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Concept of bond blocks in the kinetics of polycondensation processes

V. I. Irzhak, M. L. Tai*), N. I. Peregudov, and T. F. Irzhak

Institute of Chemical Physics, Russian Academy of Science
*) Institute of Applied Mathematics and Cybernetics, Nizhny Novgorod University, Russia

Abstract: The concept of bond blocks has been suggested for description of the formation kinetics and structure of polymer networks. The full set of concentrations of bond blocks provided full description of the polymer system. The relations between the concentrations of bond blocks and of macromolecules are derived. The law of mass action for the bond blocks is formulated. It is shown that in certain cases it is possible to replace part of differential equations describing the kinetics by the algebraic ones. Examples of applications of the concept of bond blocks are given.

Key words: Polycondensation processes – polymer structure – kinetics of polymer formation – bond blocks

Introduction

The conversions in polymer systems resulting from formation, rupture and exchange of chemical bonds are usually described as interactions between macromolecules. Taking into account that the structure of polymer is determined not only by the chemical nature of monomer units but also by bonds which link them together, the kinetic description based on the bond block concept seems to be preferable. The great significance of the bond quality is seen from the concept of isomers (tail-to-tail, tail-to-head addition, stereoisomers, and so on), i.e., bonds can be different at the same chemical composition. It is obvious that for intrachain reactions (reactions between side groups of chain, functional groups of network polymer) the description of chemical conversion in polymer systems as interaction between macromolecules is insufficient. The approach to bond as the object of chemical conversion is more suitable here. The description of chemical reactions in polymers in terms of bond conversion becomes still more significant because of the appearance of some experimental methods (NMR of high resolution, pulsed NMR) that enable one to determine concentrations of bonds [1] and of certain structural units in polymer networks (branching points, network chains, dangling chains) [2]. All this makes formulation of the kinetic theory of chemical conversion of bonds and bond blocks (BB) of certain structures a topic of much interest.

The mathematical language was developed about 10 years ago [3, 4] for the description of self-assembly models of ordered structures. Its application to polymer systems was demonstrated in our works [5, 6].

In this paper, we would like to summarize some results obtained earlier, to give the general concept of BB, to introduce the definition of the BB concentration, to show their relations to the concentrations of the components of reaction system (macromolecules), to apply them to the description of the kinetics of chemical conversion in polymer systems.

Definitions

The BB of any structure is the configuration which can be represented as a connected graph *G* independent of the macromolecuar structure in which it is located. Edges and vertexes correspond to bonds and units of polymer. Concentration of G is denoted as $y\{G\}$. The complete set of concentrations of all G characterizes composition and structure of the system unambiguously. In this sense the function $y\{G\}$ is analogous to MWD function of linear polymer.

In polymer systems consisting of definite chains there is reciprocal correspondence between the concentrations of BB and macromolecules. It is easier to grasp in the relatively simple case of linear chains of homopolymer. In this case BB are determined unambiguously by their size: G_n consists of n bonds linking $n + 1$ monomer units in any chains. If we characterize the system by a set of x_j concentrations of j-mers. the concentration y_n of the BB G_n will be:

$$y_n = \sum_{j=n}^{\infty} (j - n) \cdot x_j \tag{1}$$

Factor $(j - n)$ is the number of various realizations of G_n on the chains with j monomer units. For example, the j-mer contains only one BB with length $j - 1$, two BB with length $j - 2$, and so on.

When $n = 0$,

$$y_0 = \sum_{j=1}^{\infty} j \cdot x_j$$

is the concentration of all monomer units in the system.

When $n = 1$,

$$y_1 = \sum_{j=1}^{\infty} (j - 1) \cdot x_j$$

is the concentraton of the bonds in all polymer chains.

Equation (1) determines the BB concentrations via linear chains concentration x_j, and it leads to:

$$x_j = y_{j-1} - 2 \cdot y_j + y_{j+1} \tag{2}$$

Equation (2) expresses x_j via y_j. Therefore, there is reciprocal correspondence between the concentrations of BB and the components (macromolecules) of the polymer system.

BB's in copolymers, branched and network polymers cannot determined unambiguously by the bond number, as was possible for homo-polymers, but rather, it is necessary to list all types of bonds in the block.

Each bond in copolymers is determined unambiguously by the types of monomer units it couples. Thus, the BB structure is described by successive enumeration of all monomer units comprised by the block. $G\{a_{i1} a_{i2} \ldots a_{in} a_{i,n+1}\} = G\{a_{ij}\}$. Here, the first index denotes a type of monomer unit and the second index denotes the place number. $j = 1, 2, \ldots n, n + 1$, if G consists of n bonds and $n + 1$ units.

The systems of equations describing the linear copolymers are analogous to (1)–(2) but are more complicated.

$$y\{a_{ij}\} = \sum x\{a_{kl} a_{ij} a_{mn}\} \; . \tag{3}$$

where summation is made for all k, m (types of monomer units) and l, n (place in copolymer chains).

$y\{a_{ij}\}$ and $x\{a_{ij}\}$ are concentrations of BB and chains, correspondingly.

$$x\{a_{ij}\} = y\{a_{ij}\} - \sum a_{k0} a_{ij} - \sum a_{ij} a_{k,n+2} + \sum a_{k0} a_{ij} a_{k,n+2} \; , \tag{4}$$

where summation is produced for all k, i.e., types of monomer units taking places before (0) and after $(n + 2)$ the j-block. We remind that block consisting of n bonds contains $n + 1$ monomer units.

In the case of branched polymers the situation is the same: branching and unbranching units can be considered as comonomer ones. But for arbitrary graphs general equations describing the relationship between the concentration of components and BB becomes too cumbersome: one must include additional information about neighbor graphs, set of edges neighboring the considered edge and their division into subsets. Therefore, we shall not analyze here these equations. However, the logic of formulating the equations is the same as in the case of copolymer systems.

The notion of chain concentration has no meaning for network polymers (excluding sol-fraction). In this case we can characterize the system using the set of BB's concentrations and this method is the only exhaustive one.

The law of mass action

Analysis of kinetic problems of polymer chemistry allow us to estimate degree of profit of the concept of BB. Let us consider the simplest case of linear homopolymer.

The general kinetic equation of linear chain polycondensation process has the following form:

$$dx_j/dt = k \cdot \left[1/2 \cdot \sum_{i=1}^{j-1} x_i \cdot x_{j-i} - x_j \cdot \sum_{i=1}^{\infty} x_i \right] . \quad (5)$$

where k is the rate constant of reaction of bond formation in an ideal system.

Equation (5) is based on the law of mass action: the components of the system (macromolecules) enter into the reaction due to real collisions. In this sense, BB's are not true reagents. At the same time, using (1) and (2), we can obtain from (5):

$$dy_n/dt = k/2 \cdot \sum_{j=0}^{n-1} (y_j - y_{j+1}) \cdot (y_{n-j-1} - y_{n-j}) . \quad (6)$$

Note that difference $(y_n - y_{n+1})$ is equal to the concentration of all chains containing G_n.

$$y_{ne} = y_n - y_{n+1} = \sum_{j>n}^{\infty} x_j \quad (7)$$

y_{ne} is the concentration of end blocks, i.e., blocks one end of which is limited of breaked bond.

The physical meaning of Eq. (7) is clear: the rate of the BB formation is proportional to the concentration product of the end BB from which one can construct the particular BB. Equation (7) expresses the law of mass action in terms of BB concentrations. Formally, BB's behave like acting components obeying the law of mass action.

It is seen that system (7) is simpler than system (6), because it is complete, i.e., the concentration y_n depends only on y_j whether $j \le n$:

$$dy_0/dt = 0$$

$$dy_1/dt = k/2 \cdot (y_0 - y_1)^2$$

$$dy_2/dt = k \cdot (y_0 - y_1) \cdot (y_1 - y_2) . \quad (8)$$

and so on.

Analysis shows [3] that solutions of the set of Eq. (7) satisfy the expression (9) at any moment of time provided that it was satisfied at some moment of time:

$$y_n/y_0 = (y_1/y_0)^n . \quad (9)$$

Since, at $t = 0$ $y_n = 0$ $(n = 1, 2, \ldots)$, the above condition is fulfilled. Therefore, we can use algebraic equations (9) instead of differential ones and we have to solve only lone differential equation for y_1. This result is the basis on which the statistical approach can be developed.

The statistical method of the calculation of macromolecule concentration is known to be applicable only to the case of ideal systems or, in other words, where the rate constants do not depend on the formation of neighbor bonds ("neighbor effect") [5.6]. The BB concept allows one to analyze systems in which the "neighbor effect" takes place.

Consider the following system:

$$x_1 + x_1 \xrightarrow{k_1} x_2$$

$$x_1 + x_i \xrightarrow{k_2} x_{i+1},\ i = 2, 3, \ldots .$$

$$x_1 + x_j \xrightarrow{k_3} x_{i+j},\ i,j = 2, 3, \ldots . \quad (10)$$

The set of kinetic equations is:

$$dx_1/dt = -k_1 \cdot x_1^2 - k_2 \cdot x_1 \cdot \sum_{j=2}^{\infty} x_j$$

$$dx_2/dt = 1/2 \cdot k_1 \cdot x_1^2 - k_2 \cdot x_1 \cdot x_2 - k_3 \cdot x_2 \cdot \sum_{j=2}^{\infty} x_j \quad (11)$$

$$dx_i/dt = k_2 \cdot x_1 \cdot x_{i-1} - k_2 \cdot x_1 \cdot x_i - k_3 \cdot x_i \cdot \sum_{j-2}^{\infty} x_j + k_3/2 \cdot \sum_{j-2}^{j-1} x_j \cdot x_{i-j}$$

for $i = 3, 4, \ldots$

System (11) leads to:

$$dy_1/dt = k_1/2 \cdot (y_0 - y_1)^2 + (y_1 - y_2) \cdot \{(k_2 - k_1) \cdot (y_0 - y_1) + 1/2 \cdot (k_1 - 2 \cdot k_2 + k_3) \cdot (y_1 - y_2)\}$$

$$dy_i/dt = (k_2 - k_3) \cdot (y_{i-1} - y_i) \cdot (y_0 - 2y_1 + y_2) + k_3/2 \cdot \sum_{j=0}^{i-1} (y_j - y_{j+1}) \cdot (y_{i-j-1} - y_{i-j}) \quad (12)$$

for $i = 2, 3, \ldots$

It is seen that system (12) is simpler than (11) and y_i depends on y_j at $j \le i$. At the same time, system (12) is more complicated than (7). The first term in the righthand side of equations for dy_i/dt accounts for the deviation of the system (10) from the ideal one. It is not possible in this case to obtain equations analogous to (9) and to use the statistical approach.

However, if $k_2 = k_3$ then

$$y_i/y_0 = (y_2/y_0)^{i-1} ,$$

where y_2 is determined by Eqs. (12) for y_1 and y_2.

Therefore, the statistical approach turns out to be applicable in this case, but G_2 is the simplest BB which must be obtained by solving Eq. (12).

Use of BB′ concept for copolymers is considered an example of a binary copolymer with monomer units of two types, A and B. In expression of BB $G(a_{ij})$ index i has two meanings: a_{1j} is A and a_{2j} is B. j denotes the place of corresponding monomer units in BB: $j = 1, 2, \ldots, n$.

There are three types of bonds only: *A–A*, *A–B* and *B–B*. If the rate constants of bond formation k(AA), k(AB) and k(BB) do not depend on the presence of neighbor bonds, i.e., the "neighbor effect" is absent, the system of differential equations will be:

$$dy(a_{ij})/dt = \sum_{m=1}^{n} k(m, m+1) \cdot y_e(a_{im}) \cdot y_e(a_{i,m+1}) \qquad (13)$$

$k(m, m+1)$ is the rate constant of $a_{im} - a_{i,m+1}$ bond formation,

$$y_e(a_{im}) = y(a_{i,m}) - \sum_{a_{i,m+1}} y(a_{ij} a_{i,m+1}) ,$$

$$j = 1, 2, \ldots, m;$$

$$y_e(a_{i,m+1}) = y(a_{i,m+1}) - \sum_{a_{im}} y(a_{im} a_{i,j}) ,$$

$$j = m+1, \ldots, n, n+1; \qquad (14)$$

Equations (14) express the relations between concentrations of end blocks y_e and BB y. Here, summation is made on all unit types (A and B) taking places on ends of the blocks, i.e., m and $m + 1$.

Analysis of the system (13) shows that it has a property expressed by the equation analogous to (9):

$$y(a_{ij})/y(a_i) = \prod_{m=1}^{l} y(a_{im} a_{i,m+1})/y(a_i) , \qquad (15)$$

where $y(a_i)$ are [A] or [B], i.e., the concentrations of corresponding units in the system,

$$dy(\mathrm{AA})/dt = k(\mathrm{AA}) \cdot [a(\mathrm{A}) - y(\mathrm{AA}) - y(\mathrm{AB})]^2$$

$$dy(\mathrm{AB})/dt = k(\mathrm{AB}) \cdot [a(\mathrm{A}) - y(\mathrm{AA}) - y(\mathrm{AB})] \cdot [a(\mathrm{B}) - y(\mathrm{AB}) - y(\mathrm{BB})]$$

$$dy(\mathrm{BB})/dt = k(\mathrm{BB}) \cdot [a(\mathrm{B}) - y(\mathrm{AB}) - y(\mathrm{BB})]^2 ,$$

Equations (15) are valid at any moment of time, provided that they are valid at $t = 0$. Thus, Eqs. (15) are the basis on which the application of the statistical approach to ideal copolymer systems can be developed. It is obvious that this result does not depend on the number of copolymer units and bond types.

The investigation of kinetic equations describing the process of copolymer formation [5–8] has shown that the statistical approach can be used in the case of some nonideal systems if BB can be divided into subblocks, provided that the bond formation within such subblocks feels the "neighbor effect", but outside the subblock the bonds are formed independently, without "neighbor effect". Due to their autonomy, these subblocks have been named "nests" [4, 6]. The use of this term is justified because the system of corresponding differential equations is divided in a similar manner to give a number of subsets.

As an example examine the process of alternative copolymer formation with the "neighbor effect in the first sphere", i.e., where the monomer unit A, whose reactivity depends on the "neighbor effect", can react only with the monomer unit B, the reactivity of which is independent of the "neighbor effect".

In this case the system involves the following components: $\mathrm{A(BA)}_m\mathrm{B}$, $\mathrm{B(AB)}_m$, $\mathrm{A(BA)}_m$, $m = 0, 1, \ldots$. At any moment of time the process is characterized by a set of chain concentrations:

$$x\{\mathrm{A(BA)}_m\mathrm{B}\},\ x\{\mathrm{B(AB)}_m\},\ x\{\mathrm{A(BA)}_m\}$$

or by a set of BB concentrations:

$$y\{\mathrm{A(BA)}_m\mathrm{B}\},\ y\{\mathrm{B(AB)}_m\},\ y\{\mathrm{A(BA)}_m\} .$$

The rate constants of the bond formation satisfy:

$$k\{\mathrm{A,A}\} = k\{\mathrm{B,B}\} = 0$$

$$k\{\mathrm{A,B}\} = k\{\mathrm{A,B(AB)}_m\} = k\{\mathrm{A,B(AB)}_m\mathrm{A}\} = k_1$$

$$k\{(\mathrm{AB})_m\mathrm{A}, (\mathrm{BA})_n\} = k\{(\mathrm{AB})_m\mathrm{A}, \mathrm{B}(\mathrm{AB})_n\}$$
$$= k\{\mathrm{B}(\mathrm{AB})_m\mathrm{A}, (\mathrm{BA})_n\} = k\{\mathrm{B}(\mathrm{AB})_m\mathrm{A}, \mathrm{B}(\mathrm{AB})_n\}$$
$$= k_2$$

Under these assumptions $y\{\mathrm{A}\}$ and $y\{\mathrm{B}\}$ are constant; $y\{\mathrm{AB}\}$ and $y\{\mathrm{BAB}\}$ satisfy complete system of equations:

$$dy\{\mathrm{BAB}\}/dt = 2\cdot k_2\cdot[y\{\mathrm{B}\} - y\{\mathrm{AB}\}]\cdot[y\{\mathrm{AB}\} - y\{\mathrm{BAB}\}]$$
$$dy\{\mathrm{AB}\}/dt = [y\{\mathrm{B}\} - y\{\mathrm{AB}\}]\cdot f[y\{\mathrm{AB}\}, y\{\mathrm{BAB}\}] \tag{16}$$

where

$$f[y\{\mathrm{AB}\}, y\{\mathrm{BAB}\}] = k_1\cdot[y\{\mathrm{A}\} - y\{\mathrm{AB}\}] + (k_2 - k_1)\cdot[y\{\mathrm{AB}\} - y\{\mathrm{BAB}\}]$$

System (16) can be integrated to give the equation for $y\{\mathrm{ABA}\}$:

$$dy\{\mathrm{ABA}\}/dt = 2\cdot[y\{\mathrm{AB}\} - y\{\mathrm{ABA}\}]\cdot f[y\{\mathrm{AB}\}, y\{\mathrm{BAB}\}] \tag{17}$$

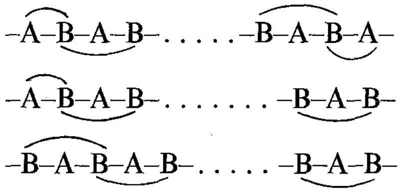
Similarly, from $m \geq 2$ BB concentrations $y\{\mathrm{AB})_m\}$ and $y\{\mathrm{B}(\mathrm{AB})_m\}$ satisfy a complete subsystem of equations, and, together with the concentrations of shorter BB, determine the concentrations $y\{(\mathrm{AB})_m\mathrm{A}\}$. Therefore, obtaining BB concentrations reduces to successive solution of subsystems for each $m = 1, 2, \ldots$.

As a consequence of such property of the system investigated, i.e., of the possibility of dividing the whole set of equations on the complete subsets, system (18) is analogous to (9) and (15):

$$y\{(\mathrm{AB})_m\mathrm{A}\}/y\{\mathrm{B}\} = [y\{\mathrm{AB}\}/y\{\mathrm{B}\}]^2\cdot[y\{\mathrm{BAB}\}/y\{\mathrm{B}\}]^{m-1}$$
$$y\{\mathrm{B}(\mathrm{AB})_m\}/y\{\mathrm{B}\} = [y\{\mathrm{BAB}\}/y\{\mathrm{B}\}]^m$$
$$y\{(\mathrm{AB})_m\}/y\{\mathrm{B}\} = [y\{\mathrm{AB}\}/y\{\mathrm{B}\}]\cdot[y\{\mathrm{BAB}\}/y\{\mathrm{B}\}]^m\,. \tag{18}$$

Equations (18) are satisfied at any moment of time, provided that they are valid at $t = 0$.

Equations (18) correspond to the following division of BB into a set of subblocks ("nests"):



Similar result can be obtained for some other copolymer systems [6]. There is only one condition for this: it should be possible to divide BB into the "nests," i.e., a set of subblocks linked together by independent bonds. In the above case the "nest" is a BAB block. It is necessary to emphasize that the smaller the number of bonds in the subblock, the simpler it is to use the relationship (18).

Consider the application of the law of mass action to network polymer. For an ideal system the network structure can be presented as a tree, designated by graph G, with corresponding set of edges $V(G)$. The concentration $y\{G\}$ is described by the system of differential equations:

$$dy\{G\}/dt = \sum k\{v\}\cdot y\{G_e(v)\}\cdot y\{G_e(\bar{v})\}\,, \tag{19}$$

where $k(v)$ is the rate constant of v bond formation (v links the units α and β together).

$G_e(v)$ and $G_e(\bar{v})$ are the end BB obtained from the block G after v bond rupture, moreover, units α and β belong to blocks $G_e(v)$ and $G_e(\bar{v})$, respectively.

Let $v(\alpha)$ be the bond set formed by monomer unit α in $G(v)$, then,

$$y\{G_e(v)\} = y\{G(v)\} - \sum_{v_1 \in v(\alpha)} y\{G(v) + v_1\}\,.$$

Equation for $G_e(\bar{v})$ is similar.

Obviously, BB concentrations are expressed in terms of concentrations of blocks in which bond number is less than the one in G. Besides, system (19) is divided into a number of complete subsystems. The simplest subsystem describes the change in the concentration of BB consisting of single bonds, the second subsystem describes the change in the concentration of BB consisting of two bonds, and so on. Therefore, as it was in cases of linear homo- and copolymers, system (19) can be solved by succesive solution of these equations starting from the simplest ones. The fact that it is possible to write equations analogous to (9) and

(15) is the immediate consequence of the above property of the system (19): one can express the BB concentration as a product of concentrations of simpler blocks. The principle according to which BB are divided into subblocks is the same as in the case of linear copolymers, but the "nests" in network polymers have more complicated topological structure.

Solving of kinetic problems with using BB's concept

Systems of equations used for processes of polymer formation are infinitive. Therefore, their solving demands application of particular methods. One of them is the method of generating functions [7, 8]. For instance, system (5) can be transformed to differential equation for function

$$F_x(q) \equiv \sum q^n \cdot x_n:$$

$$dF_x(q)/dt = -F_x(q) \cdot F_x(1) + 1/2 \cdot F_x^2(q)\,, \qquad (20)$$

which is solved very easily and, therefore, allows us to find function of MWD x_n.

The same method gives the possibility to solve the system (6) using analogous generating function:

$$F_y(q) \equiv \sum q^n \cdot y_n$$

$$dF_y(q)/dt = \{q \cdot y_0 - F_y(q) \cdot (1-q)\}^2/2q\,. \qquad (21)$$

In this case the obtained equation is solved rather easily, too.

But the situation is other when we consider the system (11). In this case the equation for the generating function has form:

$$dF_x(q)/dt = k_1 \cdot x_1 \cdot q^2/2 - k_2 \cdot x_1 \cdot (1-q) \cdot F_x(q)$$

$$k_3 \cdot F_x(q) \cdot F_x(1) + k_3 \cdot F_x^2(q):$$

$$dx_1/dt = -x_1 \cdot (k_1 \cdot x_1 + k_2 \cdot F_x(1)\,. \qquad (22)$$

It is seen that analytical solving of this equations is impossible for arbitrary significance of kinetic constants. Numerical solution does not allow to use the generating function to find MWD function.

It is more natural to use numerical methods for direct solving of the system (11) without appeal to generating functions transformations. But then the problem arises of infinity and incompleteness of the system.

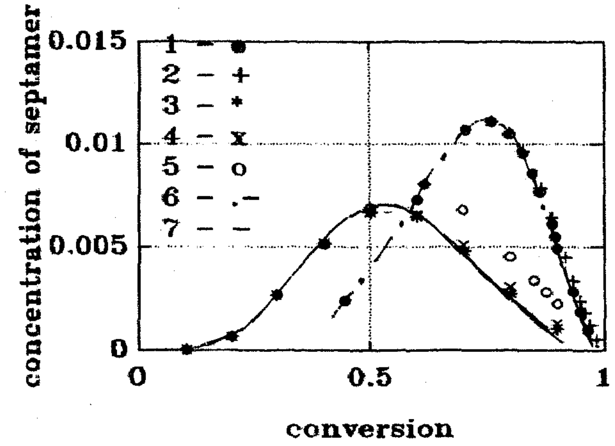


Fig. 1. Dependencies of concentration of septamer x_7 on conversion and number of equations taking into account. Kinetic constants according to scheme (10): $k_1 = k_2 = k_3 = 1$ (1, 2, 6); $k_1 = 1$, $k_2 = k_3 = 9$ (3, 4, 5, 6). Number of equations taken into account: 49(1, 6); 29(3, 7); 19(2, 4, 6, 7); 9(5, 6). 1–5 are calculated using Eq. (11); 6, 7 are calculated using (12) and (2)

To solve the infinity, incomplete systems we have to cut the infinitive row of equations. As a consequence, the possibility of error increases.

At the same time, as it has been shown above, equations for BB's concentrations are complete. Therefore, obtained solutions always lead to correct results: we can solve the system successively up to those length of chains whose concentrations are not less than a certain quantity corresponding to experimental error.

Below, we give certain results of numerical solving of the system (5), (6), (11), and (12). The number of equations taking into account was limited and different.

In Fig. 1 results for x_7 are obtained by two manners: on the one hand, by integrating of terminated systems (5) and (11); on the other hand, by integrating terminated system (6) and (12), using Eq. (2) to allow obtaining quantities x_i from y_i. The second method gives identical results in all cases, while the first one gives different results in dependence of the number of equations taken into account. For obtaining coinciding results it is necessary to consider more than 50 equations. These results are assumed to be correct.

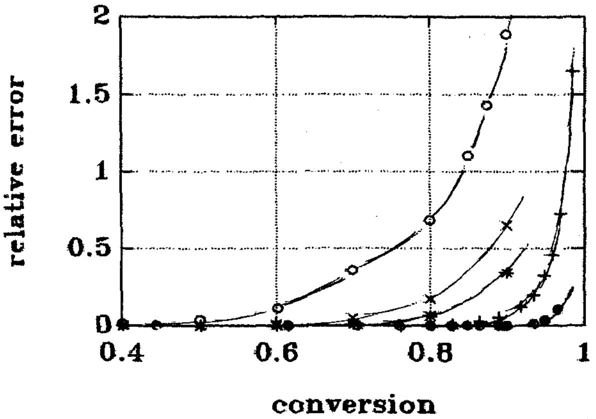


Fig. 2. Dependencies of relative errors of calculation on conversion and number of equations taking into account. All notation is the same as in Fig. 1

In Fig. 2 there are the dependencies of relative deviations δ on the number of equations taking account.

$$\delta = (x_i - x_{ic})/x_{ic} ,$$

where x_{ic} is exact quantity of x_i.

As is evident, the system termination leads to significant error when we calculate chain concentration directly and solve systems (5), (11). Using the equations for BB′s concentrations, i.e., systems (6), (12), correct results are obtained ($\delta = 0$) in spite of any terminations of infinitive systems. This is the direct consequence of their completeness.

This simple example shows a preference of application of BB′s concept to kinetic calculations for any complicated polymer systems because of the main property of corresponding systems of differential equations for BB′ concentrations: they are complicated.

Note, in the case of linear homopolymers, effect of termination of the equation system appears to a lesser degree because of increase of polymer length (increase of MWD width) with conversion being weaker than in the case of branched and network polymers. Therefore, errors in the latter cases will be sufficiently greater and appear at the earliest stages of polycondensation processes.

Conclusion

The bond block concept is a new effective method for the description of the process of polymer formation. The full set of BB concentrations characterizes the total polymer system, i.e., gives the possibility to find concentrations of all components. The law of mass action has a simple and clear form. For ideal processes of polymer formation, the system of kinetic equations is divided into simpler subsystems, and corresponding BB concentrations can be calculated by statistical methods. For nonideal processes analogous division of kinetic system is valid, too, but subsystems are more complex. The corresponding BB form subblocks ("nests"). The calculation of their concentrations requires to solve the corresponding complete subsystem of differential equations, including numerical methods. The concentrations of BB containing "nests" are calculated by statistical methods.

Such features of the BB concept give the possibility, in particular, to use the statistical approach for the problem of cycle formation. Since the kinetic constant of cycles formation depends on their size, there is the "neighbor effect" of high order (order of cycle size). Therefore, in the general case the system of kinetic equation cannot be reduced to the algebraic one. However, if the cycle size is small, one can include it in the "nest" structure and use the usual procedure for calculation of BB concentration.

References

1. Andreis M, Koenig JL (1989) Advances in Polymer Science 89:71–160.
2. Lantsov VM, Irzhak VI, Rozenberg BA (1987) In: Sedlacek B, Kahoves J (eds), de Gruyter, Berlin, 359–371
3. Tai ML (1979) Problemy peredachi informatssi (Problems of information transfer) 15 N 4:40–49
4. Tai ML (1981) ibid 17 N 1:53–61
5. Irzhak VI, Tai ML (1981) Dokl Akad Nauk SSSR, 259:856–859
6. Irzhak VI, Tai ML (1983) Vysokomol Soyedin A25:2305–2311
7. Kuchanov SI (1978) Metody kineticheskikh raschyotov v khimii polimerov (Methods of the Kinetic Calculations in the Polymer Chemistry), Khimiya, Moskva
8. Irzhak VI, Rozenberg BA, Enikolopyan NS (1979) Setchatyie polimery (Network Polymers), Nauka, Moskva

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Authors' address:
Prof. Dr. Vadim I. Irzhak
Institute of Chemical Physics
142432, Chernogolovka Moscow region, Russia