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Critical conversion in polymerization processes

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Abstract. The state of the art in calculations of the critical conversion (gel point) in three-dimensional polymerization and polycondensation is considered. The advantages and limitations of the statistical and kinetic approaches and a method for gel point calculation based on the concept of bond blocks are analyzed. The topological structure of the critical clusters is discussed. The bibliography includes 184 references.

I. Introduction

The critical conversion (α_c) in the formation of polymer networks, corresponding to the so-called gel point, is a key parameter of high-molecular-mass compounds. The gel point governs the transition of a system from viscous flow to elastic state. At degrees of conversion lower than the gel point, the polymer has a finite molecular mass. At higher degrees of conversion, one deals formally with an infinite molecular mass, or, mathematically, the higher moments of the molecular mass distribution (MMD), starting with the second moment, turn to infinity.

The gel point determines the percolation threshold in the polymeric system. Near the gel point, the macromolecules called critical clusters have a fractal topological structure.[1]

Having established a relation between the critical conversion and the structural and kinetic parameters of polymerization, one can formulate the conditions for the formation of a polymer network with specified physicomechanical characteritics.

The formation of insoluble gel or microgel particles complicates the polymerization processes. This particularly concerns the synthesis of hyperbranched polymers (HBP) by three-dimensional polymerization and polycondensation.

Flory[2–5] and Stockmeyer[6,7] determined the critical conversion for polycondensation of *f*-functional monomers, cross-linking of polymers and three-dimensional copolymerization using statistical and combinatorial methods. The relations derived were not substantiated by kinetic calculations[8,9] and experimentally.[2,9] They are applicable in the absence of intramolecular cyclization reactions. More recently, it was shown that the applicability of the probabilistic approaches is limited to the systems with no substitution effect (this means that the kinetic constants remain unchanged in the course of the process).[8,10–12] Otherwise, rigorous kinetic calculations are required. Following Flory and Stockmeyer, three-dimensional polymerization was often described within the framework of the probabilistic approach. Relations thus derived were not substantiated experimentally; however, their correctness was considered undoubtful (it is known that three-dimensional radical polymerization under ambient conditions is accompanied by intense cyclization owing to fast chain propagation and low concentration of chains in the early stages of the process).[9,13] Numerously repeated cross-linking within the same chain (secondary cyclization[13]) or within two chains (multiple cross-linking and formation of 'ladder' polymers[14]) is also considered as a factor reducing the effective concentration of inter-chain cross-links and thus increasing the critical conversion. Because of this, radical polymerization is a typical microheterogeneous process.[13,15–17] Taking account of the aforesaid, meeting certain theoretical dependences can hardly be expected.

When considering problems related to polymerization and, in particular, the gel point, the concept of functionality of the starting reactants is of paramount importance. The functionality means the number of bonds in the polymer chain that can be formed by an oligomer. One should keep in mind that the same functional group is characterized by different functionality depending on the reaction type. For instance, the double bond is bifunctional in the reactions with a reactive centre (radical, ion) and monofunctional in the reaction with an amine (Michaelis reaction).[18] Oligom-

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ers usually have nonuniform size and functionality distributions. To characterize the functionality, Entelis *et al.*[19] introduced the notion 'functionality type distribution'. It is quantitatively expressed by the number-average ($\overline{f}_n$) and weight-average ($\overline{f}_w$) values. As shown by Flory,[2] it is the weight-average functionality that plays the decisive role in the determination of the critical conversion and structural parameters of polymer networks.

The aim of this review is to consider the scopes of the statistical and kinetic approaches to the determination of critical conversion and to provide relevant substantiated results obtained in the critical conversion calculations for different polymerization mechanisms. An approach based on the concept of bond blocks [10, 20, 21] and combining the kinetic and probabilistic methods considerably facilitates the solution to the problems that cannot be solved by the pure statistical method.

The review includes five Sections. A short Introduction (Section I) is followed by the results of statistical calculations ('non-ideal' polycondensation) (Section II). Section III presents the results obtained using the concept of bond blocks ('non-ideal', or 'non-statistical' polycondensation). Section IV is devoted to the kinetic calculations that allow one, in particular, to determine the gel point in the case of three-dimensional polymerization. Finally, in Section V we describe the topological structure of critical clusters.

II. Statistical methods ('ideal' polycondensation)

It was Flory who first proposed the statistical approach for describing the kinetics of polycondensation and the structure of polymers thus synthesized.[2–5] In particular, he calculated the molecular mass distribution for f-functional polycondensation using combinatorial methods and obtained the condition for critical conversion. More recently, such calculations were carried out using a formal (and therefore simpler) method [8, 9] based on the theory of branching processes.[22] Good [23] and Gordon [24] proposed to describe the formation of polymer networks using the mathematical theory of branching processes. In the following, this approach was widely used by Galina, Gordon, Dušek, Irzhak, Kuchanov, *etc.* (see references cited in Refs 8, 9, 21 and 25).

Assuming no cyclization reactions, the structure of a macromolecule is represented [9] by a branching tree (Fig. 1). Any unit or fragment can play the role of a root. To relate the structure of the macromolecule to the polymerization process, the reactant molecules are used as such fragments. The probabilities of transitions from one generation to another (the root is treated as the zero generation) are considered as results of formation of the corresponding bonds. The transition probability depends on the kinetic parameters of the process, on the degree of conversion with respect to functional groups and on the concentration of functional groups. The probabilities are analyzed in terms of the generating functions.

The generating function $\Phi(q)$ for discrete probabilities p_i is the sum over all i

$$\Phi(q) = \sum_i q^i p_i ,$$

where q is a dummy variable. At $q = 1$, one has $\Phi(1) = 1$. The derivatives of $\Phi(q)$ with respect to q at $q = 1$ generate the moments of the probability distribution.

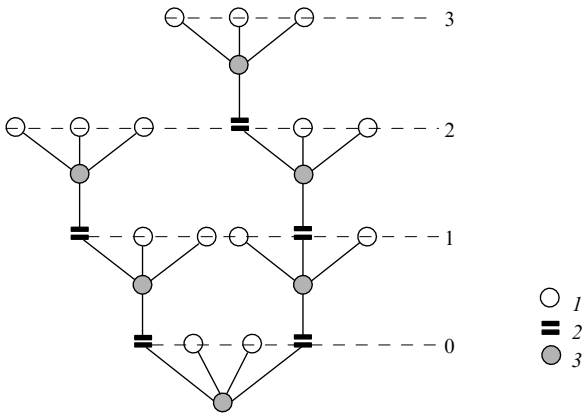


Figure 1. Representation of a product (hexamer) of polycondensation of a tetrafunctional oligomer by a tree.
Generation number varies from 0 (root) to 3: unreacted functional groups (*1*), reacted functional groups (*2*) and 'bulk' of oligomer (*3*).

A key aspect of the theory of branching processes [22] is independence of the probability of transition from one generation to another on the generation number (except the zero generation). Calculations of the generating function are reduced to solution of algebraic equations.

Taking f-functional polycondensation as a simple example, we will illustrate the principle of determination of the critical conversion.

In each generation (except the zero generation), an f-functional unit can generate at most $(f-1)$ units, the probability for each functional group to react (*i.e.*, generate a new unit) being equal to the degree of conversion (α). The probability for $(f-1)$ units to generate a total of i units is

$$p_i = \frac{(f-1)!}{i!(f-1-i)!}\alpha^i(1-\alpha)^{f-1-i} .$$

Thus, the generation function for probabilities has the form

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

The condition for gel formation is determined from the solution to the equation

$$u(q) = q\Phi\big(u(q)\big) = q[1-\alpha+\alpha u(q)]^{f-1}, \quad (2)$$

where the generating function $u(q)$ characterized the MMD of the polymer. The moments of the function $u(q)$ correspond to the MMD moments divided to the total concentration of units in the system. In particular, $u(1)$ is the first moment of the MMD, the first derivative with respect to q at $q = 1$ is the second moment, *etc.*

The critical conversion corresponds to the case where the derivative $\partial u(q)/\partial q$ turns to infinity at $q = 1$,

$$\frac{\partial u(q)}{\partial q} = [1-\alpha+\alpha u(q)]^{f-1} + q\alpha(f-1)[1-\alpha+\alpha u(q)]^{f-2}\frac{\partial u(q)}{\partial q}. \quad (3)$$

At $q = 1$, one has $u(1) = 1$ and

$$\frac{\partial u(1)}{\partial q} = \frac{1}{1-\alpha(f-1)} . \quad (4)$$

From this, the condition for gel formation has the form

$$\alpha_c(f-1) = 1. \quad (5)$$

The conversion can also be determined by solving the differential equation for the concentration of functional groups (F):

$$\frac{dF}{dt} = -kF^2,$$

$$\alpha = \frac{F_0 - F}{F_0}.$$

Here t is time, k is the rate constant for the reaction and F_0 is the initial concentration of the functional groups.

The expressions for calculating α_c in different cases of polycondensation are given below.

1. Monomers of different functionality with same-type functional groups of identical reactivity; reactions between any groups are possible,

$$\alpha_c(\overline{f}_w - 1) = 1, \quad (6)$$

$$\overline{f}_w = \sum_i i n_i,$$

$$n_i = \frac{i m_i}{\sum_j j m_j},$$

where m_i is the molar concentration of the monomer bearing i functional groups.

2. Monomers of different functionality and different-type functional groups (A and B); reactions between same-type groups are impossible, the rate constants for the reactions between different-type groups are equal to one another

$$\alpha_{cA}\alpha_{cB}(\overline{f}_{wA} - 1)(\overline{f}_{wB} - 1) = 1. \quad (7)$$

Since

$$F_{A,0} - F_A = F_{B,0} - F_B,$$

one gets

$$\alpha_A = \frac{F_{B,0}}{F_{A,0}}\alpha_B.$$

If functional groups have initially different reactivities, one can use the statistical approach. For instance, in the reaction of diisocyanate (A) with glycerol (B) the secondary and primary hydroxyl groups of glycerol have different reactivities. Therefore, the expression for the critical conversion has the form

$$\frac{2}{3}\alpha_{cA}(2\alpha_{cB_1} + \alpha_{cB_2}) = 1,$$

where the subscripts 1 and 2 refer to the primary and secondary hydroxyl groups of glycerol, respectively. The conversions of the functional groups α_{B_1} and α_{B_2} are determined by solving the corresponding kinetic equations. At identical reactivities ($\alpha_{B_1} = \alpha_{B_2}$), one gets relationship (7).

If the process involves a number of reactants B_i with different reactivities of functional groups, relation (7) should be modified. For instance, in the reaction

$$A_f + \sum_i B_i$$

(the subscripts denote the numbers of reactive functional groups in the monomer molecules) the functional groups of each monomer B_i are characterized by their own rate constants for the reactions with A and each reaction at a given instant is characterized by its own α_i value.

Taking into account the aforesaid, one gets

$$(f-1)\alpha_{cA}\sum_i (i-1)n_i\alpha_{cB_i} = 1.$$

Clearly, this expression transfoms to Eqn (7) at $\alpha_i = \alpha$.

3. Cross-linking of polymer chains by a bifunctional agent. If each unit in the polymer chain bears a functional group, one deals in essence with the preceding case except that the weight-average functionality of the polymeric reactant is equal to the weight-average degree of polymerization (P_w), which usually much exceeds unity. In addition, the concentration of the cross-linking agent (m_A) is usually much lower than that of functional groups of the polymer. It follows that $\alpha_{cA} \approx 1$; therefore, Eqn (7) is transformed to

$$\alpha_{cB}\overline{P}_w = 1.$$

Formally, this equation coincides with expression (6).

If not all units bear reactive functional groups and their mole fraction $\rho < 1$, then one has

$$f_w = \rho P_w,$$

and, correspondingly,

$$\alpha_{cB}(\rho\overline{P}_w - 1) = 1.$$

Simple relations obtained by the statistical method are widely used in the analysis of various polycondensation processes. However, typical of polyfunctional reactants is the substitution effect, *i.e.*, changes in the reactivity of functional groups after the first group has reacted. For instance, in the reactions of epoxy compounds with a primary amine the rate constants for the reactions of the primary amino group (k_1) and the secondary amino group (k_2) formed as a result of the first reaction are different (Table 1).

Table 1. Relative rate constants (k_2/k_1) for the second addition of epoxy group to amine.[26]

T/°C	DDS	MDA	MDEA	MCDA
80	0.46	0.65	–	0.67
135	0.42	–	0.66	0.64
160	0.51	–	–	0.70

Note. Notations: DDS is 4,4′-diaminodiphenylsulfone, MDA is 4,4′-methylenediamine, MDEA is 4,4′-methylenebis(2,6-diethylaniline), MCDA is 4,4′-methylenebis(3-chloro-2,6-diethylaniline).

MMD calculations for linear polycondensation in the presence of the substitution effect by the kinetic and statistical methods showed[8] that the results obtained depend on the computational method employed. Therefore, the statistical method is inapplicable in this case. Statistical

calculatios of α_c give erroneous results in the presence of the substitution effect.[27,28]

The statistical method is also inappropriate for solving the cyclization problem.[29] In this case, correct results can also be obtained only by the kinetic method.[30]

More recently, the applicability range of the statistical approach was hypothesized.[31] This range was exactly determined using the concept of bond blocks.[10,32]

III. The concept of bond blocks

There is a method for solving polycondensation problems, which is based on the concept of bond blocks.[10,32] Its development, key features and advantages have been documented.[20,33–40]

A bond block is a relatively small configuration (a fragment of the topological structure typical of a given polymer).[10,20,33–35] The bond block is represented by a connected graph G whose edges and vertices are the chemical bonds † and units connected by these bonds. A complete set of concentrations of all bond blocks unambiguously characterizes the composition and topological structure of the polymeric system. In this sense, the concentration $y(G)$ is analogous to the MMD of a linear polymer.

We wil consider the notion 'bond block' taking the linear chain of a copolymer (Table 2) as an example. We

Table 2. Bond blocks for the copolymer chain a–b–a–a–b–b–a–a–a–b–b–a–b–a.

Bond block	Number of bonds in block	Number of blocks in chain	'Broken' blocks
a–a	1	3	a–
a–b	1	8	a–, b–
b–b	1	2	b–
a–a–a	2	1	a–a–
a–a–b, b–a–a	2	4	a–a–, b–a–
a–b–a	2	2	a–b–
a–b–b, b–b–a	2	4	a–b–, b–b–
b–a–b	2	1	b–a–
a–a–a–b, b–a–a–a	3	2	a–a–a–, b–a–a–
a–a–b–a, a–b–a–a	3	1	a–a–b–, a–b–a–
a–a–b–b, b–b–a–a	3	3	a–a–b–, b–b–a–
b–a–b–b, b–b–a–b	3	1	b–a–b–, b–b–a–

will restrict ourselves to consideration of blocks including at most three bonds. The set of bond blocks of all sizes unambiguously characterizes the structure of the polymer chain. As can be seen, a bond in the block is denoted by the units connected by the bond in question.

In a linear homopolymer, blocks only differ in length, *i.e.*, the number of bonds in the block. In this case, the relation between the concentrations of blocks (y_i) and chains (x_i) has a simple form

$$y_n = \sum_{i=n}^{\infty} (i-n)x_i\,, \tag{8}$$

$$x_i = y_{i-1} - 2y_i + y_{i+1}. \tag{9}$$

The total concentration of units in the system including monomers (y_0) is a constant; therefore, the total concentration of bonds y_1 correlates with the degree of conversion

$$\alpha = \frac{y_1}{y_0}\,.$$

Equality (9) can be generalized with ease using the notion of 'broken' terminal blocks (see Table 2). The concentration of such blocks with a k-type broken bond (z_i^k) is given by

$$z_i^k = y_i - y_{i+1}^k = y_i(1 - y_1^k), \tag{10}$$

where y_{i+1}^k is the conventional block with the k-type terminal bond and y_1^k is the unit k-type block. Here, we use the symbolic multiplication where the subscripts corresponding to the block size are summed up by analogy with the summation of exponents in conventional multiplication.

For blocks with two (k- and m-type) 'broken' bonds one has

$$z_i^{k,m} = z_i^k(1 - y_1^m) = y_i(1 - y_1^k)(1 - y_1^m) \tag{11}$$

etc.

A chain of any configuration containing i bonds and n terminals can be represented by a block of the same configuration (the number of units is $i + 1$) with n broken terminal bonds. Thus, one has

$$x_{i+1} = y_i \prod_{j=1}^{n} (1 - y_1^j), \tag{12}$$

where j is the type of the broken bonds.

Indeed, according to expression (12), for a linear chain (two termini) one gets

$$x_i = y_{i-1}(1 - y_1^1)(1 - y_1^2) =$$

$$= y_{i-1} - y_i^1 - y_i^2 + y_{i+1}^{1,2} = y_{i-1} - 2y_i + y_{i+1},$$

i.e., equality (9) because the types of the termini are of no concern.

Thus, information on the structure of bond blocks, obtained from relationship (12), allows one to characterize the topological structure of the polymer.

A method for constructing kinetic equations for the formation of bond blocks was developed.[20,33,34] In the absence of the substitution effect and bond disssociation reactions, the kinetics can be described by enumerating all possible methods of assembling bond blocks of any configuration from fragments ('building blocks'), *i.e.*, structures that are simpler and no larger than the bond block under consideration. Under these admissions, one can use the probabilistic methods.

A similar method was independently proposed by Dušek [10] and used by other authors.[41] However, no relevant

† Only the bonds formed in the course of the process under study are implied. Correspondingly, the vertices of the graph (branching points) are occupied by the reacting oligomers.

mathematical substantiation was reported and the method was used intuitively.

The possibility of exact calculations of the concentrations of bond blocks is basic to the structure determination of copolymers. When this parameter is calculated using the kinetic approach provided a sufficient copolymer length and a large number of comonomers, one should take into account all possible chain configurations whose number is rather large (comparable with the Avogadro constant). But this only means that the number of macromolecules of each type is too small for the law of mass action to 'operate'.‡ This difficulty disappears if one uses the concept of bond blocks. Indeed, modern NMR spectroscopy techniques allows one to determine the concentrations of relatively small fragments in the copolymer chain, *viz*., dyads, triads and tetrads.[9,42–45] These fragments are suitable for assembling blocks of any size and, correspondingly, the copolymer chains of any configuration using the procedure mentioned above.

The advantage of the method based on the concept of bond blocks is due to combination of the kinetic and probabilistic approaches and consists in the possibility of exact solution to the polycondensation kinetics problems including the formation of the structure of polymer networks in the presence of the substitution effect.

The systems of kinetic equations for the description of the formation of bond blocks can be divided[20,34] into closed groups, each corresponding to a relatively small block. Since the number of equations in each system is small, a direct solution of differential equations is straightforward even in the presence of the substitution effect. Larger blocks and corresponding chains are built of the kinetically calculated fragments using probabilistic calculations. This is possible in the absence of the substitution effect in the reactions ensuring such an assembly. An example is provided by the simulation of the reaction of a bifunctional epoxy oligomer with diamine.

Following a known algorithm,[39,40] assume that the diamine units form nodes of the polymer network while the epoxy oligomer forms internode chains. The reactions of primary amino groups with the epoxy groups result in the secondary amino groups. But the reactivities of these amines are different (see Table 1). Thus, we deal with a typical manifestation of the substitution effect.

The network structure is determined by the concentration of nodes of different functionality. It is these structural fragments that are the bond blocks whose concentrations in this case should be calculated using the kinetic approach, *i.e*., by solving the corresponding kinetic equations. The functionality of a node is characterized by the number of oligomeric fragments bound to it. Using two-digit notation where the digits in parentheses denote the number of the primary (first digit) and secondary (second digit) hydrogen atoms, the groups involved in the construction of the network can be classified as follows:

$A(40)$ denotes the initial amine, a zero-functional node (A_0);

$A(21)$ denotes the reaction product of a primary amino group, a monofunctional node (A_1);

$A(20)$ denotes a bifunctional node (A_2);

$A(02)$ denotes a bifunctional node (A_2);

$A(01)$ denotes a trifunctional node (A_3);

$A(00)$ denotes a tetrafunctional node (A_4).

Transformations of the nodes are described by the following scheme:

$$A(40) \xrightarrow{k_1B} A(21) \begin{array}{l} \xrightarrow{k_1B} A(02) \xrightarrow{k_2B} \\ \xrightarrow{k_2B} A(20) \xrightarrow{k_1B} \end{array} \longrightarrow A(01) \xrightarrow{k_2B} A(00),$$

where B is the concentration of epoxy groups.

The system of equations for all amino groups has the form:

$$\frac{dB}{dt} = -k_1B[4A(40) + 2A(21) + 2A(20)] - k_2B[A(21) + 2A(02) + A(01)], \quad (13)$$

$$\frac{dA(40)}{dt} = -4k_1BA(40),$$

$$\frac{dA(21)}{dt} = 4k_1BA(40) - (2k_1 + k_2)BA(21),$$

$$\frac{dA(02)}{dt} = 2k_1BA(21) - 2k_2BA(02),$$

$$\frac{dA(20)}{dt} = -2k_1BA(20) + k_2BA(21),$$

$$\frac{dA(01)}{dt} = 2k_1BA(20) + 2k_2BA(02) - k_2BA(01),$$

$$\frac{dA(00)}{dt} = k_2BA(01).$$

The initial conditions are $A(40) = A_0$, $A(21) = A(20) = A(02) = A(01) = A(00) = 0$.

The reaction is accompanied by changes in the relative concentrations of nodes ($a_i = A_i/A_0$) of different functionality (Fig. 2). Noteworthy is that the curves for different values for the relative rate constant for the second addition reaction ($\beta = k_2/k_1$) plotted in the concentration–conversion coordinates have similar shapes, namely, the maximum concentration a_i corresponds to the same degree of conversion irrespective of the magnitude of the relative rate constant for the reaction involving the secondary amino group. At the same time, the maximum value changes depending on the kinetic parameters of the polycondensation reaction.

It is assumed that the reactivity of epoxy groups is constant in the course of the reaction. Therefore, the network structure can be calculated using the probabilistic approach and the calculated node concentrations. According to the theory of branching processes, one should introduce a generating function $u(q)$ which characterizes the probability of generating an oligomer chain in the next generation by the same chain in the preceding generation,

$$u(q) = q\left[1 - \alpha + \alpha \sum_i n_{a_i} u^{i-1}(q)\right], \quad (14)$$

where q is the dummy variable, α is the degree of conversion with respect to epoxy groups and n_{a_i} is the fraction of i-functional nodes:

$$n_{a_i} = \frac{iA_i}{\sum_i iA_i}.$$

‡ This was first noted by Academician I M Lifshitz at the Seminar in Polymer Physics at the Department of Physics, M V Lomonosov Moscow State University.

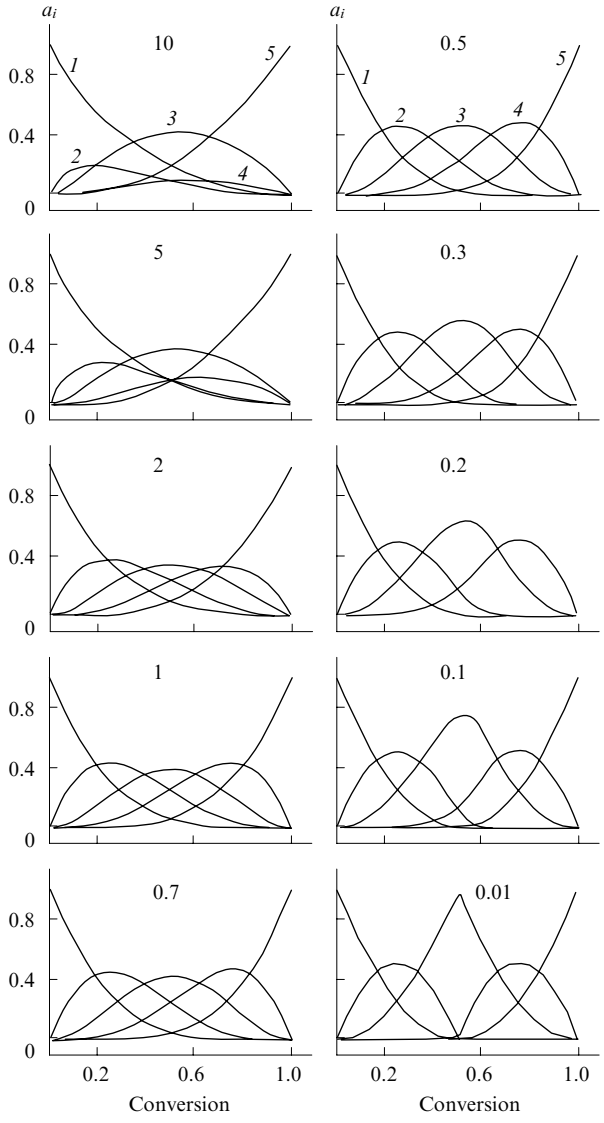


Figure 2. Relative concentrations of nodes of different functionality plotted *vs.* degree of conversion: a_0 (*1*), a_1 (*2*), a_2 (*3*), a_3 (*4*) and a_4 (*5*). Here and in Fig. 3 the numbers above the abscissa axes denote the substitution effect $\beta = k_2/k_1$.

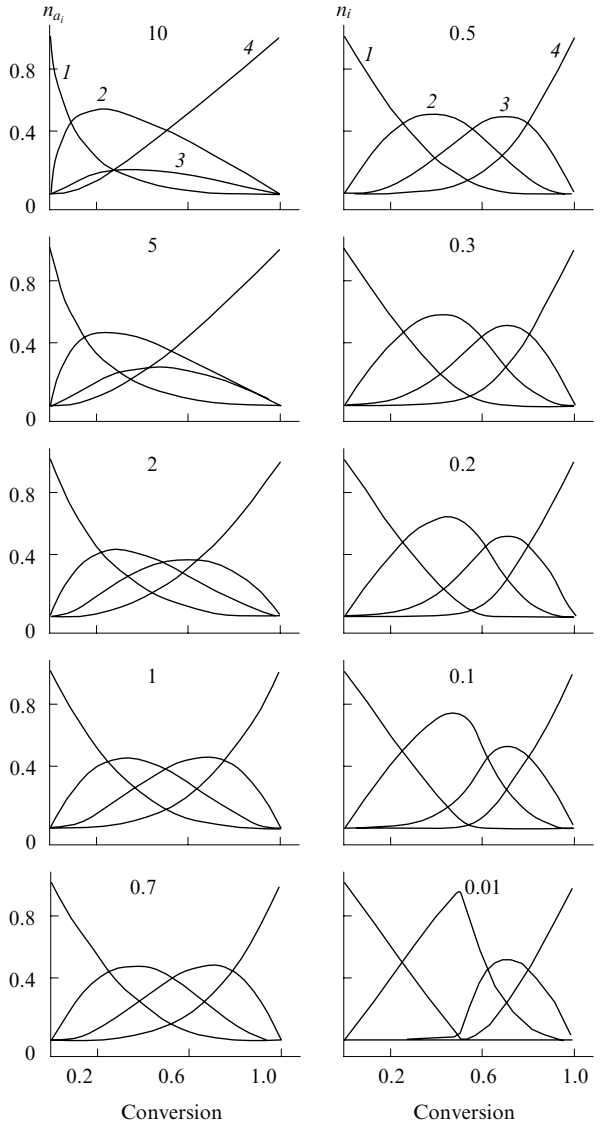


Figure 3. Changes in parameters n_{a_i} in the course of polycondensation: n_{a_1} (*1*), n_{a_2} (*2*), n_{a_3} (*3*) and n_{a_4} (*4*).

Changes in the parameters n_{a_i} in the course of polycondensation at different ratios of the rate constants for the first and second addition reactions are shown in Fig. 3.

As can be seen, n_{a_1} decreases from unity in the whole range of conversions despite the fact that the molar concentration of the monofunctional nodes (a_1) increases from zero, reaches a maximum value and then decreases. This mismatch is understandable because the early stage of the reaction involves the formation of only monofunctional nodes whose relative fraction is unity and decreases as nodes of higher functionality are formed. The proportion of bifunctional nodes increases, apparently indicating the formation of linear chains.

It is this idea of the synthesis of polymer networks that was proposed by Berlin,[46] *viz.*, the formation of a linear polymer (β-polymer) in the first stage is followed by the formation of branched chains in the second stage and subsequent formation of a polymer network in the third stage after the gel point. In terms of node functionality, branching is treated as the appearance of nodes of higher functionality (tri- and tetrafunctional ones). From the data in Figs 2 and 3 it follows that the first and second stages can be distinguished if the relative constant β is much lower than unity. At higher β values, in the early stages of the process the bifunctional nodes are accumulated faster than trifunctional ones; however, branching occurs immediately after the reaction begins. Thus, in fact there are only two stages, namely, the formation of a branched polymer before the gel point and the formation of a polymer network after the gel point. The idea of the β-polymer is probably natural of three-dimensional polymerization, but it seems to be exotic in the case of polycondensation.

Differentiation of Eqn (14) gives the condition for gel formation

$$\frac{\partial u(q)}{\partial q} = \tag{15}$$

$$= \left[1 - \alpha + \alpha \sum_i n_{a_i} u^{i-1}(q)\right] + \left[q\alpha \sum_i (i-1) n_{ai} u^{i-2}(q)\right] \frac{\partial u(q)}{\partial q}.$$

At $q = 1$, one has $u(1) = 1$ and

$$\frac{\partial u(1)}{\partial q} = \frac{1}{1 - \alpha \sum_i (i-1) n_{a_i}}. \quad (16)$$

Thus, the critical conversion with respect to epoxy groups is defined as the soluton to the equation

$$\alpha_c \sum_i (i-1) n_{a_i} = 1, \quad (17)$$

which formally coincides with the critical condition in the case of *f*-functional polycondensation (6) except that the weight-average functionality in Eqn (17) varies in the course of polymerization, being a function of the degree of conversion rather than a characteristic of the initial system.

The curves of the equation

$$y(\alpha) = 1 - \alpha \sum_i (i-1) n_{a_i} \quad (17a)$$

for different β values are shown in Fig. 4. The α_c value is determined from the condition $y(\alpha) = 0$.

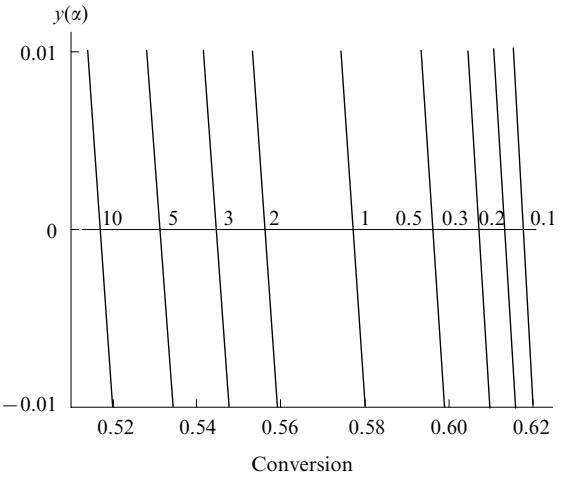


Figure 4. Curves of Eqn (17a) plotted at different β values (numbers above the abscissa axis).
The system $B_2 + A(40)$.

Figure 5 shows the critical conversions that are plotted *vs*. kinetic constant β for the systems $B_2 + A(41)$ (curve *1*), $B_2 + A(40)$ (curve *2*), $B_2 + A(21)$ (curve *3*) and $B_2 + B_3 + A(20)$ (curve *4*). In the last-mentioned case, a trifunctional reactant B_3 was introduced to provide the formation of the polymer network because the cross-linking agent $A(20)$ is bifunctional.

As can be seen, if the node concentration is determined by the substitution effect, the solution depends on the parameter β (curves *1–3*); this is not related to the statistical theory. Curve *4* demonstrates the lack of such a dependence because the substitution effect influences only the conversion $\alpha_A(t)$ rather than the node concentration related to α_B probabilistically.

This feature of manifestation of the substitution effect was first noted by Kuchanov[8, 31, 47] who showed that in the last-mentioned case the polycondensation develops as an

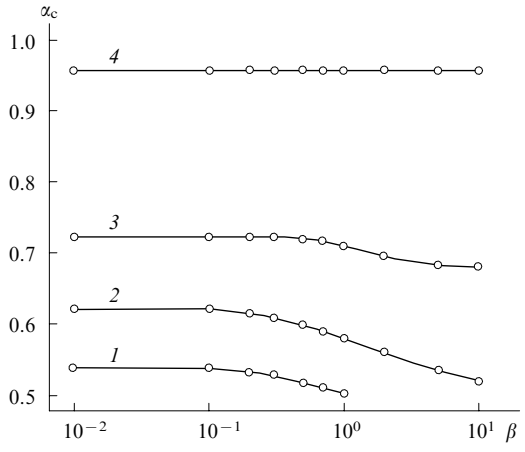


Figure 5. Critical conversion α_c plotted *vs*. parameter β. For notations (*1–4*), see text.

'ideal' process, which can be described in terms of the probability theory.

One can show with ease that if the statistical criteria for the dependence of n_{a_i} on the degree of conversion are met, one gets the known relation.

Indeed, according to probability theory, one has

$$A_i = A \frac{f!}{i!(f-i)!} \alpha_A^i (1 - \alpha_A)^{f-i}, \quad (18)$$

where A_i is the concentration of the *i*-functional node, *f* is its maximum possible functionality and α_A is the conversion with respect to amine.

Since

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

substitution of expression (18) to Eqn (17) gives:

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

which corresponds to relation (7) for the copolycondensation of bi- and *f*-functional reactants.

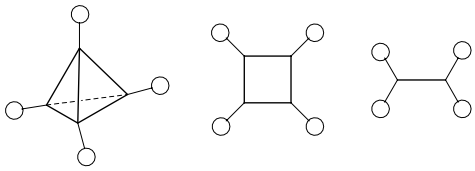
Noteworthy is that at small (but not zero!) values of the constant β the critical conversion tends to a constant value, in particular, $\alpha_c = 0.618$ for the system $B_2 + A_4$. This is due to the fact that polycondensation becomes stepwise in character. In the first stage, the smaller the β value the greater the degree of conversion of the primary amino groups. The degree of conversion reaches a particular value, *e.g.*, 50% with respect to groups *B* for the equifunctional system $B_2 + A_4$. The second stage involves accumulation of polyfunctional nodes until the gel point. Clearly, the additional conversion should have a particular value in this case.

Kuchanov developed a method for solving problems in homopolycondensation of *f*-functional monomers, which combines the kinetic and statistical approaches.§ The key

§ S I Kuchanov, A G Kholostyakov *J. Polym. Sci., Polym. Chem.* **37** 2145 (1999); S I Kuchanov, T V Zharnikov *J. Stat. Phys.* **111** 1273 (2003); S I Kuchanov, K V Tarasevich, T V Zharnikov *J. Stat. Phys.* **122** 875 (2006); K V Tarasevich, S I Kuchanov *J. Polym. Sci., Polym. Phys.* **45** 3093 (2007).

feature of the technique is consideration of the evolution of monads, *i.e.*, monomer units of the polymeric system.[8] Since the f value is small, the corresponding system including $(f+1)$ kinetic equations is also small and closed. Therefore, at any values of the rate constants for all reactions including those with the substitution effect, one can obtain the temporal dependence of the concentrations of all monads [analogously to system (13)]. Simultaneously, one gets the set of all possible bonds (more exactly, their probabilities). Using these data, one can design the branching process and then determine the α_c value and the parameters of the network structure.

The key advantage of the method is the possibility of taking account the monad configuration. For instance, a tetrafunctional monomer may have the following structures:



A fundamental difference between them is that in the presence of the substitution effect, the conversion of a functional group changes the reactivities of three groups in the pyramid, two groups in the square and one group in the dumb-bell.

IV. The kinetic approach

The kinetic approach to the description of polymerization involves a solution of the system of differential equations, corresponding to the kinetic scheme of the reaction. In this case, it is impossible to restrict ourselves to consideration of consumption of the initial reactants. One should consider the formation of at least the topological structure of the polymer and therefore the kinetic scheme and the corresponding system of differential equations are rather complicated. Taking into account the fact that the system of equations is in principle infinite even in the simplest case of linear polymerization, special computational methods are required,[48–59] *e.g.*, numerical integration techniques[49–52] implemented on modern personal computers. Since the system of equations is infinite, it should be truncated in some way, although there are, in essence, no physically substantiated truncation criteria.

In some cases, one can use the method of the MMD moments,[8,9,21,60] *i.e.*, consideration of the system in convoluted form. Physical substantiation of the applicability of this technique is due to the fact that, practically, the MMD is characterized using the average molecular masses $\bar{M}_n$, $\bar{M}_w$ or, more rarely, $\bar{M}_z$ (the ratio of the first three or four MMD moments). It is important that the right parts of the differential equations for each moment include no higher moments, that is, the zero moment depends only on the zero moment, the first moment depends only on the zero and first moments, the second moment depends on the zero, first and second moments, *etc*. In other words, the system of equations for the MMD moments is closed and can therefore be solved successively so one can stop at a desired point. However, if macromolecules just formed are involved in the process as, *e.g.*, chain transfer agents,[61–63] the method of moments is no more applicable because the system of differential equations becomes open, *i.e.*, the solution to the equation for the second moment requires information on the third moment, the solution to the equation for the third moment depends on the fourth moment, *etc*. Therefore, in this case, one should also solve an infinite system of equations for the MMD moments.

Consider separately two kinetic types of reactions, polymerization and polycondensation.

1. Polymerization

Chemistry apart, it is convenient to describe the reactants involved in polymerization processes by vectors.[8,21,60] Let us use the notation $R(m,n,p)$ for a macromolecule containing m units, n functional groups (for vinyl polymers, n is the number of double bonds) and p reactive centres ($m, n, p = 0, 1, 2, 3 \ldots$, *etc*.). The initial f-functional oligomer is denoted $R(1,f,0)$. Of course, this is the simplest method of description of a simple kinetic scheme, which ignores some details of the topological structure; however, it is sufficient for demonstration of the principles of the approach in question.

A simplest scheme of radical polymerization involves the following stages: initiation (I is the initiator, φ is the initiation efficiency, k_i is the rate constant for initiation), chain propagation with the rate constant k_p, quadratic chain termination due to recombination (k_{tr}) and disproportionation (k_{td}), chain transfer to the transfer agent X (k_x) and linear chain termination using an inhibitor Y (k_y). For simplicity, we assume that the process is initiated by monomolecular decomposition of the initiator I. The initial and 'pendant' functional groups have identical reactivities (no substitution effect). This type of polymerization is described by the following scheme:

$$I \xrightarrow{k_i} 2\varphi R(0,0,1), \tag{19}$$

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

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

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

$R(0,0,1)$ is the primary reactive centre.

As can be seen, in the chain propagation step, the numbers of units and reactive centres are summed while the total number of functional groups decreases by unity. The reactions of quadratic chain termination lead to a decrease in the total number of reactive centres by two.

Scheme (19) gives an infinite system of equations

$$\frac{dI}{dt} = -k_i I, \tag{20}$$

$$\frac{dR(0,0,1)}{dt} = 2\varphi k_i I - R(0,0,1)(k_p F + k_x X + k_t R + k_y Y) + k_x X R,$$

$$\frac{dR(i,j,l)}{dt} = -R(i,j,l)\left[k_p(lF + jR) + l(k_x X + k_t R)\right] + R(i,j,l+1)(k_y Y + k_x X + k_{td} R) + k_p \sum_{m,n,p}^{i,j,l} [n(l-p)R(i-m, j-n+1, l-p) +$$

$$+p(j-n+1)R(i-m,j-n+1,l-p)]R(m,n,p)+$$

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

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

Here

$$R=\sum_{i,j,l}^{\infty} lR(i,j,l)$$

is the total concentration of reactive centres and $k_t = k_{tr} + k_{td}$ is the total rate constant for quadratic chain termination.

Ii is convenient to solve infinite systems of differential equations in convoluted form. The simplest way is to use the generating functions

$$\Phi(q_1,q_2,q_3)=\sum_{m,n,p}^{\infty} q_1^m q_2^n q_3^p R(m,n,p), \tag{21}$$

where q_i are dummy variables, each corresponding to a particular structural characteristic, *viz*., the number of units (q_1), the number of functional groups (q_2) and the number of reactive centres in the macromolecule (q_3).

The generating functions contain full information on the system to be convoluted. Indeed,

$$R(m,n,p)=\frac{\partial^{m+n+p}}{\partial q_1^m \partial q_2^n \partial q_3^p}\Phi(q_1,q_2,q_3)\bigg|_{q_1=q_2=q_3=0}.$$

At the same time, the generating functions allow one to determine the moments of the distribution $R(m,n,p)$ over all characteristics (m, n and p).

This method is used to derive relatively simple equations in partial derivatives, which can be solved in principle (in the simplest cases, analytically).[8] In terms of the generating functions, the system (20) leads to the following equation in partial derivatives (for details, see, *e.g*., a monograph [8]):

$$\frac{\partial\Phi(\vec{q})}{\partial t}=\varphi k_i q_3 I+k_p\left(q_3\frac{\partial\Phi(\vec{q})}{\partial q_2}\,\frac{\partial\Phi(\vec{q})}{\partial q_3}-\right. \tag{22}$$

$$\left.-q_3F\,\frac{\partial\Phi(\vec{q})}{\partial q_3}-q_2R\,\frac{\partial\Phi(\vec{q})}{\partial q_2}\right)+(k_yY+k_xX)(1-q_3)\frac{\partial\Phi(\vec{q})}{\partial q_3}+$$

$$+\frac{1}{2}\,k_{\mathrm{tr}}\left(\frac{\partial\Phi(\vec{q})}{\partial q_3}\right)^2+(k_{\mathrm{td}}-q_3k_{\mathrm{t}})\frac{\partial\Phi(\vec{q})}{\partial q_3}R,$$

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

It is convenient to solve Eqn (22) after transformation to the system for the moments of the generating function rather than in the general form.

After differentiation over all q_i and having set all the derivatives thus obtained to unity, one gets the system of differential equations for the moments of the generating function and, therefore, for the moments of the distributions of macromolecules over their length, functionality and number of reactive centres:

$$N=\Phi(\vec{1})=\sum_{m,n,p}R(m,n,p)$$

is the total concentration of chains (the zero moment);

the first moments:

$$M=\frac{\partial\Phi(\vec{1})}{\partial q_1}=\sum_{m,n,p}mR(m,n,p)$$

is the total concentration of monomer units in the system;

$$F=\frac{\partial\Phi(\vec{1})}{\partial q_2}=\sum_{m,n,p}nR(m,n,p)$$

is the total concentration of functional groups;

$$R=\frac{\partial\Phi(\vec{1})}{\partial q_3}=\sum_{m,n,p}pR(m,n,p)$$

is the total concentration of reactive centres;

the second moments:

$$\Phi_{ij}\equiv\frac{\partial^2\Phi(\vec{1})}{\partial q_i\partial q_j},\ i,j=1,2,3:$$

$$\Phi_{11}=\sum_{m,n,p}m(m-1)R(m,n,p),$$

$$\Phi_{12}=\sum_{m,n,p}mnR(m,n,p),$$

$$\Phi_{13}=\sum_{m,n,p}mpR(m,n,p),$$

$$\Phi_{22}=\sum_{m,n,p}n(n-1)R(m,n,p),$$

$$\Phi_{23}=\sum_{m,n,p}npR(m,n,p),$$

$$\Phi_{33}=\sum_{m,n,p}p(p-1)R(m,n,p).$$

The system of differential equations for the moments has the form

$$\frac{\mathrm{d}I}{\mathrm{d}t}=-k_{\mathrm{i}}I, \tag{23}$$

$$\frac{\mathrm{d}N}{\mathrm{d}t}=2\varphi k_{\mathrm{i}}I-\mathrm{k_p}FR-\frac{1}{2}\mathrm{k_t}R^2-k_y\mathrm{Y},$$

$$\frac{\mathrm{d}M}{\mathrm{d}t}=0,$$

$$\frac{\mathrm{d}F}{\mathrm{d}t}=-k_{\mathrm{p}}FR,$$

$$\frac{\mathrm{d}R}{\mathrm{d}t}=2\varphi k_{\mathrm{i}}I-\mathrm{k_t}R^2-k_y\mathrm{YR},$$

$$\frac{\mathrm{d}X}{\mathrm{d}t}=-k_x\mathrm{XR},$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t}=-k_y\mathrm{YR},$$

$$\frac{\mathrm{d}\Phi_{11}}{\mathrm{d}t}=2\,k_{\mathrm{p}}\Phi_{12}\Phi_{13}+k_{\mathrm{t}}(\Phi_{13})^2,$$

$$\frac{\mathrm{d}\Phi_{12}}{\mathrm{d}t}=k_{\mathrm{p}}(\Phi_{13}\Phi_{22}+\Phi_{12}\Phi_{23}-R\Phi_{12})+k_{\mathrm{t}}\Phi_{13}\Phi_{23},$$

$$\frac{\mathrm{d}\Phi_{13}}{\mathrm{d}t}=k_{\mathrm{p}}(\Phi_{13}\Phi_{23}+\Phi_{12}\Phi_{33}+R\Phi_{12})-(k_x\mathrm{X}+k_y\mathrm{Y})\Phi_{13}+$$

$$+k_{\mathrm{t}}(\Phi_{33}-R)\Phi_{13},$$

$$\frac{\mathrm{d}\Phi_{22}}{\mathrm{d}t}=2\,k_{\mathrm{p}}(\Phi_{22}\Phi_{23}-R\Phi_{22})+k_{\mathrm{t}}(\Phi_{23})^2,$$

$$\frac{d\Phi_{23}}{dt} = k_p\left[(\Phi_{23})^2 + \Phi_{22}\Phi_{33} - R\Phi_{23} + R\Phi_{22}\right] - $$
$$-(k_y Y + k_x X)\Phi_{23} + k_t(\Phi_{33} - R)\Phi_{23},$$
$$\frac{d\Phi_{33}}{dt} = 2k_p\Phi_{23}(\Phi_{33} + R) - 2(k_y Y + k_x X)\Phi_{33} +$$
$$+ k_t(\Phi_{33} - 2R)\Phi_{33}.$$

Clearly, all these quantities are time-dependent.

Solution to the system (23) allows one to obtain full information on the polymerization process.

a. 'Living' polymerization

Consideration of the kinetics of 'living' polymerization is both theoretically and practically important. Polymer networks have long been synthesized using ionic processes (see, *e.g.*, Refs 64–68). In the last decade, polymers with complex architecture are often obtained by controlled radical polymerization [69–72] which has some characteristic kinetic features of 'living' process [73] irrespective of a particular mechanism. In particular, the kinetics of structure formation of polymer networks was studied in Refs 60 and 74–95.

The simplest case is a 'living' polymerization with instantaneous initiation. Here, the following conditions are met: $k_i = k_t = k_x = k_y = 0$. At $t = 0$, one has $R(1,f,0) = M = M_0$, $F = F_0$, $R(0,0,1) = R$, $N = M + R$ and $M \gg R$.

For the zero and first moments one gets

$$N = R + M + F - F_0,$$

$$F = F_0 e^{-k_p R t}.$$

The degree of conversion with respect to functional groups is given by

$$\alpha = \frac{F_0 - F}{F_0} = 1 - e^{-k_p R t},$$

$$\frac{dR(1,f,0)}{dt} = -f k_p R(1,f,0) R,$$

$$R(1,f,0) = M e^{-f k_p R t}.$$

Taking account of the functionality type distribution, for the concentration m of unreacted oligomers one gets

$$m = \sum_n M_n (1-\alpha)^n,$$

where M_n is the initial concentration of the n-functional oligomer; the parameters M and R are time-independent.

The concentration of polymer chains is

$$P = N - m.$$

Now for the number-average degree of polymerization one gets

$$\overline{P}_n = \frac{M - m}{N - m} = \frac{M - \sum_n M_n (1-\alpha)^n}{R + M - \sum_n M_n (1-\alpha)^n - F_0 \alpha}. \quad (24)$$

Equality (24) defines the critical conversion according to Carothers [96]

$$\overline{P}_n \to \infty, \quad (25)$$
$$R + M - \sum_n M_n (1-\alpha_c)^n - F_0 \alpha_{rmc} = 0.$$

Expansion of the expression under the summation symbol in terms of α_c gives

$$R - \frac{1}{2}\alpha_c^2 \sum_n n(n-1) M_n \simeq 0, \quad (26)$$

i.e.,

$$\alpha_c^2 \simeq \frac{2R}{\Phi_{22}(0)}.$$

However, the condition (26) overestimates α_c. As was shown by Flory [2–5] and Stockmeyer,[6,7] the true value of critical conversion is determined by the second moments, *i.e.*, $\overline{P}_w$ rather than $\overline{P}_n$.

It is accepted that, mathematically, the gel point corresponds to the situation where the second moment of the molecular mass distribution turns to infinity. However, taking into account the physical meaning of the process of gel formation, it becomes clear that it is the number of functional groups (and reactive centres) that ensures the rate of chain propagation. Therefore, the decisive role is played by the functionality distribution of macromolecules. In terms of moments of the generating function this is the second moment ¶ of the generating function with respect to functionality,

$$\Phi_{22}(t) = \sum_{m,n,p} n(n-1) R(m,n,p,t).$$

As can be seen, analytical calculations of the second moments are practically impossible even for the simplest kinetic scheme. The results of particular numerical calculations are shown in Fig. 6.

¶ More exactly, the difference between the second and first moments of the distribution over functional groups

$$\Phi_{22} = \sum_{m,n,p} n^2 R(m,n,p) - \sum_{m,n,p} n R(m,n,p).$$

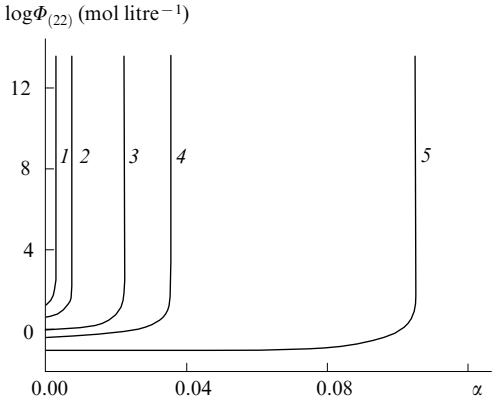


Figure 6. The second moments of the functionality distribution $\Phi_{22}(t)$ plotted *vs.* conversion under instantaneous initiation.[97]
$I_0 = 10^{-3}$ mol litre^{-1}, $\Phi_{22}(0) = 20$ (*1*), 5 (*2*), 1 (*3*), 0.5 (*4*) and 0.1 mol litre^{-1} (*5*).

The curves of changes in $\Phi_{22}(t)$ in the course of 'living' polymerization with instantaneous initiation assuming no chain transfer reactions have a characteristic shape, *viz*., in a very narrow range of conversions the $\Phi_{22}(t)$ values increase by some orders of magnitude and tend to infinity. Therefore, without introducing a large error the critical conversion is equal to the value intercepted on the abscissa axis by the asymptote to the curve $\log \Phi_{22}(t) - \alpha$. This is much smaller than the value determined by the number-average functionality.

This method was used to study different mechanisms of three-dimensional polymerization including 'living' polymerization with instantaneous and slow initiation in the absence and in the presence of chain transfer reactions as well as polymerization with quadratic and linear chain termination.[97–101] More recently, a similar approach was used to analyze the kinetics of reversible addition fragmentation chain transfer (RAFT).[60]

According to calculations,[97] the α_c value obtained assuming instantaneous initiation and no chain termination and chain transfer reactions is a one-to-one function of the ratio of the second moment of the generating function with respect to functionality $\Phi_{22}(0)$ to the number of chains and is independent of the initial concentration of functional groups (F_0).

The dependences of α_c on $\Phi_{22}(0)$ in the double logarithmic coordinates at different initial concentrations of the initiator I_0 is shown in Fig. 7 *a*. At any I_0 value, the plots obey the power law with an exponent of 1/2. Each straight line plotted in the corresponding coordinates (Fig. 7 *b*) intercepts the value equal to the corresponding I_0 value on the ordinate axis.

Thus, for 'living' polymerization with instantaneous initiation ($R = I_0$) the critical conversion is given by

$$\alpha_c^2 = \frac{R}{\Phi_{22}(0)}. \qquad (27)$$

According to expression (27), the α_c is almost 1.5 times lower than the value determined by the condition (26). In addition, the quadratic dependence of α_c in this case has a clear physical meaning, being not a result of approximation. The physical meaning is that the formation of a cross-link requires at lest two successive reactions of functional groups to occur. First, this is a reaction resulting in incorporation of the polyfunctional oligomer into the polymer chain and, therefore, in the appearance of a 'pendant' functional group (X). Second, the reaction of this 'pendant' group resulting in the formation of a cross-link (Z). For a bifunctional oligomer M_2 one has

$$\frac{d\alpha}{dt} = k_p(1-\alpha)R,$$

$$\frac{dM_2}{dt} = -2k_pM_2R,$$

$$\frac{dX}{dt} = 2k_pM_2R - k_pXR,$$

$$\frac{dZ}{dt} = k_pXR,$$

$$\frac{dM_2}{d\alpha} = -2\frac{M_2}{1-\alpha},$$

$$\frac{dX}{d\alpha} = 2\frac{M_2}{1-\alpha} - \frac{X}{1-\alpha},$$

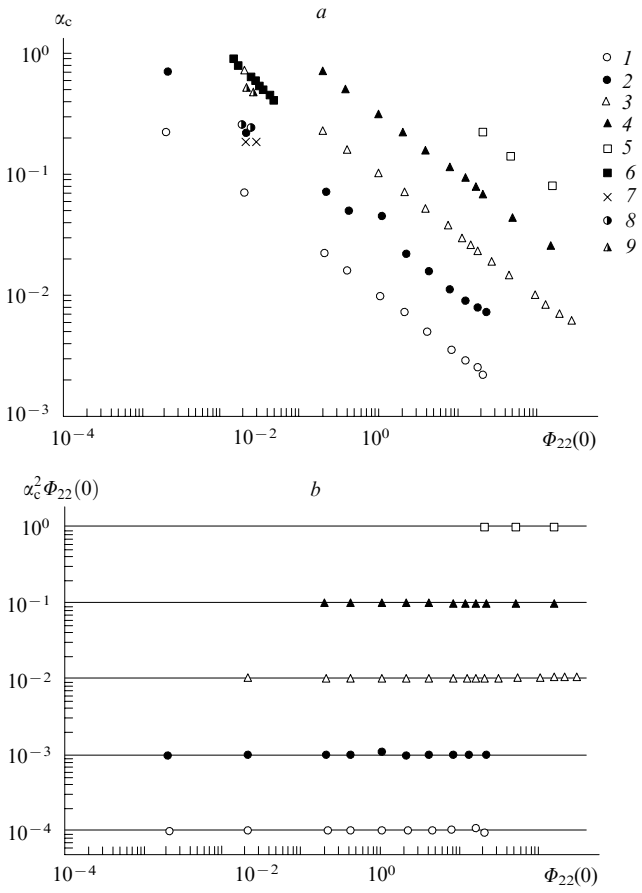


Figure 7. Plots of α_c (*a*) and $\alpha_c^2\Phi_{22}(0)$ (*b*) *vs*. $\Phi_{22}(0)$ for 'living' polymerization with instantaneous initiation.
$I_0 = 10^{-4}$ (*1*), 10^{-3} (*2*), 10^{-2} (*3*), 10^{-1} (*4*), 1.0 (*5*), 0.023 (*6*), 0.0061 (*7*), 0.0099 (*8*) and 0.034 mol litre^{-1} (*9*). Calculated values (plots *1–5*)[97] and the data taken from Ref. 75 (plots *6–9*).

$$\frac{dZ}{d\alpha} = \frac{X}{1-\alpha},$$

$$Z = M_{2.0}\alpha^2$$

(here $M_{2.0}$ is the initial value of M_2).

Taking account of the Flory criterion for gel formation (the gel point corresponds to one cross-link unit per chain), one gets with ease

$$2Z = R,$$

therefore,

$$\alpha_c^2 = \frac{R}{2M_{2.0}},$$

which corresponds to Eqn (27) because in this case one has $\Phi_{22}(0) = 2M_{2.0}$.

This conclusion was also reported in Refs 60 and 92. Kurochkin[102] derived this expression using the d'Alember test for functional series.

Experimental evidence for dependence (27) was obtained in Refs 75, 88 and 91–94. Figure 7 *a* reproduces the results obtained by Ide and Fukuda[75] (Fig. 2 in their paper) in a study of three-dimensional copolymerization of styrene and 4,4′-divinylbiphenyl in the NMRP (nitroxide-

Table 3. Experimental and theoretical α_c values for 'living' copolymerization of styrene with 4,4′-divinylbiphenyl.[75]

Initiator concentration /mmol litre^{-1}	Mole fraction of 4,4′-divinylbiphenyl	α_c	
		experiment	calculations [a]
34	0.005	0.90	0.58
	0.0075	0.80	0.47
	0.009	0.65	0.43
	0.01	0.55	0.41
	0.015	0.48	0.33
	0.02	0.42	0.29
	0.025	0.375	0.26
	0.03	0.325	0.22
	0.04	0.26	0.20
23	0.01	0.41	0.34
	0.015	0.35	0.27
9.9	0.01	0.26	0.22
	0.015	0.23	0.18
6.1	0.01	0.175	0.17
	0.015	0.16	0.14

[a] Calculated from the expression $\alpha_c = \left(\frac{I}{\Phi_{22}(0)}\right)^{1/2}$.

Initiator *I*: a complex of low-molecular-mass polystyrene with 2,2′,6,6′-tetramethylpiperidin-1-oxyl.

mediated radical polymerization [103]) regime. As can be seen, the data obey the power law to a good accuracy. However, some differences between the measured α_c values and those calculated from relation (27) do occur (Table 3). This is probably due to the cyclization reaction.

This is also indicated by the results obtained by Matyjaszewski and co-workers [88] in a study of the copolymerization of methyl acrylate and ethylene glycol diacrylate by the atom transfer radical polymerization (ATRP) mechanism.[104, 105] The dependence of α_c on the diacrylate/initiator concentration ratio (x) is shown in Fig. 8.

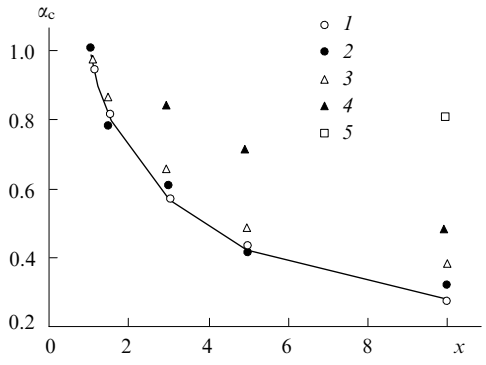


Figure 8. Critical conversion plotted *vs.* ethylene glycol diacrylate/initiator concentration ratio for ATRP-copolymerization of methyl acrylate with ethylene glycol diacrylate.[91]
Results of calculations (*1*) and experimental data (*2*–*5*). Methyl acrylate concentration /mol litre^{-1}: 8.5 (*2*), 6 (*3*), 2.5 (*4*) and 1 (*5*).

As in the preceding case, experimental points lie above the theoretical curve, the more dilute system the larger the deviation between them. This regularity suggests that the reason for the shift of the gel point is intramolecular cross-linking. It is noteworthy that the theoretically and experimentally determined α_c values for the block polymerization at a methyl acrylate concentration of 8.5 mol litre^{-1} almost coincide (data set *2*).

Wang and Zhu [87, 106] also showed that the degree of branching of the polymers prepared by ATRP of divinylbenzene and ethylene glycol dimethacrylate and by copolymerization of ethylene glycol dimethacrylate with methyl methacrylate was at most 0.5, and this was followed by gel formation. Apparently, agreement with the Flory condition suggests a small contribution of the cyclization reaction.

Now we will complicate the problem by rejecting instantaneous initiation. The plots of α_c *vs.* $\Phi_{22}(0)$ at different initiation rates (W_i) are shown in Fig. 9. As can be seen, the dependences still obey the power law, but the exponent changes from $-1/2$ (line *1*) to $-2/3$ as W_i decreases (line *5*).

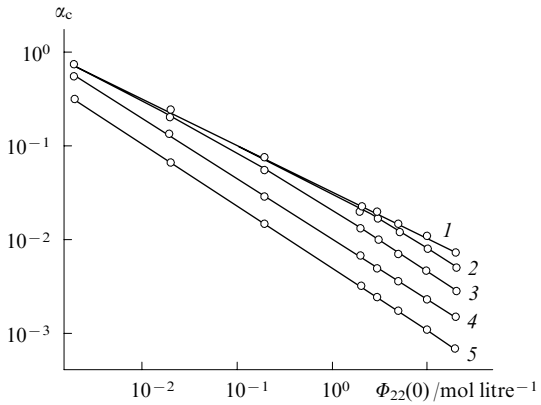


Figure 9. Critical conversion α_c plotted *vs.* $\Phi_{22}(0)$ in the course of 'living' polymerization at arbitrary initiation rate.
$W_i = k_i I_0/k_p$; $I_0 = 10^{-3}$ mol litre^{-1}; $k_i/k_p = 1$ (*1*), 10^{-1} (*2*), 10^{-2} (*3*), 10^{-3} (*4*), 10^{-4} mol litre^{-1} (*5*).

An essentially similar dependence of the critical conversion on the initiation rate was also established by Dušek and Šomvársky (see Table 2 in Ref. 107).

This dependence can be understood taking account of the following relations:

$$\frac{dR}{dt} = k_i I,$$

$$R = I_0\left(1 - e^{-k_i t}\right) \approx I_0 k_i t,$$

$$\frac{d\ln(1-\alpha)}{dt} = k_p R,$$

$$-\ln(1-\alpha) \approx \alpha = \frac{1}{2} k_p k_i I_0 t^2 = \frac{k_p R^2}{2 k_i I_0}.$$

Taking into account the Flory criterion, one gets

$$\alpha_c^3 = \frac{W_i}{k_p \Phi_{22}^2(0)}. \qquad (28)$$

To substantiate this relationship, one should analyze the changes in the concentration of reactive centres. The kinetics of accumulation of reactive centres (an increase in the concentration of chains) at different initiation rates is illustrated in Fig. 10. All curves exhibit two regions; in the

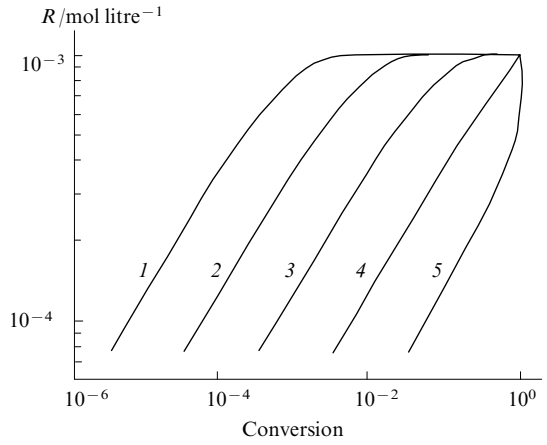


Figure 10. Kinetics of accumulation of macroradicals in the course of 'living' polymerization at arbitrary initiation rate.
$I_0 = 10^{-3}$ mol litre^{-1}; $k_i/k_p = 1$ (*1*), 10^{-1} (*2*), 10^{-2} (*3*), 10^{-3} (*4*), 10^{-4} mol litre^{-1} (*5*).

first region one has $R \propto \alpha^{1/2}$, whereas for the second region $R = I_0$. At high initiation rate (curve *1*), the first region corresponds to very low conversions and at the experimentally determined α values (from 10^{-2} to 1) one has R = const. At slow initiation (curves *4* and *5*), the accumulation of reactive centres by the power law does occur in the valuable range of conversions. Correspondingly, expression (27) holds in the first case while relation (28) holds in the second case.

The chain transfer reaction is a method of shift of the gel point up to inhibition of gel formation when preparing hyperbranched polymers.[16,108] Now we will consider a 'living' polymerization at arbitrary rates of the initiation and chain transfer to agent X.

Figure 11 demonstrates how the chain transfer reaction affects the critical conversion. At low concentration (X_0) of the chain transfer agent, the character of the dependence of α_c on $\Phi_{22}(0)$ is governed by the initiation rate (lines *1* in Fig. 11 *a* and Fig. 11 *b* corresponding to the high and low initiation rate, respectively). At high X_0, the critical conversion α_c becomes inversely proportional to $\Phi_{22}(0)$ and independent of the initiation rate (lines *4*). Owing to the chain transfer reaction, α_c is shifted towards high conversions and the gel point may appear to be unreachable at a particular concentration (X_{lim}). The data in Fig. 11 *c*,*d* show a correlation between X_{lim} and $\Phi_{22}(0)$, namely, they are linearly related in a wide range of $\Phi_{22}(0)$ values, the coefficient of proportionality being somewhat more than unity for both high and low initiation rates.

b. Polymerization involving chain termination

A conventional radical polymerization accompanied by quadratic chain termination is characterized by establishment of a steady-state concentration of reactive centres R at very low conversions. The R value is determined by the ratio of the initiation rate to the kinetic constant for chain termination [109]

$$R = \left(\frac{W_i}{k_t}\right)^{1/2}.$$

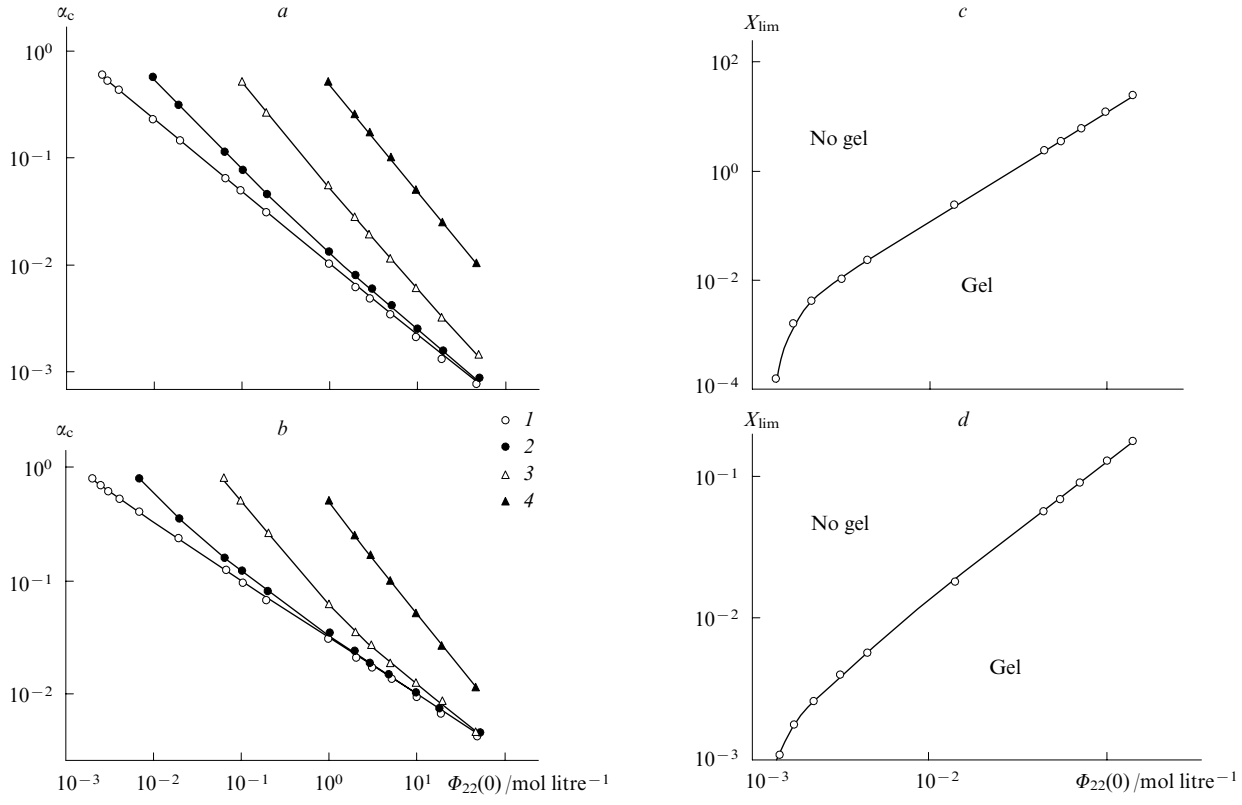


Figure 11. Plots of α_c (*a*, *b*) and X_{lim} (*c*, *d*) *vs.* $\Phi_{22}(0)$ in the course of 'living' polymerization with arbitrary initiation.
$I_0 = 10^{-3}$ mol litre^{-1}; $k_i/k_p = 1$ (*a*, *c*), 10^{-3} mol litre^{-1} (*b*, *d*); $X_0 = 10^{-3}$ (*1*), 10^{-2} (*2*), 10^{-1} (*3*), 1 mol litre^{-1} (*4*).

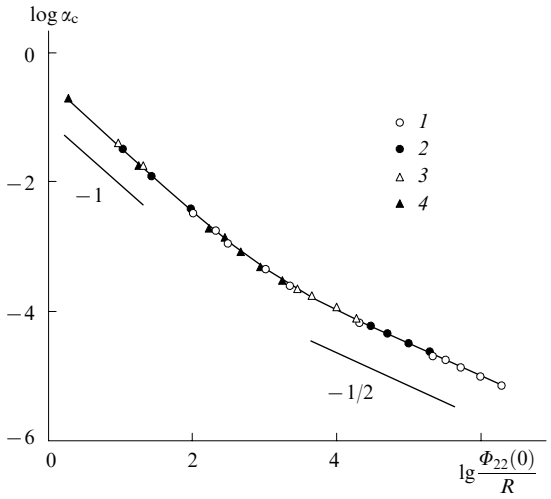


Figure 12. Plots of α_c *vs.* $\Phi_{22}(0)$ at different R values.
$-\log R$ (mol litre^{-1}) = 9 (*1*), 8 (*2*), 7 (*3*) and 6 (*4*).

The plots of α_c *vs.* $\Phi_{22}(0)$ at different R values are shown in Fig. 12. As the concentration of the cross-linking agent increases, the character of the dependence is changed from inverse proportionality (region denoted '-1') to the power law (region denoted '$-1/2$'), the latter corresponding to very low α_c values. An analysis of the data presented in Fig. 13 shows that in the first region one has

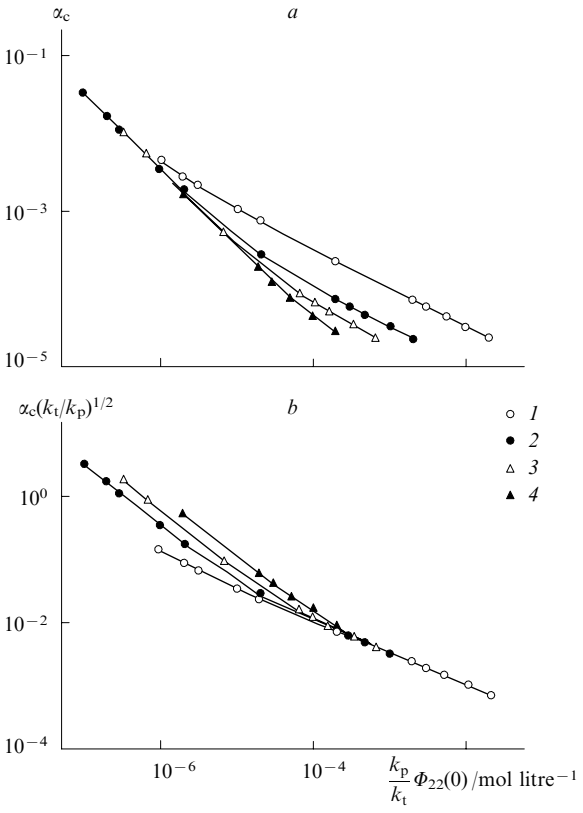


Figure 13. Plots of α_c (*a*) and $\alpha_c(k_t/k_p)^{1/2}$ (*b*) *vs.* $\Phi_{22}(0)$ at different values of the ratio k_t/k_p.
$\log(k_t/k_p)$ = 3 (*1*), 4 (*2*), 4.5 (3) and 5 (*4*).

$$\alpha_c = \frac{1}{3}\frac{k_t R}{k_p \Phi_{22}(0)}, \tag{29}$$

while in the second region one has

$$\alpha_c = \left(\frac{R}{\Phi_{22}(0)}\right)^{1/2}. \tag{29a}$$

If chain termination occurs by disproportionation, an analogue to relation (29) has the form

$$\alpha_c = \frac{1}{2}\frac{k_t R}{k_p \Phi_{22}(0)}. \tag{29b}$$

The effect of linear chain termination on the critical conversion in a wide range of initiation rates (see Fig. 14) is described by the expression

$$\alpha_c = \frac{1}{2}\frac{k_y Y_0}{k_p \Phi_{22}(0)}. \tag{30}$$

Here Y_0 is the initial concentration of inhibitor.

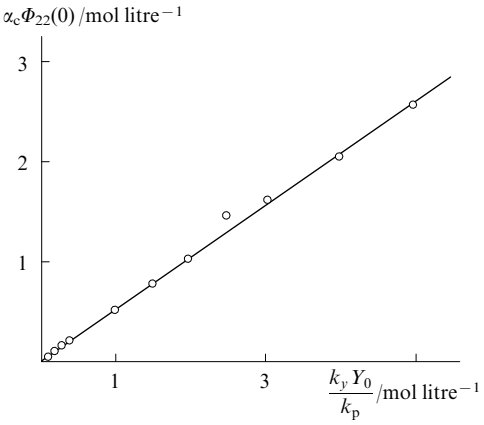


Figure 14. Critical conversion plotted *vs.* conditions for inhibited polymerization.[2]
$W_i/k_p = 10^{-9}-10^{-1}$ mol^2 litre^{-2}.

Experimental validation of these relationships is difficult because the initial stage of three-dimensional radical polymerization may be accompanied by a highly probable inefficient cyclization reaction (or intra-chain cross-linking).[9, 13, 16, 17, 110–116] Since chain formation takes a time of the order of a second (in terms of conversion, this corresponds to fractions of a per cent), this stage of polymerization involves the formation of a dilute solution of polymer in the monomer. Therefore, the reactive centre will more probably react with pendant functional groups from its own chain rather than with functional groups from 'alien' chains. In other words, intramolecular cyclization will dominate the intermolecular cross-linking reaction. Indeed, if the degree of polymerization is P, the coil volume of the propagating chain is to a first approximation proportional to $P^{3/2}$. Correspondingly, the average concentration of pendant functional groups is proportional to $P^{-1/2}$. Then, the probability for at least one group to react with the terminal radical, *i.e.*, to form an intra-chain cross-link, is proportional to $P^{1/2}$. Further evolution has a pronounced self-accelerated character,[7, 117] *viz.*, the higher the concen-

tration of cross-links within the chain the smaller the coil and, therefore, the higher the concentration of pendant groups and the more probable the intramolecular cross-linking reaction. The propagation of chains also means a decrease in their concentration and, correspondingly, a decrease in the probability of formation of inter-chain cross-links. At the same time, inter-chain cross-linking in this stage not only results in the formation of branched macromolecules, but also causes the cyclization probability to increase because the higher the degree of branching the smaller the volume of the macromolecule.[118]

Cyclization is a prerequisite to the formation of a microgel. A clear example of the microgel mechanism of three-dimensional radical polymerization is provided by the polymerization of oligoester acrylates, which was comprehensively studied by Korolev (see, *e.g.*, Refs 15, 16, 119–122).

The formation of microgel as a result of intramolecular cross-linking leads unavoidably to ν-syneresis, *i.e.*, displacement of low-molecular-mass components of the reaction system (co-monomers, initiator) from the bulk of the microgel particle.[15, 120, 123–125] This is a self-accelerated process, *i.e.*, a decrease in the local concentration of oligomer within the microgel particle makes the intra-chain cross-linking more probable; also microsyneresis increases as the degree of cross-linking increases. Yet another contribution comes from the gel effect, *viz.*, the mobility of macroradicals in the polymer network abruptly decreases, their lifetimes increase and the length of the kinetic chain made of the pendant functional groups increases. Even at low conversions this leads to formation of a highly inhomogeneous structure of the reaction system, namely, microgel particles characterized by an almost limiting conversion in the unreacted oligomer.

According to Korolev,[16] starting with some instant, namely, that where the conversion is given by

$$\alpha_{c1} = \frac{1}{(f-1)\overline{P}_n},$$

all reactive chains formed unavoidably react with the double bonds of microgel particles and no new particles are formed; the polymerization occurs as growth of the microgel particles. The degree of conversion within the microgel particles reaches a limiting value. Then, the reaction mainly proceeds in the transient zone of the microgel rather than in the bulk.[16, 112] The microgel particles may have radii as large as 10^2-10^3 nm, thus being macroscopic species compared to macromolecules. In other words, the condition $\overline{M}_w \to \infty$ is met. In addition, the situation is typical of the post-gel region for any gel formation processes. Starting with the formation of an infinite cluster, the process occurs as the growth of this cluster. Thus, α_{c1} can be considered as the gel point.

As the microgel particles grow, their volume fraction reaches a value corresponding to the percolation threshold at some conversion value. This is the second gel point (α_{c2}) usually treated as the start of gel formation. One has

$$\alpha_{c2} > \alpha_{c1} > \alpha_c,$$

where α_c is the theoretical value.

As shown above, ionic and controlled radical polymerization can also be accompanied by cyclization which, however, is little pronounced. This can be explained by the fact that, compared to the radical processes the concentration of initially growing chains is high while their growth occurs more slowly. Thus, the possibility of comparing the theoretical and experimental data free from the cyclization effect is due to an increase in the initial concentration of chains and to their fundamental shortening. In other words, one should increase the initiation rate and/or use an inhibitor.

The last-mentioned approach was used in a study[98] of the polymerization of triethylene glycol dimethacrylate initiated by dicyclohexylperoxy carbonate at an initiator : inhibitor ratio of 2 : 1 (except for the experiments denoted by footnote [a] in Table 4). Note that the rate constant for chain termination (k_y) is about 10^2 litre mol^{-1} s^{-1} for trinitrotoluene and nearly 2×10^3 litre mol^{-1} s^{-1} for benzoquinone.

Table 4. Dependence of critical conversion on the inhibitor concentration.[98]

Inhibitor concentration /mol litre^{-1}	α_c	
	experiment	calculations
Trinitrotoluene as the inhibitor		
0.05	~0.01	0.0009
0.1	0.06	0.0018
0.2	0.08	0.0036
0.5	0.11	0.009
Benzoquinone as the inhibitor		
0.005 (4) [a]	0.065	0.0018
0.005 (2) [a]	0.055	0.0018
0.005 (1) [a]	0.045	0.0018
0.01	0.085	0.0036
0.05	0.125	0.018
0.1	0.135	0.036
0.3	0.16	0.072
0.5	0.19	0.18

[a] Numbers in parentheses denote the initiation rate ($W\times10^7$ mol litre^{-1} s^{-1}).

As the concentration of the inhibitor (especially, more reactive benzoquinone) increases, there is a clearly seen trend of approach of the theoretical and measured α_c values to one another. Thus, one can believe that in an ideal case the relations given above are suitable for the description of three-dimensional radical polymerization.

Three-dimensional polymerization can be additionally complicated due to different reactivities of the initial and pendant functional groups in polyfunctional comonomers. Formally, this can be treated as the substitution effect.

Unfortunately, relevant experimental data are scarce. Landin and Macosko[126] found that in the radical copolymerization of methyl methacrylate with ethylene glycol dimethacrylate nearly 3% of pendant double bonds are consumed in the early stage of the process for cyclization and that their reactivities in the subsequent stages are nearly halved compared to that of methyl methacrylate and the lower the reactivity the higher the concentration of the cross-linking agent:

Dimethacrylate (mol.%)	0.57	1.14	1.70
k_{11}/k_{13}	1.86	2.22	2.86

Here, k_{11} and k_{13} are the kinetic constants for the reactions of the radical with the monomer and pendant group, respectively.

An increased consumption of pendant groups in the early stage of the homopolymerization of divinylbenzene and copolymerization of divinylbenzene with styrene in dilute solution was observed.[127] The authors of that study concluded that, ignoring cyclization and multiple cross-links leading to the formation of a microgel, the pendant bonds are more reactive owing to their higher concentration near the radical centre. Interaction between microgel particles leads to formation of a macrogel. In this process, the pendant double bonds are one or two orders of magnitude less reactive than the vinyl groups of the starting comonomers.

According to Matsumoto,[13] the allylic bonds of comonomers and the pendant groups are comparable in reactivity; however, lower reactivities of the latter are due to structural reasons.† Measurements of the concentration of pendant double bonds in radical copolymerization of styrene and ethylene glycol dimethacrylate[128] showed that in the early stage these bonds are consumed for cyclization resulting in a microgel. Then, their fraction increases owing to the fact that the reaction in the bulk proceeds nonuniformly, being localized in the peripheral regions of microgel grains.[13, 16, 17, 129]

Ide and Fukuda[74] reported a ^{1}H NMR study of the kinetics of copolymerization of styrene with 4,4′-divinylbiphenyl in the nitroxide-mediated radical polymerization (NMRP) regime. They estimated the copolymerization constant (r_p) for the reaction of styrene with the second double bond of 4,4′-divinylbiphenyl that reacted at the first double bond at $r_p = 1.0 \pm 0.1$.

Summing up, in contrast to the polycondensation-type reactions, the substitution effect in polymerization seems to be due to steric hindrances rather than have a chemical nature. Nevertheless, the influence of this effect on the critical conversion should be studied. This was done in Ref. 99.

To account for the initial and pendant functional groups, let us introduce the generating function characterizing the system in the initial state,

$$Z(q) = \sum_i q^i m_i ,$$

where $i = 1, 2, \ldots, f$; m_i are the concentrations of the i-functional monomers.

The system of kinetic equations can be represetned in the form

$$\frac{dm_i}{dt} = -ik_{p1} m_i R$$

(k_{p1} is the rate constant for chain propagation with respect to the primary groups), from which one gets a simple equation for the generating function

$$\frac{\partial Z(q)}{\partial t} = -qk_{p1} \frac{\partial Z(q)}{\partial q} R. \qquad (31)$$

† Collision between a functional group and a radical are hampered by, first, connectivity (dependence of the collision probability on the length of the chain separating them), and, second, diffusion-related difficulties.

A solution of Eqn (31) by the method of characteristics gives

$$Z(q) = \sum_{i=1}^{f} q^i m_{i,0} e^{-ik_{p1}\tau},$$

where $m_{i,0}$ is the initial concentration of the i-functional monomer,

$$\tau = \int_0^t R(\xi) d\xi,$$

ξ is the integration variable.

Equation (31) can be solved by the method of moments (as earlier, the subscript '2' characterizing the reactant functionality means differentiation with respect to q as many times as the subscript occurs). Successive differentiation of expression (31) leads to the open system of equations

$$\frac{dZ}{dt} = -k_{p1} R Z_2 , \qquad (32)$$

$$\frac{dZ_2}{dt} = -k_{p1} R (Z_2 + Z_{22}),$$

$$\frac{dZ_{22}}{dt} = -k_{p1} R (2Z_{22} + Z_{222}),$$

$$\frac{dZ_{222}}{dt} = -k_{p1} R (3Z_{222} + Z_{2222}),$$

etc.

It should be noted that owing to limited functionalities of the initial system of monomers, the system of equations (32) can be truncated. Indeed,

$$Z_2(q) = \sum_{i=1} i q^{i-1} m_i ,$$

$$Z_{22}(q) = \sum_{i=1} i(i-1) q^{i-2} m_i ,$$

$$Z_{222}(q) = \sum_{i=1} fi(i-1)(i-2) q^{i-3} m_i ,$$

etc.

For linear polymerization ($f = 1$), one has $Z_{22} = 0$. If the functionality is at most two, one has $Z_{222} = 0$; and $Z_{2222} = 0$ at $f = 3$.

Of course, the scheme describing three-dimensional polymerization taking account of changes in the rate constant for chain propagaton with respect to pendant groups (k_{p2}) becomes more complicated. Correspondingly, the systems of differential equations for the concentrations of macromolecules and for the moments of the generating functions will also change. It was shown[99] that, first, α_c depends only on the second moment of the functionality distribution of the initial monomers (Z_{22}, see above) and, second, the following relations are applicable in the case of 'living' polymerization:

$$\alpha_c = \left(\frac{k_{p1} I_0}{k_{p2} Z_{22}(0)} \right)^{1/2},$$

$$\alpha_c = \left(\frac{k_{p1}^2 k_i I_0}{k_{p2}^2 k_p Z_{22}^2(0)} \right)^{1/3}.$$

For a radical polymerization with quadratic chain termination one has

$$\alpha_c = \phi \frac{k_{p1} R}{k_{p2} Z_{22}(0)}. \tag{33}$$

Here R is the steady-state concentration of radicals and the coefficient ϕ equals 1/3 if chain termination occurs by recombination and 1/2 if it occurs by disproportionation.

2. Polycondensation

In the case of polycondensation there are no reactive centres and the macromolecule is represented by $R(m,n)$, where m is the number of units in the chain and n is the number of functional groups. Of course, this is a simplified model which assumes reactions between same-type functional groups.

This type of reactions is described by the following scheme

$$R(i,j) + R(m,n) \xrightarrow{k} R(i+m, j+n-2), \tag{34}$$

which leads to an infinite system of differential equations of the general form

$$\frac{dR(i,j)}{dt} = -kjR(i,j)\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} nR(m,n) + \frac{1}{2}k\sum_{n=1}^{j-1}\sum_{m=1}^{i-1}(j-n)R(i-m,j-n)nR(m,n), \tag{35}$$

which belong to the Smoluchowski-type equations.[130] Generally, such processes are treated assuming that the kinetic constants depend on the size of the reacting species. Equation (35) describes a wide range of coagulation processes and therefore considerable literature concerned with its analysis and solution is available (see, *e.g.*, Refs 8, 9, 21, 41, 130–140). For simplicity, here we assume that $k_{ij} \equiv k$.

In terms of the generating function, the system (35) has the form

$$\frac{\partial \Phi(\vec{q})}{\partial t} = -kq_2 \frac{\partial \Phi(\vec{q})}{\partial q_2} F + \frac{1}{2}k\left(\frac{\partial \Phi(\vec{q})}{\partial q_2}\right)^2, \tag{36}$$

where

$$F = \sum_{i,j,l}^{\infty} jR(i,j)$$

is the total concentration of reactive functional groups.

Since there is a one-to-one relation between the size of a macromolecule i and the number of functional groups j attached to the macromolecule, namely,

$$j = (\bar{f}_n - 2)i + 2, \tag{37}$$

expressions (34)–(36) can be simplified by restricting ourselves to consideration of one variable, *e.g.*, the number of units. Then, Eqn (36) takes the form

$$\frac{\partial \Phi(q)}{\partial t} = -kq \frac{\partial \Phi(q)}{\partial q} F + \frac{1}{2}k\left(\frac{\partial \Phi(q)}{\partial q}\right)^2. \tag{37a}$$

Equation (37a) has the following analytical solution:

$$\Phi(q) = \sum_i R_i(0)\chi^i - \left[kt\left(\sum_i iR_i(0)\chi^{i-1}\right)\right] \Big/ 2(1 + kF(0)t),$$

$$q = \chi + \left\{\chi - \left[\sum_i iR_i(0)\chi^{i-1}\right] \Big/ F(0)\right\} kF(0)t. \tag{38}$$

Here $R_i(0)$ is the initial concentration of the i-functional oligomers, χ is a parameter and $F(0)$ is the total initial concentration of functional groups.

Dušek [141] showed that the solution of Eqn (38) becomes branched at the instant t_c corresponding to the gel point,

$$\alpha_c = \frac{1 - F(t_c)}{F(0)}.$$

If the process proceeds in the presence of substitution effect in the first sphere (*i.e.*, after reaction of the first functional group all other groups are characterized by an identical reactivity which, however, differs from the initial reactivity), the scheme (34) and the system of equations (35) become complicated. The reactivities of functional groups in the initial molecule (R_1) and in the reaction products (R_i, $i > 1$) differ owing to the substitution effect in the first sphere. Therefore, they should be considered separately. Thus, one has

$$R_1 + R_1 \xrightarrow{k_1} R_2, \tag{39}$$

$$R_1 + R_n \xrightarrow{k_2} R_{n+1},$$

$$R_m + R_n \xrightarrow{k_3} R_{m+n}.$$

In scheme (39), which takes account of functionality according to expression (37), the subscript denotes the number of units in the macromolecule. The substitution effect is reflected by different kinetic constants.

Consider a simplified version based on the assumption of additivity of the activation energy (because of this, one has $k_2/k_1 = \varepsilon$, $k_3/k_1 = \varepsilon^2$). Then one gets

$$\begin{aligned}
\frac{dR_1}{k_1 dt} &= -fR_1(fR_1 + \varepsilon F) - f^2 R_1^2, \\
\frac{dR_2}{k_1 dt} &= -\varepsilon(2f-2)R_2(fR_1 + \varepsilon F) + f^2 R_1^2, \\
\frac{dR_3}{k_1 dt} &= -\varepsilon(3f-4)R_3(fR_1 + \varepsilon F) + \varepsilon fR_1(2f-2)R_2, \\
\frac{dR_n}{k_1 dt} &= -\varepsilon(nf - 2n + 2)R_n(fR_1 + \varepsilon F) + \\
&\quad + \varepsilon fR_1\Big[(n-1)(f-2) + 2\Big]R_{n-1} + \\
&\quad + \frac{\varepsilon^2}{2}\sum_{i=2}^{n-2}(if - 2i + 2)R_i\Big[(f-2)(n-i) + 2\Big]R_{n-i},
\end{aligned} \tag{40}$$

where

$$F = \sum_{i=2}(if - 2i + 2)R_i, \text{ a } n = 4, 5, \ldots.$$

Unlike the preceding case, the generating function is independent of the initial reactants

$$\Phi(q) = \sum_{i=2} q^i R_i.$$

The equation for the generating function has the form:

$$\frac{\partial\Phi(q)}{k_1\partial t} = q^2f^2R_1^2 - \varepsilon^2\Big[q(f-2)\Phi'(q) + 2\Phi(q)\Big]F + \tag{41}$$

$$+\varepsilon(q-1)fR_1\Big[q(f-2)\Phi'(q) +$$

$$+2\,\Phi(q)\Big] + \frac{\varepsilon^2}{2}\Big[q(f-2)\Phi'(q) + 2\Phi(q)\Big]^2,$$

where $\Phi'(q)$ is the first derivative with respect to q. At $t = 0$, one has $R_i = 0$, $\Phi(q) = 0$, $R_1 = R_0$.

The gel point is found by solving Eqn (41) by the method of moments of the generating function,

$$\frac{\mathrm{d}\Phi}{k_1\mathrm{d}t} = \frac{1}{2}f^2R_1^2 - \frac{\varepsilon^2}{2}F^2, \tag{42}$$

$$\frac{\mathrm{d}\Phi_1}{k_1\mathrm{d}t} = f^2R_1^2 + \varepsilon fR_1F,$$

$$\frac{\mathrm{d}\Phi_2}{k_1\mathrm{d}t} = f^2R_1^2 + 2\,\varepsilon fR[(f-2)\Phi_2 + f\Phi_1] + \varepsilon^2[(f-2)\Phi_2 + f\Phi_1]^2,$$

$$\frac{\mathrm{d}R_1}{k_1\mathrm{d}t} = -f^2R_1^2 - \varepsilon fR_1F,$$

$$F = (f-2)\Phi_1 + 2\Phi.$$

The result of this solution is presented in Fig. 15.

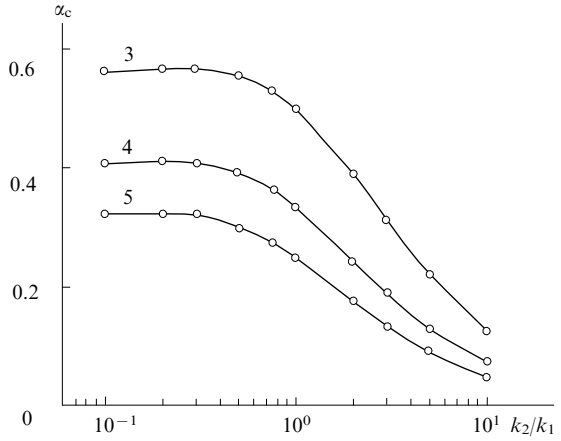


Figure 15. Illustration of the substitution effect: critical conversion α_c plotted *vs.* k_2/k_1 ratio at *f*-functional polycondensation. The functionality *f* values are given above the curves.

As can be seen, the negative substitution effect ($k_2/k_1 < 1$) causes an increase in α_c, whereas the positive substitution effect ($k_2/k_1 > 1$) leads to an appreciable decrease in this parameter.

Most often, the reaction occurs between different-type functional groups; this requires the introduction of a second parameter

$$R(i,j) + R(m,n) \xrightarrow{k} R(i+m-1, j+n-1).$$

In this case, we omit the size of the macromolecule and define it by the number of functional groups for each type.

Correspondingly, one has

$$\frac{\mathrm{d}R(i,j)}{\mathrm{d}t} = \tag{43}$$

$$-kiR(i,j)\sum_{m,n=1}^{\infty} nR(m,n) - kjR(i,j)\sum_{m,n=1}^{\infty} mR(m,n) +$$

$$+k\sum_{m,n=1}^{i-1,\,j-1}(j-n+1)R(i-m, j-n+1)(m+1)R(m+1,n),$$

and

$$\frac{\partial\Phi(\vec{q})}{\partial t} = -kq_1\frac{\partial\Phi(\vec{q})}{\partial q_1}F_2 - kq_2\frac{\partial\Phi(\vec{q})}{\partial q_2}F_1 + k\frac{\partial\Phi(\vec{q})}{\partial q_1}\frac{\partial\Phi(\vec{q})}{\partial q_2}. \tag{44}$$

Here the dummy variables q_1 and q_2 correspond to different functional groups.

The solution to this equation in the parametric form is as follows:

$$\Phi(\vec{q},t) = \sum_i a_i\chi_1^i + \sum_j b_j\chi_2^j - a\alpha_a, \tag{45}$$

$$a\alpha_a = b\alpha_b,$$

$$q_1 = \frac{b\chi_1 - \alpha_a\sum_j jb_j\chi_2^{j-1}}{b(1-\alpha_a)},$$

$$q_2 = \frac{a\chi_2 - \alpha_b\sum_i ia_i\chi_1^{i-1}}{a(1-\alpha_b)}.$$

Here the subscripts a and b refer to the type-1 and type-2 functional groups; a_i and b_i are the initial concentrations of the *i*-functional oligomers (a functionality distribution is implied), $\sum ia_i = a$, $\sum jb_j = b$; α is the degree of conversion with respect to the corresponding groups; χ_1 and χ_2 are the parameters to be determined.

Differentiation of α with respect to q_1 and q_2 gives the expression for the gel point:

$$(\alpha_a\alpha_b)_c = \frac{1}{(\bar{f}_{aw}-1)(\bar{f}_{bw}-1)},$$

where

$$\bar{f}_{aw} = \sum_i i^2a_i,$$

$$\bar{f}_{bw} = \sum_i i^2b_i$$

are the weight-average functionalities of the type-*a* and type-*b* groups, respectively.

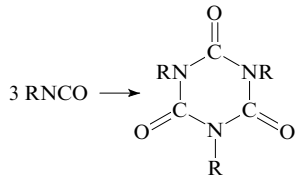
In more complicated situations (*e.g.*, reactions involving several types of functional groups with different reactivity), no simple solutions are available.

If the substitution effect occurs in one component and is absent in the other component, the problem can be solved using a method based on the concept of bond blocks (see Section III). If the substitution effect is intrinsic in both components, one should use a general kinetic method, as was demonstrated above for *f*-functional polycondensation in the presence of substitution effect.

3. The cyclotrimerization reaction

The cyclotrimerization reaction is characteristic of isocyanates,[142–144] cyanic acid derivatives[145,146] and

alkynes.[147–149] Kinetically, this is a particular case of polycondensation because propagation of the polymer chain is due to the interaction of three rather than two functional groups. For instance, irrespective of chemical features and a rather complex reaction mechanism,[150] the cyclotrimerization of isocyanates can be treated as trimolecular reaction on a certain fictitious time scale.[151]



Taking account of the aforesaid, a general scheme of cyclotrimerization of mono- and bifunctional oligomers with allowance for different reactivities of functional groups and the substitution effect is as follows (the type of the group is denoted by the subscript, their number is shown in parentheses, the kinetic constant is given on the right):[152, 153]

reactants and kinetic constants

— three monofunctional monomers (type *a*)

$R_a(1) + R_a(1) + R_a(1) \longrightarrow R_c(0), k_{111};$

— two monofunctional monomers and one bifunctional monomer (type *b*)

$R_a(1) + R_a(1) + R_b(2) \longrightarrow R_c(1), k_{112};$

— two monofunctional monomers and one polyfunctional oligomer (type *c*)

$R_a(1) + R_a(1) + R_c(n) \longrightarrow R_c(n-1), k_{113};$

— one monofunctional monomer and two bifunctional monomers

$R_a(1) + R_b(2) + R_b(2) \longrightarrow R_c(2), k_{122};$

— one mono-, one bi- and one polyfunctional oligomers

$R_a(1) + R_b(2) + R_c(n) \longrightarrow R_c(n), k_{123};$

— one mono- and two polyfunctional oligomers

$R_a(1) + R_c(n_1) + R_c(n_2) \longrightarrow R_c(n_1 + n_2 - 2), k_{133};$

— three bifunctional oligomers

$R_b(2) + R_b(2) + R_b(2) \longrightarrow R_c(3), k_{222};$

— two bifunctional oligomers and one polyfunctional oligomer

$R_b(2) + R_b(2) + R_c(n) \longrightarrow R_c(n+1), k_{223};$

— one bifunctional oligomer and two polyfunctional oligomers

$R_b(2) + R_c(n_1) + R_c(n_2) \longrightarrow R_c(n_1 + n_2 - 1), k_{233};$

— three polyfunctional oligomers

$R_c(n_1) + R_c(n_2) + R_c(n_3) \longrightarrow R_c(n_1 + n_2 + n_3 - 3), k_{333}.$

The assumption of additivity of the activation energy allows ten kinetic constants to be reduced to three following the principle

$k_{abc} = k_a k_b k_c.$

Now the corresponding system of differential equations takes the form

$$\frac{dR(n)}{dt} = -nk_3R(n)F^2 + k_1^2R_a^2(1)k_3R_c(n+1) + \quad (46)$$
$$+ k_1R_a(1)k_3^2\sum_{j=1}^{n+1} j(n-j+2)R_c(j)R_c(n-j+2) +$$
$$+ 4k_2^2R_b^2(2)k_3R_c(n-1) + k_1R_a(1)k_2R_b(2)k_3R_c(n) +$$
$$+ 2k_2R_b(2)k_3^2\sum_{j=1}^{n} j(n-j+2)R_c(j)R_c(n-j+2) +$$
$$+ \frac{1}{3}k_3^3\sum_{i=1}^{n-2}\sum_{j=1}^{i} ij(n-i-j+1)R_c(i)R_c(j)R_c(n-i-j+1),$$

where

$$F = k_1A + k_2B + k_3C,$$

$A = R_a(1)$ is the total concentration of the type-*a* functional groups, $B = 2R_b(2)$ is the total concentration of the type-*b* functional groups and $C = \sum nR_c(n)$ is the total concentration of the type-*c* functional groups.

At $t = 0$, one has $A = A_0$, $B = B_0$ and $C = 0$.

Using the generating function

$$\Phi(q) = \sum_n q^n R_c(n),$$

one can describe the kinetics of cyclotrimerization by the following system of equations:

$$\frac{dR_a(1)}{dt} = -k_1R_a(1)F^2, \quad (47)$$
$$\frac{dR_b(2)}{dt} = -2k_2R_b(2)F^2\frac{\partial\Phi(q)}{\partial t} =$$
$$= -k_3q\frac{\partial\Phi(q)}{\partial q}F^2 + \frac{1}{3}\left(k_1R_a(1) + 2qk_2R_b(2) + k_3\frac{\partial\Phi(q)}{\partial q}\right)^3,$$

where $\Phi(1) = N$ is the number of chains,

$$\frac{\partial\Phi(1)}{\partial q} \equiv \Phi_q = C,$$

$$\bar{f}_n = \frac{\Phi_q}{\Phi(1)}.$$

The second moment is given by

$$\frac{\partial^2\Phi(1)}{\partial q^2} \equiv \Phi_{qq},$$

$$\bar{f}_w = \frac{\Phi_{qq}}{\Phi_q} + 1.$$

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

$$\frac{d\Phi}{dt} = -k_3\Phi_qF^2 + \frac{1}{3}F^3,$$

$$\frac{d\Phi_q}{dt} = 2k_2R_b(2)F^2 - k_3\Phi_qF^2,$$

$$\frac{d\Phi_{qq}}{dt} = 2F\left[\left(k_3\Phi_{qq} + 2k_2R_b(2)\right)^2 - k_3\Phi_{qq}F\right].$$

The initial conditions are as follows: A_0, B_0, $C = 0$, $\Phi(q) = 0$. Correspondingly, all moments of the generating function are also equal to zero.

The results of calculations[152] of the dependence of α_c on the composition of the reaction mixture and on the relative

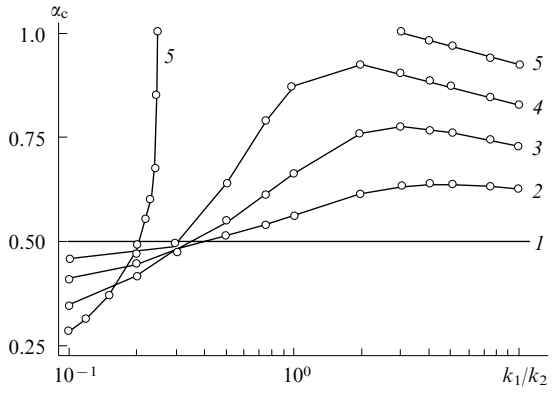


Figure 16. Critical conversion plotted *vs.* concentration of monofunctional isocyanate and its reactivity.
$k_3 = k_2$; $n_1 = 0$ (*1*), 0.2 (*2*), 0.4 (*3*), 0.6 (*4*), 0.8 (*5*).

reactivity of functional groups ignoring the substitution effect (*i.e.*, $k_1 \neq k_2 = k_3$) are shown in Fig. 16.

At a high content of the monofunctional component (curve *5*), one gets a logical result, *viz.*, no gel point. However, this is observed only if the reactivities of the reactants are similar (see the singularity region for curve *5*). If they differ appreciably, the gel point is reachable.

Noteworthy is an exotic chcracter of this dependence, namely, a decrease in α_c with an increase in the concentration of the chain termination agent, monofunctional agent (if it has low reactivity). This is due to the fact that the network is mainly formed at the expense of the bifunctional agent and α_c decreases as the fraction of the bifunctional agent decreases.

This example could also be analyzed by statistical methods. However, this cannot be done for the next example.

Figure 17 presents the results of calculations [153] of the dependence of α_c on the composition of the reaction mixture and on the substitution effect, *i.e.*, on the relative reactivity of the functional groups *C* (kinetic constant k_3) provided that $k_1 = k_2$. Interestingly, α_c decreases if the substitution effect is positive and increases to some extent if the substitution effect is negative. It should be noted that this regularity is typical of conventional polycondensation proc-

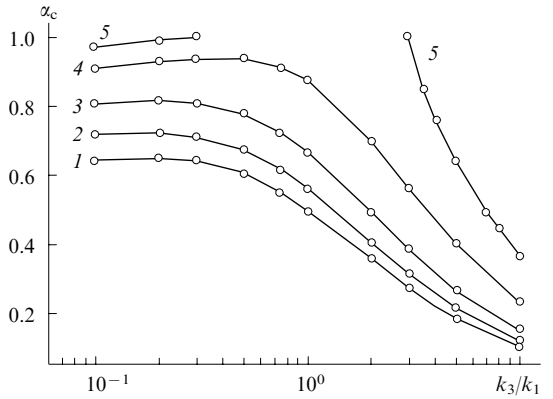


Figure 17. Critical conversion plotted *vs.* composition of reaction mixture and magnitude of the substitution effect.
$k_1 = k_2$; $n_1 = 0$ (*1*), 0.2 (*2*), 0.4 (*3*), 0.6 (*4*), 0.7 (*5*).

esses (see, *e.g.*, Fig. 15). The position of singularity in curve *5* indicates that the high concentration of the monofunctional agent suppresses the formation of the polymer network only if the substitution effect is relatively weak.

Curve *1* in Fig. 17 was earlier obtained by the recursive technique.[154] This approach developed by Miller and Macosko [155, 156] is in essence similar to the method based on the concept of bond blocks (see above), where the role of the bond block is played by the cyclic trimer.

V. Critically branched macromolecules (critical clusters)

Irrespective of the method of formation of polymer networks (polycondensation, polymerization or cross-linking), the molecular mass considerably increases and broadening of the MMD occurs as the critical conversion is approached.[9] At the same time, after the gel point, the MMD of the components of the sol fraction (finite-size macromolecules) narrows. Thus, at the gel point the polymer has a specific topological structure characterized using the fractal formalism.[1, 157] The fractal dimension of a cluster (D_f) is determined by the ratio of its volume to its mass

$$R \propto M^{1/D_f},$$

where R is the radius and M is the mass of the cluster (for a dense system, one has $D_f = 3$). For linear 'immaterial' chains one has $D_f = 2$; taking account of the effect of excluded volume gives $D_f = 5/3$.[158, 159] According to percolation theory,[1, 157] $D_f = 2.53$ in the region of critical conversion.

The character of changes in the molecular mass of critical clusters on approach to the gel point is usually described [1, 157–159] by scaling relations of the type

$$\bar{M}_w \propto |\alpha_{rmc} - \alpha|^{-\gamma}. \quad (48)$$

At $\alpha < \alpha_c$, expression (48) describes the bulk of the polymer, whereas at $\alpha > \alpha_c$ it refers to the sol fraction only.

According to statistical calculations,[2, 3] for a simple *f*-functional polycondensation one has

$$\bar{P}_w = \frac{1+\alpha}{1-(f-1)\alpha} \equiv \frac{1+\alpha}{1-\alpha/\alpha_c} \propto (\alpha_c - \alpha)^{-1}$$

at $\alpha \to \alpha_c$.

Thus, the statistical method gives $\gamma = 1$.

This result was also obtained in the kinetic calculations [152] (Fig. 18).

In both cases we ignored the possibility of cyclization. Computer simulation of gel formation taking into account this reaction as well as the effect of excluded volume led to $\gamma \approx 1.7$.[1, 157]

Experimental data are scarce and contradictory. For instance, one has $\gamma \approx 1$ (Fig. 19 *a*; data taken from Ref. 160) *vs.* $\gamma \approx 2.7$ (Fig. 19 *b*; data taken from Ref. 161). It should be noted that both studies were concerned with polycondensation of decamethylene glycol + benzene-1,3,5-triacetic acid in the former and $Si(OMe)_4 + H_2O$ in the latter case.

Probably, the case in point is the numerical value of the ratio $(\alpha_c - \alpha)/\alpha_c$: in the former case, it is an order of magnitude smaller than in the latter. However, Fig. 18 shows that the scaling relations manifest themselves only at sufficiently small values of this ratio ($< 10^{-2}$). Schmidt

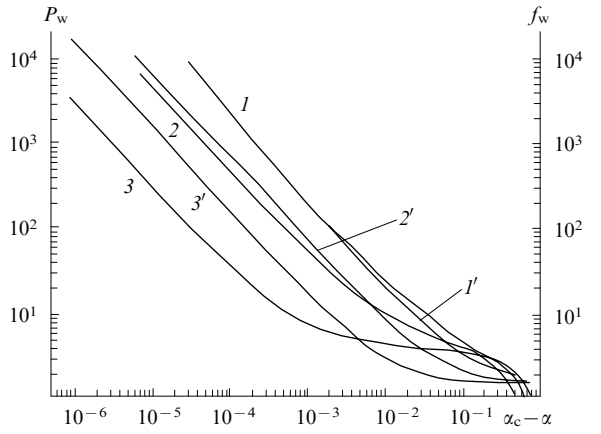


Figure 18. Structural characteristics of branched products of cyclotrimerization reaction.[152]
P_w (*1*, *2*, *3*) and f_w (*1′*, *2′*, *3′*) near the gel point; $n_1 = 0.18$ (*1*, *1′*), 0.57 (*2*, *2′*), 0.65 (*3*, *3′*); $k_1 = k_2 = k_3$.

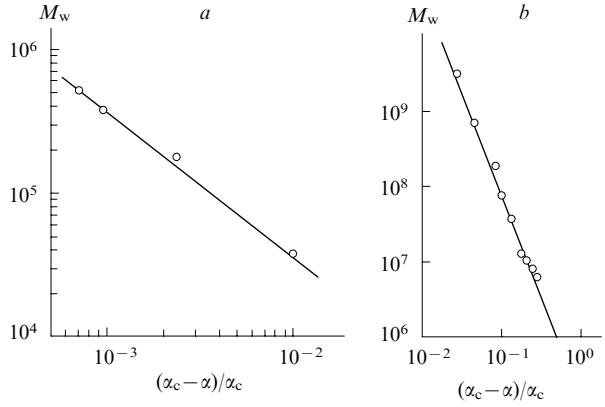


Figure 19. Molecular mass of a polymer plotted *vs.* conversion near the gel point. Data taken from Refs 160 (*a*) and 161 (*b*).

and Burchard [162] studied anionic copolymerization of styrene and divinylbenzene and found that $\gamma \approx 1$ in the interval $(\alpha_c - \alpha)/\alpha_c \approx 10^{-1} - 10^{-2}$. Yet another possible reason is the difference in the degree of cyclization. It was established [160, 162] that intra-chain cross-linking is minimum but the authors of Ref. 161 left this process out of consideration; they carried out the reaction in solution, which probably was favourable for cyclization. This conclusion is confirmed by the results obtained in a study [163] of critically branched polyurethanes by static and dynamic light scattering. It was shown that the polymer synthesized in bulk obeys the classical Flory–Stockmeyer criterion, whereas the polymer prepared in a solution in DMF is described in terms of percolation theory.

The relaxation properties of the polymeric system at the gel point are described by a power rather than exponential law [164–166]

$$G(t) \propto t^{-n}, \tag{49}$$

where G is the relaxation shear modulus. The coefficient n is related to the fractal dimension [167]

$$n = \frac{D}{D_f + 2},$$

where D is the dimension of the space (for the three-dimensional space, one has $n = 0.66$).

A consequence of relation (49) is the power law for the frequency dependence of the relaxation modulus:

$$G' = \omega^n \cos\left(\frac{\pi n}{2}\right),$$

$$G'' = \omega^n \sin\left(\frac{\pi n}{2}\right).$$

Therefore, $\tan\delta$ is frequency-independent;

$$\delta = \frac{\pi n}{2}.$$

Theoretical estimation [168] gives $n = 0.706$.

VI. Conclusion

The aforesaid demonstrates the possibility of exact calculations of the critical conversion based on the ideas of the mechanism and kinetics of gel formation. Of course, in this case we ignore a number of complicating factors, such as the side reactions, the effect of structural organization of the initial system or changes in the structural organization in the course of reaction.[17, 111] However, it is clear that estimation of α_c even in this 'ideal' case is not only useful, but also necessary for solving problems faced by industrial processes including three-dimensional polymerization (or polycondensation).

There is a specific problem concerned with correctness of experimental methods for the determination of the gel point when the medium has a complex and variable (in the course of reaction) molecular, supramolecular and phase structure. For instance, it was shown [169] that the degree of curing of bisphenol A diglycidyl ether by 4,4′-diaminodicyclohexylmethane, which corresponds to the abrupt kink of rheokinetic curves, is lower than the critical conversion (the lower the curing temperature the lower the degree of curing). In the case of polycondensation of oligomers (polyepoxides, polyurethanes, *etc.*), which is accompanied by the formation of functional groups capable of being involved in strong intermolecular interaction (a network of labile intermolecular bonds is formed), α_c is usually determined by viscosimetry or other rheokinetic methods.[170]

A typical example of limited use of relaxation methods is provided by dielectric spectroscopy studies. For instance, an inflection point on the logarithmic plot of conductivity *vs.* time was treated [171] as the gel point because of good agreement between the times corresponding to the inflection points and the gel formation times obtained by rheological methods. However, most researchers (see, *e.g.*, Refs 172–177) did not reveal such a correspondence. The reach-through conductivity was extrapolated [178] to zero and it was shown that the times corresponding to that point contradict the results of gel–sol analysis, although correlate with the data obtained by the torsional pendulum technique.[169]

There are at least two physical reasons for such a mismatch.

First, at the gel point the relaxation properties of the system become split. The formation of an infinite cluster, which is transformed to the gel fraction in later stages, causes the macroviscosity of the system to become infinitely high. At the same time, the microviscosity of the sol fraction shows no stepwise changes in the vicinity of critical conversion. Moreover, since the average molecular mass of the sol fraction decreases, one can even expect a decrease in microviscosity. Therefore, there are no grounds to believe that the mobility of low-molecular-mass charge carriers turns zero at the gel point. Correspondingly, in this case the reach-through conductivity will not be affected by gel formation.

The second reason to be taken into account is the formation of a labile network of physical bonds. In this case, one can expect a decrease in the mobility of charge carriers prior to the onset of formation of the network of chemical bonds. It is this behaviour that was observed in Refs 174 and 178. Finally, a number of studies (see, *e.g.*, Refs 179 – 184) revealed that changes in the relaxation time in the course of curing are first of all determined by the glass transition of the system rather than gel formation.

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