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Methods of description of the polycondensation kinetics and the structures of the polymers formed

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Abstract. The modern mathematical methods which make it possible to describe the kinetics of the formation reactions and the structures of polymers formed via polycondensation are examined: direct differentiation of an infinite system of differential equations, statistical approaches, and the concept of bond blocks. The possibilities and limits of applicability of each method are demonstrated. The bibliography includes 83 references.

I. Introduction

The mathematical procedures for the analysis of the kinetics of chemical reactions, based on the Law of Mass Action,[1] have been well developed. It would appear that the entire problem should reduce to finding procedures for the solution of a more or less complex system of differential equations describing the variation of the concentrations of the reactants as a function of time. However, when the formation reactions of polymers are examined, a series of problems arise. The first of them is that the kinetics of polymerisation processes depend significantly on the state of the reaction medium, which frequently varies in the course of the reaction.[2] The inhomogeneity of the distribution of the reaction centres in the initial stage of three-dimensional radical polymerisation, leading to cyclisation and ultimately to a high degree of localisation of the process,[3,4] the variation of the viscosity inducing the gel effect in the radical polymerisation of certain monomers,[5] as well as the inhibition of the reaction as a result of the vitrification of the system [2,6–9] may serve as examples. Finally, the system frequently undergoes phase decomposition in the course of the process,[10] which results in a change of the spatial distribution of the concentrations of the reactants. These factors are extremely difficult to take into account within the framework of formal kinetics.

Another difficulty consists in the need to analyse and solve an infinite system of differential equations because in principle, there is a possibility of the formation of an infinite number of reaction products — macromolecules of different size and with different structures. The approaches to the solution of such a system of equations have already been outlined by Flory [11] and were later developed in many studies and surveyed in monographs.[3,12,13] However, recently a series of new problems arose, particularly in connection with the wide scale employment of numerical methods based on the application of modern computational techniques. The principle of these is how to attain the required accuracy of the numerical solution and how to control it.

The development of modern experimental methods has reached a level such that the calculations of certain average quantities (for example, the number-average and weight-average molecular masses) have already become inadequate; more detailed information about the structure of the polymer is required from the kinetic calculation. However, any experimental methods for the study of the structures of polymers are also subject to an intrinsic error, which in fact determines the required accuracy of the calculation.

Hitherto statistical computational methods have been applied in kinetic investigations, which is due both to their simplicity and to the possibility of obtaining with their aid detailed information about the structures of complex formations such as, for example, network polymers. However, investigators do not always estimate correctly the applicability of these methods to the description of specific kinetic systems.

Finally, a new approach has appeared recently to the analysis of the formation reactions and structures of polycondensation polymers, based on the concepts of bond blocks.

All these factors have led to the writing of the present review.

It has to be stipulated immediately that the review will deal solely with the polycondensation method of synthesis of polymers. The characteristic features of the formation of the chain — unit by unit or from any fragments — actually determine the choice of qualitatively different systems of differential equations.[3,14,15] The solution and analysis of the system describing polycondensation processes are in fact the most complex. Problems of this class are solved with the aid of the Smoluchowski equation,[16] which was first proposed for the description of coagulation processes.[17,18]

II. Direct methods for the solution of the Smoluchowski equation

1. Polycondensation of polymers with isotypical functional groups

The Smoluchowski equation has the following general form:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = -x_i \sum_j k(i,j)x_j + \frac{1}{2}\sum_{j=1}^{i-1} k(i-j,j)x_{i-j}x_i \,, \qquad (1)$$

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where x_i is the concentration of the species (in the given instance, macromolecules) with size i ($i = 1, 2, 3, \ldots$ is the number of units in the chain) and $k(i, j)$ is the rate constant for the reaction between species with sizes i and j.

This equation describes a process which in the simplest case can be expressed in the form

$$X_i + X_j \longrightarrow X_{i+j}\,. \tag{2}$$

The Smoluchowski equation is suitable for the description of the kinetics of a wide variety of processes and numerous studies have therefore been devoted to its analysis (see, for example, Refs 16 and 19–25).

When applied to the reactions of polymer formation, Eqn (1) characterises polycondensation as a result of the interaction of isotypical functional groups with one another. The dependence of the kinetic constants on the dimensions of the macromolecules (subject to the condition that Flory's postulate [11] of the independence of the reactivity of functional groups on the size of the macromolecules carrying these groups is valid) is due to the fact that the number of functional groups f_i and the size of the macromolecules are directly interrelated (in the absence of intramolecular cyclisation reactions).

In the simplest case of the f-functional polycondensation, we have

$$f_i = (f-2)i + 2. \tag{3}$$

Hence it follows that the effective rate constant for the reaction between macromolecules having the ith and jth sizes is

$$k(i,j) = f_i f_j k, \tag{4}$$

where k is the rate constant for the reaction between the corresponding functional groups.

A thorough analysis of the approaches to the solution of the Smoluchowski equation has been carried out.[16] In their assessment of the functional relations $k(i, j)$, the authors do not confine themselves to Eqn (4) and consider also other more general relations:

$$k(i,j) = A + B\,(i+j) + C\,ij, \tag{5}$$

where A, B, and C are parameters the magnitude of which depends on the type of the monomer. Processes during which the relation

$$k(i,j) = A\,i^n j^m \exp(-B\,ij),$$

holds preferentially have also been analysed [19] using numerical methods for the solution of Eqn (1).

The general approach to the solution of Eqn (1) is [13] that they are convoluted with the aid of an integral transformation by introducing the so called generating function $F(s, t)$:

$$F(s,t) = \sum_i x_i(t) s^i, \tag{6}$$

where s is a parameter and t the process time.

As can be seen from Eqn (6), when the function $F(s, t)$ is expanded in series in s, the concentrations of the i-mers assume the roles of the coefficients of the corresponding powers of s. On differentiating $F(s, t)$ with respect to s for $s \to 1$, we obtain the moments of the distribution of x_i with respect to i. Eqns (1) then assume the form of a partial differential equation:

$$\frac{\partial F(s,t)}{\partial t} = -s\frac{\partial F(s,t)}{\partial s}\frac{\partial F(1,t)}{\partial s} + \frac{1}{2}\left\{\frac{\partial F(s,t)}{\partial s}\right\}^2, \tag{7}$$

which can be solved by the method of characteristics.[26]

If it is assumed that the index i in the designation of the concentrations x_i characterises not the size of the macromolecule, expressed as the number of monomer units, but its functionality, then, firstly, the relation $k(i, j)$ becomes universal, namely $k(i, j)$ is proportional to the product ij, and, secondly, Eqn (7) becomes applicable to any polycondensation system with isotypical functional groups.

The solution of Eqn (7) leads to the following result (in a parametric form):

$$F(s,t) = \sum_i x_i(0)\chi^i - \frac{t\{\sum_i i x_i(0)\chi^{i-1}\}^2}{2(1+\Phi t)}, \tag{8}$$

$$s = \chi + (\chi - \frac{\sum_i i x_i(0)\chi^{i-1}}{\Phi})\Phi t\,. \tag{9}$$

Here $x_i(0)$ is the initial concentration of molecules with i functional groups (this quantity characterises the distribution of the initial molecules with respect to the types of functionality), χ is a parameter, and Φ is the initial concentration of functional groups.

It has been shown [27] that the solution of Eqns (7) branches at a certain critical point t_c on the time scale. If $t \leqslant t_c$, then $\chi(s) = 1$ when $s = 1$. Starting from the time t_c Eqn (9) has two roots: $\chi_1(1) = 1$ and $\chi_2(1) < 1$. The critical point corresponds to the onset of gel formation, while the second root χ_2 (less than unity) characterises the sol fraction of the system. On differentiating Eqn (9) with respect to s, we obtain an expression for the critical time:

$$\frac{\partial\chi}{\partial s} = \frac{1}{1+\Phi t\left\{1 - \sum_i i(i-1)x_i(0)\chi^{i-2}/\Phi\right\}} = \frac{1}{1-\Phi t(\bar{f}_w - 2)}, \tag{10}$$

i.e.

$$\Phi\, t_c = \frac{1}{\bar{f}_w - 2}\,, \tag{11}$$

and for the critical conversion we have

$$\alpha_c = \frac{\Phi t_c}{1+\Phi t_c} = \frac{1}{\bar{f}_w - 1}\,, \tag{12}$$

where

$$\bar{f}_w = \frac{\sum i^2 x_{i0}}{\sum i x_{i0}}\,.$$

Here $\bar{f}_w$ is the weight-average functionality [3] of the initial system.

The branching of the solution of Eqn (8) may be confirmed by a general consideration of the initial Eqn (7) without resorting to its solution.[28]

Indeed, successive differentiation of Eqn (7) with respect to the parameter s leads to the appearance of a chain of equations for the distribution moments:

$$\frac{\partial F'(s)}{\partial t} = -F'(s)F'(1) + F''(s)[F'(s) - sF'(1)]\,, \tag{13}$$

$$\frac{\partial F''(s)}{\partial t} = F''(s)[F''(s) - 2F'(1)] + F'''(s)[F'(s) - sF'(1)], \tag{14}$$

etc. The primes in the equations denote the corresponding derivatives (first, second, and third) with respect to s.

When $s = 1$, the expressions in square brackets in the second terms on the right-hand sides of the equations become zero. As a result of this, the chain of equations is closed and this makes it possible to find explicitly the time variation of the distribution moments $F'(1)$, $F''(1)$, *etc*. However, as can be seen from Eqn (10), at the critical point the highest distribution moments tend to infinity. Thus the second term on the right-hand sides of the equations becomes indeterminate, because it represents the product of zero and infinity. This indeterminacy must be resolved, as it implies the appearance of the possibility of a different solution.

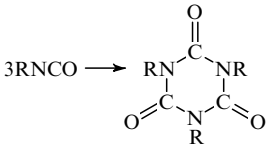
The size of the macromolecule and its functionality are unambiguously interrelated by a relation of type (3). However, in the general case, for an arbitrary initial distribution with respect

to functionality, it is not so easy to find the specific form of a relation of this kind. It is therefore reasonable, adopting the considerations put forward in a monograph,[13] to introduce a two-index definition of the chains, where one of the indices characterises the size of the macromolecule and the other its functionality. If the polycondensation takes place as a result of the interaction of different functional groups, then a larger number of indices are introduced, each corresponding to a definite type of such functional groups. Thus it is possible to describe adequately a process occurring in an arbitrarily complex system.

2. Cyclotrimerisation

It is noteworthy that reactions with participation of only isotypical functional groups are encountered extremely rarely. One of the examples is the cyclotrimerisation of isocyanates[29,30] and cyanic acid derivatives.[31] Although these reactions can be formally regarded as polycondensation with participation of isotypical groups, a wide variety of aspects of which have been well investigated, the fact that the formation of a trifunctional unit takes place in one step must introduce certain characteristic features into the process kinetics. We shall discuss this problem.

The trimerisation process represents formally the simultaneous condensation of three functional groups, *i.e.* a termolecular reaction. For example, in the case of isocyanates, it can be described as follows:



(15)

However, the reaction mechanism is fairly complex.[32] For example, the trimerisation of isocyanates takes place as a first-order reaction.[33–35] It is of first order with respect to both the isocyanate groups and the catalyst and proceeds via a complex system of equilibria. In particular, the first stage is the formation of carbamates.[35] The time law governing the consumption of functional groups is determined by this factor. However, since the functional groups are distributed between different macromolecules, the probability of the reaction of each of them (the reaction rate) must be proportional to the product of the rate of reaction of the functional groups and the product of the concentrations of the corresponding macromolecules. Thus the differential equations describing the growth of macromolecules assumes form (1), but in terms of a certain fictitious time. We shall explain this in relation to a simple example.[36]

Suppose that the functional groups Y are bound in a complex with a reagent Z:

$$Z + Y \overset{K}{\rightleftharpoons} S, \tag{16}$$

where K is the equilibrium constant.

The rate of formation of the Y–Y bond as a result of, say, the interaction of species bound in a complex has been described by the expression

$$\frac{d[YY]}{dt} = k\left(\frac{Kz_0y}{1+Ky}\right)^2, \tag{17}$$

where the symbols z and y designate the concentrations of the corresponding reactants and k is the reaction rate constant.

Evidently, depending on the product Ky, the reaction can be of both second and zero order with respect to the concentration of the functional groups y. However, if the formation reaction of the dimer X_2 is described, then the multiplier x_1 appears in brackets in the numerator on the right-hand side of the equation whilst the denominator remains the same as before. Thus the kinetic equation for the formation of the dimer assumes the form

$$\frac{d[X_2]}{dt} = k\left(\frac{Kz_0y}{1+Ky}\right)^2 x_1^2 = \frac{d[YY]}{dt}x_1^2, \tag{18}$$

or, after the introduction of the fictitious time,

$$\tau = \int \frac{d[YY]}{dt}dt, \tag{19}$$

$$\frac{d[X_2]}{dt} = kx_1^2. \tag{20}$$

A similar problem arises also in the case of reactions between an amine and an epoxide. The interaction of these reactants is also known[37,38] to proceed via a complex system of donor–acceptor equilibria. The kinetic law governing the consumption of the epoxide groups should therefore be fairly complex.[37–40] Thus the following kinetic equation has been proposed:[40]

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^{n_1} + k_2\alpha^m(1-\alpha)^{n_2},$$

where α is the degree of conversion with respect to the epoxide groups.

The simplest way of taking into account the complexity of the kinetic law consists in the use of an equation of type (19) in formulating the kinetic equations for the concentrations of macromolecules of different size, the consumption of the functional groups and the hydroxy- and epoxide groups (E) being disregarded.[41] In this case

$$\tau = k[OH][E]_0^2 t.$$

Evidently, this approach may lead to significant errors. The system of donor–acceptor interactions, which determines the complexity of the process kinetics, varies over the course of the reaction[38] because not only the initial system components, the concentration of which falls as the process proceeds, but also the reaction products, the concentration of which increases, may participate directly in the equilibrium. Thus it would be more correct to express the fictitious time in an integral form, as in Eqn (19).

The question whether the complexity of the reaction mechanism may preclude the formulation of kinetic equations in the form of Eqn (1) was apparently first posed in the study of Stanford and Stepto[42] in relation to the reaction of urethane formation. The problem was solved as follows: the application of Eqn (1) is possible if the degree of conversion is used instead of time as the independent variable. In essence, this claim agrees with Eqn (18). However, this conclusion has not been demonstrated rigorously and is more in the nature of an intuitive postulate.

When equations of type (1) are formulated for a cyclotrimerisation reaction, account is actually taken of its termolecularity,[43,44] neglecting the complexity of the kinetic law.

Since the reaction products may contain only an odd number of oligomeric units and the chain length obeys the condition

$$i = 2n + 1, \tag{21}$$

whilst the number of functional groups in the macromolecule is defined by the relation

$$f_i = n + 2, \tag{22}$$

where n is the number of ternary knots arising as a result of cyclotrimerisation, an equation of type (1) can be written as follows:[43,44]

$$\frac{dx_{2n+1}}{dt} = -(n+2)x_{2n+1}\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}(i+2)(j+2)x_{2i+1}x_{2j+1} + \quad (23)$$

$$+\frac{1}{3}\sum_{i=0}\sum_{j=0}\sum_{k=0}(i+2)(j+2)(k+2)x_{2i+1}x_{2j+1}x_{2k+1}$$

$i + j + k = n - 1$.

Eqn (23) was solved by the method of generating functions.[43]

If account is taken of the fact that the relation between the degree of polymerisation of the macromolecules i and the functionality is specified by the relation

$$f_i = \frac{i+3}{2}, \quad (24)$$

which follows from conditions (21) and (22), then the equation thus obtained assumes the form

$$\frac{\partial F(s,t)}{\partial t} = -\frac{1}{8}[sF'(s,t) + 3F(s,t)][(F'(1,t) + 3F(1,t)]^2 + \quad (25)$$

$$+\frac{1}{24}[sF'(s,t) + 3F(s,t)]^3 .$$

It has been shown that the degree of critical conversion $\alpha_c = 0.5$, which agrees with experimental data.[45–48]

An attempt has been made[44] to explain the experimentally observed[49] deviations of the observed value of α_c (0.60–0.66) by the decrease in the reactivity of the 'suspended' functional group compared with the initial reactivity, *i.e.* by the effect of substitution in the first sphere. A statistical approach was used as a method for the solution of the problem. The authors[44] found that, as the reactivity approaches zero, the degree of critical conversion tends to 0.66.

Several comments need to be made concerning the result obtained. Firstly, it has been shown[32, 33] that the reactivities of the initial and 'suspended' isocyanate groups are the same, *i.e.* that there is no substitution effect at least in the case of 1,6-hexamethylene diisocyanate. Secondly, as shown above, the gel formation point in the cyclotrimerisation of cyanate esters corresponds to 50% conversion.[45–48] Finally, it has been established[13] that the use of the statistical method of calculation in the presence of the substitution effect may lead to erroneous results. A striking confirmation of this conclusion has been obtained.[50]

The kinetic effect of substitution in the first sphere implies that, when a polycondensation reaction, which in the simplest case can be represented by the scheme

$$X_1 + X_1 \xrightarrow{k_1} X_2 , \quad (26)$$

$$X_1 + X_i \xrightarrow{k_2 f_i} X_{i+1} ,$$

$$X_i + X_j \xrightarrow{k_3 f_i f_j} X_{i+j} ,$$

is carried out, the kinetic constants are not equal to one another: $k_1 \neq k_2 \neq k_3$. As in Scheme (2), in Scheme (26) the index designates the number of monomer units in the macromolecule and f_i represents the functionality of the i-mer.

As shown in Fig. 1, the degrees of critical conversion calculated for the equilibrium polycondensation (where the results of the statistical calculation are applicable) and nonequilibrium polycondensation differ not only quantitatively but also qualitatively.

The cyclotrimerisation reaction is not of interest solely as a method of synthesis of a wide variety of thermally stable and heat-resistant polymers from a fairly wide class of monomers.[31] The fact that three functional groups entering into the composition of three different macromolecules participate in the reaction introduces definite characteristic features also into the formal features

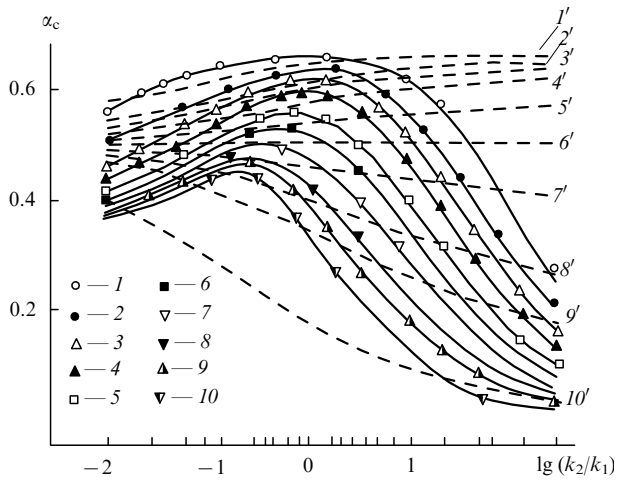


Figure 1. Dependence of the critical conversion (gel point) on the constant k_2/k_1 [see Scheme (26)] in irreversible (continuous lines) and equilibrium (dashed lines) 3-functional polycondensation.[50] The constants k_3/k_1: (*1*) and (*1′*) 0.01; (*2*) and (*2′*) 0.05; (*3*) and (*3′*) 0.1; (*4*) and (*4′*) 0.2; (*5*) and (*5′*) 0.5; (*6*) and (*6′*) 1; (*7*) and (*7′*) 2; (*8*) and (*8′*) 5; (*9*) and (*9′*) 10; (*10*) and (*10′*) 100.

of the polycondensation. In particular, the solution of Eqn (25) by the method of characteristics affords the following result for the number-average degree of polymerisation $\bar{P}_n$ and the critical conversion α_c

$$\bar{P}_n = \frac{1}{1 - 2/3\,(\bar{f}_n\alpha)}, \quad (27)$$

$$\alpha_c = \frac{1}{2(\bar{f}_w - 1)}, \quad (28)$$

where

$\bar{f}_n = \dfrac{\sum i x_{i0}}{\sum x_{i0}}$ is the number-average functionality.[3]

Evidently Eqns (27) and (28) differ from the classical equations, including Eqn (12), which characterises the critical conditions in f-functional polycondensation. This is why monofunctional monomers (for example, 1-chloro-6-hexamethylene isocyanate[33, 34]) do not terminate the network chain but play the role of a chain propagator, displacing the gel formation point towards higher conversions up to the formation of linear polymers. We shall carry out below a more thorough comparison of the cyclotrimerisation and 3-functional polycondensation processes on the basis of statistical analysis. Despite all the differences, these processes lead to the formation of 3-functional knots.

3. Polycondensation of monomers with heterotypical functional groups

The reaction between functional groups of different types (epoxide + amine, isocyanate + hydroxyl, hydroxyl + carboxyl, *etc.*) is a more common instance of polycondensation processes. If the polycondensation takes place as a result of the interaction of heterotypical functional groups and reaction between isotypical groups is impossible, then Eqn (7) is replaced by the expression

$$\frac{\partial F(\bar{s})}{\partial t} = -s_1\frac{\partial F(\bar{s})}{\partial s_1}\frac{\partial F(\bar{1})}{\partial s_2} - s_2\frac{\partial F(\bar{1})}{\partial s_1}\frac{\partial F(\bar{s})}{\partial s_2} + \frac{\partial F(\bar{s})}{\partial s_1}\frac{\partial F(\bar{s})}{\partial s_2}, \quad (29)$$

in which $\bar{s}$ is a vector, consisting in the given instance of two components, s_1 and s_2, which refer to functional groups of two types.

The solution of the above equation by the method of characteristics leads to the following result, which has also been obtained in a parametric form:

$$F(\bar{s}, t) = \sum_i (x_{ai}\chi_1^i + x_{bi}\chi_2^i) - a\,\alpha_a\,, \tag{30}$$

$$a\,\alpha_a = b\,\alpha_b\,, \tag{31}$$

$$s_1 = \frac{\chi_1 - \alpha_a \sum_i i x_{bi}\chi_2^{i-1}/b}{1-\alpha_a}, \tag{32}$$

$$s_2 = \frac{\chi_2 - \alpha_b \sum_i i x_{ai}\chi_1^{i-1}/a}{1-\alpha_b}, \tag{33}$$

$$\alpha_a = b\frac{e^{(b-a)t}-1}{be^{(b-a)t}-a}, \tag{34}$$

$$\alpha_b = a\frac{e^{(b-a)t}-1}{be^{(b-a)t}-a}, \tag{35}$$

where x_{ai} and x_{bi} are the initial concentrations of the reactants carrying i functional groups of types A and B respectively (the initial distribution with respect to types of functionality), α_a and α_b are the degrees of conversion of groups A and B respectively, a and b are their initial concentrations, and χ_1 and χ_2 are parameters.

Differentiation of Eqns (32) and (33) with respect to s_1 and s_2 makes it possible to find the critical conditions:

$$\frac{\partial\chi_1(\bar{1})}{\partial s_1} = \frac{1-\alpha_a}{1-\alpha_a\alpha_b(\bar{f}_{wa}-1)(\bar{f}_{wb}-1)}, \tag{36}$$

i.e.

$$(\alpha_a\alpha_b)_c = \frac{1}{(\bar{f}_{wa}-1)(\bar{f}_{wb}-1)}, \tag{37}$$

where $\bar{f}_{wa}$ and $\bar{f}_{wb}$ are the weight-average functionalities with respect to groups A and B respectively.

4. Certain general comments

An analytical solution of Eqn (1) with the aid of generating functions can be found in rare instances. A kinetically complex system of equations with a large set of kinetic constants is usually susceptible only to a numerical solution. A convenient method involves the creation of a system of equations for the distribution moments. The system can be characterised experimentally by the first three moments (more precisely, the number-average and weight-average molecular masses and the yield of the polymer). In order to find these parameters in the case of the polycondensation of monomers with isotypical functional groups, a system of three equations has to be solved. Additional equations for mixed second moments appear in copolymerisation. Thus the system of equations increases to 10 components. Modern computational techniques makes it possible to readily solve problems of this kind (see, for example, Dzhavadyan *et al.*[51]).

However, the applicability of the method of moments is extremely limited. In particular, the equation for the moments cannot be obtained when Flory's principle of the independence of the constants of the size of the macromolecule does not hold or when the system is such that intramolecular cyclisation cannot be neglected. In the latter case, it is impossible to convolute Eqn (1) with the aid of the method of generating functions because an additional term arises in the equation, the dependence of which on the index has a fractional exponent.[3, 12, 52] The system of equations (1) therefore has to be solved numerically. Complexities due to the incompleteness of the system then arise. Indeed, the first term on the right-hand side of Eqn (1) contains an infinite sum, which represents the overall concentration of the functional groups. In the absence of cyclisation, this quantity can be easily found by solving Eqn (13) with $s = 1$. However, as already stated above, an equation of type (13) cannot be obtained in the presence of the additional term taking cyclisation into account. Therefore the system of Eqns (1) has to be solved directly and, since it is incomplete, the problem of the termination of infinite series of equations arises.

In the case of a direct solution of the system of equations, the only reasonable approach involves the estimation of the results of the calculation as a function of the number of equations solved. When the latter increases, the accuracy of the calculation should also increase. The attainment of the instant when the result obtained ceases to depend on the number of equations implies the possibility of terminating the chain of equations.

Examples of this approach to the solution of the problem of linear polycondensation when cyclisation reactions take place may be found in a number of communications.[52–54]

In the analysis of the results of their investigation, Irzhak *et al.*[52] observed an interesting phenomenon — the attainment of a limiting yield of cyclic products (Fig. 2). Physically this effect is due to the fact that the rate of cyclisation is lower the longer the chain. Consequently, with increase in the degree of conversion and in the size of the macromolecules, the rate of cyclisation diminishes to a greater extent than the decrease in the rate of polycondensation as a consequence of the exhaustion of functional groups.

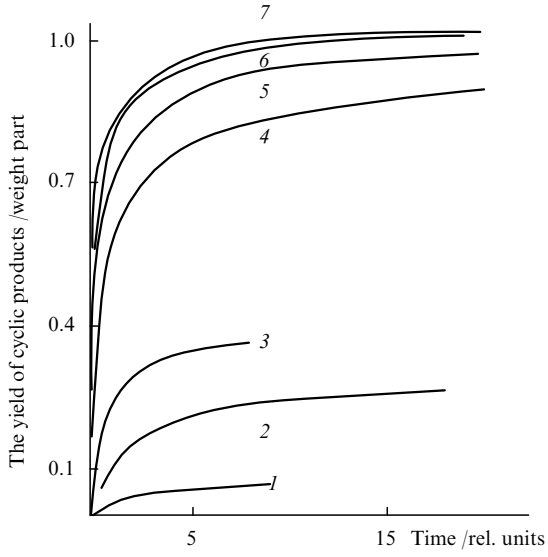


Figure 2. Kinetic curves for the accumulation of cyclic condensation products.[52] Cyclisation constant k: (*1*) 0.1; (*2*) 0.5; (*3*) 1.0; (*4*) 5.0; (*5*) 10.0; (*6*) 20.0; (*7*) 50.0.

Another example refers to the determination of the conditions for the appearance of a nonmonotonic molecular mass distribution (MMD).

Direct calculation of the concentration of chains [55, 56] made it possible to find a criterial relation between the kinetic constants of Scheme (26), which determines the nature of the MMD for a linear polymer. It has been observed [57–60] that in certain cases a polymer with a nonmonotonic 'saw tooth' MMD is formed (Fig. 3). Analysis showed [55, 56] that this is possible for a definite ratio of the kinetic constants. The condition

$$\frac{k_2^2}{k_1k_3} \leqslant \frac{2}{3}, \tag{38}$$

is necessary, while the condition

$$\frac{k_2^2}{k_1k_3} \leqslant \frac{\sqrt{2}-1}{2}. \tag{39}$$

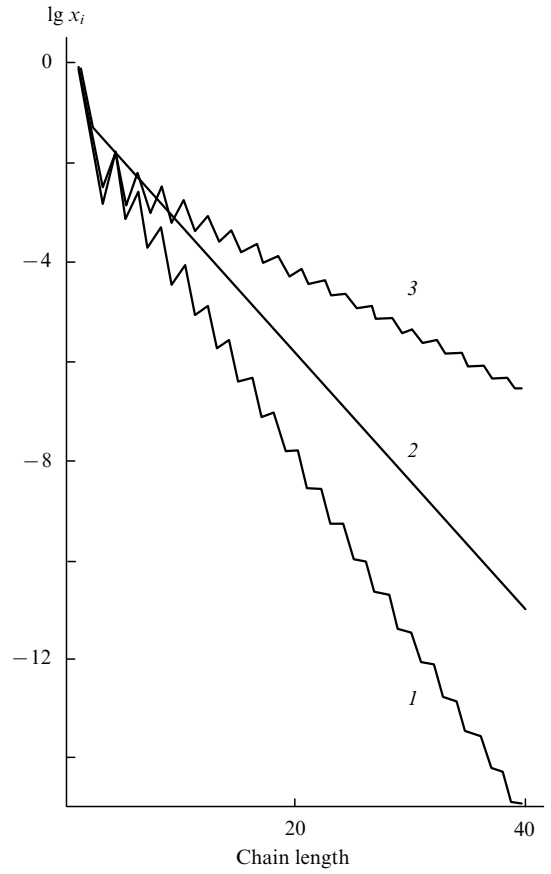


Figure 3. Numerical MMD function for a linear homopolymer [55] with the kinetic constants of Scheme (26); k_2/k_1: (*1*) 0.1; (*2*) 3.0; (*3*) 0.4; k_3/k_1: (*1*) and (*2*) 9; (*3*) 100. Degree of conversion 0.2.

is necessary and sufficient. As shown in Fig. 4, the above relations make it possible to separate the regions of existence of monotonic (region *I*) and nonmonotonic (region *II*) MMD.

Physically the nonmonotonic nature of MMD is due to the decisive role of the dimerisation rate constant. In this case, the formation of polymers with an even number of units is somewhat preferred. If a copolycondensation method is applied, then polymers with heterotypical end groups accumulate preferentially.

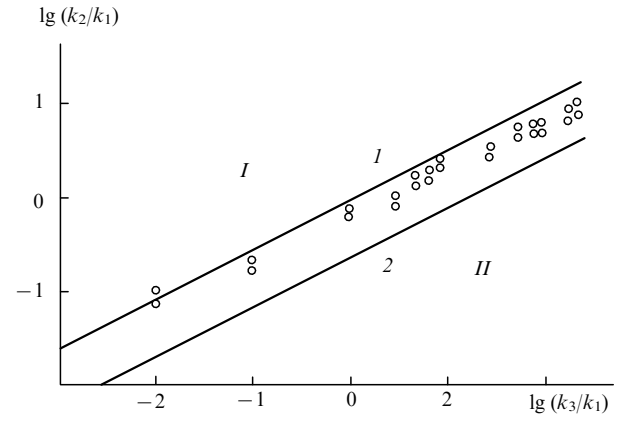


Figure 4. Regions corresponding to the existence of the monotonic (*I*) and nonmonotonic (*II*) MMD defined by the kinetic constants. Line *1* corresponds to Eqn (38) and line *2* to Eqn (39). The points in the transition region were obtained by direct calculation.

As early as 1942, Zel'dovich proposed a qualitatively different method for the analysis of an infinite system of differential equations.[61] Its essential feature is that the particle growth process is regarded as random movement in the phase space of their sizes and is described by a partial differential equation. This idea was expressed in a more concrete form in other studies.[24, 25]

In formulating partial differential equations, it is assumed that the parameter Δi is the elementary step in the size space — it is small for a small particle size, *i.e.* for the first members of the series the system of differential equations must nevertheless be regarded as discrete. In this case, the question of the number of the equation from which one should go over to a continuous system and replace the sum by an integral assumes the main importance. In the analysis of a specific kinetic scheme, it has been shown [25] that the transition from a discrete series to a continuous equation was impossible up to numbers 50 – 100. Since the result obtained was expressed in the form of a certain function of particle size, the proposed approach made it possible to establish the distribution function also in the region of large sizes, which cannot be achieved in the numerical solution of a limited number of equations (1).

In conclusion of this section, we emphasise that the subdivision of the formation reactions of polymers in terms of a kinetic feature into polymerisation and polycondensation is extremely arbitrary. Indeed, even in radical polymerisation with formation of linear polymers, chain termination may occur as a result of the recombination of radicals. This implies that, together with the unit-by-unit addition (chain propagation reaction), the chain is formed also as a result of the combination of fragments (macroradicals), which is characteristic of reactions of the polycondensation type. This effect is manifested even more explicitly in three-dimensional polymerisation of any type. The polymerisation results in the appearance of branched macromolecules carrying both active centres and 'suspended' functional groups; the reaction between them leads to the combination of macromolecules. Thus, in this case too the formation of macromolecules from fragments makes a significant contribution to the overall polymerisation process.

However, as a result of the effect of substitution in polycondensation, a considerable proportion of the monomer molecules may begin to fail to react with one another, adding instead to the polymer chains. For example, this may be the result of the process occurring in accordance with Scheme (26) if $k_2 \gg k_1, k_3$.

The principal disadvantage of the kinetic approach is the impossibility of calculating with its aid the structural characteristics of a network polymer (the gel fraction). The structure of the gel may be inferred to some extent from data obtained by analysing the sol fraction with the aid of the kinetic method [3, 62] but these conclusions are extremely indirect.

The full scale structural characteristics of the polymer, without limitations associated with the cyclisation reaction, can be found by the computer modelling of the formation reactions of polymers (see, for example, Refs 63 – 66). A satisfactory agreement between the data obtained by kinetic calculations and the results of modelling is then often attained.[67] However, in the present review we shall not be concerned with this approach, which is fairly specific as regards method and object of study.

III. Statistical methods

The structural characteristics of the polymer in any state can be established by statistical methods. A simple approach, based on the application of statistical calculations, was first proposed by Flory.[11] Combinatorial computational methods for the determination of the MMD function in the case of *f*-functional polycondensation were already used in classical studies.[11, 68] Later, in the 1960s – 1970s, a formalised and therefore simpler and elegant method, based on the theory of branching processes (see the detailed survey in the monograph of Irzhak *et al.*[3]), was proposed for such calculations. Attempts were made to use this method in order to solve virtually any polycondensation problem, including

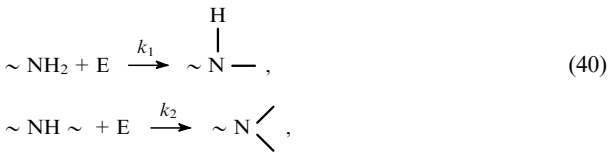
that of reactions with the effect of substitution in the first sphere and cyclisation, to which the statistical approach has been shown to be inapplicable in principle.[13, 50, 69, 70]

The statistical approaches are based on the hypothesis that the bonds formed as a result of chemical reactions, the probabilities of the formation of which can be readily calculated from the kinetic scheme, are distributed in the polymer in the most probable way. It is not difficult to calculate the concentration of any structural formation, because it is postulated that it is proportional to the probability of the occurrence of this structure. There are no limitations to the application of this approach: thus it is possible to calculate the MMD for polymer chains with any structure and complexity, the composition and structure of copolymer macromolecules, and the structure of network polymers. The attractiveness of the statistical approach frequently leads to the neglect of the problem of its applicability.

It has been shown in relation to linear polycondensation that the results of the statistical and kinetic calculations may not agree if the effect of substitution occurs.[13] The hypothesis of the limits of applicability of the statistical approach was later put forward.[70] The conditions for its applicability were fully established with the aid of the concept of bond blocks.[69, 71]

Without going into the details of the statistical method for calculations relating to the kinetics of the formation and the structure of polymers, based on the theory of branching processes, we may note that, as in the case of kinetic calculations, a type (6) generating function is analysed when it is applied. The difference consists only in the fact that algebraic and not partial differential equations are solved, which undoubtedly simplifies the problem and computational procedure.

The possibility of applying the statistical approach arises also from the fact that, as stated above, the polycondensation method of synthesis of polymers frequently presupposes the interaction of two and more monomers with heterotypical functional groups and, if the effect of substitution occurs in one of the monomers, the functional groups of the second monomer as a rule possess a constant reactivity. For example, in the interaction of epoxide monomers (usually bifunctional) with primary amines, the reactivity of the epoxide groups participating in the first and second additions remains unchanged.[36] On the other hand, the reactivities of primary and secondary amines differ. As an example, Table 1 presents the ratios of the rate constants for the reactions of the epoxide group with primary and secondary amines:[8]



(40)

E = epoxide group.

The presence of a reagent the activity of which does not change in the course of the reaction permits, as will be shown below, the application of statistical computational methods, although in a more complex form.

A thorough analysis of the approaches based on the statistical theory of branching processes has been carried out.[72] Attention is then concentrated on a multistage synthetic process in which a prepolymer with definite molecular mass characteristics and a specified number and type of functional groups is formed in the first stage. This aim is achieved by regulating the reactant ratio. If necessary, in the subsequent stages the MMD is additionally regulated and the chains are then cross-linked via the end groups. Since a large excess of one of the components is used in the initial stages in the case of such technology, the effects of substitution virtually do not affect the reaction product and such systems are susceptible to statistical analysis.[72]

The probability approach makes it possible to carry out fairly simply a comparative analysis of the cyclotrimerisation and 3-functional polycondensation process. Table 2 presents the principal initial formulae of the theory of branching processes[3] in relation to the reactions under consideration and also the dependences of the average degrees of polymerisation, number-average ($\bar{P}_n$) and weight-average ($\bar{P}_w$), and the yield of the sol fraction (s) on the degree of conversion (α). The comparison shows that, on the one hand, the use of the theory of branching processes makes it possible to obtain experimentally defined relations. On the other hand, the difference between the mechanisms of the synthesis of network polymers with seemingly identical trifunctional knots leads to a different nature of these relations, although it has been claimed,[42, 43] for example, that the result of the calculation of the gel point in the cyclotrimerisation process agrees with the Flory–Stockmayer theory.

Table 1. Relative rate constants for the second addition ($k_2/k_1 \pm 0.05$) of the epoxide group to the amine.[8]

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

Note. DDS = di(4-aminophenyl) sulfone, MDA = 4,4′-methylenediamine, MDEA = 4,4′-methylenebis(2,6-diethylaniline), MCDEA = 4,4′-methylenebis(3-chloro-2,6-diethyleneaniline).

Table 2. Formulae for the description of cyclotrimerisation and simple 3-functional polycondensation reactions.

Process characteristic	Relation	
	3-functional polycondensation	cyclotrimerisation
$F_0(s)$	$(1-\alpha+\alpha s)^3$	$(1-\alpha+\alpha s^2)^2$
$F_1(s)$	$(1-\alpha+\alpha s)^2$	$(1-\alpha+\alpha s^2)$
$\bar{P}_n$	$\frac{1}{1-3\alpha/2}$	$\frac{1}{1-4\alpha/3}$
$\bar{P}_w$	$\frac{1+\alpha}{1-2\alpha}$	$\frac{1+2\alpha}{1-2\alpha}$
s	$\left(\frac{1-\alpha}{\alpha}\right)^3$	$\left(\frac{1-\alpha}{\alpha}\right)^2$

The interest in the statistical approach has not weakened, which is indicated by the large number of reports at conferences on network polymers, in which these methods have been used to solve problems associated with the formation reactions and structure of network polymers (see, for example, Refs 73–75).

IV. Bond blocks

The method for the description of the kinetics of polycondensation reactions and the structures of polycondensation polymers in the language of bond blocks was proposed more than 15 years ago.[69, 71] Later the employment of this approach to the analysis of various polycondensation systems was described in a series of communications[55, 56, 76–79] and the characteristic features and advantages of its application were demonstrated.

A bond block is understood[71, 76, 77] as a certain structure which may belong to any macromolecule or network polymer. It is represented by a bond graph G, the edges and vertices of which

represent the bonds and atoms (units) joined by these bonds. The complete set of concentrations of all the blocks G characterises unambiguously the composition and structure of the system. In this sense, the concentration y(G) is analogous to the MMD function of the polymer.

Speaking of 'bonds', we have in mind those bonds which are formed as a result of the reaction considered. Consequently the concept of bond blocks is closely related to the chemistry of the process. Each bond is characterised by groups (units) which are joined by this bond: the bond a – a joins the units A, the bond a – b joins the units A and B, *etc*. In other words, the designations of different units have only the significance of a feature (characteristic) of the bonds.

We shall elucidate the significance of the concept of bond blocks in relation to a linear copolymer. As can be seen from Table 3, the chain may contain a large number of blocks (this number is naturally even greater in a set of chains) and larger blocks (for example, a–a–b–b) include smaller blocks (a–a, a–b, b–b, a–a–b, a–b–b). The complete set of blocks (Table 3 presents blocks containing not more than three bonds) characterises unambiguously the structure of the chain.

Table 3. The structure of the copolymer chain a–b–b–a–a–a–b–a–a–b expressed with the aid of the bond block concept.

Bond block	Number of bonds in block	Number of blocks in chain
a–a	1	3
a–b	1	4
b–b	1	1
a–a–a	2	1
a–a–b (b–a–a)	2	4
a–b–a	2	1
a–b–b (b–b–a)	2	2
a–a–a–b (b–a–a–a)	3	2
a–b–b–a	3	1
a–a–b–b (b–b–a–a)	3	1

In a linear homopolymer, the bond blocks differ only in length, *i.e*. in the number of bonds constituting the block. Therefore the relation between the bond block concentrations (y_i) and the chain concentrations (x_i) assumes an extremely simple form:

$$y_n = \sum_{i=n}^{\infty}(i-n)x_i\,. \tag{41}$$

The multiplier $(i-n)$ is equal to the number of ways in which a block comprising n bonds can be accommodated in a chain containing i units. The quantity y_0 represents the overall concentration of monomer units in the system (they include both the units in the polymer and the free monomers, *i.e*. y_0 is a constant quantity), y_1 is the overall concentration of bonds, and y_1/y_0 is the degree of conversion.

The converse relation, which follows from Eqn (41), is also valid:

$$x_i = y_{i-1} - 2y_i + y_{i+1}. \tag{42}$$

The significance of Eqn (42) is most closely related to the very concept of bond blocks. Indeed, as can be seen from Table 3, large blocks include smaller blocks. Consequently the subtraction of the concentrations y_{i-1} from the concentrations y_i yields the concentration of the terminal block of the same dimension (i) and the same operation with the concentrations of terminal blocks makes it possible to find the corresponding concentration of chains by Eqn (42).

Condition (42) may be extended to chains (macromolecules) and blocks of any configuration.

Suppose that we have a bond block of size i (i is the total number of bonds) connected to the overall polymer system *via n* terminal blocks (bonds). The concentration of blocks of the same configuration but with one 'broken' bond of type k (z_i^k) can be expressed as follows:

$$z_i^k = y_i - y_{i+1}^k = y_i(1 - y_1^k), \tag{43}$$

where y_{i+1}^k is the concentration of the block the size of which has been increased by one type k bond compared with the block of size i and y_i^k is the concentration of unit blocks of type k. The product corresponds to symbolic multiplication, *i.e*. the summation of indices (block sizes), just as in the usual multiplication the power exponents are added together.

Similarly for the concentration of blocks having the same configuration but with two 'broken' bonds, of types k and m, we obtain

$$z_i^{k,m} = z_i^k(1 - y_1^m) = y_i(1 - y_1^k)(1 - y_1^m). \tag{44}$$

Since the chain (macromolecule) containing $i + 1$ units corresponds to a block with the same configuration and size i in which all n terminal bonds are 'broken', the overall expression assumes the form

$$x_{i+1} = y_i \prod_{j=1}^{i1}(1 - y_1^j). \tag{45}$$

This postulate is illustrated below in relation to copolymer systems.

Thus there is an unambiguous reciprocal correspondence between the concentrations of bond blocks and the MMD of the chains.

It has been shown [69, 71, 76, 77] that kinetic equations can be formulated for bond blocks and the system of equations is complete in all cases: the concentration of a block of any length and complexity depends on the presence of only those blocks which do not surpass the block under consideration as regards length and complexity. This makes it possible to find by a numerical method the exact concentration of a block of any length and hence the exact concentration of the chains.

As an illustration, we shall quote data taken from Refs 76 and 77 (Table 4), where a direct calculation for the kinetic scheme (26) was carried out.

Table 4. Dependence of the relative error (δ_i) in the calculation of the concentration of chains x_i on the numerical values of the kinetic constants of Scheme (26) and on the number of equations (n) taken into account in the calculation ($k_1 = 1$).

i	k_2	k_3	δ_i			
			$n = 9$	$n = 19$	$n = 29$	$n = 49$
1	1	1	0.191	0.047	0.014	0.001
1	1	9	0.060	0.031	0.019	0.020
1	3	9	0.192	0.078	0.041	0.013
1	9	9	0.521	0.123	0.044	0.007
3	1	1	0.225	0.052	0.015	0.001
3	1	9	0.680	0.321	0.195	0.105
3	3	9	0.770	0.284	0.138	0.042
3	9	9	0.534	0.123	0.042	0.007
5	1	1	0.260	0.055	0.015	0.002
5	1	9	1.333	0.524	0.298	0.117
5	3	9	1.110	0.349	0.161	0.048
5	9	9	0.578	0.129	0.045	0.006
7	1	1	0.294	0.059	0.016	0.002
7	1	9	1.896	0.652	0.344	0.132
7	3	9	1.350	0.378	0.176	0.050
7	9	9	0.671	0.140	0.048	0.009
9	1	1	–	0.063	0.016	0.000
9	1	9	–	0.731	0.361	0.139
9	3	9	–	0.414	0.180	0.048
9	9	9	–	0.151	0.051	0.007

Table 4 presents the maximum relative errors δ_i in the calculation of x_i as a function of the number of equations taken into account in the numerical solution of the equations:

$$\delta_i = \frac{x_i - x_{i\mathrm{b}}}{x_{i\mathrm{b}}}, \tag{46}$$

where x_i is the concentration of the chains calculated on the basis of Scheme (26) and $x_{i\,\mathrm{b}}$ is the concentration of chains calculated by Eqn (42) using the concept of bond blocks and therefore independent of the number of equations considered.

The table shows that the deviations from the exact value may be considerable. At the same time, the employment of the concept of bond blocks makes it possible to find exact concentrations for any number of equations.

The possibility of the exact calculation of the bond block concentrations plays a most important role in the determination of the structures of copolymers. Indeed, the modern experimental methods make it possible to characterise the structure of a copolymer solely in terms of the number (concentrations) of blocks of not too great a size — diad, triad, tetrad.[12,72] On the other hand, the kinetic calculation of the structure in the usual version requires the consideration of copolymer chains of all possible configurations. This creates unsurmountable computational difficulties. Furthermore, for a sufficient length and a considerable number of components, the set of possible chain types becomes very large, comparable to the Avogadro number. This means that the number of molecules of each type is insufficient to ensure the operation of the statistical Law of Mass Action. I M Lifshits drew attention to this factor for the first time at one of the seminars on polymer physics at Moscow State University. This difficulty disappears when the concept of bond blocks is used in the calculations.

In the formulation of kinetic equations for the calculation of the concentrations of bond blocks, an extremely simple rule is employed: all possible ways in which the given structure can be formed are added together. The concept of the terminal block, which is an extension of the concept of a functional group, therefore assumes key importance in the consideration of kinetic problems in the language of bond blocks. Indeed, as a result of the reaction between functional groups, one bond or, in other words, a bond block of unit length is formed. If a functional group with units attached to it (one, two, and more) is considered, then one may be dealing with the formation of a larger structure, *i.e.* a larger bond block. For example, the reaction between the functional groups $\sim$a + $\sim$b leads to the appearance of the bond $\sim$a–b$\sim$. The following reactions participate in the formation of the block $\sim$aabba$\sim$:

$$\begin{aligned} &\sim\mathrm{a} + \mathrm{abba}\sim, \\ &\sim\mathrm{aa} + \mathrm{bba}\sim, \\ &\sim\mathrm{aab} + \mathrm{ba}\sim, \\ &\sim\mathrm{aabb} + \mathrm{a}\sim. \end{aligned} \tag{47}$$

The formation of terminal blocks with a complex structure, for example $\sim$aabb, is also associated with the occurrence of a series of reactions:

$$\begin{aligned} &\sim\mathrm{a} + \mathrm{abb}, \\ &\sim\mathrm{aa} + \mathrm{bb}, \\ &\sim\mathrm{aab} + \mathrm{b}, \end{aligned} \tag{48}$$

etc. However, as can be seen, all the reactions proceed with participation of reactants the structure of which is not more complex than that of the bond block being sought. Thus the system of equations is closed and the experimental requirements determine in relation to which blocks the kinetic problem is to be solved. This in fact constitutes the advantage of the approach based on the concept of bond blocks.

Analysis of the structure of the system of kinetic equations describing the bond block accumulation processes[71,77] showed that it may be subdivided into groups of equations in such a way that the concentrations of the structures described by these equations are susceptible to direct calculation. The concentrations of larger structures are found by probability computational methods. If the minimum size of a block corresponds to one bond, we arrive at the case of the absolute application of statistical methods. It is almost always possible to identify such structures of minimum size from which any structural formations, however large and complex, are made up. The use of the concept of bond blocks makes it possible to simplify still further the solution of kinetic problems, since it becomes unnecessary to formulate differential equations for blocks of all sizes: it is sufficient to solve these problems for elementary blocks, using statistical calculations for larger formations. In other words, this method combines the advantages of both the kinetic and the statistical approaches.

It was found that the criterion of 'being elementary'[71,77] is the absence of the influence of the effects of substitution on the reactivity of the functional groups on the other hand, within an 'elementary' block, these effects do occur. We shall elucidate this postulate by a simple example.

Suppose that a copolycondensation reaction takes place between units carrying functional groups of types A and B and there is a possibility of both A + A and A + B interactions, on the one hand, and B + B interactions, on the other, the effect of substitution in the first sphere being observed in groups A, while in groups B there is no such effect. The reaction results in the formation of blocks of different structure:

$$\sim\mathrm{a...a}\sim,\ \sim\mathrm{a...ab}\sim,\ \sim\mathrm{ba...ab}\sim,\ \sim\mathrm{b}\sim.$$

In order to calculate blocks of all these types, one has to begin with differential equations describing their formation. However, in more complex blocks, for example $\sim$ba...abbba...ababbabb$\sim$, it is possible to differentiate smaller blocks $\sim$ba...b$\sim$, $\sim$b$\sim$, $\sim$bab$\sim$, which are 'elementary', and from which the entire block is constructed in accordance with the laws of probability. If, as in the case of homopolycondensation in the presence of effects of substitution, it is not possible to differentiate such elementary blocks, the statistical approaches are found to be completely unsuitable.[13]

As an illustration, we shall calculate the MMD for the chains of a polymer formed as a result of the reaction between the monomers AA and BB, the substitution effect being observed in the former but not in the latter. This scheme corresponds, for example, to the reactions between phenylene diisocyanate (AA) and a diol (BB) and between an amine (AA) and a diepoxide (BB).

The formation reactions of the corresponding bond blocks can be represented in the form

$$\begin{aligned} &\mathrm{a} + \mathrm{b} \xrightarrow{k_1} \sim\mathrm{a}, \\ &\sim\mathrm{a} + \mathrm{b} \xrightarrow{k_2} \sim\mathrm{a}\sim. \end{aligned} \tag{49}$$

Component a includes functional groups belonging to the initial monomer AA and $\sim$a is a terminal block of the polymer chain. Since there is no substitution effect in group B, there is no need to differentiate groups B belonging to different molecules. For this reason, b includes any terminal blocks belonging both to the initial monomer BB and to polymer chains. In the general case, the kinetic constants are not equal to one another and

$$\frac{k_2}{k_1} = r \neq 1.$$

The solution of the system of equations describing scheme (49) leads to the following relations:

$$\alpha_A = 1 - \frac{e^{-r\tau} - (r-1)e^{-2\tau}}{2-r},$$

$$\alpha_B = Q\,\alpha_A,$$

$$p_{AB} = 2\frac{e^{-r\tau} - e^{-2\tau}}{2-r}, \qquad (50)$$

$$p_{BA} = 2\,\alpha_B(1-\alpha_B),$$

$$p_{BAB} = \frac{2rQ}{2-r}\left(\frac{1-e^{-r\tau}}{r} - \frac{1-e^{-2\tau}}{2}\right).$$

Here α_A and α_B are the conversions of the corresponding groups, Q is the initial ratio of the functional groups A and B, p_{AB}, p_{BA}, and p_{BAB} are the probabilities (relative concentrations) of the terminal bond blocks ~ba~ and ~ab and of the block ~bab~ (including both terminal and inner blocks) respectively, and τ is the fictitious time:

$$\tau = \int k_1 b\,dt. \qquad (51)$$

The concentrations of the chains AA, BB, AB, ABA, and BAB are calculated on the basis of the kinetic scheme. The concentrations of larger chains are determined with the aid of relations, analogous to Eqn (42), namely

$$x\{(BA)_iB\} = y\{(BA)_iB\} - 2y\{A(BA)_iB\} + y\{A(BA)_iBA\}, \qquad (52)$$

$$x\{A(BA)_iB\} = y\{A(BA)_iB\} - y\{BA(BA)_iB\} - y\{A(BA)_iBA\} + y\{BA(BA)_iBA\},$$

$$x\{A(BA)_iBA\} = y\{A(BA)_iBA\} - 2y\{BA(BA)_iBA\} + y\{BA(BA)_iBAB\}.$$

The concentrations of the blocks $y\{...\}$ are determined in accordance with the probability relations:

$$y\{(BA)_iB\} = (y\{BAB\})^i = (p_{BAB})^i, \qquad (53)$$

$$y\{A(BA)_iB\} = (y\{BAB\})^i\,y\{BA\} = (p_{BAB})^i\,\alpha_B,$$

$$y\{A(BA)_iBA\} = (y\{BAB\})^i\,(y\{BA\})^2 = (p_{BAB})^i\,(\alpha_B)^2.$$

Thus

$$x\{(BA)_iB\} = B_0\,(1-\alpha_B)^2\,(p_{BAB})^i, \qquad (54)$$

$$x\{A(BA)_iB\} = 2B_0\alpha_B\left(1 - \frac{p_{BAB}}{\alpha_B}\right)(1-\alpha_B)\,(p_{BAB})^i,$$

$$x\{A(BA)_iBA\} = B_0\,(\alpha_B)^2\left(1 - \frac{p_{BAB}}{\alpha_B}\right)^2(p_{BAB})^i.$$

When the equality of the kinetic constants ($r = 1$) holds then $p_{BAB}/\alpha_B = \alpha_A$ and Eqns (54) lead to simple probability formulae.

The indices [subscripts] correspond to the type of end groups in the chain the length of which i is equal to the number of BA bonds contained in it.

Figure 5 presents the concentrations of the BAB molecules found in three ways: by the direct kinetic calculation, by the probability calculation employing kinetic data on the conversion of groups A and B (α_A and α_B respectively), and by the calculation employing bond blocks (the {BAB} block). Evidently, in the absence of the substitution effect (when the constants are equal), all three methods yield concordant results. If the rate constants for the first and second additions are different, only the results of the direct kinetic calculation and the calculation based on the concept of bond blocks agree. The statistical calculation leads to an incorrect result.

The concentration of small molecules can be readily calculated. Problems arise with larger structures.

The algorithm of the procedure for the description of the structure of a network polymer, formed, for example, in the interaction of a diepoxide with a diamine [Eqn (40)], reduces in the general case to the following.

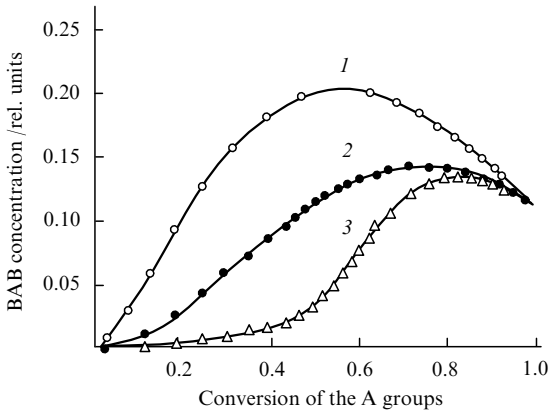
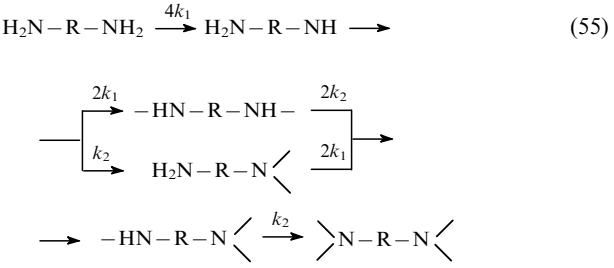


Figure 5. Variation of the concentration of the molecules BAB during the AA + BB copolycondensation process occurring in accordance with Scheme (49): (*1*) direct kinetic calculation (curve) and calculation based on bond blocks (symbols) with $r = 10$; (*2*) kinetic calculation with $r = 1.0$ and statistical calculation with $r = 10.0$, 1.0, and 0.1 (curve) as well as calculation based on bond blocks with $r = 1.0$ (symbols); (*3*) direct kinetic calculation (curve) and calculation based on bond blocks (symbols).

1. The bond block concentrations are calculated kinetically in conformity with Scheme (55) (on the assumption that the substitution effect occurs only for the amine but not for the epoxide oligomer).



(55)

2. The statistical calculation is performed for any structural fragments bearing in mind that the $H_2N-R-NH_2$ molecule enters exclusively into the sol fraction of the polymer system, $H_2N-R-NH-$ is the end group of the chains, and $-HN-R-N\langle$ and $\rangle N-R-N\langle$ are network nodes.

Thus the use of bond block data in the calculation makes it possible to solve structural problems effectively.

V. Conclusion

We have endeavoured to show that modern methods for the solution of Eqn (1) make it possible to answer all or the majority of formal kinetic questions. Naturally, the most important predictive problems, namely how and under what conditions the process should be carried out in order to obtain a polymer with a specified structure, remained outside the scope of our review. Its subject was only the establishment of a direct relation between the structure of the polymer and the kinetic parameters of the polycondensation process. Evidently, the problems of reactivity should be considered from completely different standpoints. This constitutes another field of science. If, as stated above, real processes are complicated by a possible change in the physical state of the system in the course of the reaction, which alters not merely the numerical values of the kinetic constants but the very process mechanism, then evidently the attempts at prediction become extremely problematical. Certain approaches to the solution of this problem have already been developed to some

extent (for example, attempts to take into account the vitrification of the system are known), but they are either too formal and require physical justification or are speculative and require a broad experimental test.

Reactions between rigid-chain macromolecules,[80, 81] particularly in liquid crystal polymer systems,[82, 83] carried out in order to obtain network polymers from them are nowadays of special interest. In this case the low flexibility of the chains — the carriers of functional groups — necessitates the formulation of more general questions: about the nature of the collisions of the reaction centres, about the influence of chain length on the reactivity, about the influence of the organisation of the medium on the kinetic parameters of the processes, *etc*. These problems still await their investigators.

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