine, [c] MDEA is 4,4′-methylenebis(2,6-diethylaniline), [d] MCDA is 4,4′-methylenebis(3-chloro-2,6-diethylaniline).

It was found equally fruitless to use the statistical approach for solving the cyclisation problem.[60] It was shown[61] that, as in the previous case, only a kinetic solution can give correct results.

Later, a hypothesis on the applicability limits of the statistical calculation method was proposed.[62] Its applicability limits were fully established using the BBs concept.[9,63] However, attempts to use this method to describe the kinetics of polymer formation in the presence of the substitution effect were made previously[64] and were continuing until recently.[65,66]

IV. The bond block concept as a method to solve problems involving the substitution effect

The bond block concept[9,51,63,67] assumes a combination of kinetic and statistical methods. It is this concept that made it possible to develop a general approach for determining the gel point; the formulas resulting from statistical calculations are obtained as a special case if certain conditions are met. The 'bond block' concept is not yet widespread, therefore let us consider it in more detail.

A bond block is understood as a structure that can belong to any macromolecule or cross-linked polymer.[63] It is represented as a connected graph G, whose verges and nodes are bonds and atoms (units) connected by these bonds. The total set of concentrations of all bond blocks in a system characterises unambiguously its composition and structure. In this sense, the concentration $y(G)$ is analogous to the polymer molecular mass distribution function in terms of the information it contains. On the other hand, it is richer, as it not only describes the length distribution of chains but also characterises the molecular and topologic structure of a polymeric system.

When we speak of bonds, we mean those which result from the reaction under consideration. Hence, the BB concept is closely related to the process chemistry. Each bond is determined by the groups (units) connected by that bond: an a – a bond connects A units, an a – b bond connects A and B units, *etc*. In other words, identification of different units is meaningful only as an attribute (characteristics) of a bond. The total set of BBs unambiguously characterises the chain size and structure.

In the case of a linear homopolymer, BBs only differ in the number of bonds but not in their type, as in the example presented above. Therefore, the relationship between the concentrations of BBs and chains has a simple form in this case:

$$y_n = \sum_{i=n}^{\infty}(i-n)x_i, \quad (17)$$

where y_n and x_i are the concentrations of BBs and chains, respectively; their sizes are shown by the indices. The $(i-n)$ factor equals the number of ways to arrange a BB of n bonds in a chain containing i units.

The reverse relationship follows from Eqn (17)

$$x_i = y_{i-1} - 2y_i + y_{i+1}. \quad (18)$$

The condition (18) can be generalised for chains and BBs with any configuration if the terminal block (TB) concept is introduced. A TB is understood as a BB in which one of the units bordering the block is also a terminal unit of the chain (polymeric structure).

The TB concentration (z_i) is expressed through the BB concentration:

$$z_i = y_{i-1} - y_i = y_{i-1}(1 - y_1). \quad (19)$$

(For simplicity, here we used symbolic multiplication as addition of indices.)

If the number of terminal groups z_i^k (the superscript identifies the terminal member type) in a selected polymeric structure is more than unity, then

$$z_i^{k,m} = z_i^k(1 - y_1^m) = y_{i-1}(1 - y_1^k)(1 - y_1^m). \quad (20)$$

If there are several terminal groups (branched polymer), the numbers of multiplicands and superscripts in formula (20) increase accordingly.

A polymeric chain with any topology (excluding rings!) can be defined as a TB where the number of terminal groups equals the number of terminal groups of a macromolecule (all the block's bonds are broken). This number equals two for a linear chain. In this case, we come to the relationship (17). For an arbitrary number and type of terminal groups, we obtain

$$x_i = y_{i-1}\prod_{j=1}^{n}(1 - y_1^j). \quad (21)$$

Thus,

$$x_i = \begin{cases} y_{i-1} - y_i & \text{for terminal block} \\ y_{i-1} - y_i^1 - y_i^2 + y_{i+1}^{1,2} & \text{for linear chain with terminal groups of types 1 and 2} \\ y_{i-1} - \sum_{j=1}^{3} y_i^j + y_i^{1,2,3} & \text{for branched chain with three terminal groups} \end{cases} \quad (22)$$

and so on.

An example of the use of formulas similar to those presented above [(17)–(22)] was considered by Hsieh and Randall.[68] To calculate the number of sequences in ethylene and butene copolymers, they used NMR data that allowed the concentrations of short TBs (containing one, two, and three units) to be found.

The system of kinetic equations for BBs was obtained from a usual scheme of chain formation and a (17)-type relationship. Let us develop equations for linear polycondensation

$$\begin{aligned} &X_1 + X_1 \xrightarrow{k_1} X_2, \\ &X_1 + X_i \xrightarrow{k_2} X_{i+1},\ i = 2, 3, \ldots \\ &X_i + X_j \xrightarrow{k_3} X_{i+j},\ i, j = 2, 3, \ldots, \end{aligned} \quad (23)$$

where X_1, X_2, X_i, and X_j are reagents.

The corresponding system of differential equations has the form

$$\begin{aligned} \frac{dx_1}{dt} &= -2k_1x_1^2 - k_2x_1\sum_{j=2}^{\infty}x_j, \\ \frac{dx_2}{dt} &= k_1x_1^2 - k_2x_1x_2 - k_3x_2\sum_{j=2}^{\infty}x_j, \\ \frac{dx_3}{dt} &= k_2x_1(x_2 - x_3) - k_3x_3\sum_{j=2}^{\infty}x_j, \\ \frac{dx_i}{dt} &= k_2x_1(x_{i-1} - x_i) - k_3x_i\sum_{j=2}^{\infty}x_j + \frac{1}{2}k_3\sum_{j=2}^{i-2}x_jx_{i-j},\ i = 4, 5, \ldots, \end{aligned} \quad (24)$$

where x_1, x_2, x_3, x_i, x_j are the chain concentrations.

After substituting (17) into (24) we obtain

$$\begin{aligned} \frac{dy_0}{dt} &= 0, \\ \frac{dy_1}{dt} &= k_1(y_0 - y_1)^2 + (y_1 - y_2)[(k_2 - k_1)(y_0 - y_1) + \\ &\quad + \frac{1}{2}(k_1 - 2k_2 + k_3)(y_1 - y_2)], \\ \frac{dy_2}{dt} &= (k_2 - k_3)(y_1 - y_2)(y_0 - 2y_1 + y_2) + \\ &\quad + \frac{1}{2}k_3\sum_{j=0}^{2}(y_j - y_{j+1})(y_{2-j-1} - y_{2-j}), \\ \frac{dy_i}{dt} &= (k_2 - k_3)(y_{i-1} - y_i)(y_0 - 2y_1 + y_2) + \\ &\quad + \frac{1}{2}k_3\sum_{j=0}^{i}(y_j - y_{j+1})(y_{i-j-1} - y_{i-j}),\ i = 3, 4, \ldots \end{aligned} \quad (25)$$

where the concentration of bond blocks y_0 equals the total number of units in the system and is therefore a constant; y_1 is the total number of bonds; the y_1/y_0 ratio is the conversion depth.

System (25) is as infinite as system (24). However, the distinctive feature is that it is a closed system starting from the second term of the series (y_2), and can therefore be solved numerically by a sequential method: y_i can be calculated if all the preceding values, *viz.*, y_j, $j < i$, are known. The truncation of the system occurs naturally: there is no sense in calculating the variables whose concentrations cannot be measured. For example, if an experiment allows the determination of sequences consisting of a maximum of five units, why should the concentration of a six-unit sequence be determined? Thus, in this case the system to be solved will consist of five equations. A similar statement corresponds to chain concentrations obtained from (25) by substitution of y_i into Eqn (18).

Analysis of the structure of kinetic equations for BBs showed that a simple rule is observed: all the possible ways of formation of a given block are totalled. This simplifies considerably the formulation of kinetic equations for BBs. In this case, the TB concept becomes of key importance: in essence, the TB concept is a generalisation of the 'functional group' concept. In fact, a reaction between functional groups results in one bond, or a single BB (y_1). A terminal block is a functional group with units (one, two or more) bound to it. The formation of a TB results from reactions of simpler TBs with starting reagents; the structures of all the reaction participants are simpler than the structure of the starting block. Thus, the system of equations for any arbitrary complex structure appears to be closed, and the requirements of an experiment determine the blocks for which the kinetic problem should be solved.

Analysis of the system of differential equations for BBs showed [9, 51, 67] that it can be broken into groups of equations in such a way that the concentrations of BBs described by these equations can be calculated directly by solving that group of equations. The concentrations of larger BBs can be found using probabilistic methods. If such a group consists of a single block, *i.e.*, a block involving only one bond, the probabilistic approach is applicable to calculations of a polymeric structure of any complexity. In almost all cases it is possible to separate such structures of minimum size from which structures of arbitrary complexity and size can be combined. It was found [9, 51, 67] that the criterion of 'simplicity' consists of the absence of substitution effects on the reactivity of functional groups. Such effects can exist within a 'simple' block.

Thus, the use of the BB concept makes it possible to simplify the solution of kinetic problems, because it becomes unnecessary to formulate differential equations for all sizes of blocks. It is sufficient to solve these problems for elementary blocks and to use probabilistic calculations for larger blocks. In other words, the method based on the BB concept combines the advantages of both kinetic and probabilistic approaches.

Let us illustrate the application of the BB concept to the solution of the problem of critical conversion for a particular system, *viz*., epoxide bifunctional oligomer–pentafunctional amine.[69] The presence of primary and secondary hydrogen atoms in the latter creates prerequisites for the substitution effect. If BB concentrations are used, then, as in the statistical calculation, not molar concentrations of reagents are used but functional fractions of reactive groups (n_i) and probabilities of reactions of the corresponding groups, *i.e*., conversion degree (α_i).

The functional fractions of the corresponding groups n_i that are capable of reacting with the amine (the functional fraction of which equals n_A) can be represented as

$$n_i = \frac{N_i}{\sum_j N_j},$$

where N_i is the molar concentration of the corresponding groups at a given instant in time (at a given conversion); moreover,

$$N_i = i m_i,$$

where m is the molar concentration of a reagent containing i reactive functional groups. The balance condition is

$$\sum_i N_i \alpha_i = A\alpha_A,$$

where the i index corresponds to the epoxide reagents and the A index corresponds to the amine. The values of α_i and n_i are found by solving the corresponding systems of kinetic equations.

The structure of the network is determined by the concentration of nodes with different functionality; in this case, fragments of the amine-type hardening agent play the role of nodes. It is these structural elements that are bond blocks, whose concentration in this case should be calculated by the kinetic method, *i.e*., by solving the appropriate kinetic equations. The functionality of a node is determined by the number of oligomeric fragments bound to it.

In the case of the 'bifunctional epoxide oligomer–pentafunctional amine' system [*e.g*., diethylenetriamine (DETA) contains one secondary and two primary amino groups], it is necessary to distinguish primary and secondary amino groups from the very start of the reaction. If we designate the numbers of primary and secondary hydrogen atoms by digits (the first and second digit, respectively), the following groups are involved in the building of the network:

A(41) — original amine, node of zero functionality;

A(40) — amine with reacted secondary amino group; its functionality is 1, and it is a terminal fragment in the network;

A(22) — reaction product of a primary amino group; its functionality is 1, and it is a terminal fragment;

A(21) — functionality 2, intermediate fragment;

A(03) — functionality 2, intermediate fragment;

A(20) — trifunctional node;

A(02) — trifunctional node;

A(01) — tetrafunctional node;

A(00) — pentafunctional node.

If the ratio of reaction rate constants of secondary and primary amino groups is designated as

$$\beta = \frac{k_2}{k_1},$$

then the system of equations for all amino groups can be represented as follows:

$$\begin{aligned}
\frac{dB}{dt} &= -B\{4A(41) + 4A(40) + 2A(22) + 2A(21) + 2A(20) + \\
&\quad + \beta[A(41) + 2A(22) + A(21) + 3A(03) + \\
&\quad + 2A(02) + A(01)]\},\\
\frac{dA(41)}{dt} &= -(4+\beta)BA(41),\\
\frac{dA(40)}{dt} &= [\beta A(41) - 4A(40)]B,\\
\frac{dA(22)}{dt} &= [4A(41) - 2(1+\beta)A(22)]B,\\
\frac{dA(21)}{dt} &= [4A(40) + 2\beta A(22) - (2+\beta)A(21)]B,\\
\frac{dA(03)}{dt} &= [2A(22) - 3\beta A(03)]B,\\
\frac{dA(02)}{dt} &= [3\beta A(03) + 2A(21) - 2\beta A(02)]B,\\
\frac{dA(20)}{dt} &= [\beta A(21) - 2A(20)]B,\\
\frac{dA(01)}{dt} &= [2\beta A(02) + 2A(20) - \beta A(01)]B,\\
\frac{dA(00)}{dt} &= \beta A(01)B.
\end{aligned} \tag{26}$$

The concentrations of nodes with different functionality change in the course of a reaction (Fig. 1). Characteristically, the concentration–conversion curves for different β values are similar in appearance: the maximum concentration of nodes with a given functionality corresponds to a single value of conversion depth, irrespective of the relative rate constant of the reaction involving the secondary amino group. On the other hand, the maximum value varies as a function of the kinetic parameters of polycondensation.

Since it is assumed that the reactivity of epoxy groups is unchanged during the reaction, the network structure can be calculated using a statistical approach based on calculated node concentrations.

According to the theory of branching processes,

$$u(q) = x\left[1 - \alpha + \alpha\sum n_{Ai} u^{i-1}(q)\right], \tag{27}$$

where α is the conversion degree of epoxy groups; n_{Ai} is the functional fraction of i-functional nodes.

Differentiation of the equation results in an expression for the gel formation condition

$$\alpha\sum_i (i-1)n_{Ai} = 1. \tag{28}$$

Formally, Eqn (28) coincides with the critical condition for f-functional polycondensation (15); however, the difference is that the weight-average functionality $\langle f\rangle_w$ changes during the process, *i.e*., it is a function of the conversion α.

The plots

$$y(\alpha) = 1 - \alpha\sum_i (i-1)n_{Ai}$$

are presented in Fig. 2 for different β values. The α_c value is determined by the condition $y(\alpha) = 0$. The critical conversion values for the diepoxide–DETA system for different β values are presented below.

β	1.0	0.7	0.5	0.3	0.1	0.01
α_c	0.5	0.507	0.514	0.524	0.535	0.535

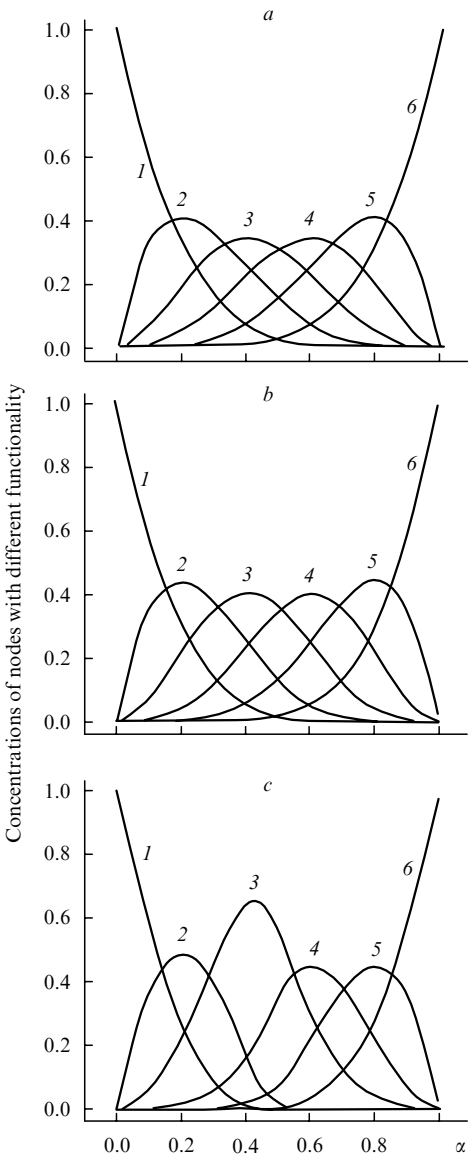


Figure 1. Dependencies of the concentrations of network nodes with different functionality on conversion for $\beta = 1$ (*a*), 0.5 (*b*), 0.1 (*c*).[69]
Node functionality: (*1*) 0, (*2*) 1, (*3*) 2, (*4*) 3, (*5*) 4, (*6*) 5.

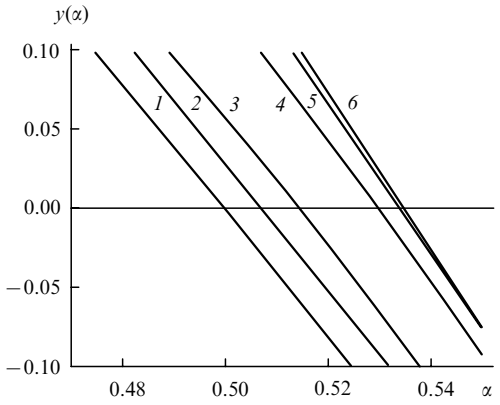


Figure 2. Graphical solution of the equation for finding the critical conversion at $\beta = 1$ (*1*), 0.7 (*2*), 0.5 (*3*), 0.2 (*4*), 0.1 (*5*), 0.01 (*6*).[69]

Thus, the solution result depends on the β value; this does not follow from the statistical theory at all. However, it can be shown easily that the known formula for the dependence of n_{Ai} on conversion is obtained if the applicability conditions of the statistical approach are met. In fact, according to statistics,

$$A_i = A\frac{f!}{i!(f-i)!}\alpha_A^i(1-\alpha_A)^{f-i}, \qquad (29)$$

where A_i is the concentration of the i-functional node and f is its maximum possible functionality ($f = 5$ for DETA).

Since

$$n_{Ai} = \frac{iA_i}{\sum_i iA_i},$$

substituting (29) into (28) we obtain

$$\alpha(f-1)\alpha_A = 1,$$

which coincides with Eqn (16) for a system of a bifunctional and an f-functional reagent.

The ratio of β constants affects considerably the gel point if the reagents are present in a non-equivalent ratio (Fig. 3).

When the scheme of a branching process is constructed (the statistical stage of solving the problem), the functionality of nodes that are formed should be taken into account. The presence of monofunctional reagents in the reaction mixture shifts the gel point towards higher conversions.[69] In this case, the gel formation condition has the form of Eqn (28); however, the presence of a monofunctional 'terminator' should be taken into account in the i index (as above, it means the node functionality). Here the functionality equals the number of added bifunctional oligomers rather than the number of hydrogen atoms that have reacted.

The strong dependence of the critical conversion on the concentration of the monofunctional modifier results from the decrease in the functionality of nodes (Table 2, Fig. 4). In comparison with the plots of changes in the concentrations of nodes with different functionality presented in Fig. 1, similar curves in Fig. 4 are shifted to the right along the x axis, the stronger the higher the content of the monofunctional modifier. While the final state of the system did not depend on the values of kinetic constants in the former case, in the latter case the presence of a monofunctional modifier strongly affects the structure of the

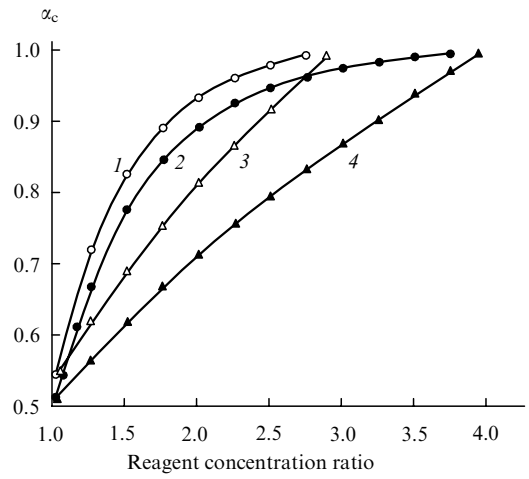


Figure 3. Dependence of the critical conversion on the ratios of the concentrations of amine (A) and epoxide oligomer (B) at different β values.[69]
A/B at $\beta = 0.1$ (*1*), 1 (*2*); B/A at $\beta = 0.1$ (*3*) and 1 (*4*).

Table 2. Critical conversion values at different monofunctional component concentrations (n_1) and different relative reaction rate constants of the modifier with primary (k_1) and secondary (β_2) amino groups (β_1 is the relative reaction rate constant of the secondary amino group with the epoxy group of the main oligomer).[69]

n_1	$k_1=1$, $\beta_1=\beta_2=1$	$k_1=5$, $\beta_1=\beta_2=1$	$k_1=1$, $\beta_1=\beta_2=0.5$	$k_1=0.5$, $\beta_1=\beta_2=1$	$k_1=0.5$, $\beta_1=\beta_2=0.5$
0	0.500	0.500	0.514	0.500	0.514
0.1	0.527	0.527	–	0.527	0.542
0.2	0.559	–	0.572	–	0.574
0.3	0.597	–	–	0.597	0.613
0.4	0.645	0.645	0.655	–	0.661
0.5	0.707	–	–	0.707	0.722
0.6	0.790	–	0.794	–	0.804
0.65	0.845	0.845	–	–	0.857
0.7	0.913	–	0.912	0.913	0.923
0.74	0.981	0.981	0.980	–	0.987

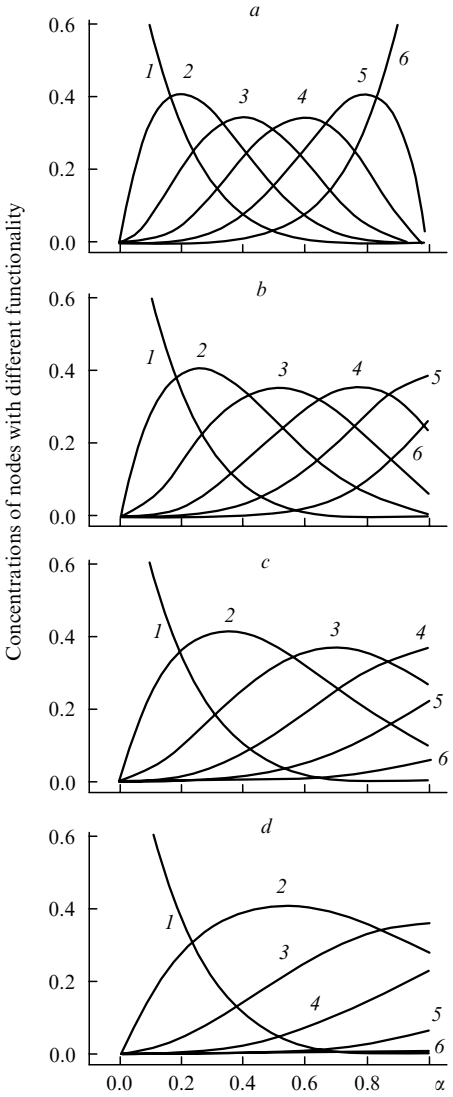


Figure 4. Dependencies of the concentrations of network nodes with different functionality on conversion for $\beta = 1$ at $n_1 = 0$ (*a*), 0.2 (*b*), 0.4 (*c*), 0.6 (*d*).
Node functionality: (*1*) 0, (*2*) 1, (*3*) 2, (*4*) 3, (*5*) 4, (*6*) 5.[69]

network formed, hence the gel point becomes unreachable at some concentration of the modifier.

Unlike a monofunctional modifier, a bifunctional modifier does not affect the critical conversion since neither of the components breaks network chains, hence the functionality of nodes does not depend on which of them is bound to an amine fragment. In this case, critical conversion is determined by the equation

$$(\alpha_b n_b + \alpha_2 n_2) \sum_i (i-1) n_{Ai} = 1, \tag{28a}$$

where the 'b' index corresponds to the main oligomer and the '2' index corresponds to the modifying one,

$$\alpha_b n_b + \alpha_2 n_2 \equiv \alpha_{ef}.$$

Both the difference of reaction rate constants of epoxy groups corresponding to different oligomers and the relative concentrations of oligomers affect the α_{ef} value but do not affect the gel point.

The use of the approach considered above for the solution of the problem of critical conversion values for other systems was considered by Deberdeev *et al.*[69,70].

V. Three-dimensional polymerisation

Polymerisation can be regarded as a process with a pronounced substitution effect. In fact, interaction of an active centre with a functional group recovers the active centre, *i.e.*, its reactivity changes. If there is no reagent with unchanged reactivity, the statistical approach to the description of such reactions is not applicable in any form (neither directly nor with the use of the BB concept). However, the statistical approach proposed long ago by Stockmayer [11,71] and improved by Gordon [72] is widely used even now.[18–20,73–76]

In essence, based on the statements of the statistical theory, the gel point condition for three-dimensional polymerisation consists of the requirement

$$\alpha_c = \frac{1}{\rho(\bar{P}_w - 1)}, \tag{16e}$$

i.e., this is considered as a cross-linking process. In this formula, α_c is the critical branching, a value introduced by Flory and Stockmayer;[5,71] ρ is the molar fraction of the bifunctional monomer if (as often happens) a mixture of mono- and bifunctional monomers is considered. The relationship between α_c and conversion was determined by solving kinetic equations describing the consumption of functional groups of monomers.[72]

Attempts were made to solve the problem kinetically. However, either the conditions used were not quite correct in some cases[77–79] or approximate and particular solutions were obtained.[7]

It should be noted that the question of experimental validation of theoretical calculations was non-topical for a long time, since it is well known that their feasibility conditions are not realised in three-dimensional polymerisation:[7,8,50] the fast chain growth by the radical mechanism and the low chain concentration at early stages of the process result in rather intense intramolecular cyclisation.[8,80–82] In this case, multiple cross-linking between a single pair of chains (formation of multiplet nodes and 'staircase'-type macromolecular structures) is also regarded as a factor decreasing the effective concentration of interchain cross-links and thus increasing the critical conversion. Because of that, microheterogeneous behaviour is typical of radical polymerisation.[8,50,83,84]

However, recent studies on living radical three-dimensional polymerisation (see, *e.g.*, Ref. 85) showed that the relationship (16e) is not fulfilled either,[86] though cyclisation does not play a significant role,[87] and the microheterogeneous character of the process does not manifest itself.[86,88]

It is convenient to solve Eqn (6) not in general form but by transforming it to a system of moments of the generating function.

Differentiation of Eqn (6) by all the q_i followed by equating them to 1 results in a system of differential equations for generating function moments and hence, moments of macromolecule distribution by length, chain functionality, and number of active centres. Obviously, all of these values are functions of time: $N = \Phi(\mathbf{1})$ is the total concentration of chains (zero moment);

first moments:

$$M = \frac{\partial \Phi(\mathbf{1})}{\partial q_1} = \sum_{i,j,l} i R(i,j,l)$$

is the total concentration of monomeric units in the system;

$$F = \frac{\partial \Phi(\mathbf{1})}{\partial q_2} = \sum_{i,j,l} j R(i,j,l)$$

is the total concentration of functional groups,

$$R = \frac{\partial \Phi(\mathbf{1})}{\partial q_3} = \sum_{i,j,l} l R(i,j,l)$$

is the total concentration of active centres;

second moments:

$$\Phi_{ij} \equiv \Phi_{ij}(\mathbf{1}) = \frac{\partial^2 \Phi(\bar{q})}{\partial q_i \partial q_j} \text{ at } \boldsymbol{q} = \mathbf{1}:$$

$$\Phi_{11} = \sum i(i-1)R(i,j,l),$$

$$\Phi_{12} = \sum ij R(i,j,l),$$

$$\Phi_{13} = \sum il R(i,j,l),$$

$$\Phi_{22} = \sum j(j-1)R(i,j,l),$$

$$F_{23} = \sum jl R(i,j,l),$$

$$\Phi_{33} = \sum l(l-1)R(i,j,l).$$

The system of differential equations for generating function moments has the form

$$\frac{dI}{dt} = -k_i I,$$

$$\frac{dN}{dt} = f k_i I - k_p FR - \frac{1}{2} k_t R^2 - k_Y Y,$$

$$\frac{dM}{dt} = 0,$$

$$\frac{dF}{dt} = -k_p FR,$$

$$\frac{dR}{dt} = f k_i I - k_t R^2 - k_Y Y,$$

$$\frac{dX}{dt} = -k_X XR,$$

$$\frac{d\Phi_{11}}{dt} = 2k_p \Phi_{12}\Phi_{13} + k_t(\Phi_{13})^2, \qquad (30)$$

$$\frac{d\Phi_{12}}{dt} = k_p(\Phi_{13}\Phi_{22} + \Phi_{12}\Phi_{23} - R\Phi_{12}) + k_t \Phi_{13}\Phi_{23},$$

$$\frac{d\Phi_{13}}{dt} = k_p(\Phi_{13}\Phi_{23} + \Phi_{12}\Phi_{33} + R\Phi_{12}) - (k_X X + k_Y Y)\Phi_{13} + k_t(\Phi_{33} - R)\Phi_{13},$$

$$\frac{d\Phi_{22}}{dt} = 2k_p(\Phi_{22}\Phi_{23} - R\Phi_{22}) + k_t(\Phi_{23})^2,$$

$$\frac{d\Phi_{23}}{dt} = k_p[(\Phi_{23})^2 + \Phi_{22}\Phi_{33} - R\Phi_{23} + R\Phi_{22}] - (k_Y Y + k_X X)\Phi_{23} + k_t(\Phi_{33} - R)\Phi_{23},$$

$$\frac{d\Phi_{33}}{dt} = 2k_p \Phi_{23}(\Phi_{33} + R) - 2(k_Y Y + k_X X)\Phi_{33} + k_t(\Phi_{33} - 2R)\Phi_{33}.$$

The solution of the system makes it possible to obtain comprehensive information about the course of polymerisation, including the value of critical conversion.

As noted above, the mathematical criterion of the formation of a cross-linked polymer is that the second moment of molecular mass distribution turns to infinity. However, it is the number of functional groups (as well as the number of active centres) that determines the chain growth rate during gel formation. Hence, distribution of macromolecules by functionality is the determining factor. In terms of generating function moments, it is the value of the second moment of the generating function by functionality

$$\Phi_{22}(t) = \sum_{i,j,l} j(j-1)R(i,j,l,t).$$

In a series of studies, Irzhak *et al.*[49,89–92] used the method considered above to study three-dimensional polymerisation processes involving different mechanisms: living polymerisation with instant and slow initiation, without and with chain transfer; polymerisation with square-law and linear termination. The main results of these studies are presented below.

The plots of $\Phi_{22}(t)$ during living polymerisation in the absence of chain transfer reactions under instant initiation conditions are presented in Fig. 5. One can see that $\Phi_{22}(t)$ increases by orders of magnitude (tends to infinity) in a very narrow range of conversions. Therefore, the critical conversion can be determined, without a considerable inaccuracy, as the x-axis intercept of the asymptote to the $\Phi_{22}(t)-\alpha$ curve. As calculations showed,[89] the critical conversion α_c obtained by this method is an unambiguous function of the starting $\Phi_{22}(0)$ value at a given concentration of active centres I_0 and does not depend on the starting concentration of functional groups, F(0).

The dependence of α_c on $\Phi_{22}(0)$ for living polymerisation with instantaneous initiation is presented in Fig. 6. It is evident that the square-root law is obeyed with good accuracy in this case; the

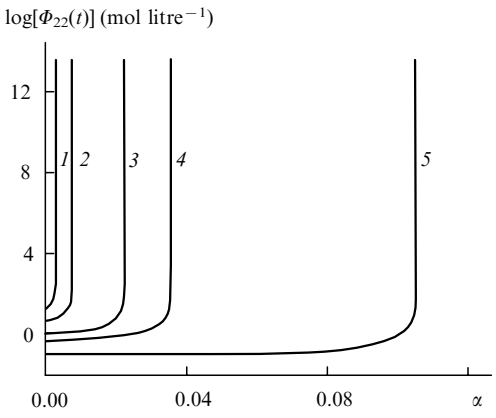


Figure 5. Kinetic curves of changes in the second moment of functionality distribution $\Phi_{22}(t)$ on instant initiation.
$I_0 = 10^{-3}$ mol litre^{-1}; $\Phi_{22}(0) = 20$ (*1*), 5 (*2*), 1 (*3*), 0.5 (*4*), 0.1 (*5*).[89]

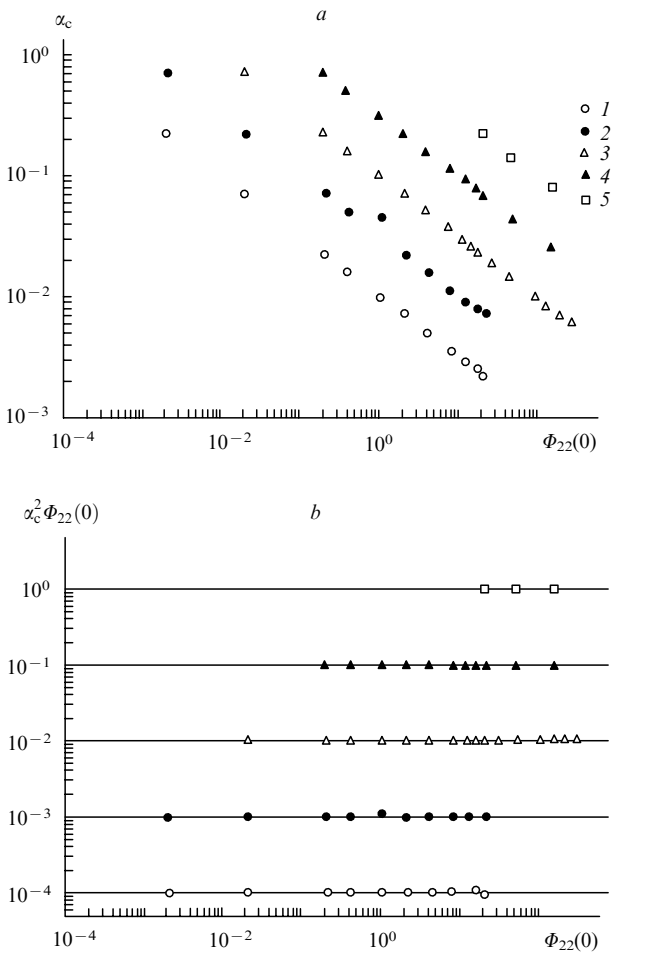


Figure 6. Dependencies of α_c on $\Phi_{22}(0)$ in the case of instant initiation. $I_0 = 10^{-4}$ (*1*), 10^{-3} (*2*), 10^{-2} (*3*), 10^{-1} (*4*), 1 mol litre^{-1} (*5*).[89]

straight lines corresponding to different concentrations of active centres are parallel to each other. Analysis showed that the critical conversion value is described by the formula

$$\frac{\alpha_c^2\Phi_{22}(0)}{I_0} = 1. \qquad (31)$$

The forms of the formulas (31) and (16) are similar. It fact, taking into account that

$$\frac{\Phi_{22}(0)}{F(0)} = \langle f\rangle_w - 1,$$

formula (31) can be converted to

$$\alpha_c^2 r(\bar{f_w} - 1) = 1. \qquad (31a)$$

However, this is just an outward similarity, since the r value, which is the ratio of concentrations of functional groups and active centres is much more than unity, whereas the F_{B0}/F_{A0} in formula (16) is close to unity. Furthermore, there is no multiplier characterising the distribution of the second reagent (active centres) by functionality. Anyway, it could not be present here because of the facts noted above, *i.e.*, that the starting molecules of active centres are monofunctional [R(0,0,1)/I_0 = 1] and that they are not consumed in polymerisation. Probably, the presence of the second power of α_c in formula (31) originates from the fact that the achievement of the critical point requires the reaction of at least two (per one chain) groups belonging to polyfunctional (branching) monomers, rather than the simultaneous reaction of two different functional groups, as is the case in Eqn (16).

Solution of the problem of radical copolymerisation of mono- and bifunctional monomers by the Monte Carlo method[93] resulted in an empirical relationship, whose form is similar to Eqn (31). The dependence of the critical conversion p_c on the inhibitor concentration C_I, the fraction of vacant lattice points C_V, and the molar fraction of bifunctional monomers f_{bif} was determined using the formula

$$p_c = \frac{C_I^{0.45}}{f_{bif}^{0.47}(1 - C_V)}.$$

As one can see, there are some differences, *viz.*, the index of power differs somewhat from 2 and the relative concentration of branching (bifunctional) comonomer appears in place of the second moment by functionality. The first difference is explained by the fact that cyclisation can be taken into account in the simulation of polymerisation. Therefore, the gel point should shift towards higher conversions in comparison with that calculated analytically. As regards the molar fraction of the branching comonomer, its use is not substantiated by any considerations.

Bansil *et al.*[93] reached the conclusion that the relationship obtained agreed with the ideas of Flory and Stockmayer. However, on the contrary, the calculation presented in that study suggests that there was no agreement.

Analysis of polymerisation processes with more complex mechanisms confirms the latter conclusion. Results for living polymerisation under slow initiation conditions are presented in Fig. 7. One can see that the α_c *vs.* $\Phi_{22}(0)$ plots in logarithmic

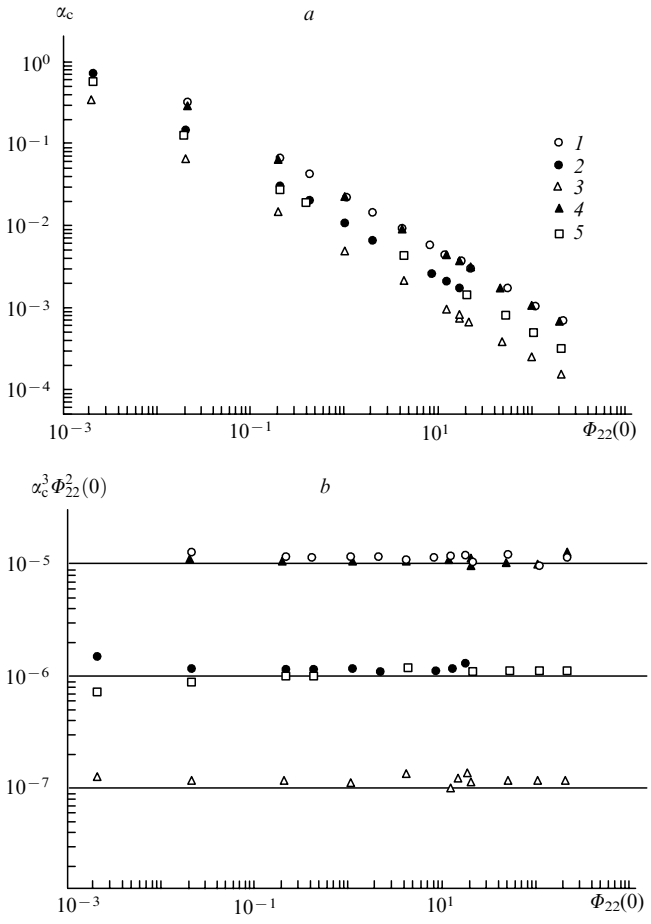


Figure 7. Dependencies of α_c on $\Phi_{22}(0)$ in the case of slow initiation. I_0 = 1 (*1*), 10^{-1} (*2*), 10^{-2} (*3*, *4*), 10^{-3} mol litre^{-1} (*5*); $k_i/k_p = 10^{-5}$ (*1*–*3*) and 10^{-3} (*4*, *5*).[89]

coordinates have the form of parallel straight lines demonstrating the relationship

$$\alpha_c \sim [\Phi_{22}(0)]^{-0.67},$$

shifted along the y-axis depending on the initiation rate. All the results are described with high accuracy by the following relationship:

$$\alpha_c^3 \frac{k_p \Phi_{22}^2(0)}{k_i I_0} = 1. \quad (32)$$

However, it is obvious that this result does not at all correlate with formulas provided by the statistical theory. On the other hand, both Eqns (31) and (32) relate the critical conversion value with the weight-average functionality of the starting monomer mixture referred to the concentration of chains [Eqn (31)] or to the rate of their accumulation [Eqn (32)].

It should be noted that the formulas (31) and (32) are some limiting cases that are obtained from a more general expression at $W_i \to \infty$ (instant initiation) or $W_i \to 0$ (slow initiation). The following formula can be an example:

$$\frac{\alpha_c^2 \Phi_{22}(0)}{I_0} = 1 - \exp\left[- \frac{k_i}{k_p \alpha_c \Phi_{22}(0)} \right] \longrightarrow$$

$$\longrightarrow \begin{cases} 1 & \text{at} \quad k_i \to \infty \\ \dfrac{k_i}{k_p \alpha_c \Phi_{22}(0)} & \text{at} \quad k_i \to 0 \end{cases}.$$

However, this result cannot be obtained in explicit form because the system (30) does not have an analytical solution. On the other hand, numeric calculation (Fig. 8) showed that the formula (31) is correct under the condition

$$\frac{k_i}{k_p \alpha_c \Phi_{22}(0)} \geqslant 6.$$

If

$$\frac{k_i}{k_p \alpha_c \Phi_{22}(0)} < 1,$$

then the critical conversion value is determined by the expression (32). The term 'instant initiation' should be used in the case $k_i/k_p > 0.1$ mol litre^{-1}.

Dusek and Somvarsky [94] gave a kinetic solution of the problem for living polymerisation with slow initiation. It was shown that the results given by the suggested approach differed from those of statistical calculations. Calculations carried out using the system (30) (taking into account that initiation occurs when an initiator reacts with a functional group) also give a somewhat different result (Table 3).

The difference between the critical conversion values is not high at a low inhibitor concentration and a low initiation constant, but it increases with an increase in these parameters.

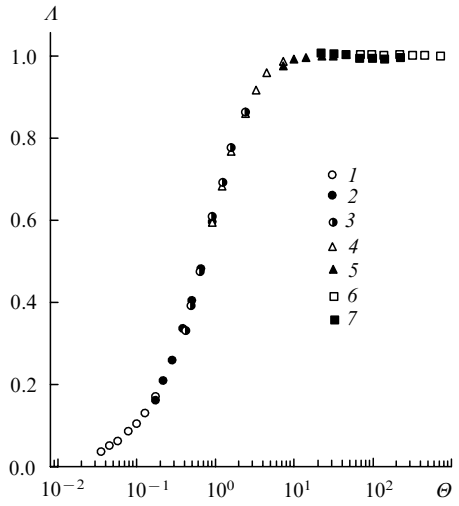


Figure 8. Dependence of α_c on the initiation rate in generalised coordinates $\Lambda - \Theta$.[49]
The curve shows the regions where the relationships (31) and (32) are obeyed.
$\Lambda = \alpha_c^2 \Phi_{22}(0)/I_0$, $\Theta = k_i/k_p \alpha_c \Phi_{22}(0)$; $\log(k_i/k_p) = -5$ (*1*), -4 (*2*), -3 (*3*), -2 (*4*), -1 (*5*), 0 (*6*), 1 (*7*).

Probably, the results of kinetic calculations differ because Dusek and Somvarsky [94] did not use the kinetic approach quite consistently: in order to take into account the interaction of active centres with 'dangling' functional groups, they derived a branching process and obtained the $G_1(z_a)$ probability generating function [see Eqns (14)–(16) in Ref. 94]. However, both variants give critical conversion values that differ considerably from those obtained using the statistical approach.

The significant dissimilarity between the results obtained and the statistical conclusions is also obtained if the concentration of chains is determined by a more complex mechanism, *viz*., chain transfer or chain termination.[89,90]

The relationships between the α_c, $\Phi_{22}(0)$ values and the chain transfer rate for instant and slow initiation are demonstrated in Fig. 9. In both cases, invariants characteristic of processes in the absence of chain transfer are plotted along the y axis. By selecting appropriate coordinates for the y axis it becomes possible to 'plot' the entire set of 'experimental' data on consolidated curves. The left branches of such curves correspond to the relationship

$$\alpha_c \approx \frac{1}{2} \frac{k_X X_0}{k_p \Phi_{22}(0)}, \quad (33)$$

i.e., critical conversion is determined by the ratio of the chain transfer rate to the growth rate on functional groups belonging to polyfunctional (branching) monomers.

The right branches of the curves for instant and slow initiation obey the relationships (31) and (32), respectively. The crossover points are described by the following relationships:

Table 3. Critical conversion calculation results: kinetic methods (I, II); statistical methods (III).

I_0/m_0	$k_i/k_p = 0.01$			$k_i/k_p = 0.1$			$k_i/k_p = 1.0$			$k_i/k_p = 10$		
	I	II	III	I	II	III	I	II	III	I	II	III
0.001	0.020	0.020	0.015	0.030	0.031	0.022	0.032	0.033	0.023	0.032	0.033	0.023
0.01	0.046	0.048	0.036	0.083	0.089	0.063	0.100	0.108	0.075	0.105	0.109	0.076
0.1	0.102	0.112	0.081	0.204	0.236	0.168	0.316	0.367	0.257	0.332	0.385	0.279
0.5	0.177	0.204	0.146	0.375	0.448	0.324	0.707	0.758	0.643	0.864	0.855	0.809

Note. I, III are data from Ref. 94, II is calculation using system (30); $F(0) = 10$, $\Phi_{22}(0) = 20$, monomer concentration $m_0 = 5$ mol litre^{-1}.

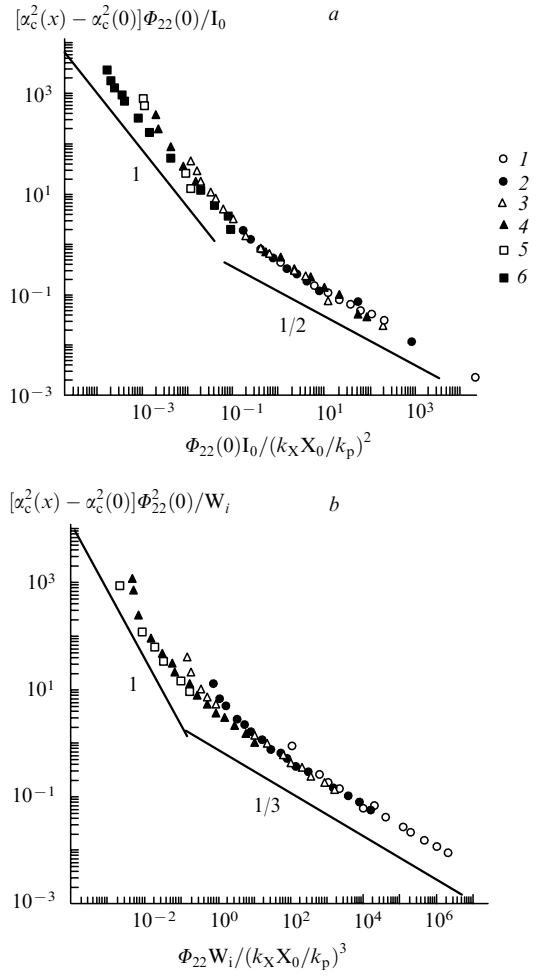


Figure 9. Dependencies of α_c on $\Phi_{22}(0)$ in the case of instant (*a*) and slow (*b*) initiation and chain transfer.[83]
$I_0 = 10^{-4}$ mol litre^{-1}: (*a*): $X_0 = 0$ (*1*), 1 (*2–4*, *6*); 10^{-1} mol litre^{-1} (*5*); $k_X/k_p = 10^{-3}$ (*1*, *2*), 10^{-2} (*3*), 10^{-1} (*4–6*); (*b*): $W_i = 10^{-4}$ (mol litre^{-1})^2 (see †). $X_0 = 0$ (*1*), 1 (*2–4*), 10^{-1} (*5*); $k_X/k_p = 10^{-3}$ (*1*, *2*), 10^{-2} (*3*), 10^{-1} (*4*, *5*). The numbers at the plots show the slopes of the straight lines.

$$\frac{k_p\Phi_{22}(0)}{k_X X_0} \approx \begin{cases} \dfrac{k_X X_0}{k_p I_0} & \text{(instant initiation)} \\ \dfrac{(k_X X_0)^2}{k_p k_i I_0} & \text{(slow initiation)} \end{cases} \qquad (34)$$

Therefore, if $k_X/k_p \approx 1$ and $X_0 \approx I_0$, one should use the formula (33) at $\Phi_{22}(0) < X_0$ and the relationships (31) and (32) at $\Phi_{22}(0) > X_0$. However, it is obvious that if $\Phi_{22}(0) < X_0$, then α_c exceeds 1, *i.e.*, the gel point cannot be reached. This means that it is the formulas (31) and (32) that make sense for practically important polymerisation conditions, *i.e.*, the chain transfer reaction and hence the actual length of the polymeric chain are not of importance in determining the critical conversion. In other words, the concentration of active centres in the former case and the initiation rate in the latter case are of importance not as factors determining the chain length but as those setting the concentration of the second reagent that participates in the formation of a macromolecule, which is an active centre.

Similar conclusions are obtained from analysis of polymerisation reactions with chain termination.[90, 92] The corresponding formulas are presented in Table 4.

† The initiation rate was attributed to the chain growth constant, therefore the (mol litre^{-1})^2 measurement units were obtained.

Table 4. Critical conversion calculation formulas.[89–92]

Process	small Φ_{22}	high Φ_{22}	Criterial conditions
Living polymerisation, instant initiation	$\frac{\alpha_c^2\Phi_{22}}{I_0} \approx 1$	$\frac{\alpha_c^2\Phi_{22}}{I_0} \approx 1$	$\frac{k_i}{k_p} > \sqrt{I_0\Phi_{22}}$
The same + chain transfer	$\alpha_c \approx \frac{1}{2}\frac{k_X X_0}{k_p\Phi_{22}}$	$\frac{\alpha_c^2\Phi_{22}}{I_0} \approx 1$	$\Phi_{22} >< \frac{(k_X X_0)^2}{k_p^2 I_0}$
Living polymerisation, slow initiation	$\frac{\alpha_c^3\Phi_{22}^2}{W_i} \approx 1$	$\frac{\alpha_c^3\Phi_{22}^2}{W_i} \approx 1$	$\frac{k_i}{k_p} < \sqrt{I_0\Phi_{22}}$
The same + chain transfer	$\alpha_c \approx \frac{1}{2}\frac{k_X X_0}{k_p\Phi_{22}}$	$\frac{\alpha_c^3\Phi_{22}^2}{W_i} \approx 1$	$\Phi_{22} >< \frac{(k_X X_0)^3}{k_p k_i^2 I_0}$
Slow initiation, termination by recombination	$\alpha_c \approx 0.33\frac{k_t R}{k_p\Phi_{22}}$	$\frac{\alpha_c^3\Phi_{22}^2}{W_i} \approx 1$	$\Phi_{22} >< \frac{\sqrt{k_1^3 W_i}}{k_p^2}$
Slow initiation, linear termination	$\alpha_c \approx \frac{1}{2}\frac{k_{tY} Y}{k_p\Phi_{22}(0)}$	–	–
'Substitution' effect, termination by disproportionation	$\alpha_c \approx \frac{1}{2}\frac{\sqrt{k_t W_i}}{k_{p2} Z_{22}}$	–	$\frac{k_{p1} Z_{22}}{\sqrt{k_t W_i}} < \frac{k_t}{k_{p2}}$

It is usual for three-dimensional radical polymerisation that a dilute solution of primary macromolecules in their own monomer is formed at early stages. Chain units carry functional ('dangling') groups; subsequent conversion of such groups is determined by two factors. On the one hand, the local concentration of these groups in the vicinity of a reactive end of a macroradical can be considerably higher than the mean bulk value, which results in their higher consumption with formation of intrachain rather than interchain cross-links. Because of that, both the apparent reactivity of 'dangling' groups and the critical conversion increase.[8] On the other hand, shielding of 'dangling' groups by the polymeric chain itself decreases the reactivity due to the steric factor, particularly if aggregation occurs. Finally, the substitution effect can manifest itself, *i.e.*, a change in the double bond reactivity, depending on whether it belongs to a monomer molecule or to a monomeric unit of a macromolecule. The combined effects of all these factors complicate the determination of the actual mechanism of the formation of cross-links in three-dimensional radical polymerisation.

In fact, conversion of double bonds (α_1) and 'dangling' groups (α_p) was observed separately in a number of studies [88, 95–97] on the kinetics of three-dimensional radical polymerisation. It was found that α_p reaches 0.2–0.4 at initial reaction stages where α_1 is close to zero. In terms of relative reactivity ε ($\varepsilon = k_{p2}/k_{p1}$, where k_{p1} and k_{p2} are reaction rate constants of chain growth on original and 'dangling' double bonds), this gives $\varepsilon \gg 1$.

The following copolymerisation systems were used: mixtures of styrene with 0.2 mol.%–2 mol.% of divinylbisphenol [88, 98–100] and mixtures of MMA with 1%–2% of ethylene glycol dimethacrylate.[98] In both cases, there are no reasons to believe that the reactivity of vinyl groups can increase when they are 'hung' on a polymeric chain. Probably, the increase in the local concentration of 'dangling' groups in the vicinity of the reactive macroradical end is the determining factor in both cases.

When three-dimensional radical polymerisation is carried out in the living chain mode,[86, 88] $k_{p2}/k_{p1} \approx 0.3$. This means that at the very start of the reaction, the concentration of macromolecules is high and the chain lengths are small, therefore the effect of local concentration of 'dangling' groups ceases and their decreased

reactivity in comparison with the original monomer is observed. It is likely that steric restrictions play a decisive role in this system.

On the other hand, it is obvious that the substitution effect can manifest itself in the three-dimensional radical polymerisation of diene monomers. This should primarily affect the structure of the cross-linked polymer:[101] a decrease in the reactivity of dangling groups in comparison with the original functional groups results in the formation of 'loose' interpenetrating clusters, while its increase results in compact, closely packed 'grains'.

Changes in the reactivity of functional groups within the suggested calculation scheme were taken into account by Korolev *et al.*[91] It was shown that it is necessary to separate original (monomeric) reagents from all polymeric chains and to introduce an own generating function for such chains

$$Z(\boldsymbol{q}) = \sum_i q_1 q_2^i m_i$$

(m_i is the concentration of the *i*-functional monomer). For example, in the case of bifunctional oligomers (*e.g.*, dimethacrylates)

$$Z(\boldsymbol{q}) = q_1 q_2^2 m_2.$$

The kinetic scheme of m_i consumption expressed by the equation

$$\frac{\mathrm{d}m_i}{\mathrm{d}t} = -k_{\mathrm{p}1} i m_i \mathrm{R}$$

($k_{\mathrm{p}1}$ is the growth rate constant on functional groups belonging to monomers) gives an ordinary differential partial equation for the generating function

$$\frac{\partial Z(\boldsymbol{q})}{\partial t} = -k_{\mathrm{p}1} q_2 \frac{\partial Z(\boldsymbol{q})}{\partial q_2} \mathrm{R}, \tag{35}$$

solution of which by the characteristics method gives

$$Z(\boldsymbol{q}) = \sum_i q_1 (q_2 \mathrm{e}^{-k_{\mathrm{p}1}\tau})^i m_i(0), \tag{36}$$

where

$$\tau = \int_0^t \mathrm{R}(\xi)\mathrm{d}\xi$$

(ξ is the variable of integration); $m_i(0)$ is the starting concentration of the *i*-functional monomer.

Equation (35) can be represented as a system for moments taking the distribution by functional groups (the '2' index) into account

$$\begin{aligned}
\frac{\mathrm{d}Z}{\mathrm{d}t} &= -k_{\mathrm{p}1}\mathrm{R}Z_2, \\
\frac{\mathrm{d}Z_2}{\mathrm{d}t} &= -k_{\mathrm{p}1}\mathrm{R}(Z_2 + Z_{22}), \\
\frac{\mathrm{d}Z_{22}}{\mathrm{d}t} &= -k_{\mathrm{p}1}\mathrm{R}(2Z_{22} + Z_{222}), \\
\frac{\mathrm{d}Z_{222}}{\mathrm{d}t} &= -k_{\mathrm{p}1}\mathrm{R}(3Z_{222} + Z_{2222}), \\
&\textit{etc.}
\end{aligned} \tag{37}$$

This system is not closed.

However, it should be taken into account that the initial reaction mixture consists of monomeric molecules with limited functionality. This fact makes it possible to truncate the system of equations. In fact, since

$$\begin{aligned}
Z_2(\boldsymbol{q}) &= q_1 \sum_{i=1}^n i q_2^{i-1} m_i, \\
Z_{22}(\boldsymbol{q}) &= q_1 \sum_{i=1}^n i(i-1) q_2^{i-2} m_i, \\
Z_{222}(\boldsymbol{q}) &= q_1 \sum_{i=1}^n i(i-1)(i-2) q_2^{i-3} m_i \\
&\textit{etc.},
\end{aligned} \tag{38}$$

$Z_{22}(1) = 0$ for linear polymerisation; $Z_{222}(1) = 0$ if the functionality does not exceed two ($n \leqslant 2$); $Z_{2222} = 0$ if n is no greater than three.

Naturally, the scheme describing radical polymerisation is more complex than Scheme (1). The system of differential equations for macromolecule concentrations and generating function moments changes accordingly. The initial conditions change as well: at $t = 0$ $m(1,i,0) = m_i(0)$, all $\mathrm{R}(i,j,l) = 0$.

Calculations showed[91] that the result obtained above is true with rather high precision, *viz.*, the critical conversion value depends only on the second distribution moment by functionality for initial molecules, $Z_{22}(0)$. Therefore, (31)- and (32)-type formulas are valid for living polymerisation. Results of calculations for radical polymerisation (with chain termination) are presented in Table 4.

As noted above, comparison of theoretical conclusions with experimental data for polymerisation processes is very difficult. Owing to the high distribution nonhomogeneity of reactive macromolecules in the reaction volume at early stages, intrachain cyclisation and aggregation of polymeric coils are highly probable at early stages. Therefore, assessment of the validity of particular formulas requires that the distribution nonhomogeneity of macromolecules be minimised. This can be achieved by minimising the degree of polymerisation by increasing the rates of chain transfer or chain termination reactions. When polymerisation occurs in the living chain mode, the steady-state concentration of active centres decreases by several orders in comparison with a similar value for polymerisation under ordinary conditions.[85,102] As a result, the concentration of chains is rather high even at small conversion levels. Therefore, the cyclisation probability decreases considerably in this case, too.[87] It can also be expected that cyclisation would contribute insignificantly to polymerisation if the content of the branching comonomer in the reaction mixture is decreased.

These approaches were used in a number of studies[75,86,87,90,98,103] on the determination of the critical conversion value in three-dimensional polymerisation processes.

Ide and Fukuda[86] carried out radical copolymerisation of styrene with certain bifunctional monomers in the presence of 2,2,6,6-tetramethylpiperidinyl 1-oxide, a stable radical that ensured the living polymerisation mode. The content of the bifunctional reagent

$$f_2 = \frac{m_2}{m_2 + m_1}$$

in the original mixture did not exceed two molar percent. As noted above, both factors (the living polymerisation mode and the small f_2 value) contribute to the insignificance of intrachain cyclisation. Some of the results obtained are presented in Table 5.

The fact that the calculation result obtained using formula (16e) exceeds the experimental critical conversion value suggests that this calculation is faulty; on the other hand, the overestimated values obtained using formula (31) can be due to the inaccuracy of determination of the number of chains, which may easily be smaller than I_0. Thus, experimental results can be regarded as evidence of the validity of the formula (31).

The use of dodecanethiol as the chain transfer agent in the polymerisation of neopentyl dimethacrylate[98] decreased the weight-average degree of polymerisation. As this value decreases from 142 to 49, the critical conversion value increases but remains higher than that calculated using formula (16e). Since formula (33) gives even lower values, it is not possible to assess the validity of the suggested approach. The cyclisation probability remains considerable even at such relatively low chain lengths.

Table 5. Critical conversion in living three-dimensional copolymerisation.[86]

f_2	I_0/m_1	$\langle P\rangle_w$	α_c		
			experiment	calculation using the formula	
				(16e)	(31) [a]
0.01	1/200	132	0.55	0.76	0.70
0.016	1/170	101	0.50	0.62	0.60
0.02	1/200	96	0.40	0.52	0.495

[a] In this case, formula (31) has the form

$$\alpha_c = \sqrt{\frac{I_0(1-f_2)}{f_2}}.$$

The effect of the number of branching links in a chain on the critical conversion value is demonstrated by data in Table 6.

Table 6. Critical conversion in three-dimensional copolymerisation of styrene with *m*-divinylbenzene (DVB).[75]

[DVN] (mol.%)	$10^{-3}\langle P\rangle_w$	$\Phi_{22}(0)$	α_c		
			experiment	calculation using the formula	
				(16e)	(see [a])
1	1.19	0.154	0.215	0.0425	0.032
0.5	0.79	0.077	0.333	0.133	0.065
0.25	0.74	0.039	0.488	0.271	0.128
0.17	0.67	0.026	0.549	0.435	0.192

[a] Calculation using the formula presented in Table 4.

Calculation gives lower critical conversion values in both versions. This suggests that cyclisation occurs at such a low content of the divinyl monomer. In fact, the molar fraction of the monomer was lower by an order of magnitude in the living polymerisation experiments described above; it is this factor that predefines the absence of cyclisation.

It is of note that statistical calculation gives overestimated gel point values. This may misguide researchers who assess the contributions of cyclisation to the polymerisation process. For example, the experimental gel point value in the polymerisation of triethylene glycol dimethacrylate in the presence of benzoquinone (0.05 mol litre^{-1}) as the inhibitor was found to be 0.19.[90] Statistical calculations gave a much higher value, *viz*., 0.72, which is physically unreasonable. Calculation with the use of formulas shown in Table 4 gave 0.18, which is very close to the experimental value. The corresponding values at the inhibitor concentration of 0.01 mol litre^{-1} are as follows: 0.135; 0.14; 0.036. In other words, cyclisation does not occur, judging by statistical calculation results. However, accurate calculation using the formulas in Table 4 indicates the opposite situation.

Thus, the statistical approach cannot be used to analyse three-dimensional polymerisation.

VI. Conclusion

In conclusion, it should be emphasised that calculation of critical conversion values in the case of the formation of network polymers can be regarded as a particular solution of a more general problem, *viz*., determination of molecular mass distribution parameters or, more exactly, distribution of macromolecules by functionality. Quite a few approaches have been proposed for this purpose; however, their physical substantiation is provided only in some cases. In this review we made an attempt to determine the applicability conditions of different solution methods, depending on the polymer formation mechanism. Calculation of molecular mass distributions is a problem of current interest for polymer technology, so the criteria formulated here appear to be quite significant.

In the review we summarise the achievements in the calculation methods for the critical sol–gel transition point during polymer formation. One can state with certainty that the principles underlying these methods are also applicable to the formation of physical gels.[104] In particular, the relationship between the temperature and the gel transition concentration of biopolymers discussed by Matveev[105] is determined, in essence, by general regularities of network structure formation, though in this case the nature of nodes is rather specific: the latter are formed due to phase separation rather than chemical reactions.

References

1. L Z Rogovina, G L Slonimskoi *Vysokomol. Soedin., Ser. B* **39** 1543 (1997) [a]
2. F Chambon, H H Winter *Polym. Bull. (Berlin)* **13** 499 (1985)
3. M Baumgaertel, H H Winter *Rheol. Acta* **28** 511 (1989)
4. A B Rodd, J Cooper-White, D E Dustan, D V Boger *Polymer* **42** 185 (2001)
5. P J Flory *Principles of Polymer Chemistry* (Ithaka: Cornell University Press, 1953)
6. W H Stockmayer *J. Chem. Phys.* **11** 45 (1943)
7. S I Kuchanov *Metody Kineticheskikh Raschetov v Khimii Polimerov* (Methods of Kinetic Calculations in the Chemistry of Polymers) (Moscow: Khimiya, 1978)
8. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery. Sintez, Struktura, Svoistva* (Cross-Linked Polymers. Synthesis, Structure, Properties) (Moscow: Nauka, 1979)
9. M L Tai, V I Irzhak *Vysokomol. Soedin., Ser. A* **25** 2305 (1983) [a]
10. H Galina *Europhys. Lett.* **3** 1155 (1987)
11. W H Stockmayer *J. Chem. Phys.* **13** 199 (1945)
12. H Tobita *J. Polym. Sci., Part B* **36** 2423 (1998)
13. H Tobita *Macromolecules* **26** 836 (1993)
14. H Tobita *Macromolecules* **29** 693 (1996)
15. H Tobita *Macromol. Theory Simul.* **7** 225 (1998)
16. A E Hamielec, J W Hodgins, K Tebbens *AIChE J.* **13** 1087 (1967)
17. A E Hamielec, J F MacGregor, A Penlidis *Macromol. Symp.* **10–11** 521 (1987)
18. H Tobita, A E Hamielec *Macromolecules* **22** 3098 (1989)
19. T Xie, A E Hamielec *Macromol. Theory Simul.* **2** 455 (1993)
20. S Fiorentino, A Ghielmi, G Storti, M Morbidelli *Ind. Eng. Chem. Res.* **36** 1283 (1997)
21. C H Bamford, A D Jenkins *Trans. Faraday Soc.* **56** 907 (1960)
22. R Zeman, N R Amundson *Chem. Eng. Sci.* **20** 331 (1965)
23. R Zeman, N R Amundson *Chem. Eng. Sci.* **20** 637 (1965)
24. D J Coyle, T J Tulig, M Tirell *Ind. Eng. Chem. Fundam.* **24** 343 (1985)
25. M F Ellis, T W Taylor, V Gonzalez, K F Jensen *AIChE J.* **34** 1341 (1988)
26. P E Bailagou, D S Soong *Chem. Eng. Sci.* **40** 87 (1985)
27. V M Gonzalez-Romero, B E Rodriguez *Chem. Eng. Commun.* **59** 185 (1987)
28. M Chaimberg, Y Cohen *Ind. Eng. Chem. Res.* **29** 1152 (1990)
29. K Nagasubramanian, W W Graessley *Chem. Eng. Sci.* **25** 1549 (1970)
30. L Blavier, J Villermeaux *Chem. Eng. Sci.* **39** 101 (1984)
31. H Tobita, K Ito *Polym. React. Eng.* **1** 407 (1992/1993)
32. T J Crowley, K Y Choi *Ind. Eng. Chem. Res.* **36** 1419 (1997)
33. P Pladis, C Kiparissides *Chem. Eng. Sci.* **53** 3315 (1998)
34. W J Yoon, J H Ryu, C Cheong, K Y Choi *Macromol. Theory Simul.* **7** 327 (1998)
35. P D Iedema, H C J Hoefsloot *Macromol. Theory Simul.* **11** 410 (2002)
36. W H Ray *Macromolecules* **4** 162 (1971)
37. W H Ray, T L Douglas, E W Godsalve *Macromolecules* **4** 166 (1971)
38. P L Mills *Comput. Chem. Eng.* **10** 399(1986)

39. H Nordhus, O Moen, P Singstad *J. Macromol. Sci., Pure Appl. Chem.* **34A** 1017 (1997)
40. U Budde, M Wulkow *Chem. Eng. Sci.* **46** 497 (1991)
41. P Canu, W H Ray *Comput. Chem. Eng.* **15** 549 (1991)
42. M Wulkow *Macromol. Theory Simul.* **5** 393 (1996)
43. F Teymour, J D Campbell *Macromolecules* **27** 2460 (1994)
44. A Batte, A Ghielmi, G Storti, M Morbidelli *Macromol. Theory Simul.* **8** 498 (1999)
45. G Papavasiliou, I Birol, F Teymour *Macromol. Theory Simul.* **11** 533 (2002)
46. S Kumar, D Ramkrishna *Chem. Eng. Sci.* **52** 4659 (1997)
47. A Batte, G Storti, M Morbidelli *Macromol. Theory Simul.* **11** 37 (2002)
48. S I Kuchanov, E S Pavolotskaya *Vysokomol. Soedin., Ser. A* **24** 2190 (1982) [a]
49. T F Irzhak, G V Korolev, V I Irzhak *Khim. Fiz.* **21** 58 (2002) [b]
50. G V Korolev, M M Mogilevich, I V Golikov *Setchatye Poliakrilaty. Strukturnaya Mikrogeterogennost', Fizicheskie Setki, Deformatsionnye i Prochnostnye Svoistva* (Cross-Linked Polyacrylates. Structural Microheterogeneity, Physical Networks, Deformation and Mechanical Properties) (Moscow: Khimiya, 1995)
51. V I Irzhak *Usp. Khim.* **66** 598 (1997) [*Russ. Chem. Rev.* **66** 541 (1997)]
52. S I Kuchanov *Adv. Polym. Sci.* **152** 157 (2000)
53. K Dusek *Polym. Bull. (Berlin)* **1** 523 (1979)
54. P J Flory *J. Am. Chem. Soc.* **63** 3083 (1941)
55. I J Good *Proc. Camb. Philos. Soc.* **56** 367 (1960)
56. M Gordon *Proc. R. Soc. London, Ser. A* **268** 240 (1962)
57. A T Bharucha-Reid *Elements of the Theory of Markov Processes and their Applications* (New York: McGraw-Hill, 1960)
58. E Girard-Reydet, C C Riccardi, H Sautereau, J-P Pascault *Macromolecules* **28** 7599 (1995)
59. H Galina, K Kaczmarski, B Sanecka *Macromol. Theory Simul.* **1** 37 (1992)
60. M Gordon, G R Scantlebury *Proc. R. Soc. London, Ser. A* **292** 380 (1966)
61. H Galina, J Lechowicz, B Paka, B Sanecka *Polimery-tworz. Wielcoszasteczk.*, **39** 429 (1994)
62. S I Kuchanov *Dokl. Akad. Nauk SSSR* **249** 899 (1979) [c]
63. M L Tai, V I Irzhak *Dokl. Akad. Nauk SSSR* **259** 856 (1981) [c]
64. M Gordon, G R Scantlebury *Trans. Faraday Soc.* **60** 604 (1964)
65. H Tobita *J. Polym. Sci., Polym. Phys.* **36** 2423 (1998)
66. T Nakao, F Tanaka, S Kohjiya *Macromolecules* **35** 5649 (2002)
67. V I Irzhak, M L Tai, N I Peregudov, T F Irzhak *Colloid Polym. Sci.* **272** 523 (1994)
68. E T Hsieh, J C Randall *Macromolecules* **15** 353 (1982)
69. T R Deberdeev, R M Garipov, R Ya Deberdeev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **46** 412 (2004) [a]
70. T R Deberdeev, R M Garipov, R Ya Deberdeev, T F Irzhak, V I Irzhak *Dokl. Akad. Nauk* **393** 209 (2003) [c]
71. W Stockmayer *J. Chem. Phys.* **12** 125 (1944)
72. M Gordon *J. Chem. Phys.* **22** 610 (1954)
73. C W Macosco, D R Miller *Macromolecules* **9** 199 (1976)
74. D Durand, C M Bruneau *Makromol. Chem.* **183** 1007 (1982)
75. A Matsumoto, Y Kitaguchi *Macromolecules* **32** 8336 (1999)
76. A Matsumoto, S Asai, S Shimizu, H Aota *Eur. Polym. J.* **38** 863 (2002)
77. H H Tvorogov *Vysokomol. Soedin., Ser. A* **18** 1919 (1976) [a]
78. H H Tvorogov, A A Berlin *Vysokomol. Soedin., Ser. A* **19** 1274 (1977) [a]
79. N N Tvorogov, A G Kondrat'eva *Vysokomol. Soedin., Ser. A* **20** 1550 (1978) [a]
80. H Galina, K Dusek *Polymer* **17** 185 (1980)
81. K S Anseth, Ch N Bowman *J. Polym. Sci., Polym. Phys.* **33** 1769 (1995)
82. J E Elliott, C N Bowman *Macromolecules* **32** 8621 (1999)
83. O Okay, M Kurz, K Lutz, W Funke *Macromolecules* **28** 2728 (1995)
84. X Sun, Y Y Chiu, J Lee *Ind. Eng. Chem.* **36** 1343 (1997)
85. G V Korolev, A P Marchenko *Usp. Khim.* **69** 447 (2000) [*Russ. Chem. Rev.* **69** 409 (2000)]
86. N Ide, T Fukuda *Macromolecules* **32** 95 (1999)
87. J H Ward, N A Peppas *Macromolecules* **33** 5137 (2000)
88. N Ide, T Fukuda *Macromolecules* **30** 4268 (1997)
89. G V Korolev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **43** 970 (2001) [a]
90. G V Korolev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **43** 2106 (2001) [a]
91. G V Korolev, T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **44** 5 (2002) [a]
92. V I Irzhak, T F Irzhak, G V Korolev *Macromol. Symp.* **171** 11 (2001)
93. R Bansil, H J Herrmann, D Stauffer *J. Polym. Sci., Polym. Symp.* **73** 175 (1985)
94. K Dusek, J Somvarsky *Polym. Bull. (Berlin)* **13** 313 (1985)
95. J Holdway, R N Haward, W Parsons *Makromol. Chem.* **179** 1939 (1978)
96. L Mrkvichkova, P Kratochvil *J. Polym. Sci., Polym. Phys. Ed.* **19** 1675 (1981)
97. D T Landlin, C W Macosco *Macromolecules* **21** 846 (1988)
98. D Mitomi, A Matsumoto, H Aota, J Ikeda *Polymer* **41** 1321 (2000)
99. A Matsumoto, Y Yamashita, M Oiwa. *Netsukokasci Yushi (J. Thermoset. Plast. Jpn.)* **14** 139 (1993)
100. B Soper, R N Haward, E F T White *J. Polym. Sci., Polym. Chem. Ed.* **10** 2545 (1972)
101. V A Sal'nikov, N M Bol'bit *Vysokomol. Soedin., Ser. A* **30** 2551 (1985) [a]
102. T F Irzhak, V I Irzhak *Vysokomol. Soedin., Ser. A* **42** 2137 (2000) [a]
103. A Matsumoto, S Okuno, H Aota *Angew. Makromol. Chem.* **240** 275 (1996)
104. K Te Nijenhuis *Adv. Polym. Sci.* **130** 1 (1997)
105. Yu I Matveev *Vysokomol. Soedin., Ser. B* **45** 841 (2003) [a]

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Chem. Phys. Rep. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*