

# Configurational Effects in Statistical Theory of Branched Non-Random Polycondensation

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The statistical theory of gelation in the simplest process of the non-random polycondensation (S. I. Kuchanov, T. V. Zharnikov, *J. Stat. Phys.*, 111(5/6), 1273 (2003)) has been refined as to be able to take into account the effect of a monomer configuration on topological characteristics of the polymer network of the gel. Proceeding from the kinetic analysis of such a polycondensation, we rigorously prove that it can be described in terms of some stochastic branching process. The parameters of the process depend on the overall number of functional groups in the monomer as well as on the pattern of their mutual arrangement. Examples of some model systems illustrate the effect of kinetic and configurational factors on the topology of a polymer network formed in the course of non-random polycondensation.

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**KEY WORDS:** gelation, polymer networks, statistical kinetics, stochastic branching process.

## 1. INTRODUCTION

Polycondensation is one of the aggregation processes<sup>(1)</sup> wherein polymer molecules (clusters) are formed by the integration of small elements (monomers). Each of them comprises functional groups, the chemical reaction between which just leads to the aggregation. If this reaction is irreversible, all chemical bonds formed will be stable. During such an irreversible polycondensation (which will be scrutinized in the present paper) processes of the degradation of polymer molecules do not proceed. Therefore their number gradually decreases with time, whereas the average molecular weight of the polycondensation products increases. When

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among the initial monomers there are those containing more than two functional groups, branched polymer molecules will appear.

The distinctive feature of the branched polycondensation of such a kind is the gelation phenomenon. It consists in the appearance in the system at a certain moment (referred to as the gel-point) of a macroscopic size giant molecule occupying the whole volume of a reactor. Then the weight of this gel molecule grows due to the addition of the sol molecules right up to their complete depletion.

Under a theoretical description of branched polycondensation, the problems of two kinds are generally encountered.<sup>(2)</sup> The first of them is concerned with the description of the evolution of the distribution of sol molecules for number of monomeric units. The other group of problems deals with the calculation of the elasticity properties of the polymer network of a gel formed by fixed instant of time.

When tackling these problems, the recourse is normally made to both the kinetic and the statistical approaches.<sup>(2,3)</sup> The first of them implies the derivation and the solution of the material balance equations for the concentrations of molecules with fixed number of monomeric units participating in the process of interest. Under the second approach, the fraction of molecules is calculated with given configuration among those involved in the reaction mixture. This fraction is identified with the probability for the molecule chosen at random to have such a configuration. Mathematically speaking, this procedure means the construction of the probability measure on the set of conceivable configurations of polymer molecules.

The statistical method is widely engaged in the quantitative theory of polycondensation.<sup>(2,3)</sup> According to the most general version of this method, the realization of some stochastic process is put in correspondence to each polymer molecule. The probability measure on the set of macromolecules in a reaction system and that on the set of realizations of a stochastic process are presumably coincident. The main advantage of the statistical method is its ability to exhaustively describe in a straightforward manner the configurational structure of both sol and gel in terms of just several probability parameters.

However, it should be stressed that the problem of the choice of the type of a stochastic process producing the probability measure on the set of configurations of polymer molecules can not be settled in principle in the framework of the statistical method itself. To cope with this problem, should be employed the kinetic method. This enables one to simultaneously express the probability parameters of the stochastic process through the rate constants of the reactions between functional groups and the initial monomers' concentrations.

Invoking the kinetic method for the description of the polycondensation, it is necessary to find the solution of a set of infinite number of nonlinear ordinary differential equations for the concentrations of polymer molecules with specified sets of numbers  $\{l_{\alpha}\}$  of different monomeric units. These equations have many

features in common with the discrete version of the Boltzmann equation<sup>(4)</sup> as well as with the Smoluchowski equation.<sup>(5-7)</sup> This similarity is most apparent for the simplest system where polycondensation proceeds of only one monomer,  $RA^f$ , consisting of monomeric unit R and  $f$  identical functional groups A. Since the vast majority of the theoretical works on polycondensation have to do with just this system (see reviews<sup>(2-8)</sup> and references therein), we will also restrict ourselves in this paper to its consideration.

Among kinetic models of branched polycondensation, the most popular is the *ideal* model. It assumes that no sol molecule is involved in the cyclization reaction and the Flory principle holds. In consonance with this fundamental principle the reactivity of any functional group of a particular type does not depend on which molecule this group belongs to as well as on where it is located in a molecule. Considering reaction systems wherein the Flory principle is a good approximation, we are obviously dealing with the random polycondensation. Here the evolution with time  $t$  of concentration of polymers  $C(l; t)$  comprising  $l$  monomeric units is found from the Smoluchowski equation with bilinear kernel.<sup>(5-8)</sup> This equation admits exact analytic solution found by Stockmayer more than sixty years ago.<sup>(9)</sup> Later,<sup>(10)</sup> offered the statistical interpretation of this solution in terms of a stochastic branching process. This made possible the derivation of the expressions describing the elasticity properties of a polymer network.<sup>(11)</sup>

There is a considerable body of experimental evidence reported in literature testifying to the fact that, despite its simplicity, the *ideal* model provides an adequate treatment of experimental data obtained in an appreciable number of real polycondensation processes.<sup>(3)</sup> Nevertheless, for some of them the ideality condition is known to be violated because of the effects related to steric, induction, catalytic or some other type of influence of reacted functional groups on the reactivity of neighboring unreacted groups. In the simplest manner these effects are taken into account by the First Shell Substitution Effect (FSSE) model,<sup>(2,3)</sup> by which this influence is believed to be essential only on the scale of a single monomeric unit. In the framework of this model, a group A reactivity is unambiguously governed by the configuration of the monad incorporating this particular group as well as by its position in this monad.<sup>(12)</sup> In order to discriminate the chemically identical groups A by their reactivity, let us designate them  $A^{(i)}$ , where the superscript  $i$  stands for the kind of the functional group A.

Clearly, the FSSE model of non-random polycondensation of monomer  $RA^f$  is fully specified by kinetic matrix  $\mathbf{k}$  whose element  $k_{ij}$  is the rate constant of the chemical reaction between groups  $A^{(i)}$  and  $A^{(j)}$ . The dependencies on matrix  $\mathbf{k}$  elements of the most important parameters of a gel polymer network formed during polycondensation of the monomer  $RA^f$  were theoretically analyzed in detail in our preceding paper.<sup>(13)</sup> This analysis was performed by means of the original approach based on the kinetic and statistical examination (see review<sup>(2)</sup> and references therein) put forward by one of the authors of the present publication

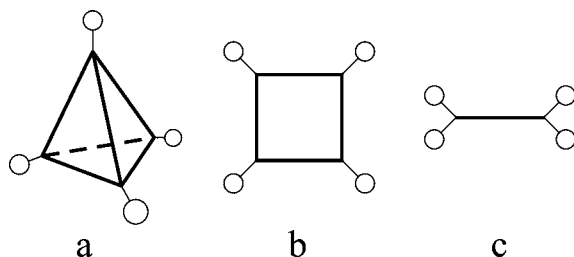


Fig. 1. Examples of monomer  $RA^4$  configurations: regular tetrahedron (a), square (b), dumb-bell (c).

to describe a non-random polycondensation. This approach enables a rigorous kinetic substantiation of the statistical method characterizing the products of the aforementioned process in terms of the theory of stochastic branching processes.

A serious drawback of all works on the theory of non-random polycondensation issued so far is a disregard of the peculiarities of the chemical structure of the initial monomer  $RA^f$ . For functionality  $f = 3$  this is likely to be quite justified bearing in mind that this monomer has the only configuration, isomorphic to the equilateral triangle. However, already at  $f = 4$ , the number of such configurations may be more than one (see Fig. 1). It should be emphasized that all theoretical results relevant to the non-random polycondensation of monomer  $RA^4$  reported by now remain valid only provided its configuration is isomorphic to the regular tetrahedron. The present paper aims at extending the results of the preceding article<sup>(13)</sup> by allowing for the configurational effects. The potentialities of the general theory are exemplified by considering the non-random polycondensation of four-functional monomers with configurations isomorphic to the square and dumb-bell (Fig. 1b and 1c). This will make possible to scrutinize the effect of the chemical structure of a monomer on the statistical characteristics of the products of its non-random polycondensation. To the authors' knowledge, no attempts to tackle the problems of such a kind in the aggregation theory based on the Smoluchowski equation have been undertaken so far.

The paper is organized as follows. First, the key ideas of the kineticostatistical approach used in the present paper are comprehensively explained. Then the kinetic model is outlined and a set of kinetic equations is presented for finding the generating function ( $gf$ ) of the weight molecular-weight distribution (MWD) of the products of non-random polycondensation. In the next Section, a probabilistic interpretation of the results achieved from the solution of the kinetic equations is proposed in terms of a stochastic branching process. Then the Markov processes characterizing the evolution of a monomeric unit configuration have been used to discuss some expressions derived by the kinetic method. The subsequent Section is devoted to the description of topological characteristics of the gel polymer network. Additionally, modifications are discussed

which the theoretical expressions undergo when one switches from the general FSSE model to its simplified versions. The last Section illustrates some results of the numerical calculations of the statistical characteristics of the polymer network obtained in the course of non-random polycondensation. In the conclusion the specific features of the original theoretical approach are highlighted. Some important details of the mathematical apparatus used are presented in appendices.

## 2. PRINCIPLES OF THE THEORETICAL APPROACH

The key points of this approach are most easily elucidated by considering the polycondensation of monomer  $RA^f$  describable by the *ideal* model. In this case, all molecules of the sol have the tree-like configurations, and, consequently, each  $l$ -mer contains  $a = (f - 2)l + 2$  functional groups A. In the framework of the ideal model, all these groups are of equal reactivity interacting to one another with the same constant  $k$  of the rate of the elementary condensation reaction. That is why the rate constant of the bimolecular chemical reaction between  $l'$ -mer and  $l''$ -mer is, apparently, equal to  $ka'a'' = k[(f - 2)l' + 2][(f - 2)l'' + 2]$ . Thus, the differential-difference equation of the random polycondensation for the concentration of  $l$ -mers  $C(l, t)$  at the moment of time  $t$  has the following appearance

$$\begin{aligned} \frac{dC(l, t)}{dt} &= \frac{k}{2} \sum_{l'=1}^{\infty} \sum_{l''=1}^{\infty} [(f - 2)l' + 2][(f - 2)l'' + 2] C(l', t) C(l'', t) \\ &\quad \times \delta(l, l' + l'') - k[(f - 2)M^0 + 2N] \\ &\quad \times [(f - 2)l + 2] C(l, t) \quad C(l, 0) = M^0 \delta(l, 1) \end{aligned} \tag{1}$$

where  $N$  and  $M^0$  stand for the overall concentrations in the reaction system, respectively, of molecules and monomeric units

$$N(t) = \sum_l C(l, t) \quad M^0 = \sum_l l C(l, t) \tag{2}$$

It is readily seen that the equation 2 is the well-known Smoluchowski coagulation equation with the kernel representing a bilinear form. Its exact analytic solution has been first reported by Stockmayer,<sup>(9)</sup> and later repeatedly re-derived by other researchers in different ways. By one of them, the equation 2 reduces to the equivalent equation

$$\frac{\partial g}{\partial \tau} = \frac{1}{2} \left[ (f - 2)s \frac{\partial g}{\partial s} + 2g \right]^2 - \mu \left[ (f - 2)s \frac{\partial g}{\partial s} + 2g \right] \quad g(s, 0) = s \tag{3}$$

$$\tau = kM^0 t \quad \mu(\tau) \equiv \left( f - 2 + \frac{2N}{M^0} \right) = \frac{f}{1 + f\tau} \tag{4}$$

for the generating function (*gf*)

$$g(s, \tau) = \frac{1}{M^0} \sum_{l=1}^{\infty} C(l, \tau) s^l \quad (5)$$

Of prime importance for the theory of polymers is the weight molecular-weight distribution (MWD)  $f_W(l, \tau) = lC(l, \tau)/M^0$  that equals the fraction of units involved in an  $l$ -mer molecules. The *gf* of this distribution is related in a simple way

$$G_W(s, \tau) \equiv \sum_{l=1}^{\infty} f_W(l, \tau) s^l = s \frac{\partial g}{\partial s} \quad (6)$$

with the *gf* (5) representing the solution of Eq. (3), which is obtainable by the method of characteristics. The analytic expression for the *gf* (6) can be presented by expression

$$G_W(s, \tau) = s(1 - p + pu)^f \quad (7)$$

in which  $p = f\tau/(1 + f\tau)$  denotes the fraction of the reacted functional groups  $\bar{A}$ , while the auxiliary function  $u(s, \tau)$  is found from the solution of the algebraic equation

$$u = s(1 - p + pu)^{f-1} \quad (8)$$

Using the Lagrange's theorem (14), it is an easy matter to obtain from (7), (8) the exact expression for the weight MWD

$$f_W(l, p) = \frac{f[(f-1)l]!}{(l-1)![(f-2)l+2]!} p^{l-1} (1-p)^{(f-2)l+2} \quad (9)$$

The value of the critical conversion  $p = p^* = 1/(f-1)$ , at which the gel appears in the reaction system for the first time, is determined from the condition of turning into infinity of the weight-average degree of polymerization  $P_W$ , i.e., the first-order statistical moment of the distribution (9). To have it found, there is no need to perform the summation of the infinite series, since the value  $P_W = (1+p)/[1-(f-1)p]$  represents the derivative of the function (7) with respect to the variable  $s$  at point  $s = 1$ .

Formulas (7), (8) derived by the kinetic method from the solution of the Smoluchowski coagulation equation have rather transparent statistical meaning, which is clearly interpreted in terms of the theory of branching stochastic processes. The simplest among them is the Galton-Watson process.<sup>(15)</sup> Its essence can be better understood in the context of the evolution of a population of stochastically reproducing identical particles.

Let the initial number of such particles be  $n_0$ . Each of them during its life time can produce  $n_1$  daughter particles, any of which before dying will, in turn, give birth to  $n_2$  grand-daughter particles, and so on. Further inspection of the subsequent

generations enables one to reconstruct the whole history of the propagation of the population (family) originated by the initial particle. The evolution of such a population can be most readily described by setting the sequence of the numbers of particles  $n_0, n_1, n_2, \dots$  in all generations  $j = 0, 1, 2, \dots$ . It is convenient to consider any such a sequence as the realization of a certain stochastic process with discrete time  $j$  and the infinite set of denumerable states  $n = 0, 1, 2, \dots$ . It will be referred to as the Galton-Watson branching process, provided all particles reproduce independently. Mathematically speaking, this means that any of them for its life time produces  $n$  particles with the same probability  $P_n$ . Therefore, the Galton-Watson branching process is completely specified by the probability distribution  $P_0, P_1, \dots, P_n, \dots$  which is identical in all generations  $j$ , as well as by the distribution of the probabilities  $P_0^{(0)}, P_1^{(0)}, \dots, P_n^{(0)}, \dots$  of the number of daughter particles produced by the particle ancestor in the zero generation. The *gf*s of these distributions

$$F^{(0)}(s) = \sum_n P_n^{(0)} s^n \quad F(s) = \sum_n P_n s^n \quad (10)$$

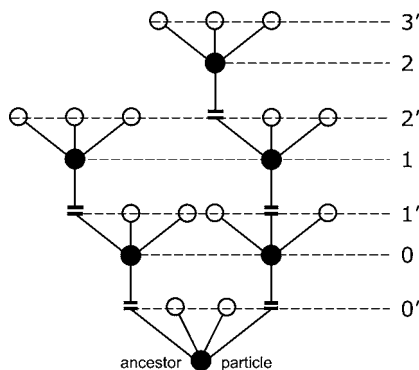
permit finding (15) the *gf* of the distribution of the overall number of particles  $l = n_0 + n_1 + \dots + n_j + \dots$  of a population

$$G_{pop}(s) = sF^{(0)}(u) \quad u = sF(u) \quad (11)$$

The comparison of expressions (11) with those, (7), (8), obtained from the solution of the kinetic equation (2), enables the following conclusions. The formulas for the *gf* of the weight MWD (7), (8) can be formally derived by means of the statistical method in terms of the Galton-Watson branching process with the probabilities of particles' reproduction specified by the Bernoulli distributions

$$P_n^{(0)} = \frac{f!}{n!(f-n)!} p^n (1-p)^{f-n} \quad P_n = \frac{(f-1)!}{n!(f-1-n)!} p^n (1-p)^{f-1-n} \quad (12)$$

Let us explain briefly the main ideas of the statistical method as applied to the theoretical description of branched polymers whose molecules do not comprise cycles. To each of them there corresponds the molecular graph known as "molecular tree," whereas to the whole polymer specimen the ensemble of such trees corresponds, which is termed "molecular forest." The latter can be unambiguously transformed into "clone," i.e., the forest of rooted trees obtained from the molecular trees by virtue of the successive choice of each their vertex as a root. Such a transformation retains the probability measure, so that the only thing which remains to be done is to find the distribution of the probabilities of the rooted trees in a clone. Each of them, in turn, may be conceived as a genealogical tree describing the history of a certain family or (which is the same) as a realization of the stochastic branching process of reproducing particles. An example



**Fig. 2.** The rooted tree schematically presents one of the molecules consisting of  $l = 6$  units formed during the polycondensation of monomer  $RA^f$ . Open circles correspond to the unreacted functional groups A, filled circles denote monomeric units R, whereas symbol  $\equiv$  represents a chemical bond consisting of a pair of reacted groups  $\bar{A}$ . Numbers of generations are indicated by figures supplied or not by prime symbol for the branching process whose reproducing particles are functional groups or monomeric units, respectively.

of one of such realizations is given in Fig. 2. Essentially, in the framework of the statistical method, the choice of the structural elements of the polymer molecules associated with the reproducing particles is ambiguous.<sup>(16)</sup> As it can be seen from Fig. 2, as such elements can act either monomeric units R or reacted functional groups  $\bar{A}$ . In the first case, the stochastic process begins with the sole particle ancestor, whereas in the second one the population starts propagating with  $n_0$  particles. Their number is a random variable with the distribution function  $P_n^{(0)}$ . All particles, except for the particle ancestor, stochastically reproduce with the identical probability distribution  $P_n$ . Noteworthy, the probabilities of the reproduction  $P_n^{(0)}$  and  $P_n$  are mutually dependent. Thus, these probabilities, as well as their generating functions, are related in the following manner

$$P_n = (n + 1)P_{n+1}^{(0)} / \sum_n nP_n^{(0)} \quad F(s) = \frac{dF^{(0)}(s)}{ds} / \frac{dF^{(0)}(s)}{ds} \Big|_{s=1} \quad (13)$$

Therefore, in order to exhaustively specify the branching process of interest, it will suffice to indicate only the probabilities  $P_n^{(0)}$  or their generating function  $F^{(0)}(s)$ . As evident from Fig. 2, the quantity  $P_n^{(0)}$  equals the probability for the root of the graph to have  $n$  adjacent nodes, i.e., the probability that the monomeric unit associated with this root is linked with  $n$  reacted functional groups. The probabilities for a randomly chosen group to be reacted  $\bar{A}$  or unreacted A are equal to  $p$  or  $1 - p$ , respectively. Because in the framework of the *ideal* model of polycondensation all groups react independently of one another, the probability of the arbitrary



monad  $R\bar{A}^n A^{f-n}$  is given by expression (12) wherein the combinatorial factor equals the number of manners in which  $n$  groups can be chosen from  $f$  identical groups.

The gelation phenomenon admits a simple interpretation in terms of the theory of the branching processes. The possibility of the existence in a reaction system of macroscopic polymeric structures is associated with the non-vanishing probability of the emergence in the corresponding branching process of non-degenerate populations where the number of the descendants of the ancestor particle is, by definition, infinite. Such populations can exist only if the average number of the daughter particles (equal to the derivative of the *gf*  $F(s)$  at point  $s = 1$ ) is more than unity. The value of parameter  $p = p^* = 1/(f - 1)$  at which the above-mentioned derivative equals unity just corresponds to the critical conversion at the gel-point.

When dealing with the theory of the branched polycondensation the statistical method has an indisputable advantage over the kinetic method because of its ability to provide a description of a reaction system not only before the gel-point but also after it. Particularly, the weight fraction of sol  $\omega_s$  is found from expression

$$\omega_s = G_W(1) = F^{(0)}(\theta) \tag{14}$$

where  $\theta$  is the sole within the interval  $0 < \theta < 1$  root of the algebraic equation

$$\theta = F(\theta) \tag{15}$$

Quantities  $\theta$  and  $\omega_s$  have the sense of the probability of the degeneration of the population produced by an ordinary particle and by the particle ancestor, respectively. Given the probability  $\theta$ , one can find the *gf* of the MWD of sol molecules using the modified generating functions

$$\hat{F}^{(0)}(s) = \frac{F^{(0)}(s\theta)}{\omega_s} \qquad \hat{F}(s) = \frac{F(s\theta)}{F(\theta)} \tag{16}$$

The above-presented formulas working before the gel-point turn out to be true for the sol, provided the *gfs* (10) are replaced in these formulas by their modified expressions (16). Specifically, expressions (11) after their extension will read

$$G_W^{sol}(s) = sF^{(0)}(\hat{u}) \qquad \hat{u} = s\hat{F}(\hat{u}) \tag{17}$$

where  $\hat{u}(s)$  is the *gf* of the distribution of the overall number of particles in a finite population produced by one ordinary particle. Upon going over in expressions (17) from  $\hat{u}$  to variable  $u = \hat{u}\theta$ , one gets

$$G_W^{sol}(s) = s \frac{F^{(0)}(u)}{\omega_s} \qquad u = sF(u) \tag{18}$$

The weight average degree of polymerization of the finite molecules can be calculated by the formula

$$P_W^{sol} \equiv \frac{dG_W^{sol}}{ds} \Big|_{s=1} = 1 + \frac{1}{\omega_s} \frac{dF^{(0)}(u)}{du} \Big|_{u=\theta} \times \frac{du}{ds} \Big|_{s=1} = 1 + \frac{UF(\theta)}{\omega_s} z \quad (19)$$

in which the following designations are used

$$U = \frac{dF^{(0)}(u)}{du} \Big|_{u=1} \quad z = \frac{du}{ds} \Big|_{s=1} \quad (20)$$

The value of variable  $z$  meaning the average number of particles in a finite population originated by one ordinary particle can be found from the equation

$$\Gamma z = \theta, \quad \text{where} \quad \Gamma \equiv 1 - \frac{dF(\theta)}{d\theta} \quad (21)$$

The quantity  $z$ , as well as  $P_W$ , becomes infinite just at the gel-point where  $\Gamma$  vanishes.

The statistical method is especially efficient when calculating the characteristics of a polymer network responsible for its elasticity properties. Among the challenges of the theory of branched polycondensation is the determination of the weight fraction of the gel  $\omega_g = 1 - \omega_s$  as well as of the fractions of its units,  $\omega_{ge}$  and  $\omega_{gp} = \omega_g - \omega_{ge}$ , involved, respectively, in the active and passive material of a network. The latter, as distinct from the former, makes no contribution to the elastic properties of such a network.

Among the characteristics of a polymer network the most significant is the cyclic rank  $\mathcal{R}$  of its molecular graph. This topological parameter (equal to the least number of edges in a graph that should be removed from it to ensure its transformation into a tree) enters in the expression for the elasticity modulus of a polymer network. Quantity  $\mathcal{R}$  equals the difference of the number  $\nu$  of elastically active chains and that  $\mu$  of elastically effective nodes. These latter are such nodes from which at least three paths in the infinite graph of a gel lead to infinity. A chain linking two such nodes is referred to as elastically active one. Since under theoretical consideration the molecular graph of a gel is believed to be infinite, it is natural that quantities  $\mathcal{R}$ ,  $\nu$ ,  $\mu$  are intensive, i.e., defined per one vertex of this graph. Given  $\omega_{ge}$  and  $\nu$ , one can calculate the average length  $N_e = \omega_{ge}/\nu$  of an elastically active chain.

Thus one of the fundamental problems of the quantitative theory of branched polycondensation is the determination of the dependencies of fractions  $\omega_g$ ,  $\omega_{ge}$  as well as the statistical characteristics of the topological structure of a polymer network on functional groups' conversion.

To describe a gel by the statistical method, the necessity arises to distinguish monads not by their kind but by number of paths  $k$  going from the monad under consideration to infinity. Let us, by analogy with paper<sup>(13)</sup>, the  $\lambda^{(k)}$  denotes fractions

of all such monads involved in a gel molecule. All statistical characteristics of interest can be expressed through these fractions using formulas

$$\begin{aligned} \omega_g &= 1 - \lambda^{(0)} = \sum_{k=1}^f \lambda^{(k)} & \omega_{ge}\omega_g &= 1 - \lambda^{(0)} - \lambda^{(1)} = \sum_{k=2}^f \lambda^{(k)} \\ \mu\omega_g &= 1 - \lambda^{(0)} - \lambda^{(1)} - \lambda^{(2)} = \sum_{k=3}^f \lambda^{(k)} & \nu\omega_g &= \frac{1}{2} \sum_{k=3}^f k\lambda^{(k)} \quad (22) \\ N_e &= \frac{\omega_{ge}}{\nu} & \mathcal{R} &= \nu - \mu \end{aligned}$$

In the process of a branched polycondensation, describable by the ideal model, fraction  $\lambda^{(k)}$  and parameter  $\nu$  are defined by the following expressions

$$\lambda^{(k)} = \frac{1}{k!} (1 - \theta)^k \left. \frac{d^k F^{(0)}(u)}{du^k} \right|_{u=\theta} = \frac{f!}{k! (f - k)!} [p(1 - \theta)]^k (1 - p + p\theta)^{f-k} \quad (23)$$

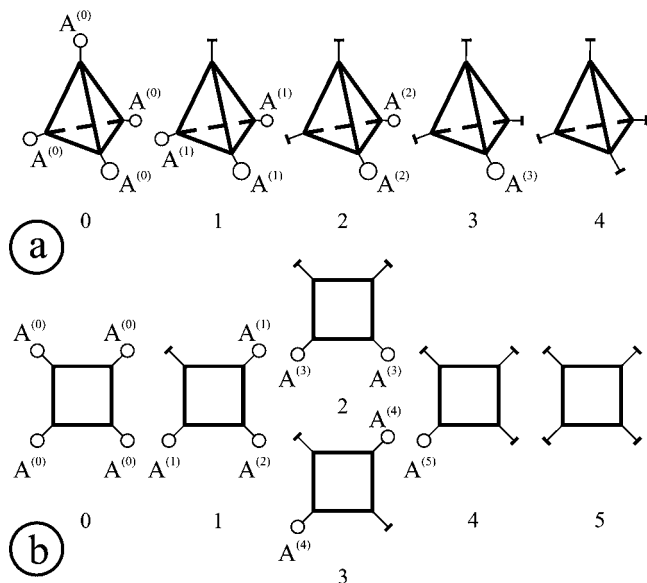
$$\nu = \frac{1}{2} (1 - \theta) U[1 - F(\theta)] - \lambda^{(2)} = \frac{1}{2} f p (1 - \theta)^2 \left[ 1 - \frac{(f - 1) p \theta}{1 - p + p\theta} \right] \quad (24)$$

The theoretical approach to the description of a *random* branched polycondensation exhaustively discussed above provides an idea how combining the formalisms of the kinetic and statistical methods, one can find the most important statistical characteristics of the polymer obtained. In the subsequent Sections it will be shown in which manner this approach can be extended to consider the *non-random* polycondensation with allowance for the effect of the configuration of monomeric units.

### 3. KINETIC DESCRIPTION OF THE POLYCONDENSATION PROCESS

Let us consider the general FSSE model of irreversible polycondensation of monomer  $RA^f$ . Here the entry into the reaction of any functional group leads to the alteration of the reactivity of all the remaining unreacted groups attached to the monomeric unit. Overall number of kinds of functional groups  $A^{(i)}$  at fixed value of functionality  $f$  of monomer  $RA^f$  is prescribed by its configuration. As it can be seen from Fig. 3, this number will be equal to four or six for monomer  $RA^4$  whose configuration is isomorphic to regular tetrahedron or square, respectively.

Along with the kinetic matrix  $k$ , the FSSE model in hand is additionally characterized by the pair of stoichiometric matrices  $f$  and  $\Delta$ . Matrix element  $f_{\alpha i}$  of the first of them equals the number of groups of the kind  $i$  in the  $\alpha$ -th kind monad. Below Latin and Greek letters will denote the kind of functional groups and monads, respectively. As for matrix  $\Delta$ , its element  $\Delta_{i\gamma}$  will be distinct from



**Fig. 3.** Complete sets of monads of different kinds occurring under consideration of the polycondensation of monomer  $RA^4$  with configuration of regular tetrahedron (a) and square (b) described by the FSSE model. The number ascribed to a monad corresponds to its kind  $\alpha$ . Open circles and bars correspond to unreacted functional groups of kind  $A^{(i)}$  and reacted groups, respectively.

zero being equal to unity only provided any reacted functional group of  $i$ -th kind is involved in  $\gamma$ -th kind monad. These matrices, corresponding to the monomer configurations depicted in Fig. 1a and 1b, look as follows

$$\mathbf{f} = \begin{pmatrix} 4 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \Delta = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad (25)$$

$$\mathbf{f} = \begin{pmatrix} 4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \Delta = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad (26)$$

Note that matrices  $\mathbf{f}$  and  $\Delta$  for the configuration appearing in Fig. 1c coincide completely with those presented above (26).

To find  $gf$   $G_W(s)$  of the weight MWD of the products of a polycondensation

$$G_W(s) \equiv \sum_{l=1}^{\infty} f_W(l) s^l = \sum_{\alpha} s_{\alpha} \left. \frac{\partial g}{\partial s_{\alpha}} \right|_{s_{\alpha}=s} \quad (27)$$

it is necessary to determine  $gf$   $g(\mathbf{s}, t)$  of distribution  $c(\mathbf{l}; t)$  of macromolecules with given value of vector  $\mathbf{l}$

$$g(\mathbf{s}, t) = \sum_{\mathbf{l}} c(\mathbf{l}, t) \prod_{\alpha} s_{\alpha}^{l_{\alpha}} \quad (28)$$

Each its component is equal to the number of  $\alpha$ -th kind monads in a polymer molecule. Dimensionless function  $c(\mathbf{l}; t)$  equals the ratio of concentration of polymer molecules  $C(\mathbf{l}; t)$  to overall number of monomeric units  $M^0$  in a reaction system. Generating function  $g(\mathbf{s}, t)$  is the solution of the set of the first order nonlinear partial differential equations

$$\frac{\partial g}{\partial t} = M^0 \sum_{\alpha, \beta} \left\{ -\mathbb{k}_{\alpha\beta} \lambda_{\alpha} s_{\beta} S_{\beta} + \frac{1}{2} \sigma_{\alpha\beta}(\mathbf{s}) S_{\alpha} S_{\beta} \right\} \quad g(\mathbf{s}, 0) = s_0 \quad (29)$$

obtained immediately from the set of material balance equations for concentrations  $C(\mathbf{l}; t)$ . In formula (29) the following designations are used

$$S_{\alpha}(\mathbf{s}, t) = \frac{\partial g}{\partial s_{\alpha}} \quad \sigma_{\alpha\beta}(\mathbf{s}) = \sum_{\gamma, \delta} \tilde{k}_{\alpha\beta}^{\gamma\delta} s_{\gamma} s_{\delta} \quad (30)$$

Here the rate constant of the reaction between monads, whose kinds are  $\alpha$  and  $\beta$ , resulting in the formation of monads of kinds  $\gamma$  and  $\delta$ , respectively, is characterized by formula

$$\tilde{k}_{\alpha\beta}^{\gamma\delta} = \sum_{i, j} f_{\alpha i} f_{\beta j} k_{ij} \Delta_{i\gamma} \Delta_{j\delta} \quad (31)$$

The dependencies on time  $t$  of average fractions of  $\gamma$ -th kind monads  $\lambda_{\gamma}(t)$  are determined from the solution of the set of ordinary differential equations

$$\frac{d\lambda_{\gamma}}{dt} = M^0 \sum_{\alpha, \beta} \mathbb{k}_{\alpha\beta}^{\gamma} \lambda_{\alpha} \lambda_{\beta} - \theta_{\gamma} \lambda_{\gamma} \quad \lambda_{\gamma}(0) = \delta_{\gamma 0} \quad (32)$$

where  $\delta_{\gamma 0}$  is the Kronecker delta. Infinitesimal probability  $\theta_{\alpha}(t)$  of the disappearance at moment  $t$  of an  $\alpha$ -th kind monad as well as parameters  $\mathbb{k}_{\alpha\beta}^{\gamma}$  and  $\mathbb{k}_{\alpha\beta}$  are defined by the following expressions

$$\theta_{\alpha} = M^0 \sum_{\beta} \mathbb{k}_{\alpha\beta} \lambda_{\beta} \quad \mathbb{k}_{\alpha\beta}^{\gamma} = \sum_{\delta} \tilde{k}_{\alpha\beta}^{\gamma\delta} \quad \mathbb{k}_{\alpha\beta} = \sum_{\gamma} \mathbb{k}_{\alpha\beta}^{\gamma} = \sigma_{\alpha\beta}(\mathbf{1}) \quad (33)$$

Essentially, in the particular case when the configuration of a monomer is isomorphic to that portrayed in Fig. 1a, matrix function  $\sigma_{\alpha\beta}(\mathbf{s})$  has the appearance  $\mathbb{k}_{\alpha\beta} s_{\alpha+1} s_{\beta+1}$ , and Eq. (29) is reduced to the one already known.<sup>(13,17)</sup>

When comparing theoretical results with experimental data, it is often proves more convenient to consider the statistical characteristics of polycondensation products at fixed conversion  $p$  of functional groups A. The transition from time  $t$  to conversion  $p$  in theoretical formulas for these characteristics can be easily carried out, provided the following expressions are employed

$$p = 1 - \frac{1}{f} \sum_{\alpha,i} \lambda_{\alpha} f_{\alpha i} \qquad \frac{dp}{dt} = \frac{1}{f} \sum_{\alpha,\gamma} \lambda_{\alpha} \varphi_{\alpha\gamma} \sum_i (f_{\alpha i} - f_{\gamma i}) \quad (34)$$

where matrix function  $\varphi_{\alpha\gamma}(\tau)$  (A9) is defined in Appendix A.

One of the major challenges of a quantitative theory of polycondensation is the calculation of critical conversion  $p^*$  under which an infinite molecule of gel emerges. Such a calculation is possible to realize, as it has been already done, in two different ways detailed in Appendix A.

Expression for  $gf$  of the weight MWD (27) derived from Eq. (29) can be written down as follows

$$G_W(s) = s \mathcal{F}^{(0)}[\mathbf{u}] \qquad \mathcal{F}^{(0)}[\mathbf{u}] = \sum_{n=0}^f \sum_{\alpha_n} \mathcal{F}_{\alpha_n}^{(n)}[\mathbf{u}] \quad (35)$$

Here functional  $\mathcal{F}_{\alpha_n}^{(n)}[\mathbf{u}]$  is determined by expression

$$\mathcal{F}_{\alpha_n}^{(n)}[\mathbf{u}] = \sum_{\{\alpha_0, \dots, \alpha_{n-1}\}} \int \dots \int P_{\alpha_0, \dots, \alpha_n}^{(n)\text{mon}}(t; \tau_0, \dots, \tau_{n-1}) \prod_{k=0}^{n-1} u_{\alpha_k \alpha_{k+1}}(\tau_k) d\tau_k \quad (36)$$

where the coefficients read

$$P_{\alpha_0, \dots, \alpha_n}^{(n)\text{mon}}(t; \tau_0, \dots, \tau_{n-1}) = \exp[-I_{\alpha_n}(t)] \prod_{k=0}^{n-1} v_{\alpha_k \alpha_{k+1}}(\tau_k) \varphi_{\alpha_k \alpha_{k+1}}(\tau_k) \quad (37)$$

with the following designations used

$$I_{\alpha}(t) = \int_0^t \theta_{\alpha}(t') dt' \qquad v_{\alpha\gamma}(t) = \exp[I_{\gamma}(t) - I_{\alpha}(t)] \quad (38)$$

The time  $\tau_{n-1}$  is the moment of formation of the  $\alpha_n$ -th kind monad. Functions  $\theta_{\alpha}(t)$  and  $\varphi_{\alpha\gamma}(\tau)$  entering in these formulas have been defined earlier (33), (A9). Notice that any functional  $\mathcal{F}_{\alpha_n}^{(n)}[\mathbf{u}]$  is the solution of the set of linear ordinary differential equations

$$\frac{d\mathcal{F}_{\gamma}^{(n)}}{dt} = M^0 \sum_{\alpha} \mathcal{F}_{\alpha}^{(n-1)} \sum_{\beta} u_{\alpha\beta} \mathbb{k}_{\alpha\beta}^{\gamma} \lambda_{\beta} - \theta_{\gamma} \mathcal{F}_{\gamma}^{(n)} \qquad \mathcal{F}_{\gamma}^{(n)}(0) = \delta_{n0} \delta_{\gamma 0} \quad (39)$$

Each function  $u_{\alpha\beta}$ , on the set of which the functional  $\mathcal{F}^{(0)}[\mathbf{u}]$  has been specified, is dependent on variable  $s$ . These dependencies can be found from the solution of the set of nonlinear integral equations

$$u_{\alpha\gamma}(\tau) = s\mathcal{F}_{\alpha\gamma}(\tau; [\mathbf{u}]) \tag{40}$$

where variable  $s$  is involved as a parameter. Functional  $\mathcal{F}_{\alpha\gamma}(\tau; [\mathbf{u}])$  appearing in the right-hand side of equation (40) is defined as

$$\mathcal{F}_{\alpha\gamma}(\tau; [\mathbf{u}]) = \sum_{\beta} \sum_{\delta} \frac{\tilde{k}_{\alpha\beta}^{\gamma\delta} \lambda_{\beta}(\tau) \delta \mathcal{F}^{(0)}[\mathbf{u}]}{\varphi_{\alpha\gamma}(\tau) \delta u_{\beta\delta}(\tau) \varphi_{\beta\delta}(\tau) \lambda_{\beta}(\tau)} \tag{41}$$

through the variational derivatives of functional  $\mathcal{F}^{(0)}[\mathbf{u}]$ .

Relationships (35), (40) and (41), obtained from the solution of kinetic equation (29), after their transformations admit a statistical interpretation in terms of some stochastic branching process analogous to that put forward earlier.<sup>(13)</sup>

### 4. STATISTICAL METHODS

In order to interpret statistically the formulas derived by the kinetic method in the previous Section, they should be transformed in the following way.

Expressions (35), (40) and (41) comprise functions  $\varphi_{\alpha\gamma}(\tau)$  (A9) having the sense of the infinitesimal probabilities of the transformation at moment  $\tau$  of an  $\alpha$ -th kind monad to the  $\gamma$ -th kind monad. Such a transition is due to the entry into the reaction of a certain kind functional group, which is one of those involved in the  $\alpha$ -th kind monad. As a consequence, in all formulas containing  $\varphi_{\alpha\gamma}(\tau)$ , this can be replaced by  $\varphi_i(\tau)$ . Similarly, function  $u_{\alpha\gamma}(\tau)$  is possible to replace by  $u_i(\tau)$ . As regards the rate constant  $\tilde{k}_{\alpha\beta}^{\gamma\delta}$  of the chemical reaction between monads whose kinds are  $\alpha$  and  $\beta$  leading to their transformation into  $\gamma$ -th kind and  $\delta$ -th kind monads, respectively, it can be presented as matrix element  $\tilde{k}_{ij}$ . With this in mind, it is possible to reduce expressions (35), (40) and (41) to the following ones

$$G_W(s) = s\mathcal{F}^{(0)}[\mathbf{u}] \quad u_i(\tau) = s\mathcal{F}_i(\tau; [\mathbf{u}]) \quad (i = 0, 1, \dots) \tag{42}$$

$$\begin{aligned} \mathcal{F}^{(0)}[\mathbf{u}] &= P^{(0)}(t) + \sum_{n=1}^f \sum_{\{i_0, \dots, i_{n-1}\}} \int \dots \int P_{i_0, \dots, i_{n-1}}^{(n)}(t; \tau_0, \dots, \tau_{n-1}) \\ &\quad \times \prod_{k=0}^{n-1} u_{i_k}(\tau_k) d\tau_k \end{aligned} \tag{43}$$

$$\mathcal{F}_i(\tau; [\mathbf{u}]) = \sum_j \pi_{ij}(\tau) \mathcal{F}_j^{\dagger}(\tau; [\mathbf{u}]) \quad \mathcal{F}_j^{\dagger}(\tau; [\mathbf{u}]) = \frac{\delta \mathcal{F}^{(0)}[\mathbf{u}]}{\delta u_j(\tau)} \frac{1}{U_j(\tau)} \tag{44}$$

$$U_j(\tau) \equiv \left. \frac{\delta \mathcal{F}^{(0)}[\mathbf{u}]}{\delta u_j(\tau)} \right|_{u(\tau)=1} = \varphi_j(\tau) \sum_{\alpha} \lambda_{\alpha}(\tau) \Gamma'_{\alpha j} \quad \pi_{ij}(\tau) = \frac{\tilde{k}_{ij}}{\varphi_i(\tau) \varphi_j(\tau)} \tag{45}$$

allowing a simple probabilistic interpretation. Here matrix  $\mathbf{f}'$  is obtained from matrix  $\mathbf{f}$  (exemplified in the foregoing, (25) and (26) via replacing all non-vanishing elements of the latter by unity.

The stochastic branching process, which produces the probability measure on the set of polymer molecules formed during the non-random polycondensation in hand, is characterized by a set of reproducing particles whose kind is specified by discrete index  $i$  (color) and label  $\tau$ . These particles correspond to the functional groups of kind  $i$  which have reacted at moment  $\tau$ .

Function  $P_{i_0, \dots, i_{n-1}}^{(n)}(t; \tau_0, \dots, \tau_{n-1})$  is the density of the probability for the particle-ancestor during the time lapse  $(0, t)$  to give birth to  $n$  descendants  $\bar{A}_{i_0}(\tau_0), \bar{A}_{i_1}(\tau_1), \dots, \bar{A}_{i_{n-1}}(\tau_{n-1})$  at moments  $0 < \tau_0 < \tau_1 < \dots < \tau_{n-1} < t$ , respectively. Every such a particle is incapable of reproducing until it becomes active particle. The latter in the course of such a transformation (happening right after particle  $\bar{A}_i(\tau)$  is born) retains the same label  $\tau$  differing, generally speaking, from the former by color. Conditional probability  $\pi_{ij}(\tau)$  (45) of this transformation upon the summation over index  $j$  yields, naturally, unity. In the next generation each active particle  $\bar{A}_j^\dagger(\tau)$  produces a set of non-active particles. The probability distribution of such sets is characterized by generating functional ( $GF$ )  $\mathcal{F}_j^\dagger(\tau; [\mathbf{u}])$ , which is related by expression (44) with  $GF$   $\mathcal{F}^{(0)}[\mathbf{u}]$  (43) of the probability distribution of sets of the particle-ancestor descendants.

The development of a population of the branching process in every generation starting with the first one proceeds in the same manner. Each non-active particle belonging to the  $m$ -th generation turns immediately into active one with the same label. Once formed, this active particle will later give birth in  $(m + 1)$ -th generation to some set of non-active daughter particles. The probability distribution of particle  $\bar{A}_i(\tau)$  transformation into particle  $\bar{A}_j^\dagger(\tau)$  is described in all generations by the stochastic matrix with elements  $\pi_{ij}(\tau)$  (45), whereas the subsequent reproduction by particle  $\bar{A}_j^\dagger(\tau)$  of the descendants is characterized by  $GF$   $\mathcal{F}_j^\dagger(\tau; [\mathbf{u}])$  (44). Using the statistical method, we can skip the first transformation to consider the branching process exclusively in terms of the set of non-active particles  $\{\bar{A}_i(\tau)\}$  whose reproduction is described by the  $GF$  representing the vector with elements  $\mathcal{F}_i(\tau; [\mathbf{u}])$  (44).

To give an account of the branching process in hand, it is enough to specify the  $GF$   $\mathcal{F}^{(0)}[\mathbf{u}]$  (43) of the distribution of the probabilities of particles produced by the particle-ancestor in the zero generation. This statement is apparently true since the other  $GF$ s appearing in relationships (42) and (44) are variational derivatives of functional  $\mathcal{F}^{(0)}[\mathbf{u}]$ . For this  $GF$  to be given, it is necessary to indicate all sets of daughter particles and to write down the expressions for their probabilities. Obviously, the collection of these sets varies, generally speaking, for monomers of different configurational structure. As it can be seen from Fig. 4a, the specificity of the branching process describing the products of polycondensation of a monomer



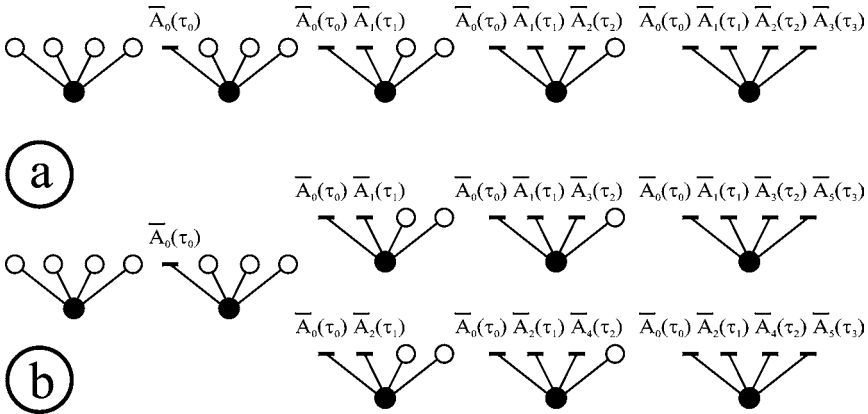


Fig. 4. Ensemble of all sets of daughter particles produced by the particle-ancestor in the branching process describing the products of non-random polycondensation of monomer  $RA^4$  whose configuration is isomorphic to regular tetrahedron (a) and square (b).

with tetrahedral configuration resides in the fact that at given number of daughter particles the only their set is possible. For monomers of other configurational structure this is not the case (see, for example, Fig. 4b).

Function  $u_i(s; \tau)$ , entering in Eq. (42), under the statistical approach has a simple meaning. This is the *gf* of the probability of the number of descendants produced by particle  $\bar{A}_i(\tau)$  in all generations. When dealing with a branching process, of prime importance are two functions

$$\theta_i(\tau) = u_i(1; \tau) \quad z_i(\tau) = \left. \frac{du_i}{ds} \right|_{s=1} \quad (46)$$

The first of them represents the probability for the particle  $\bar{A}_i(\tau)$  to have in all generations finite number of the descendants, while the second function is their average number. Probabilities  $\{\theta_i(\tau)\}$  that the reacted groups  $\{\bar{A}_i(\tau)\}$  enter in polymer molecules of finite size are found from the solution of the set of nonlinear integral equations

$$\theta_i(\tau) = \mathcal{F}_i(\tau; [\theta]) \quad (i = 0, 1, \dots) \quad (47)$$

derivable from equations (42) upon setting in them variable  $s$  to be equal to unity. Equations (47) before the gel-point  $p < p^*$  have only the trivial solution  $\theta = \mathbf{1}$  where all components of vector  $\theta$  are unity. After the gel-point  $p > p^*$  equations (47), as it has been rigorously proved (19), have one more solution located within hypercube  $0 < \theta_i(\tau) < 1$ , which describes the sol. Its weight fraction in a reaction system can be calculated from expression

$$\omega_s \equiv G_W(1) = \mathcal{F}^{(0)}[\theta] \quad (48)$$

where the dependence of vector  $\theta$  components on the process duration  $t$  or its conversion  $p$  is found from the solution of Eqs. (47).

As shown in Sec. 2, the  $gf$  of the MWD of the sol molecules formed in the course of the *random* polycondensation can be obtained by mere modification of the  $gf$ 's of the MWD of the products, which are prepared in the course of the pre-gel stage. These results are easy to extend to the *non-random* polycondensation. Taking into account this modification, the weight average degree of polymerization of the sol molecules can be calculated by formula

$$P_W^{sol}(t) \equiv \left. \frac{dG_W^{sol}}{ds} \right|_{s=1} = 1 + \frac{1}{\omega_s(t)} \int_0^t d\tau \sum_i \mathcal{F}_i^\dagger(\tau; [\theta]) U_i(\tau) z_i(\tau) \quad (49)$$

where functions  $z_i(\tau)$  (46) are found from the set of linear integral equations

$$\int_0^t d\xi \sum_j \Gamma_{ij}(\tau, \xi) z_j(\xi) = \theta_i \quad (i = 0, 1, \dots) \quad (50)$$

Their left-hand part can be considered as a result of the action upon the vector function  $z(\tau)$  of the linear integro-matrix operator  $\Gamma$  with kernel

$$\Gamma_{ij}(\tau, \xi) = \delta_{ij} \delta(\tau - \xi) - \mathcal{F}_{ij}(\tau, \xi) \quad (51)$$

Here  $\delta_{ij}$  denotes the Kronecker delta-symbol,  $\delta(\tau - \xi)$  is the Dirac delta-function, while  $\mathcal{F}_{ij}(\tau, \xi)$  stands for the matrix function

$$\begin{aligned} \mathcal{F}_{ij}(\tau, \xi) &\equiv \left. \frac{\delta \mathcal{F}_i(\tau; [\mathbf{u}])}{\delta u_j(\xi)} \right|_{\mathbf{u}=\theta} = \sum_k \pi_{ik}(\tau) \mathcal{F}_{kj}^\dagger(\tau, \xi) \\ &= \sum_k \frac{\tilde{k}_{ik} \mathcal{F}_{kj}^{(0)}(\tau, \xi)}{\varphi_i(\tau) \varphi_k(\tau)}, \quad \text{where} \quad \mathcal{F}_{kj}^{(0)}(\tau, \xi) \equiv \left. \frac{\delta^2 \mathcal{F}^{(0)}[\mathbf{u}]}{\delta u_k(\tau) \delta u_j(\xi)} \right|_{\mathbf{u}=\theta} \end{aligned} \quad (52)$$

Note, formula (49) describes, in fact, the evolution of the weight average degree of polymerization of finite size molecules not only before the gel-point, but after it as well. At this stage of polycondensation, expressions (49)–(52) can be employed for the calculation of the quantity  $P_W(t)$  taking into consideration that the values  $\theta(\tau)$ ,  $\omega_s(t)$  and  $\mathcal{F}_i^\dagger(\tau; [\mathbf{1}])$ , according to their definition, vanish identically up to the instant  $t = t^*$  of the polymer network formation. There is another method to calculate the value of  $t^*$ , apart from those two presented in Appendix A. This method implies finding the least eigenvalue of the self-conjugate operator  $\Gamma$ . It equals unity at  $t = 0$  decreasing in the course of the polycondensation to vanish eventually at  $t = t^*$ . Just at this moment the solution  $z$  of the equation 50 becomes infinite as well as the value of  $P_W(t^*)$  does.

In order to calculate the most important statistical characteristics of a polymer network, recourse should be made to formulas (23). However, the dependence on time of the parameters  $\lambda^{(k)}$  and  $\nu$  entering in these formulas, for the FSSE model

of polycondensation will be defined by the expressions other than (23) and (24)

$$\lambda^{(k)} = \frac{1}{k!} \int \cdots \int \prod_{v=1}^k d\tau_v \sum_{i_v} [1 - \theta_{i_v}(\tau_v)] \mathcal{F}_{i_1 \dots i_k}^{(0)}(\tau_1, \dots, \tau_k; [\boldsymbol{\theta}]) \quad (53)$$

$$v = \frac{1}{2} \int_0^t d\tau \sum_i [1 - \theta_i(\tau)] U_i(\tau) \{1 - \mathcal{F}_i^\dagger(\tau; [\boldsymbol{\theta}])\} - \lambda^{(2)} \quad (54)$$

Expressions (23), (53), (54) will be used below to calculate particular model polycondensation systems.

### 5. MARKOV STOCHASTIC PROCESS DESCRIBING THE EVOLUTION OF A MONOMERIC UNIT CONFIGURATION

Functions  $P_{\alpha_0, \dots, \alpha_n}^{(n)\text{mon}}(t; \tau_0, \dots, \tau_{n-1})$  (37) in the expressions (35) (36) for functional  $\mathcal{F}^{(0)}[\boldsymbol{u}]$  admit two simple probabilistic interpretations, provided these functions are written down as

$$P_{\alpha_0, \dots, \alpha_n}^{(n)\text{mon}}(t; \tau_0, \dots, \tau_{n-1}) = \mathcal{P}_{\alpha_0 \alpha_1}(0, \tau_0) \prod_{k=1}^{n-1} \mathcal{P}_{\alpha_k \alpha_{k+1}}(\tau_{k-1}, \tau_k) \mathcal{P}_{\alpha_n}(\tau_{n-1}, t) \quad (55)$$

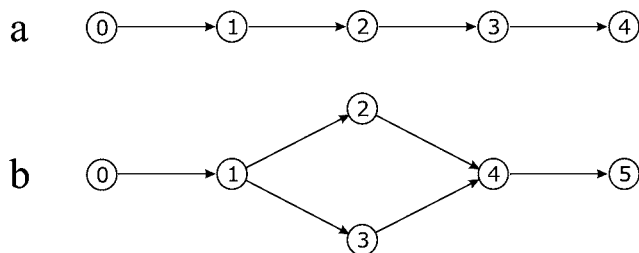
where the following designations are employed

$$\mathcal{P}_{\alpha\gamma}(\eta, \tau) = \exp[-I_\alpha(\eta, \tau)] \varphi_{\alpha\gamma}(\tau) \quad \mathcal{P}_\alpha(\eta, t) = \exp[-I_\alpha(\eta, t)] \quad (56)$$

$$I_\alpha(\eta, \tau) = \int_\eta^\tau \theta_\alpha(\xi) d\xi \quad (57)$$

In both interpretations, the function (37) is imparted the sense of the probability of the trajectory of a particular Markov process.

The first of them is a stochastic process with discrete “time”  $n$  having a meaning of the number of reacted groups in a monad. The set of regular states  $\{S_\alpha(\tau)\}$  of this process coincides with the set of monads of different types  $\alpha$ , each being marked by time  $\tau$  of its formation. The transition from regular state  $S_\alpha(\tau)$  into absorbing one implies that an  $\alpha$ -th kind monad formed at moment  $\tau$  will retain its configuration during the interval of real time  $(\tau, t)$ . In terms of this stochastic process, function  $\mathcal{P}_{\alpha\gamma}(\eta, \tau)$  (56) signifies the probability of the transition in a unit interval of “time”  $n$  from regular state  $S_\alpha(\eta)$  into regular state  $S_\gamma(\tau)$ . In order for this event to happen, an  $\alpha$ -th kind monad should necessarily retain its configuration within the interval of real time  $(\eta, \tau)$  to go over into configuration  $\gamma$  by the end of this interval. Probabilities of these two events are equal to the first and the second factors, respectively, in the right-hand side of the first of formulas (56). The second of functions (56) equals the probability of the transition from regular state  $S_\alpha(\tau)$  into the absorbing state.



**Fig. 5.** Examples of evolutionary orgraphs describing the evolution of a monomeric unit during non-random polycondensation of a monomer with configuration of regular tetrahedron (a) and square (b).

To every trajectory of this stochastic process, representing the particular sequence of transitions between its states, a certain path unambiguously corresponds on some labeled orgraph whose vertices are supplied with discrete  $\alpha$  and continuous  $\tau$  labels. The probability of such a trajectory coincides with the weight of the associated path on this orgraph. This weight is equal to the product of the weights of all arcs (i.e., directed edges) constituting this path multiplied by the probability of the transition into the absorbing state from the last vertex of this path. The weight of the arc corresponding to the transition from state  $S_\alpha(\eta)$  to state  $S_\gamma(\tau)$  equals  $P_{\alpha\gamma}(\eta, \tau)$  (56). Some examples of such an orgraph for monomers with different configurations are presented in Fig. 5. Special attention should be paid to the fundamental distinction between two kinds of orgraphs depicted in this figure. It consists in the presence of a loop in the second of them. This signals the existence in such an orgraph of vertices to which more than one path conduces from the zero vertex. Noteworthy that up to now all theoretical works dealing with non-random branched polycondensation did not examine monomers to which evolutionary orgraphs other than linear ones correspond (orgraph in Fig. 5a). At the same time, the presence of loops in an evolutionary orgraph may be responsible for some peculiarities in the formation of the polymer network at different sets of kinetic parameters of a reaction system. For example, at some relationship between elements of kinetic matrix  $k$ , the probability of trajectories 012 and 013 on the orgraph shown in Fig. 5b may differ dramatically. If so, the distinction in values of fractions of monads of each kind, i.e., the second and the third one, is strongly pronounced in products of the synthesis, that can lead to noticeable distinction in topological structure of molecules of both sol and gel.

One more statistical interpretation is possible for the expression (55). It can be considered as the probability of the trajectory at moment  $t$  of some extended Poisson stochastic process. In such a stochastic process, the trajectory is given apart from the sequence of states  $S_{\alpha_0}, \dots, S_{\alpha_n}$ , which a system passes through, also by the values of moments  $\tau_0, \dots, \tau_{n-1}$  at which these transitions have happened. The role of this process states is played by monads of different kinds, while the

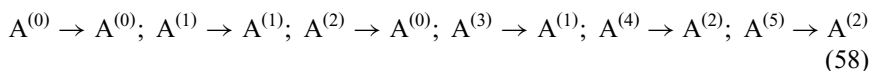
infinitesimal probability of the transition from state  $S_\alpha$  to state  $S_\gamma$  at moment  $\tau$  equals  $\varphi_{\alpha\gamma}(\tau)$  (A9). The initial state of any trajectory of this process naturally corresponds to the monad of the zero kind, whereas the absorbing state corresponds to the monad free from unreacted groups.

It should be stressed that the aforementioned stochastic process is not, strictly speaking, the Poisson process because the infinitesimal probabilities  $\varphi_{\alpha\gamma}(\tau)$ , according to formula (A9), depend on functions  $\lambda_\alpha(\tau)$  (32) which are one-dimensional sections of the process in hand. However, once these functions are found from the solution of closed set of Eqs. (32) and substituted in formula (A9) for  $\varphi_{\alpha\gamma}(\tau)$ , these latter may be viewed as known functions of time. Having performed such a procedure, it is possible to resort to the Kolmogorov equations to obtain the conditional probability  $R_{\alpha\gamma}(\eta, \tau)$  for the trajectory which was at moment  $\eta$  in state  $S_\alpha$  to be found at moment  $\tau$  in state  $S_\gamma$ .

## 6. SIMPLIFIED KINETIC MODELS

All formulas presented in the foregoing are derived in the framework of the general FSSE model. However, in macromolecular chemistry along with this model several its simplified versions are also currently used. These are characterized by smaller number of the rate constants of elementary reactions between functional groups.<sup>(2,21)</sup> Every such a model is given by kinetic matrix *boldsymbol* of special appearance. We will consider the modifications which theoretical expressions undergo when switching from the general FSSE model to its simplified versions.

Let us start with the “neighboring groups effect” (NGE) model.<sup>(20,21)</sup> It is based on the assumption that the reactivity of any functional group can be affected exclusively by the reacted functional groups neighboring with it in a monad. Evidently, in the case of the regular tetrahedron configuration of monomer  $RA^4$  (Fig. 1a), the NGE model is equivalent to the general FSSE model. As for square (Fig. 1b) and dumb-bell (Fig. 1c) configurations, in the general case, these are mutually topologically isomorphic. That is why it will suffice to restrict our consideration of the NGE model only to the first of them. For this configuration each functional group has two neighboring groups. Hence, just three kinds of functional groups,  $A^{(i)}$  ( $i = 0, 1, 2$ ), should be distinguished in this case where superscript  $i$  denotes the number of neighboring reacted groups. In other words, functional groups of three “colors” appear when considering the kinetics of polycondensation in the framework of the NGE model. Thus, when leaving the general FSSE model for the NGE model, it is necessary to “recolor” some functional groups in accordance with the following rule



In the model under examination, the kinetic matrix of elementary reactions between functional groups  $\mathbf{k}$  upon the transposition of its columns 2 and 3 and rows 2 and 3 will read

$$\mathbf{k} = \begin{pmatrix} \mathcal{K}^{00} & \mathcal{K}^{01} & \mathcal{K}^{02} \\ \mathcal{K}^{01} & \mathcal{K}^{11} & \mathcal{K}^{12} \\ \mathcal{K}^{02} & \mathcal{K}^{12} & \mathcal{K}^{22} \end{pmatrix} \quad (59)$$

where matrix cells  $\mathcal{K}^{ij}$  look as

$$\mathcal{K}^{ij} = \hat{k}_{ij} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad \hat{\mathbf{k}} = \begin{pmatrix} k_{00} & k_{01} & k_{02} \\ k_{01} & k_{11} & k_{12} \\ k_{02} & k_{12} & k_{22} \end{pmatrix} \quad (60)$$

Such a rearrangement of matrix  $\mathbf{k}$  virtually implies the inversion in labeling the functional groups of the second and the third kinds. This inversion should be carried out also in matrices  $\mathbf{f}$  and  $\mathbf{\Delta}$  (26) by inverting columns and rows in the first and the second of them, respectively. Having substituted matrices  $\mathbf{f}$ ,  $\mathbf{k}$  and  $\mathbf{\Delta}$  modified in the above-discussed manner, we will get some expressions for the rate constants of the reactions between monads (31). Substituting these constants into corresponding relationships presented in the foregoing, we will find formulas 42 and (44) retaining their appearance. It means that their statistical interpretation in terms of a branching process remains unchanged (see Sec.4), except that the number of kinds of reproducing particles will reduce from six to three. As to formulas (45), these will undergo substantial modifications

$$U_j(\tau) = \varphi_j(\tau) \mu_j(\tau) \quad \pi_{ij}(\tau) = \frac{\hat{k}_{ij} \mu_j(\tau)}{\varphi_i(\tau)} \quad (61)$$

where the following designations are adopted

$$\mu_j(\tau) = \sum_{\alpha} \lambda_{\alpha}(\tau) \hat{\mathbf{f}}_{\alpha j} \quad \varphi_i(\tau) = \sum_j \hat{k}_{ij} \mu_j(\tau) \quad (62)$$

Here matrix  $\hat{\mathbf{f}}^{\top}$  is the transpose of matrix  $\hat{\mathbf{f}}$

$$\hat{\mathbf{f}}^{\top} = \begin{pmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 0 & 2 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 1 & 0 \end{pmatrix} \quad (63)$$

Interestingly, all results, rigorously derived in the framework of this model in the above-discussed way, may be arrived at by considering the kinetics of polycondensation with participation of the functional groups of three kinds,  $A^{(0)}$ ,  $A^{(1)}$  and  $A^{(2)}$ . Under such a treatment all expressions of the theoretical approach invoked above to consider the general FSSE model can be employed. The only

distinction will be that instead of matrices  $\mathbf{f}$ ,  $\mathbf{k}$  and  $\mathbf{\Delta}$ , one should resort to their modifications  $\hat{\mathbf{f}}$  63,  $\hat{\mathbf{k}}$  60 and  $\hat{\mathbf{\Delta}}$

$$\hat{\mathbf{\Delta}} = \begin{pmatrix} 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 \end{pmatrix} \quad (64)$$

Let us address now the model dealing with the partial substitution effect (PSE) that is relevant to polycondensation of monomers composed of kinetically independent blocks. The entry into the reaction of a functional group involved in such a block inevitably leads to the change in the reactivity of the remaining groups of this block leaving, however, unaffected the reactivity of functional groups belonging to other blocks. As regards polycondensation of monomer  $\text{RA}^4$  with regular tetrahedron configuration, it, obviously, consists of the sole block. The simplest example of monomer  $\text{RA}^4$  that admits partitioning into two kinetically independent blocks is the monomer whose configuration is isomorphic to dumb-bell (Fig. 1c). In this case, every such a block comprises two groups. Each of them is able to be of either of two "colors," depending on whether its neighbor has already reacted or not. The "recoloring," analogous to that described above (58), should be realized in the following manner

$$\text{A}^{(0)} \rightarrow \text{A}^{(0)}; \text{A}^{(1)} \rightarrow \text{A}^{(0)}; \text{A}^{(2)} \rightarrow \text{A}^{(1)}; \text{A}^{(3)} \rightarrow \text{A}^{(1)}; \text{A}^{(4)} \rightarrow \text{A}^{(0)}; \text{A}^{(5)} \rightarrow \text{A}^{(1)} \quad (65)$$

Upon the inversion of kinds 3 and 5 of functional groups, kinetic matrix  $\mathbf{k}$  can be presented as

$$\mathbf{k} = \begin{pmatrix} \mathcal{K}^{00} & \mathcal{K}^{01} \\ \mathcal{K}^{01} & \mathcal{K}^{11} \end{pmatrix} \quad \mathcal{K}^{ij} = \hat{k}_{ij} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \quad \hat{\mathbf{k}} = \begin{pmatrix} k_{00} & k_{01} \\ k_{01} & k_{11} \end{pmatrix} \quad (66)$$

The chain of reasoning concerning the NGE model is also valid for the model under examination. The only exclusion is that here matrices  $\hat{\mathbf{f}}$ ,  $\hat{\mathbf{k}}$  and  $\hat{\mathbf{\Delta}}$  have appearance different from (63), (60) and (64)

$$\hat{\mathbf{f}}^\top = \begin{pmatrix} 4 & 2 & 0 & 2 & 0 & 0 \\ 0 & 1 & 2 & 0 & 1 & 0 \end{pmatrix} \quad \hat{\mathbf{\Delta}} = \begin{pmatrix} 0 & 1 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 & 1 \end{pmatrix} \quad (67)$$

As for the branching process describing polycondensation products by formulas (42) and (44), the number of kinds of reproducing particles equals two.

The most salient feature of the PSE model is the factorization of  $GF \mathcal{F}^{(0)} [u]$  (43), which represents the product of  $GF$ s of kinetically independent blocks

$$\mathcal{F}^{(0)} [u] = \left( \mathcal{F}_{bl}^{(0)} [u] \right)^2 \quad (68)$$

Here GF  $\mathcal{F}_{bl}^{(0)} [u]$  describes polycondensation of monomer  $RA^2$  in the framework of the complete FSSE model. There are serious grounds to believe that similar factorization will be the case under the statistical description of non-random polycondensation of arbitrary monomers consisting of kinetically independent blocks.

Let us turn now to the factorisable model. Here each element of matrix  $k$  is the product  $k_{ij} = k_i k_j$  of two factors,  $k_i$  and  $k_j$ , which characterize the reactivity of functional groups  $A^{(i)}$  and  $A^{(j)}$ , respectively. The rate constant of any reaction between monads (31) factorizes as

$$\tilde{k}_{\alpha\beta}^{\gamma\delta} = \tilde{k}_{\alpha\gamma} \tilde{k}_{\beta\delta} \quad \tilde{k}_{\alpha\gamma} = \sum_i f_{\alpha i} k_i \Delta_{i\gamma} \quad \tilde{k}_\alpha = \sum_\gamma \tilde{k}_{\alpha\gamma} \quad (69)$$

It can be readily shown that formulas (42–45) for polycondensation of monomer  $RA^f$  in the framework of the factorisable model are reducible to

$$G_W(s) = s\mathcal{F}^{(0)}[u] \quad u(\tau) = s\mathcal{F}(\tau; [u]) \quad (70)$$

$$\begin{aligned} \mathcal{F}^{(0)}[u] &= P^{(0)}(t) + \sum_{n=1}^f \sum_{\{i_0, \dots, i_{n-1}\}} \int \dots \int P_{i_0, \dots, i_{n-1}}^{(n)}(t; \tau_0, \dots, \tau_{n-1}) \\ &\times \prod_{k=0}^{n-1} u(\tau_k) d\tau_k \end{aligned} \quad (71)$$

where the density of probability is determined by expression

$$\begin{aligned} P_{\alpha_0, \dots, \alpha_n}^{(n)\text{mon}}(t; \tau_0, \dots, \tau_{n-1}) &= \exp[-\tilde{k}_{\alpha_n} I(t)] \prod_{k=0}^{n-1} \exp[(\tilde{k}_{\alpha_{k+1}} - \tilde{k}_{\alpha_k}) I(\tau_k)] \\ &\times \tilde{k}_{\alpha_k \alpha_{k+1}} \varphi(\tau_k) \end{aligned} \quad (72)$$

and the following simplification takes place

$$\mathcal{F}(\tau; [u]) = \mathcal{F}^\dagger(\tau; [u]) = \frac{\delta \mathcal{F}^{(0)}[u]}{\delta u(\tau)} \frac{1}{U(\tau)} \quad (73)$$

$$\begin{aligned} I(t) &= \int_0^t \varphi(t') dt' \quad U(\tau) = [\varphi(\tau)]^2 \\ \varphi(\tau) &= M^0 \sum_\alpha \tilde{k}_\alpha \lambda_\alpha(\tau) \end{aligned} \quad (74)$$

These expressions admit the statistical interpretation in terms of a branching process with one kind of reproducing particles which are marked by just the label  $\tau$ . The probability for the overall number of particle  $\bar{A}(\tau)$  descendants to be finite,



$\theta(\tau)$ , as well as the average number of particles in a population  $z(\tau)$  originated by this particle is, respectively, defined by formulas

$$\theta(\tau) = u(1; \tau) \quad z(\tau) = \left. \frac{du}{ds} \right|_{s=1} \tag{75}$$

where function  $\theta(\tau)$  is found from the solution of nonlinear integral equation

$$\theta(\tau) = \mathcal{F}(\tau; [\theta]) \tag{76}$$

As for expressions (49)–(52) for the calculation of the weight average degree of polymerization  $P_W(t)$ , they look as follows

$$P_W^{sol}(t) \equiv \left. \frac{dG_W^{sol}}{ds} \right|_{s=1} = 1 + \frac{1}{\omega_s(t)} \int_0^t d\tau U(\tau) z(\tau) \tag{77}$$

where function  $z(\tau)$  (75) is obtainable from the solution of the linear integral equation

$$\int_0^t d\xi \Gamma(\tau, \xi) z(\xi) = \theta \tag{78}$$

Here the kernel of the integral operator is

$$\Gamma(\tau, \xi) = \delta(\tau - \xi) - \frac{1}{U(\tau)} \left. \frac{\delta^2 \mathcal{F}^{(0)}[u]}{\delta u(\tau) \delta u(\xi)} \right|_{u=\theta} \tag{79}$$

If kinetic parameters  $k_i$  in the factorisable model are not controlled by subscript  $i$  and are equal to  $k$ , we are obviously dealing with the ideal model of polycondensation. In this case, it is easy to show that the generating functionals (43), (44) become generating functions<sup>(3,10)</sup>

$$F^{(0)}(u) = (1 - p + pu)^f \quad F(u) = (1 - p + pu)^{f-1} \tag{80}$$

with  $p$  representing the conversion of functional groups A. It can be easily demonstrated as well, that integral Eq. (76) reduces to the algebraic one

$$\theta = (1 - p + p\theta)^{f-1} \tag{81}$$

whose solution does not depend on  $\tau$ . This result comes as no surprise since the products of random polycondensation are statistically described by a branching process whose particles  $\bar{A}$  are not supplied with label  $\tau$ .

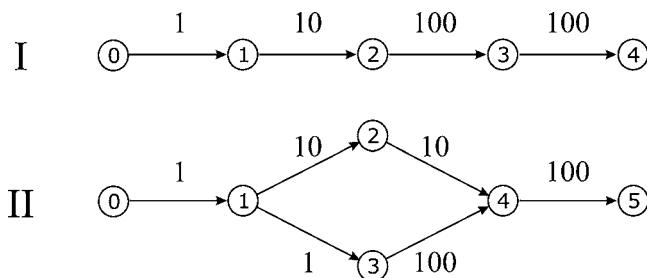
## 7. EXAMPLES OF THE CALCULATION OF THE STATISTICAL CHARACTERISTICS OF A POLYMER NETWORK

In order to calculate conversion  $p = p^*$  at which a polymer network appears for the first time, we resorted to two methods described in Appendix A. A number

of polycondensation systems differing by elements of kinetic matrix  $k$  have been calculated. Values of  $p^*$  obtained by these methods were found to coincide one with another as well as with those calculated earlier<sup>(18)</sup> with an accuracy not worse than 0.1 per cent.

With calculation of the topological characteristics of a polymer network (23) in mind we developed a computer program doing better than that employed in the preceding work.<sup>(13)</sup> Our new program makes redundant the recourse to any method of interpolation. The employment of such methods was absolutely inevitable earlier<sup>(13)</sup> to substantially reduce the calculation time which dramatically increases when  $p$  approaches  $p^*$ . The reason is the exponential retardation of the convergence of iterations under the solution of nonlinear integral equations (47).<sup>(19)</sup> Essentially, the computer program in hand provides an opportunity to calculate in a couple of hours necessary characteristics of a polymer network whose weight fraction  $\omega_g$  is 1.5–2 per cent. The computer program employed for the calculations in the preceding work<sup>(13)</sup> did not give a chance to escape some interpolation methods for achieving such results. It is worth emphasizing that with practical purposes in view, at values  $\omega_g \approx 1 - 2$  per cent there is no need to find a numerical solution of nonlinear integral Eqs. (47) by interpolation methods, since in such a close vicinity of the gel-point the asymptotic formulas are working quite well.

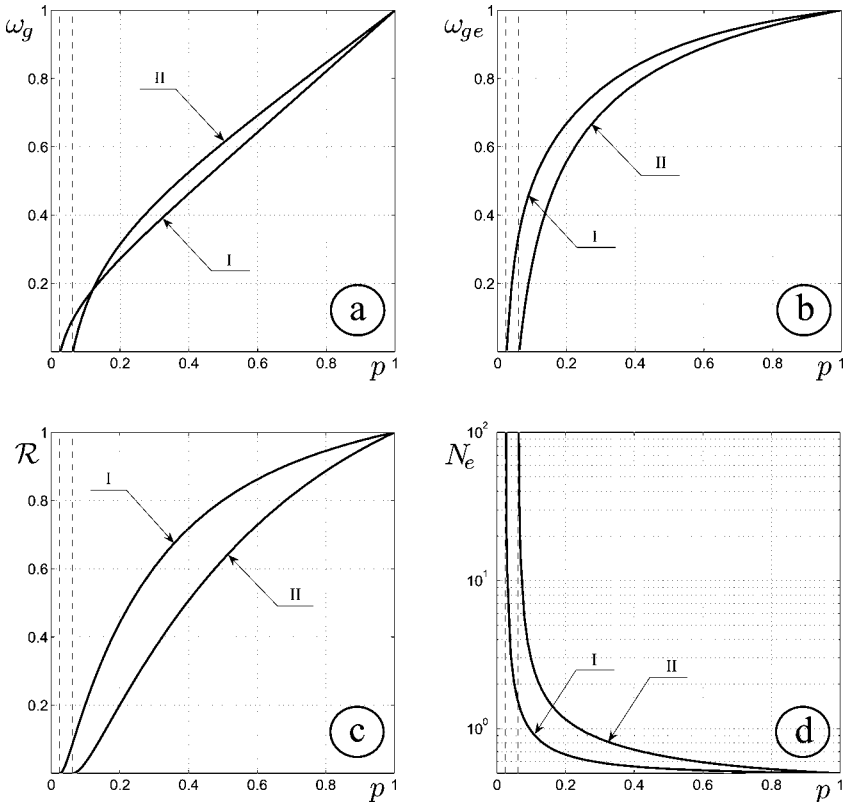
To illustrate the peculiarities of a polymer network formation caused by the configuration effects, we examined in the framework of the “neighboring group effect” model two particular systems of the non-random polycondensation at identical values ( $\kappa_0 = 1$ ,  $\kappa_1 = 10$ ,  $\kappa_2 = \kappa_3 = 100$ ) of kinetic parameters  $\kappa_i = k_i/k_0$  (see Fig. 6). In macromolecular chemistry, analogous systems are perfectly known<sup>(20)</sup>, in which the redistribution of electronic density in a monomeric unit due to the entry into the reaction of the neighboring functional groups results



**Fig. 6.** Evolutionary graphs of two polycondensation systems describable by the NGE model which have been chosen to exemplify the implementation of the theory proposed. The number every  $i$ -th arc is supplied with represents the value of kinetic parameter  $\kappa_i = k_i/k_0$ , where subscript  $i$  denotes the kind of the functional group whose entry into the reaction leads to the transformation of a monad consisting in alteration of its kind.

in an appreciable increase of the reactivity of the functional group of interest. Note, choosing in the configurational graph depicted in Fig. 5b for the kinetic parameters  $\kappa_1 = \kappa_2$  and  $\kappa_3 = \kappa_4$  (corresponding, respectively, to arcs 12, 13 and 24, 34) values 10 and 100, one will get a system kinetically equivalent to the system I in Fig. 6. However, in some systems, where equalities  $\kappa_1 = \kappa_2$  and  $\kappa_3 = \kappa_4$  are markedly broken, the topological characteristics of the molecular graph of a polymer network considerably differ from those peculiar to the system I (Fig. 6). The system II presented in Fig. 6, characterized by the following values of kinetic parameters  $\kappa_0 = 1, \kappa_1 = 10, \kappa_2 = 1, \kappa_3 = 10, \kappa_4 = 100, \kappa_5 = 100$ , makes an excellent example.

The results of kinetic calculations of the statistical characteristics of a polymer network for systems I and II are given in Fig. 7. It can be seen from Fig. 7a



**Fig. 7.** Dependencies on conversion  $p$  of the main statistical characteristics (22) of a polymer network formed in the course of non-random polycondensation of monomer  $RA^4$  which is described by the NGE model in systems I and II (see Fig. 6). Each vertical dashed line denotes the border of the gelation region.

that the gel forms first in the system I. However, the rate of its formation is initially substantially less than that in the system II. That is why within the region of moderate conversions, the value of  $\omega_g$  in the system II will noticeably exceed that in the system I. Such a distinction, for instance at  $p = 0.4$ , constitutes more than ten per cent. As Fig. 7b shows, the same happens to the fraction of elastically effective material  $\omega_{ge}$  of a polymer network. In regard to the conversional dependence of cyclic rank  $\mathcal{R}$  of its molecular graph, the distinction between systems I and II is of quantitative rather than of qualitative nature. On turning to Fig. 7c, it is easy to notice that value of  $\mathcal{R}$  at all  $p$  is smaller for the system II than that for the system I. For example, at conversion  $p = 0.3$  the relative distinction  $\Delta = (\mathcal{R}_I - \mathcal{R}_{II})/\mathcal{R}_I$  of values of cyclic rank  $\mathcal{R}_I$  and  $\mathcal{R}_{II}$  in systems I and II is 39.6 per cent. Such a pronounced discrepancy is easy to explain. Indeed, the value of the cycling rank  $\mathcal{R} = 0.5\lambda^{(3)} + \lambda^{(4)}$  is expressed in a straightforward manner through the fractions  $\lambda^{(k)}$  of monads characterized by number  $k$  of paths leading to infinity. We have calculated that at conversion  $p = 0.3$  in the system I monad fractions  $\lambda^{(3)} = 0.069$ ,  $\lambda^{(4)} = 0.189$  and the cyclic rank  $\mathcal{R}$  have the following values 0.604, whereas in the system II they are  $\lambda^{(3)} = 0.075$ ,  $\lambda^{(4)} = 0.120$ ,  $\mathcal{R} = 0.365$ . These findings point to a minor difference in values of the fraction of monads  $\lambda^{(3)}$  in both systems. Conversely, the distinction in values of  $\lambda^{(4)}$  is clear cut. The last circumstance is responsible for a significant difference in values of  $\mathcal{R}_I$  and  $\mathcal{R}_{II}$ , since the contributions of monads with  $k = 4$  to the cyclic rank for the case in point is well above that of monads with  $k = 3$ . Average length of an elastically active chain in a polymer network, which at the instant of its formation equals infinity, monotonically decreases with conversion. It can be inferred from Fig. 7d that at any conversion  $p$  the value of  $N_e$  is higher in the system II. However, this property is not universal. We managed to discover systems where the curve of the dependence  $N_e$  on conversion  $p$  for polycondensation of monomer  $RA^4$  with square configuration crosses the analogous curve for polycondensation of monomer  $RA^4$  with regular tetrahedron configuration.

## 8. CONCLUSION

A branched polycondensation possesses a number of specific features setting it apart from other aggregation processes. This stipulates some peculiarities which one should take into account under theoretical consideration of a branched polycondensation. Among these peculiarities (which have not been addressed so far in vast majority of publications on the theory of aggregation) are the following:

### 1. *Polycondensation under consideration is non-random*

It is a common knowledge that for any process of random irreversible polycondensation (aggregation), the theoretical problem of finding the distribution  $C(l, t)$  of molecules (clusters) for number of

constituent monomeric units  $l$  is reduced to the solution of an infinite set of ordinary differential equations. This set represents a discrete analogue of the Smoluchowski integro-differential equation with kernel  $R(l', l'')$  depending only on numbers of units  $l'$  and  $l''$  of reacting molecules. For non-random polycondensation, this statement proves to be incorrect because the evolution of distribution  $C(l, t)$  can not be described, in principle, by any Smoluchowski-type equation. In this case one is supposed to resort to approaches which are non-traditional for the regular aggregation theory. Just one of these approaches is employed in the present paper.

2. *Necessity to calculate the topological characteristics of the molecular graph of a gel (polymer network)*

When considering a gel in the theory of aggregation of colloid particles, it is customary to restrict the calculation to the evolution with time of its weight fraction. However, in the theory of polymers' aggregation of prime concern are the elastic properties of a polymer network which are predetermined by the topology of its molecular graph. Here some topological problems arise for the description of a gel that have no analogue in the traditional theory of coagulation. The above-presented theoretical approach permitted us to solve these problems.

3. *Recourse to the mathematical apparatus of the theory of stochastic processes*

Presently in quantitative theory of polycondensation, both kinetic and statistical methods are concurrently used to calculate the statistical characteristics of sol and gel. The first of them implies the solution of the material balance equations describing the evolution with time of concentrations of different molecules. However, for the calculation of the statistical characteristics of a gel, the second method turns out to be more efficient, for it enables one to find these characteristics from simple probabilistic considerations. Such a statistical method is rigorously substantiated in statistical chemistry of polymers where today it has found a wide utility. However, for a theorist dealing with aggregation processes in non-polymeric systems, the statistical method is far from being as familiar as the kinetic one. Meanwhile the use of the statistical formalism alike to that employed in the foregoing appears to be quite efficient under a theoretical description of arbitrary aggregation processes.

The results reported in the present paper certainly point to the importance of the allowance for the configurational effect in the quantitative theory of non-random polycondensation. This effect has been experimentally found in some polycondensation systems,<sup>(22)</sup> in which the value  $f$  of monomer  $RA^f$  functionality lies within the range between 6 and 12. In order to describe the polycondensation of such systems it would be pertinent to resort to the theory advanced in the present

paper. The comparison of our theoretical results with the experimental findings<sup>(22)</sup> will be reported elsewhere.

**APPENDIX A. METHODS FOR CALCULATION OF THE GEL-POINT**

There are several methods for finding the critical value of the conversion at gel-point  $p = p^*$ . One of them is based on the solution of a closed set of equations for the second order statistical moments of  $c(\mathbf{I}; t)$ , which are related in a simple way to the second derivatives of function  $g(\mathbf{s}, t)$  (28) taken at point  $\mathbf{s} = \mathbf{1}$

$$\mu_{\alpha\beta} \equiv \sum_{\mathbf{I}} I_{\alpha}(I_{\beta} - \delta_{\alpha\beta})c(\mathbf{I}, t) = \left. \frac{\partial^2 g}{\partial s_{\alpha} \partial s_{\beta}} \right|_{\mathbf{s}=\mathbf{1}} \tag{A1}$$

These equations obtained via term by term differentiation of the equation for function  $g(\mathbf{s}, t)$  (29) look as follows

$$\begin{aligned} \frac{d\mu_{\alpha\beta}}{dt} = M^0 \sum_{\gamma, \delta} \left\{ \tilde{k}_{\gamma\delta} \mu_{\gamma\alpha} \mu_{\delta\beta} + \left( \Gamma_{\gamma\delta}^{\alpha} \mu_{\gamma\beta} + \Gamma_{\gamma\delta}^{\beta} \mu_{\gamma\alpha} \right) \lambda_{\delta} \right. \\ \left. + \frac{1}{2} \Gamma_{\gamma\delta}^{\alpha\beta} \lambda_{\gamma} \lambda_{\delta} \right\} - \mu_{\alpha\beta} (\theta_{\alpha} + \theta_{\beta}) \quad \mu_{\alpha\beta}(0) = 0 \end{aligned} \tag{A2}$$

where the designations are used

$$\Gamma_{\alpha\beta}^{\gamma\delta} = \left. \frac{\partial^2 \sigma_{\alpha\beta}}{\partial s_{\gamma} \partial s_{\delta}} \right|_{\mathbf{s}=\mathbf{1}} = \tilde{k}_{\alpha\beta}^{\gamma\delta} + \tilde{k}_{\alpha\beta}^{\delta\gamma} \quad \Gamma_{\alpha\beta}^{\gamma} = \left. \frac{\partial \sigma_{\alpha\beta}}{\partial s_{\gamma}} \right|_{\mathbf{s}=\mathbf{1}} = \sum_{\delta} \Gamma_{\alpha\beta}^{\gamma\delta} \tag{A3}$$

Mathematical condition of gel-point  $t = t^*$  (or  $p = p^*$ ) is simultaneous divergence of all functions  $\mu_{\alpha\beta}(t)$ .

Another method for the calculation of critical conversion  $p = p^*$  implies the consideration of a set of ordinary differential equations for characteristics  $S_{\alpha}$  and  $s_{\gamma}$

$$\begin{aligned} \frac{dS_{\alpha}}{dt} = \sum_{\beta} S_{\beta} \phi_{\beta\alpha} - \theta_{\alpha} S_{\alpha} \quad S_{\alpha}(0) = \delta_{\alpha 0} \\ \frac{ds_{\gamma}}{dt} = \theta_{\gamma} s_{\gamma} - \sum_{\delta} \phi_{\gamma\delta} s_{\delta} \quad s_{\gamma}(0) = \zeta_{\gamma} \end{aligned} \tag{A4}$$

with the following designations employed

$$\phi_{\alpha\gamma}(\mathbf{s}) = M^0 \sum_{\beta, \delta} \tilde{k}_{\alpha\beta}^{\gamma\delta} S_{\beta} s_{\delta} \tag{A5}$$

The solution of the set of equations (A4) can be presented as

$$S_{\alpha} = H_{\alpha}(\boldsymbol{\zeta}, t) \quad s_{\gamma} = h_{\gamma}(\boldsymbol{\zeta}, t) \tag{A6}$$

The components of vector-function  $\zeta_\gamma = q_\gamma(\mathbf{s}, t)$  represent before the gel-point the only solution of the second equation (A6). At the very gel-point this uniqueness proves to be broken. Mathematical condition of this is vanishing of the determinant of matrix  $\mathbf{x}$  whose elements are  $x_{\alpha\beta}$ , that in combination with elements  $y_{\alpha\beta}$  of matrix  $\mathbf{y}$

$$x_{\alpha\beta} \equiv \frac{\partial h_\alpha(\mathbf{1}, t)}{\partial \zeta_\beta} \quad y_{\alpha\beta} \equiv \frac{\partial H_\alpha(\mathbf{1}, t)}{\partial \zeta_\beta} \tag{A7}$$

is determined from the solution of ordinary differential equations

$$\begin{aligned} \frac{dx_{\alpha\beta}}{dt} &= \theta_\alpha x_{\alpha\beta} - \sum_\gamma \varphi_{\alpha\gamma} x_{\gamma\beta} - M^0 \sum_{\delta, \mu} \mathbb{k}_{\delta\alpha}^\mu (\lambda_\delta x_{\mu\beta} + y_{\delta\beta}) \quad x_{\alpha\beta}(0) = \delta_{\alpha\beta} \\ \frac{dy_{\alpha\beta}}{dt} &= \sum_\gamma \varphi_{\gamma\alpha} y_{\gamma\beta} - \theta_\alpha y_{\alpha\beta} + M^0 \sum_\gamma \lambda_\gamma \\ &\quad \times \sum_{\delta, \mu} \tilde{k}_{\delta\gamma}^{\mu\alpha} (\lambda_\delta x_{\mu\beta} + y_{\delta\beta}) \quad y_{\alpha\beta}(0) = 0 \end{aligned} \tag{A8}$$

Here infinitesimal probability  $\varphi_{\alpha\gamma}$  for an  $\alpha$ -th kind monad to turn at moment  $t$  into  $\gamma$ -th kind monad is defined as

$$\varphi_{\alpha\gamma} = \phi_{\alpha\gamma}(\mathbf{1}) = M^0 \sum_{\beta, \delta} \tilde{k}_{\alpha\beta}^{\gamma\delta} \lambda_\beta \quad \theta_\alpha = \sum_\gamma \varphi_{\alpha\gamma} \tag{A9}$$

Monads' fractions  $\lambda_\alpha$  appearing in the right-hand side of Eqs. (A8) are solutions of Eqs. (32). Elements of the first row of matrix  $\mathbf{y}$  are equal to zero, as also are the elements of the last row of matrix  $\mathbf{x}$ . The sole exclusion here is the last element of this row which equals unity. Moreover, it can be readily shown that the elements of the first column of matrix  $\mathbf{y}$  and those of the first column of matrix  $\mathbf{x}$  (with the exception of the first element  $x_{00}$  in this column) are zero as well. As for element  $x_{00}$ , it remains positive at any moment as it stems from the equation which may be integrated separately. So, in order to calculate critical conversion  $p = p^*$  it is enough to consider square matrices  $\mathbf{x}'$  and  $\mathbf{y}'$  (obtained from matrices  $\mathbf{x}$ ,  $\mathbf{y}$  by excluding the first and the last of rows and columns) as well as to specify the moment at which matrix  $\mathbf{x}'$  determinant vanishes for the first time.

## APPENDIX B. EQUATIONS FOR FINDING TRANSITION PROBABILITIES

When calculating the statistical characteristics of the topological structure of a polymer network, one inevitably encounters the problem of the calculation of the variational derivatives of functional  $\mathcal{F}^{(0)}[\mathbf{u}]$  (43). For instance, the knowledge of its first order variational derivatives are indispensable in finding the right-hand

side of Eqs. (47) for the calculation of vector-function  $\theta(\tau)$ , as well as under the calculation of the fraction of gel  $\omega_g$  (23), fractions of elastically active material  $\omega_{ge}$  (23) and cyclic rank  $\mathcal{R}$  (23). To calculate the fraction of elastically effective nodes  $\mu$  (23), the number of elastically active chains per one node  $\nu$  (23) as well as average length of an elastically active chain  $N_e$  (23), it is necessary to know the second variational derivatives of functional  $\mathcal{F}^{(0)}[\mathbf{u}]$ . This can be regarded as  $GF$  of the extended Poisson process (see Sec. 5), wherein “counter”  $u_{\alpha\gamma}(\tau)$  (representing a dummy variable) is ascribed to the transition from state  $S_\alpha$  into state  $S_\gamma$  at moment  $\tau$ . The derivatives of this functional are in a straightforward manner expressed

$$\begin{aligned} \frac{\delta \mathcal{F}^{(0)}[\mathbf{u}]}{\delta u_{\alpha_n \alpha_{n+1}}(\tau)} &= R_{0\alpha_n}(0, \tau; [\mathbf{u}]) \varphi_{\alpha_n \alpha_{n+1}}(\tau) \sum_{\gamma} R_{\alpha_{n+1}\gamma}(\tau, t; [\mathbf{u}]) \\ &\quad \delta^2 \mathcal{F}^{(0)}[\mathbf{u}] / \delta u_{\alpha_m \alpha_{m+1}}(\xi) \delta u_{\alpha_n \alpha_{n+1}}(\tau) \\ &= R_{0\alpha_n}(0, \xi; [\mathbf{u}]) \varphi_{\alpha_m \alpha_{m+1}}(\xi) R_{\alpha_{m+1}\alpha_n}(\xi, \tau; [\mathbf{u}]) \varphi_{\alpha_n \alpha_{n+1}}(\tau) \\ &\quad \times \sum_{\gamma} R_{\alpha_{n+1}\gamma}(\tau, t; [\mathbf{u}]) \eta_s(\tau - \xi) \\ &\quad + R_{0\alpha_n}(0, \tau; [\mathbf{u}]) \varphi_{\alpha_n \alpha_{n+1}}(\tau) R_{\alpha_{n+1}\alpha_m}(\tau, \xi; [\mathbf{u}]) \varphi_{\alpha_m \alpha_{m+1}}(\xi) \\ &\quad \times \sum_{\gamma} R_{\alpha_{m+1}\gamma}(\xi, t; [\mathbf{u}]) \eta_s(\xi - \tau) \end{aligned} \quad (\text{B1})$$

through the infinitesimal probabilities of transition  $\varphi_{\alpha\gamma}(\tau)$  (A9) of the above stochastic process and functional  $R_{\alpha\gamma}(\xi, \tau; [\mathbf{u}])$  of the conditional transition probabilities. This latter is calculated analogously to the conditional transition probability  $R_{\alpha\gamma}(\xi, \tau)$  (see Sec. 5) itself, with the only distinction that the infinitesimal probability of every transition in the trajectory should be additionally multiplied by corresponding counter  $u_{\alpha\gamma}(\tau)$ . From this it immediately follows that functional  $R_{\alpha\gamma}(\xi, \tau; [\mathbf{u}])$  satisfies direct differential equations

$$\begin{aligned} \frac{dR_{\alpha\gamma}(\xi, \tau; [\mathbf{u}])}{d\tau} &= \sum_{\beta} \varphi_{\beta\gamma}(\tau) u_{\beta\gamma}(\tau) R_{\alpha\beta}(\xi, \tau; [\mathbf{u}]) - \theta_\gamma(\tau) R_{\alpha\gamma}(\xi, \tau; [\mathbf{u}]), \\ R_{\alpha\gamma}(\xi, \xi; [\mathbf{u}]) &= \delta_{\alpha\gamma} \quad R_{\alpha\gamma}(\xi, \tau; [\mathbf{u}]) \equiv 0, \quad \xi > \tau \end{aligned} \quad (\text{B2})$$

and reverse differential equations

$$\begin{aligned} \frac{dR_{\alpha\gamma}(\xi, \tau; [\mathbf{u}])}{d\xi} &= - \sum_{\delta} \varphi_{\alpha\delta}(\xi) u_{\alpha\delta}(\xi) R_{\delta\gamma}(\xi, \tau; [\mathbf{u}]) + \theta_\alpha(\xi) R_{\alpha\gamma}(\xi, \tau; [\mathbf{u}]), \\ R_{\alpha\gamma}(\tau, \tau; [\mathbf{u}]) &= \delta_{\alpha\gamma} \quad R_{\alpha\gamma}(\xi, \tau; [\mathbf{u}]) \equiv 0, \quad \xi > \tau \end{aligned} \quad (\text{B3})$$



which are a modification of the Kolmogorov equations (23). Note, the equation for the calculation of  $\lambda_\gamma(t)$  is obtained directly from (B2), provided all elements of matrix  $\mathbf{u}$  are put in them equal to unity. Summing term by term all items in equation (B2) over index  $\alpha$  and integrating it over variable  $\xi$ , we will get equation (32) for fractions of different kind monads.

Formula (B1) represents a particular case of the general expression for the variational derivative of any  $k$ -th order of the  $GF$  (43). This expression will be a sum of  $k$  items, each corresponding to a region of the  $k$ -dimensional space of variables  $\{\tau_\nu\}$ , characterized by their specified ordered sequence  $0 < \tau_{\nu_1} < \tau_{\nu_2} < \dots < \tau_{\nu_k}$ . The first of these items corresponds to the principle sequence  $0 < \tau_1 < \tau_2 < \dots < \tau_k$ , whereas the remaining items correspond to sequences with different permutations of indices  $\nu_1, \nu_2, \dots, \nu_k$ . The algorithm enabling one to write down the expression for the first item is rather simple if recourse is made to the evolutionary orgraph (see Fig. 5). In fact, taking variational derivative of functional  $\mathcal{F}^{(0)}[\mathbf{u}]$  (43) with respect to variable  $\delta u_{\alpha_n \alpha_{n+1}}(\tau)$  corresponds to setting apart in this orgraph the arc (i.e., directed edge) with label  $\tau$  which links vertices  $\alpha_n$  and  $\alpha_{n+1}$ . We will ascribe to this arc weight  $\varphi_{\alpha_n \alpha_{n+1}}(\tau)$ . Thus, to the  $k$ -th order derivative there corresponds a set consisting of  $k$  labeled arcs, separated one from another by some subgraphs. Analogous subgraphs can be situated both at the beginning and the end of the evolutionary graph. In every such a subgraph a pair of vertices,  $\alpha_{n+1} \alpha_m$ , are specified which are adjacent to arcs with labels  $\tau$  and  $\xi$ . We will ascribe weight  $R_{\alpha_{n+1} \alpha_m}(\tau, \xi; [\mathbf{u}])$  to every of these subgraphs. Then the expression for variational derivative of an arbitrary order will equal the product of weights of all labeled arcs of the orgraph and corresponding subgraphs adjacent to them.

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