Stochastic Branching Process for Description of Non-Random Irreversible Polycondensation

Semion I. Kuchanov[1] **and Timur V. Zharnikov**[2]

For the first time the possibility of the description of the products of non-random irreversible polycondensation by the theory of branching processes is rigorously substantiated. The formalism of this theory is shown to be efficient in finding any statistical characteristics not only of finite molecules but those of a polymer network as well. Exact equations are derived and their simplified forms are presented for networks being formed in the vicinity of the gel-point. Errors arising under the application of an approximation based on the traditional statistical approach are evaluated proceeding from the analysis of the numerical solutions of these equations.

1. INTRODUCTION

An extremely important phenomenon in a wide variety of processes in physics, chemistry, biology, medicine, and engineering is the formation of large clusters by the union of many separate, small elements. Among such processes are branched polycondensation in polymer science, floccullation, and coagulation in colloid physics, nucleation in statistical physics of phase transitions, antigen-antibody aggregation in immunology and etc.[1] Despite differences between these processes, mathematical approaches used for their description are quite similar. They imply the derivation and solution of an infinite set of kinetic equations of material balance for the concentrations of different size' clusters. The most popular of them is the

---

[1] Physics Department, Moscow State University, 119992, Moscow, Russia; e-mail: kuchanov@ polly.phys.msu.ru

[2] Nesmeyanov Institute of Elementoorganic Compounds, Vavilov str., 28, 119991, Moscow, Russia.

Smoluchowski equation which has much in common with nonlinear Boltzmann equation.[2] The steady interest to the cluster formation kinetics in aggregation processes from physicists-theorists is witnessed by the great number of works devoted to this problem (see reviews 3–5 and references therein). Many of them deal with the gelation effect, i.e., the appearance of an infinite-size cluster, which in the polycondensation theory corresponds to a polymer network. Problems of the calculation of its topological characteristics can not be solved by straightforward recourse to the Smoluchowski kinetic equation but call for a statistical method. Its rigorous substantiation for the non-random aggregation accompanied by formation of polymer gel has apart from scientific value also a practical significance for the mathematical modeling of industrial processes of the network polymers' synthesis.

The point is that many of such polymers are manufactured by step-growth polymerization of monomers with number of functional groups exceeding two. For such a branched polycondensation the average size of a polymer molecule progressively increases to diverge at a certain instant when an infinite gel network appears. Thereafter the weight fraction of gel ω_g in the reaction system will grow whereas the fraction of sol $\omega_s = 1 - \omega_g$ will diminish in parallel with the decrease of the average size of its constituent finite molecules. Finding their distribution for size and composition as well as determining the statistical moments of this distribution are among major challenges to a quantitative theory of branched polycondensation. One of them that is of crucial practical significance consists in establishing the dependence of quantity ω_g and statistical characteristics of the topological structure of a polymer network on conversion of functional groups.

The most important among these characteristics of a network are the number of elastically active chains v and the number of elastically effective nodes μ per one monomeric unit. To these latter there belong the nodes from which not less than three paths in the infinite molecular graph of a gel connect to infinity. A chain linking two such nodes is referred to as elastically active one. Parameters v and μ play a leading role in the theory of polymer networks' elasticity since they enter into the expressions for the elasticity modulus. The latter under the simplest theoretical approach is proportional to the cyclic rank $\mathscr{R} = v - \mu$ of the molecular graph of a network. This topological parameter equals, by definition, the least number of edges of a graph, which should be removed to convert it into a tree.

Any polymer network comprises a pendant material that makes no contribution into its elastic properties. Fraction of units ω_{gp} pertaining to this material may be regarded as a criterion characterizing the quality of a particular network. This will be the more attractive for practical implication the larger is the fraction of units $\omega_{ge} = \omega_g - \omega_{gp}$ involved in elastically

effective material. Given ω_{ge} and v it is possible to calculate the number-average length of an elastically active chain ω_{ge}/v.

The foregoing characteristics of sol and gel are found in a standard manner by a statistical method for the processes of branched polycondensation describable by the ideal kinetic model. This is based on two assumptions:

1. The absence of intramolecular reactions in molecules of finite size.

2. The fulfillment of the Flory principle for all reacting functional groups.

The second assumption means that the reactivity of any such a group depends neither on the configuration of a molecule (i.e., its size, composition and chemical structure) it belongs to nor on this group position in a molecule. Otherwise stated the reactivities of all functional groups remain unaltered throughout the synthesis being equal to the values, which these groups possessed in monomers.

Nowadays the elaboration of the theory of random polycondensation describable by the ideal model may be considered as completed.[6, 7] Proceeding from kinetic analysis of this model it was rigorously proved that the statistical method can be employed for the calculation of any characteristic of both sol and gel. Central idea of this method resides in reducing the procedure of averaging over configurations of polymer molecules to that over realizations of a certain branching process subsequently using an advanced mathematical apparatus of the theory of these stochastic processes. Bearing in mind indisputable advantages of statistical methods in calculating configurational characteristics of polycondensates it is of prime importance to reveal the potentialities of this method as applied to systems where the Flory principle is violated.

This fundamental principle whose validity has been established for a great many polycondensation systems is a good approximation for the description of chemical transformations proceeding in them. However a multitude of particular systems (mainly with participation of aromatic monomers) have been revealed where the above principle does not hold. The reason is the so called "substitution effect" due to steric, induction, catalytic and other kinds of the influence of the reacted functional groups on the reactivity of the neighboring unreacted groups. Originally this effect was taken into account by Gordon and Scantlebury[8] who theoretically studied the homopolycondensation of monomer RA^f with f identical functional groups within the framework of the First Shell Substitution Effect (FSSE) model. This implies that the reactivity of any group A attached to the monomeric unit is entirely controlled by its kind i, i.e., by number i of

molecular bonds connecting this unit with other ones. When considering a kinetic scheme of elementary reactions such a group may be ascribed the kind i. Thus the FSSE model is completely specified by a matrix of kinetic parameters with elements k_{ij} equal to the rate constants of elementary reactions between functional groups of different kinds.

The authors of paper[8] postulated that all characteristics of the configurational structure of non-random polycondensation products examined are possible to calculate from the equations of the branching process that describes random polycondensation but with other probability distribution characterizing the reproduction of particles. In the zeroth generation the probability to produce i descendants equals the fraction λ_i of monads of kind i, i.e., the fraction of monomeric units R with i reacted groups $\bar{A}$. In all generations but the zeroth one particles reproduce with other probabilities whose generating function (gf) F is expressible in a simple manner through gf $F^{(0)}$ of probabilities λ_i

$$F^{(0)}(u) = \sum_{i=0}^{f} \lambda_i u^i \qquad F(u) = \frac{dF^{(0)}(u)}{du} \bigg/ \frac{dF^{(0)}(u)}{du}\bigg|_{u=1} \tag{1}$$

The mathematical apparatus of the branching processes theory enables one to calculate any statistical characteristic of polycondensates provided probability parameters $\lambda_0,\ldots,\lambda_f$ are given. To find them it was suggested[8] to use thermodynamic or kinetic equations for equilibrium or irreversible polycondensation regimes, respectively. In the framework of this monad approach there were considered various problems of finding by the statistical method of the characteristics of sol and gel formed during monomer RA^f polycondensation described by the FSSE model.[8–12] This system being the simplest among non-ideal ones features, however, all main peculiarities of the non-random step-growth polymerization. That is why we will consider in this paper just this system with the perspective to address the theory of non-random polycondensation of an arbitrary monomer mixture in the framework of the FSSE model elsewhere.[13]

For a time the question of the validity of the Gordon branching process for the description of the products of non-random polycondensation remained open. By the end of 70s it was established[6, 14, 15] that the recourse to this stochastic process leads to the expression for the molecular-weight distribution (MWD) other than that obtained from the solution of the kinetic equations of irreversible polycondensation. The partial differential equation was derived[15] for the generating function (gf) of this distribution allowing one to get the equations for the statistical moments of MWD. From the condition of their divergence the value of the conversion $p = p^*$ was calculated at the gel point for a wide range of kinetic

parameters.[16] The equations of non-random polycondensation reported in papers[15, 16] were rederived more than fifteen years later[17–19] as applied only to the particular case of the simplified variant of the FSSE model where the rate constants of elementary condensation reactions k_{ij} between groups of kinds i and j are factorisable $k_{ij} = k_i k_j$. In the framework of this "factorisable" model Mikes and Dusek[20] examined the dependence of the gel-point p^* under polycondensation of monomer RA_3 on kinetic parameters k_0, k_1, k_2 invoking for this purpose the Monte-Carlo method. The comparison of the results of the computer simulations with those achieved using the Gordon statistical method, i.e., the monad approach, prompted the authors[20] to conclude that the values of p^* found in two ways are virtually identical excluding some specific values of kinetic parameters. However this conclusion should be viewed with due caution because of two circumstances. Firstly, Mikes and Dusek[20] confined themselves to the value of monomer functionality f equal to three. Secondly, they performed simulations in the framework of the factorisable FSSE model only. These restrictions were relaxed in paper[21] where a comprehensive study was undertaken of the influence of different factors on the error in value p^* that arises under the application of the approximation based on the Gordon branching process. The calculations revealed the existence of an appreciable region of values of the kinetic parameters where the employment of this approximation produces too large error in the value of critical conversion in gel-point.[21]

Of special significance in the theory of non-random polycondensation is the paper by Sarmoria and Miller.[22] They came up with the idea to use the recursive statistical approach for the calculation of the molecular weight of the products of this process formed during the pre-gelation stage. This approach, being distinct from the Gordon statistical approach,[8, 9] yields for random polycondensation the same results.[23] Because these latter coincide with the results of the kinetic examination the employment of the recursive approach in this case is well justified. Conversely, such a substantiation for the non-random polycondensation is missing so far.

Critically important for a quantitative theory of non-random polycondensation is to answer the question of whether there is a branching process capable of providing an exact statistical description of sol and gel. In the present paper a rigorous kinetic substantiation of the existence of such stochastic process is offered and the expressions for its probability parameters are presented. Subsequent employment of the statistical method permits one to calculate, in particular, the topological characteristics of a polymer network governing its elasticity. The results of such a calculation are reported below for polycondensation systems with various values of elements k_{ij} of the matrix of the constants of elementary reactions. The

comparison of the values of the above topological characteristics obtained from the equations of the new branching process and the traditional one makes possible to estimate the error occurring under the application of the latter for mathematical modeling of the gelation processes.

The paper is organized as follows. In Section 2 we give brief presentation of the traditional statistical approach to the approximate calculation of the characteristics of sol and gel. In Section 3 a new branching process is introduced, and equations are presented enabling the calculation of the exact values of the above characteristics. In Section 4 we discuss the simplification of general relationships in particular case of factorisable model. Section 5 is devoted to the comparison of the values of polymer network's characteristics obtained in the framework of the rigorous theory with the approximate ones found using the formalism of the branching process put forward by Gordon and co-workers.[8, 9]

2. GORDON'S STATISTICAL APPROACH

In the framework of this approach the statistical characteristics of a polymer are found by means of the formalism of the branching process with the only type of the reproducing particles. Their role is played here by the reacted functional groups. The generating functions (gf) of this branching process (1) are governed exclusively by fractions $\lambda_0,\ldots, \lambda_i,\ldots, \lambda_f$ of different type monomeric units the dependence on time t or conversion p of which is obtainable from the solution of the set of equations

$$\frac{d\lambda_i}{dt} = \varphi_{i-1}\lambda_{i-1} - \varphi_i\lambda_i \qquad \lambda_i(0) = \delta_{i0} \qquad p = \frac{1}{f}\sum_{j=0}^{f} j\lambda_j \qquad (2)$$

Here the following designations are employed

$$\varphi_i = M^0 \sum_{j=0}^{f-1} \tilde{k}_{ij}\lambda_j \qquad \tilde{k}_{ij} = (f-i)(f-j)\, k_{ij} \qquad (3)$$

while M^0 stands for overall concentration of all monomeric units. The mathematical apparatus of the theory of branching processes makes possible to calculate in terms of the probability parameters $\{\lambda_i\}$ any statistical characteristic of finite molecules and infinite network. Thus, for instance, gf $G_W(s)$ of the weight molecular-weight distribution (MWD) of polycondensates $f_W(l)$ can be found by formula

$$G_W(s) \equiv \sum_{l=1}^{\infty} f_W(l)\, s^l = sF^{(0)}(u) \qquad (4)$$

where the dependence $u(s)$ of function u on dummy variable s can be found from the solution of algebraic equation

$$u = sF(u) \tag{5}$$

satisfying the condition $u(0) = 0$. Derivatives of gf $G_W(s)$ at point $s = 1$ are connected in a simple manner with the statistical moments of MWD. This enables one by differentiating $G_W(s)$ to derive expressions for weight average P_W, z-average P_Z and other average numbers of units in a polymer molecule. So, for the first of them we have

$$P_W \equiv \frac{dG_W}{ds}\bigg|_{s=1} = 1 + \frac{pf}{1-\Lambda}, \qquad \text{where} \quad \Lambda \equiv \frac{dF}{du}\bigg|_{u=1} \tag{6}$$

The condition of the gel-point (where P_W becomes infinite) is turning into unity of quantity Λ that has the probabilistic sense of average number of particles reproduced by a particle in one generation. When $\Lambda > 1$ relationships (4) and (5) will define the MWD of the sol provided $F^{(0)}$ and F are changed for their modified values

$$\hat{F}^{(0)}(u) = \frac{F^{(0)}(u\theta)}{F^{(0)}(\theta)} \qquad \hat{F}(u) = \frac{F(u\theta)}{F(\theta)} \tag{7}$$

These are possible to get from relationships (1) where probability parameters λ_i should be replaced by the fractions $\hat{\lambda}_i$ of units of different kinds in the sol

$$\hat{\lambda}_i = \frac{\lambda_i \theta^i}{\omega_s}, \qquad \text{where} \quad \omega_s = \sum_{i=0}^{f} \lambda_i \theta^i \tag{8}$$

Quantity $\theta = u(1)$ entering into expressions (7) and (8) has the meaning of the probability for the number of the descendants generated by a particle in all generations to be finite. This quantity represents the root of equation

$$\theta = F(\theta) \tag{9}$$

which is the least in the unit interval between 0 and 1. Being equal to unity before the gel-point $p = p^*$ this root then decreases with conversion p to vanish at $p = 1$.

Given expressions (7) any statistical characteristics of the MWD of finite molecules can be found. In particular, value P_W^s of such molecules will be

$$P_W^s = 1 + \frac{\hat{p}f}{1-\hat{\Lambda}}, \qquad \text{where} \quad \hat{\Lambda} \equiv \frac{d\hat{F}}{du}\bigg|_{u=1} = \frac{dF}{du}\bigg|_{u=\theta} \tag{10}$$

Quantities $\hat{p}$ and $\hat{\Lambda}$ have here just the same sense that p and Λ in expression (6) referring, however, only to the sol but not to the entire system. In terms of the theory of branching processes this signifies that among all its realizations quantities $\hat{p}$ and $\hat{\Lambda}$ characterize only those, which do not tend to the infinity. In order to calculate the dependence of the conversion of sol functional groups $\hat{p}$ on overall conversion of all groups p recourse should be made to formula $\hat{p} = p\theta^2/\omega_s$.

Turning to the statistical description of the gel one should recognize monomeric units not only by kinds i but also by the number of paths k conducing from a unit to the infinity. The fraction of such units equals

$$\lambda_i^{(k)} = \lambda_i C_i^k \theta^{i-k}(1-\theta)^k, \qquad \text{where} \quad C_i^k = i!/(k!(i-k)!) \tag{11}$$

Statistical sense of this formula is quite transparent. Indeed, every path may either approach the infinity or not. The probabilities of these events are equal to $1-\theta$ and θ, respectively. Because all paths in the molecular graph of a network are statistically independent their probabilities have to be multiplied. Hence, the conditional probability that among i paths just k tend to the infinity while the remaining $i-k$ do not is described by the Bernoulli binomial distribution (11).

Under a statistical description of a gel of prime importance is the probability distribution $\lambda^{(k)}$ and its generating function $T(y)$

$$\lambda^{(k)} \equiv \sum_{i=k}^{f} \lambda_i^{(k)} \qquad T(y) \equiv \sum_{k=0}^{f} \lambda^{(k)} y^k \tag{12}$$

Knowing quantities $\lambda^{(k)}$ one can calculate the fraction of units occurring in gel ω_g, in its pendant material ω_{gp} and elastically active material $\omega_{ge} = \omega_g - \omega_{gp}$ as well as the fraction of units μ that are elastically effective nodes

$$\omega_g = 1 - \lambda^{(0)} = \sum_{k=1}^{f} \lambda^{(k)}; \qquad \omega_{ge} = 1 - \lambda^{(0)} - \lambda^{(1)} = \sum_{k=2}^{f} \lambda^{(k)};$$

$$\mu = 1 - \lambda^{(0)} - \lambda^{(1)} - \lambda^{(2)} = \sum_{k=3}^{f} \lambda^{(k)} \tag{13}$$

Besides through $\lambda^{(k)}$ such significant statistical characteristics of a gel are also expressed as the number of elastically active chains of polymer network per one unit v, number-average length of such a chain N_e and cyclic rank of polymer network $\mathcal{R}$

$$v = \frac{1}{2}\sum_{k=3}^{f} k\lambda^{(k)} \qquad N_e = \frac{\omega_{ge}}{v} \qquad \mathcal{R} = v - \mu \tag{14}$$

The above introduced quantities ω_{ge}, v, μ and $\mathcal{R}$ are defined per one monomeric unit of polycondensation system, which is convenient when considering this system theoretically. However, when the results obtained are meant for the description of the properties of a polymer network, then these characteristics should be defined per one monomeric unit of this network. To do so one should divide the calculated values of the above mentioned characteristics of a polymer network by the weight fraction of the gel

$$\hat{\omega}_{ge} = \frac{\omega_{ge}}{\omega_g}; \qquad \hat{v} = \frac{v}{\omega_g}; \qquad \hat{\mu} = \frac{\mu}{\omega_g}; \qquad \hat{\mathcal{R}} = \frac{\mathcal{R}}{\omega_g}; \qquad \hat{N}_e = N_e \quad (15)$$

To have gel structure parameters (13) and (14) calculated it will suffice to find expressions for gf T (12), its first-order T' and second-order T'' derivative at point $y = 0$ as well as derivative T' at point $y = 1$. This is quite apparent from expressions

$$\lambda^{(0)} = T(0) \qquad \lambda^{(1)} = T'(0) \qquad \lambda^{(2)} = T''(0)/2 \quad (16)$$

$$v = [T'(1) - T'(0) - T''(0)]/2 \quad (17)$$

which hold for any model of the branched polycondensation. In the framework of the monad approach the substitution of $\lambda_i^{(k)}$ (11) into (12) leads to the following expression

$$T(y) = \sum_{i=0}^{f} \lambda_i (\theta + (1-\theta)\,y)^i = F^{(0)}(\theta + (1-\theta)\,y) \quad (18)$$

where function $F^{(0)}(u)$ has been determined earlier (1). Differentiating gf (18) and setting $y = 0$ or $y = 1$ it is an easy matter to get with allowance for (16) and (17) the following relationships

$$\lambda^{(0)} = F^{(0)}(\theta); \qquad \lambda^{(1)} = pf(1-\theta)\,F(\theta); \qquad \lambda^{(2)} = pf(1-\theta)^2\,F'(\theta)/2 \quad (19)$$

$$v = pf(1-\theta)[1 - F(\theta) - (1-\theta)\,F'(\theta)]/2 \quad (20)$$

where dependence θ on conversion p is to be found from the solution of Eq. (9). Substituting quantities (19) and (20) into expressions (13) and (14) it is possible to determine the dependence on conversion of the statistical characteristics of the topological structure of a polymer network.

Of great practical value are responsive gels[24–26] which have one crosslinking per hundreds units. They are capable of absorbing and retaining great amount of solvent that exceeds the mass of the polymer constituting gel by several orders of magnitude. Such gels are formed at conversions just slightly exceeding the critical one p^*. Gordon[27] proposed to call

such polymer networks, synthesized in the very vicinity of the gel-point, critically branched networks. The values of the characteristics of their topological structure are found in the asymptotic limit $p \rightarrow p^*$ from general relationships (13), (14), (19), and (20)

$$\omega_g = \gamma^{(1)}\varepsilon; \qquad \omega_{ge} = \gamma^{(2)}\varepsilon^2; \qquad \mu = \gamma^{(3)}\varepsilon^3;$$
$$v = \frac{3}{2}\gamma^{(3)}\varepsilon^3; \qquad \mathscr{R} = \frac{1}{2}\gamma^{(3)}\varepsilon^3; \qquad N_e = \frac{2\gamma^{(2)}}{3\gamma^{(3)}\varepsilon} \qquad (21)$$

The small parameter ε occurring in these expressions has the following form

$$\varepsilon = \Delta\varepsilon', \qquad \text{where} \quad \varepsilon' = p - p^*, \quad \Delta = 2b/a \qquad (22)$$

Relationships for the coefficients $\gamma^{(1)}$, $\gamma^{(2)}$, and $\gamma^{(3)}$ as well as for the quantities a and b, entering formulas (21) and (22), in the framework of the Gordon approach are as follows

$$a = \sum_{i=3}^{f} i(i-1)(i-2)\,\lambda_i(p^*);$$
$$b = -f\sum_{i=0}^{f}(2i-1)\,\varphi_i(p^*)\,\lambda_i(p^*)\bigg/\sum_{i=0}^{f}\varphi_i(p^*)\,\lambda_i(p^*) \qquad (23)$$
$$\gamma^{(1)} = p^*f; \qquad \gamma^{(2)} = \gamma^{(1)}/2; \qquad \gamma^{(3)} = a/6 \qquad (24)$$

3. RIGOROUS THEORY

When considering the irreversible non-random homopolycondensation of monomer RA^f the role of kinetically independent elements in consonance with the extended Flory principle[6, 7] is performed by monomeric units of different kinds. Here the dependence of their fractions λ_i on time or conversion is obtainable from the solution of kinetic equations (2) and (3). Using the kinetic approach in order to study the non-random polycondensation of monomer RA^f in the framework of the FSSE model it was suggested[7, 15, 16] to characterize each molecule by vector $\boldsymbol{l}$ with components $l_0, \ldots, l_i, \ldots, l_f$ equal to the numbers of its monomeric units of different kinds. Under such an approach the reaction system at every moment t is described by concentration of molecules with fixed value of vector $\boldsymbol{l}$. To make this concentration dimensionless it is convenient to divide it by overall concentration of monomeric units M^0. For gf $g(s, t)$ of this

dimensionless concentration $C(l, t)$ there was derived the following equation in partial derivatives

$$\frac{\partial g}{\partial t} = M^0 \sum_{i=0}^{f} \sum_{j=0}^{f} \tilde{k}_{ij} \left\{ -\lambda_i s_j \frac{\partial g}{\partial s_j} + \frac{1}{2} s_{i+1} s_{j+1} \frac{\partial g}{\partial s_i} \frac{\partial g}{\partial s_j} \right\} \quad (25)$$

whose solution at initial condition $g(s, 0) = s_0$ permits finding gf of weight MWD

$$G_W(s) \equiv \sum_{l=1}^{\infty} f_W(l) \, s^l = \sum_{i=0}^{f} s_i \frac{\partial g}{\partial s_i}\bigg|_{s_i = s} \quad (26)$$

Unlike for the ideal polycondensation the exact analytical solution of Eq. (25) is hardly attainable. However, differentiating it term by term with respect to the components of vector s and setting all of them equal to unity it is possible to derive a closed set of ordinary differential equations for the statistical moments of distribution $C(l, t)$. Numerical solution of these equations enables one to predict, for instance, the evolution with conversion of weight-average P_W, z-average P_Z degree of polymerization of finite molecules as well as to determine critical conversion p^* at the gel-point. It should be emphasized that working perfectly before the gel-point a kinetic method fails to describe a reaction system at the gelation stage. Such a description can be carried out, however, by the statistical method in terms of a branching process.

To have this process defined the results reported in paper[16] should be presented as follows

$$G_W(s) = s\mathscr{F}^{(0)}[\boldsymbol{u}] \qquad u_i(\tau) = s\mathscr{F}_i(\tau; [\boldsymbol{u}]) \qquad (i = 0,..., f-1) \quad (27)$$

where the following designations are employed

$$\mathscr{F}^{(0)}[\boldsymbol{u}] = \sum_{i=0}^{f} \int \cdots \int P_i(t; \tau_0,..., \tau_{i-1}) \prod_{j=0}^{i-1} u_j(\tau_j) \, d\tau_j \quad (28)$$

$$\mathscr{F}_i(\tau; [\boldsymbol{u}]) = \sum_{j=0}^{f-1} \pi_{ij}(\tau) \, \mathscr{F}_j^{\dagger}(\tau; [\boldsymbol{u}]) \qquad \mathscr{F}_j^{\dagger}(\tau; [\boldsymbol{u}]) = \frac{\delta \mathscr{F}^{(0)}[\boldsymbol{u}]}{\delta u_j(\tau)} \frac{1}{U_j(\tau)} \quad (29)$$

$$U_j(\tau) \equiv \frac{\delta \mathscr{F}^{(0)}[\boldsymbol{u}]}{\delta u_j(\tau)}\bigg|_{u(\tau) = I} = \varphi_j(\tau) \, \lambda_j(\tau) \qquad \pi_{ij}(\tau) = \frac{\tilde{k}_{ij}\lambda_j(\tau)}{\varphi_i(\tau)} \quad (30)$$

$$P_i(t; \tau_0,..., \tau_{i-1}) = \exp[-I_i(t)] \prod_{j=0}^{i-1} v_j(\tau_j) \, \varphi_j(\tau_j) \quad (31)$$

$$v_i(\tau) = \exp[I_{i+1}(\tau) - I_i(\tau)] \qquad I_i(t) = \int_0^t \varphi_i(\tau) \, d\tau \quad (32)$$

It is easy to see that expressions (27) being similar to those (4) and (5) show yet an essential distinction. Instead of gf $F^{(0)}(u)$ and $F(u)$ (1), generating functionals (GF) $\mathscr{F}^{(0)}[u]$ (28) and $\mathscr{F}_i(\tau; [u])$ (29) appear. In order to find gf $G_W(s)$ of the weight MWD it is necessary according to expressions (27) to solve a set of f integral equations for functions $u_0(\tau),..., u_{f-1}(\tau)$ and to substitute the solution obtained into the expression for $\mathscr{F}^{(0)}[u]$.

Relationships (27)–(29) admit simple probabilistic interpretation in terms of the branching process. To its reproducing particles reacted functional groups $\bar{A}$ correspond distinguished by "color" i and label τ. Integer i characterizes the kind of monomeric unit to which a given group was attached at the moment τ of its formation.

Function $P_i(t; \tau_0,..., \tau_{i-1})$ represents the density of probability for the particle-ancestor for the time lapse $(0, t)$ to give birth to i descendants $\bar{A}_0(\tau_0), \bar{A}_1(\tau_1),..., \bar{A}_{i-1}(\tau_{i-1})$ at the instants $0 < \tau_0 < \tau_1 < \cdots < \tau_{i-1} < t$, respectively. Any of these particles $\bar{A}_j(\tau)$ is incapable of reproducing until it transforms into active particle $\bar{A}_k^\dagger(\tau)$. This latter during such a transformation, that happens immediately after particle $\bar{A}_j(\tau)$ is born, differing, generally speaking, from the former by color has the same label. Conditional probability $\pi_{jk}(\tau)$ (30) of this transformation upon the summation over index k yields, naturally, unity. In the next generation each active particle $\bar{A}_k^\dagger(\tau)$ produces a set of non-active particles. The probability distribution of such sets has GF $\mathscr{F}_j^\dagger(\tau; [u])$ related to GF $\mathscr{F}^{(0)}[u]$ (28) of the probability distribution of the sets of the descendants of the particle-ancestor by expression (29) resembling formula (1) which connects gf $F(u)$ with gf $F^{(0)}(u)$. Fundamental distinction between them is that the role of ordinary derivative (1) is played now by functional derivative (29). Normalizing function $U_j(\tau)$ (30) entering in this expression has the sense of the rate of the formation of groups $\bar{A}_j(\tau)$. Erasing of their labels and colors results in obvious relationships

$$\int_0^t U_j(\tau)\, d\tau \equiv \bar{\mu}_j(t) = \sum_{i=j+1}^{f} \lambda_i(t) \qquad \sum_{j=0}^{f} \bar{\mu}_j(t) = \sum_{i=0}^{f} i\lambda_i(t) = pf \quad (33)$$

where $\bar{\mu}_j(t)$ is the overall number of color j reacted groups per one monomeric unit which are present in the reaction system by moment t.

The development of a population of the branching process in every generation, beginning with the first one, proceeds in the same manner. Each non-active particle from n-th generation immediately transforms into active one with the same label. This newly formed particle gives later birth in $(n+1)$-th generation to some set of daughter non-active particles. The probability distribution of the transformation of particle $\bar{A}_i(\tau)$ into $\bar{A}_j^\dagger(\tau)$ is described by the stochastic matrix with elements $\pi_{ij}(\tau)$ (30) while the

subsequent producing by particle $\bar{A}_j^\dagger(\tau)$ of the offspring is controlled by GF representing the vector with elements $\mathscr{F}_j^\dagger(\tau; [\boldsymbol{u}])$ (29). Using the statistical method one may well skip the first transformation to consider the branching process exclusively in terms of particles $\bar{A}_i(\tau)$ whose reproduction is governed by GF that is the vector with elements $\mathscr{F}_i(\tau; [\boldsymbol{u}])$ (29).

Under the statistical approach function $u_i(s; \tau)$ occurring in Eqs. (27) has simple meaning. It represents gf of the probability of the number of the descendants produced in all generations by particle $\bar{A}_i(\tau)$. Of considerable importance here are functions

$$\theta_i(\tau) = u_i(1; \tau) \qquad z_i(\tau) = \frac{du_i}{ds}\bigg|_{s=1} \qquad (34)$$

The first of them is the probability for the overall number of particle $\bar{A}_i(\tau)$ descendants to be finite whereas the second one is average number of particles in a population produced by this particle. Probabilities $\theta_0(\tau),...,$ $\theta_{f-1}(\tau)$ that the reacted groups $\bar{A}_0(\tau),...,\bar{A}_{f-1}(\tau)$ are involved in polymer molecules of finite size is found from the solution of the set of f nonlinear integral equations

$$\theta_i(\tau) = \mathscr{F}_i(\tau; [\boldsymbol{\theta}]) \qquad (i = 0, 1,..., f-1) \qquad (35)$$

which result from Eqs. (27) provided variable s is put unity. Equations (35) before gel-point $p < p^*$ have the sole solution $\boldsymbol{\theta} = \boldsymbol{1}$ where all components of vector $\boldsymbol{\theta}$ are unity. Under conversions $p > p^*$ within hypercube $0 < \theta_i(\tau) < 1$ $(i = 0,..., f-1)$ a nontrivial solution emerges describing the sol. Its weight fraction in the reaction system is defined by expression

$$\omega_s \equiv G_W(1) = \mathscr{F}^{(0)}[\boldsymbol{\theta}] \qquad (36)$$

where the dependence of vector $\boldsymbol{\theta}$ components on conversion p is obtainable from the solution of Eqs. (35).

Weight average degree of polymerization of finite molecules can be calculated by formula

$$\mathrm{P}_W(t) \equiv \frac{dG_W}{ds}\bigg|_{s=1} = \mathscr{F}^{(0)}[\boldsymbol{\theta}] + \int_0^t d\tau \sum_{i=0}^{f-1} U_i(\tau)\, z_i(\tau) \qquad (37)$$

where functions $z_i(\tau)$ (34) are found from the solution of the set f of linear integral equations

$$\int_0^t d\xi \sum_{j=0}^{f-1} \Gamma_{ij}(\tau, \xi)\, z_j(\xi) = \theta_i(\tau) \qquad (i = 0,..., f-1) \qquad (38)$$

Their left-hand part may be considered as the action upon vector $z(\tau)$ of linear integro-matrix operator Γ with kernel

$$\Gamma_{ij}(\tau, \xi) = \delta_{ij}\delta(\tau-\xi) - \mathscr{F}_{ij}(\tau, \xi) \tag{39}$$

Here δ_{ij} is the Kroneker-delta, $\delta(\tau-\xi)$ denotes the Dirac delta-function while $\mathscr{F}_{ij}(\tau, \xi)$ stands for the matrix-function

$$\mathscr{F}_{ij}(\tau, \xi) \equiv \frac{\delta\mathscr{F}_i(\tau; [\boldsymbol{u}])}{\delta u_j(\xi)}\bigg|_{\boldsymbol{u}=\boldsymbol{\theta}} = \sum_{n=0}^{f-1} \pi_{in}(\tau)\,\mathscr{F}_{nj}^{\dagger}(\tau, \xi)$$
$$= \sum_{n=0}^{f-1} \frac{\tilde{k}_{in}\mathscr{F}_{nj}^{(0)}(\tau, \xi)}{\varphi_i(\tau)\,\varphi_n(\tau)}, \qquad \text{where} \quad \mathscr{F}_{nj}^{(0)}(\tau, \xi) \equiv \frac{\delta^2\mathscr{F}^{(0)}[\boldsymbol{u}]}{\delta u_n(\tau)\,\delta u_j(\xi)}\bigg|_{\boldsymbol{u}=\boldsymbol{\theta}} \tag{40}$$

Weight average degree of polymerization of sol (37)

$$\mathrm{P_W}(t) = \mathscr{F}^{(0)}[\boldsymbol{\theta}] + \sum_i \sum_j \int_0^t \int_0^t U_i(\tau)\,\Gamma_{ij}^{(-1)}(\tau, \xi)\,\theta_j(\xi)\,d\tau\,d\xi \tag{41}$$

is expressed through the Green function $\Gamma_{ij}^{(-1)}(\tau, \xi)$ which represents the kernel of operator Γ^{-1}, inverse to that Γ with kernel (39).

Expressions (37)–(41) hold not only at the stage of a polymer network formation but before the gel-point as well. In the last case vector $\boldsymbol{\theta}$ should be replaced by vector $\boldsymbol{1}$ with all components equal unity. Value $\mathrm{P_W}$ (41) diverges when the largest eigenvalue of operator Γ^{-1} turns into infinity. To this moment of time, $t = t^*$, (conversion $p = p^*$) there corresponds vanishing of minimal eigenvalue of operator Γ and, thus, turning into unity of the largest eigenvalue of operator with kernel $\mathscr{F}_{ij}(\tau, \xi)$ (40).

To derive the relationships for gel structure parameters (13) and (14) it is enough to have the expression for gf $T(y)$ (12). A straightforward reasoning enables its derivation for the FSSE model in hand

$$T(y) = \mathscr{F}^{(0)}[\boldsymbol{\theta} + (\boldsymbol{1}-\boldsymbol{\theta})\,y] \tag{42}$$

where GF $\mathscr{F}^{(0)}[\boldsymbol{u}]$ was determined in the foregoing (28). Differentiating gf $T(y)$ (42) with respect to y it is easy, proceeding from (16), to get expressions

$$\lambda^{(0)} = \mathscr{F}^{(0)}[\boldsymbol{\theta}] \qquad \lambda^{(1)} = \int_0^t d\tau \sum_{i=0}^{f-1} [1-\theta_i(\tau)]\,U_i(\tau)\,\mathscr{F}_i^{\dagger}(\tau; [\boldsymbol{\theta}])$$
$$\lambda^{(2)} = \frac{1}{2}\int_0^t \int_0^t d\tau\,d\xi \sum_{i=0}^{f-1} \sum_{j=0}^{f-1} [1-\theta_i(\tau)][1-\theta_j(\xi)]\,\mathscr{F}_{ij}^{(0)}(\tau, \xi) \tag{43}$$

$$\nu = \frac{1}{2}\int_0^t d\tau \sum_{i=0}^{f-1} [1-\theta_i(\tau)]\,U_i(\tau)\{1-\mathscr{F}_i^{\dagger}(\tau; [\boldsymbol{\theta}])\} - \lambda^{(2)} \tag{44}$$

analogous to those arrived at in the framework of the monad approach (19) and (20).

A rigorous theoretical analysis shows that in the case of critically branched networks asymptotic expressions (21) and (22) retain their appearance. The values of coefficients $\gamma^{(1)}$, $\gamma^{(2)}$, and $\gamma^{(3)}$ as well as those of quantities a and b calculated in the framework of the rigorous theory by relationships we derived are distinct from those (23) and (24) arrived at in the framework of the Gordon approach. However, it is not worthwhile to present them here because of their relatively cumbersome appearance.

4. FACTORISABLE MODEL

Within the framework of this kinetic model of polycondensation any element k_{ij} of matrix of the constants of elementary reactions between groups A_i and A_j is presumed to be equal to the product $k_i k_j$ of the factors characterizing the reactivity of each of them. When this condition holds the statistical description of the sol and the gel becomes far more simple as compared to the general model. This simplification consists in the fact that only one type of particles corresponding to the reacted functional groups irrespective of their kinds participates in the branching process, which appears under such a description. However, these particles, $\bar{A}(\tau)$, unlike those involved in the traditional branching process (see Section 2), are supplied with label τ indicating the instant of the formation of reacted group $\bar{A}$. In this case general equations (27)–(30) are reduced to

$$G_W(s) = s\mathscr{F}^{(0)}[u] \qquad u = s\mathscr{F}(\tau; [u]) \tag{45}$$

where GFs $\mathscr{F}^{(0)}$ and $\mathscr{F}$ look as follows

$$\mathscr{F}^{(0)}[u] = \sum_{i=0}^{f} \int \cdots \int P_i(t; \tau_0, ..., \tau_{i-1}) \prod_{j=0}^{i-1} u(\tau_j)\, d\tau_j \tag{46}$$

$$\mathscr{F}(\tau; [u]) = \mathscr{F}^{\dagger}(\tau; [u]) = \frac{\delta\mathscr{F}^{(0)}[u]}{\delta u(\tau)} \frac{1}{U(\tau)}, \qquad U(\tau) = \left(\sum_j \tilde{k}_j \lambda_j\right)^2 \tag{47}$$

Expressions (34)–(44), derived in the preceding Section, in particular case of the factorisable model turn out to be markedly simplified since all vector and tensor functions entering in them become scalars. Besides, no operations of summation over indices that characterize kinds of particles are present in these formulas any longer. As a result, calculations of the statistical characteristics of the sol and the gel prove to be noticeably facilitated. Thus, for instance, within the framework of the factorisable model instead

of the solution of the set of f nonlinear integral equations (35) only one such equation is supposed to be solved

$$\theta = \mathscr{F}(\tau; [\theta]) \tag{48}$$

5. RESULTS OF CALCULATIONS

The theory presented above makes it possible to calculate any statistical characteristics of the molecular structure of a network formed in the course of irreversible polycondensation of monomer with any functionality f. Two aspects are of special interest when conducting calculations and discussing their results. The first of them consists in the analysis of the dependencies of the quantities ω_g, ω_{ge} (13) and $\mathscr{R}$ (14) on conversion p at different values of the kinetic parameters of the system. The second aspect implies the comparison of the results of calculations performed by the formulas of the rigorous theory and those of the Gordon approach as well as the determination of the degree of accuracy of the latter. These aspects will be exemplified in this section by homopolycondensation of the three-functional monomer. The expressions employed for the calculations can be readily obtained from general formulas of Section 3 written for particular case of f = 3 provided one goes in them from time to conversion using relationship

$$f\frac{dp}{dt} = U, \qquad \text{where} \quad U \equiv \sum_{i=0}^{f} U_i \tag{49}$$

which immediately follows from Eqs. (2), (3), and (30). Under such transition all formulas will comprise only reactivity ratios $\kappa_{ij} = k_{ij}/k_{00}$, rather than the kinetic constants k_{ij} themselves. The relationships for statistical characteristics of the topological structure of a polymer network for the case in hand have especially simple appearance in the framework of the Gordon approach. Under such an approach the quantity θ (9) is determined from the solution of the square equation

$$3p\theta = \lambda_1 + 2\lambda_2\theta + 3\lambda_3\theta^2 \tag{50}$$

that in the region $p > p^*$ has nontrivial solution $\theta = \lambda_1/(3\lambda_3)$. The expressions for ω_g, ω_{ge} and $\mathscr{R}$ (13) and (14) are as follows

$$\begin{aligned}
\omega_g &= 1 - \lambda_0 - \lambda_1\theta - \lambda_2\theta^2 - \lambda_3\theta^3 \qquad \mathscr{R} = \lambda_3(1-\theta)^3/2 \\
\omega_{ge} &= \lambda_2(1-\theta)^2 + \lambda_3(1-\theta)^3 + 3\lambda_3\theta(1-\theta)^2
\end{aligned} \tag{51}$$

To calculate the statistical characteristics of the topological structure of a polymer network in the framework of the rigorous theory it is necessary to find the solution of the set of Eqs. (35) and to calculate on this solution the corresponding integrals. In order to solve this problem we employed the simple iterations method.[28] Our calculations revealed, that irrespective of the choice of the initial approximation the iterations converge at fixed conversion p to the same unique solution $\theta(p')$. This identically equals unity before the gel-point $p < p^*$ and represents certain function of p' at $p > p^*$. Essentially, the number of iterations necessary here to calculate the solution with the given accuracy dramatically rises in the vicinity of the gel-point. So, for instance, it goes from several tens to several hundreds under change of the conversion from the values, at which the fraction of gel is several tens percent to those corresponding to $\omega_g \lesssim 10\%$. This peculiarity substantially hinders the construction of the curves $\omega_g(p)$, $\omega_{ge}(p)$ and $\mathcal{R}(p)$ in the neighborhood of the gel-point. The arising difficulties can be overcome in various ways whose efficiency will be discussed for gels the characteristics of which are calculated according to the monad approach. The results of such calculations are shown for the certain system in Table I which demonstrates that the asymptotic expression works well only in the very vicinity of the gel-point.

Therefore we resorted to two variants, A and B, of the spline-interpolation.[29] According to the A method we perform interpolation in the interval between the critical conversion and the least one where the iterations still converge quickly enough and the characteristic in question can be calculated with reasonable accuracy. So at the right boundary we use the tabulated value of the function to be interpolated, which is obtained by calculations. At the left boundary we impose the condition of vanishing of

Table I. Gel-Fraction Values Calculated Using Different Methods in the Vicinity of the Gel-Point $p^* = 0.1325$ in the Framework of the Factorisable Model for Kinetic Parameters $\kappa_1 = 10$, $\kappa_2 = 10$

p, %	$\omega_g \cdot 100^a$	$\omega_g \cdot 100^b$	$\omega_g \cdot 100^c$	$\omega_g \cdot 100^d$
13.81	3.00	3.06	2.89	3.05
14.23	5.00	5.38	4.84	5.07
15.43	10.00	12.01	9.84	10.11

^{a} Exact dependence.

^{b} Asymptotic.

^{c} A method of spline interpolation.

^{d} B method of spline interpolation.

this characteristic at the gel-point. The B method differs from the A method in that an additional condition on the dependence's first derivative is placed at the left boundary. The curve's $\omega_g(p)$ slope at the gel-point is found from asymptotic formulas (21–24). Turning to Table I one can note that the employment of the spline-interpolation leads to significantly better results as compared to that of asymptotic formulas (21)–(24), for ω_g. The most effective is the B method, which permits calculating the gel-fraction with the accuracy sufficient for the comparison with the results of the majority of experimental data on critically branched networks. We checked that analogous conclusions about the efficiency of the above methods can be drawn for the calculations of other topological characteristics of the responsive gels as well. These inferences remain valid if the calculations are conducted not only for the monad approach but also for the rigorous theory as well. When discussing the results of the calculations we will focus on the simplest case of the factorisable model. This is uniquely determined at f = 3 by merely two parameters, κ_1 and κ_2.

As it was already mentioned one of the main goals of our calculations lies in the elucidation of the degree of accuracy of the Gordon approach in the various regions of the values of kinetic parameters κ_1, κ_2. This can be done in several ways, two of which are illustrated below. The first of them allows a direct estimate of the error arising under the monad approach. The results obtained when using such an approach are presented on Fig. 1. It is of interest to compare this figure with the analogous one (see Fig. 1 in paper 21) showing the degree of inaccuracy of the Gordon approach under the calculation of the critical conversion p^* at the same values of the kinetic parameters κ_1, κ_2. Such comparison leads to the important conclusion that for half of the considered systems employment of monad approach for the calculation of the structure characteristics of a polymer network is completely incorrect. This is connected with the fact that the approximate and the true values of the quantities calculated can differ several times and even more. However, the application of the Gordon approach seems to be justified for certain systems. Among them are those where $\kappa_1 = 1$, as well as the systems with monotonic acceleration ($\kappa_2 > \kappa_1 > 1$), for instance, with $\kappa_1 = 10$, $\kappa_2 = 10$. The results presented in paper 21 give ground, at the first glance, for the conclusion that to such systems those with monotonic retardation ($\kappa_2 < \kappa_1 < 1$) can be also assigned. However, such a conclusion turns out to be incorrect as it can be easily seen from Fig. 1. In the system with parameters $\kappa_1 = 0.1$, $\kappa_2 = 0.1$ the dramatic discrepancy in the approximate and the true values of all gel structure characteristics can be observed despite tiny difference (3%) in the respective values of critical conversion p^*. For this system the distinction in the values of the cyclic rank amounts to nearly three times. Noteworthy, the error of the cyclic rank $\hat{\mathscr{R}}$ (15)
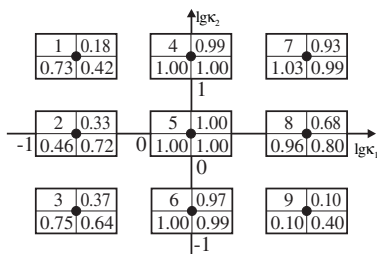
Fig. 1. Ratios of quantities ω_g, $\hat{\omega}_{ge}$ and $\hat{\mathscr{R}}$ calculated on the basis of the Gordon approach to those computed in the framework of the rigorous theory at fixed conversion, where the weight fraction of gel calculated by the second method equals 0.5. Each rectangle corresponds to certain system with given values of kinetic parameters κ_1 and κ_2 whose decimal logarithms are the coordinates of the dot in the center of this rectangle. In its upper left corner there stands the system number, while the above mentioned ratios are presented in the remaining corners. Such ratios for ω_g, $\hat{\omega}_{ge}$ and $\hat{\mathscr{R}}$ are shown in the lower left, lower right and upper right corners, respectively.

calculation at other values of the kinetic parameters as well is noticeably higher than that of ω_g and $\hat{\omega}_{ge}$. For the vast majority of the systems presented on Fig. 1 the approximate values of all these characteristics happen to be lower as compared to the true ones. However, there exist systems with such values of parameters, for example $\kappa_1 = 10$, $\kappa_2 = 10$, where this is not the case.

The second criterion, which we employed to estimate the error of the monad approximation is as follows. A polymer network of given weight is considered, which has been synthesized in the course of homopolycondensation of monomers with known concentration. For such networks with fixed ω_g the possibility of theoretical prediction of their topological characteristics is of practical interest. This can be realized in the framework of both the rigorous theory and the Gordon approach. The described criterion is especially useful when considering critically branched networks where the employment of the first criterion often makes no sense. Indeed, under the application of the latter to such networks there are systems in which the gel is absent according to the Gordon approach.

We calculated the fraction of elastically effective material, the cyclic rank of the network and the average length of the elastically active chain by both methods and compared the values obtained. The results of such comparison presented in Fig. 2 demonstrate that the discrepancy between the monad approximation and the rigorous theory, estimated by the second criterion, proves, as a rule, to be noticeably smaller than that, assessed by the first criterion. However, despite for the majority of the systems in
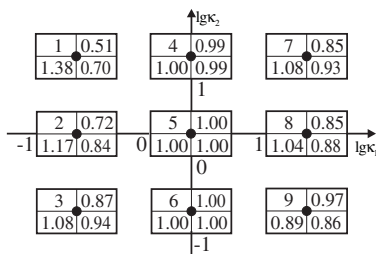
Fig. 2. Ratios of quantities N_e, $\hat{\omega}_{ge}$ and $\hat{\mathscr{R}}$ calculated on the basis of the Gordon approach to those computed in the framework of the rigorous theory at fixed weight fraction of gel $\omega_g = 0.1$. The designations are the same as in Fig. 1 except lower left corner, where the above mentioned ratio for N_e now stands.

Fig. 2 the inaccuracy of the Gordon approach is less than 15%, there exist systems (e.g., the first one) where such an error reaches 50%. Noteworthy, under consideration of polycondensation systems 1-9 proceeding from the second criterion, their set, where the monad approximation is good enough, turns out to be almost the same as that indicated earlier[21] on the basis of the analysis of the critical conversion p^* value.

   Some notion about how well the Gordon approach works for the calculation of the topological characteristics of a gel in the whole range of conversions is given by Fig. 3. It shows that for systems 4-6 with $\kappa_1 = 1$ the monad approximation at any value of κ_2 yields results practically indiscernible from the precise ones. The reason is weak dependence of the probability distribution of reproducing particles $\bar{A}(\tau)$ on instant τ of their formation (see Section 4). It shows up, for example, in the fact that the solution of Eq. (48) for the case $\kappa_1 = 1$ in the range of parameter κ_2 considered is, according to our calculations, practically independent of τ. The physical reason has to do with the random character of elementary reactions between functional groups, leading to formation of linear chains entering polymer network. Looking at Fig. 3 one may get impression that this approximation works well also for systems 3 and 7 characterized by monotonic retardative and accelerating FSSE, respectively. However, this conclusion as applied to system 3 is valid only if the comparison of the approximate and precise numerical results is performed by the second criterion. Conversely, when such a comparison is carried out by the first criterion the discrepancy between these results is tangible, as it was mentioned above. The reason is the steep slope of the conversion dependence of ω_g. In systems 1, 2, 8, 9 characterized by nonmonotonous constant ratios, the employment of the Gordon approach leads to noticeable errors which are
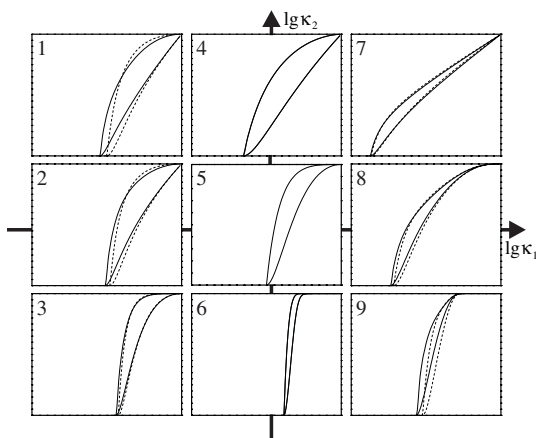
Fig. 3. Solid lines depict the dependencies of the gel-fraction ω_g (upper curve) and of the fraction of elastically effective material ω_{ge} (lower curve) on conversion, calculated by the equations of the rigorous theory for various systems. The conversion dependencies of these quantities computed in the framework of the monad approximation are shown as dashed lines.

the greater the more pronounced the nonmonotonicity. These inferences qualitatively agree with those made earlier[21] from the analysis of the gel-point position. It can also be seen from Fig. 3 that the decrease of the parameter κ_2 value at any fixed κ_1 results in the rise of the critical conversion p^* (which was established earlier[21]) along with the sharpening of the conversion dependencies of ω_g and ω_{ge}.

Having in mind possible applications it is interesting to analyze the dependence of the topological characteristics of the critically branched networks on kinetic parameters of a system. Turning to the Table II, it can be noted that with the diminishing of κ_2 the appreciable decrease of the cyclic rank value is observed concurrently with the increase of the average length of the elastically active chain. These tendencies are the most pronounced when $\kappa_1 = 10$. Among the systems analyzed system 9 is that, where the cyclic rank takes on the minimal value while the average lengths of elastically active chain assumes the largest value. Similar values of $\hat{\mathscr{R}}$ and N_e (15) in other systems are obtainable only for networks of significantly lesser weight which is impractical. Essentially, for the calculation of the topological characteristics of gel in system 9 the application of the Gordon approach is conducive to substantial error. Hence, such a calculation should be performed by resorting to the equations of the rigorous theory.

Table II. Fraction of Elastically Effective Material $\hat{\omega}_{ge}$, Cyclic Rank of Polymer Network $\hat{\mathscr{R}}$ and Average Length of Elastically Active Chain N_e for the Systems Presented in Fig. 3 at the Gel-Fraction $\omega_g = 0.1$

system	1	2	3	4	5	6	7	8	9
$\hat{\omega}_{ge} \cdot 10^2$	4.98	3.98	3.22	5.00	3.49	2.84	14.8	7.20	4.31
$\hat{\mathscr{R}} \cdot 10^4$	7.87	4.35	1.66	7.33	2.05	0.47	42.3	3.49	0.31
N_e	21	30	65	23	57	201	12	69	463

The above conclusion that the monad approximation works well for the calculation of the topological characteristics of gel for the systems with monotonous constant ratios was arrived at by the analysis of the results of the calculations performed in the framework of the factorisable model. However, when turning to the general model the degree of the accuracy of the Gordon approach can, generally speaking, deteriorate.[21] To illustrate this inference we chose one of the simplest nonfactorisable kinetic models with reactivity ratios

$$\kappa_{ij} = \kappa + (1-\kappa)\, \delta_{i0}\delta_{j0} \tag{52}$$

In the framework of this model we considered two systems, I and II, characterized by the strong retardative ($\kappa = 0.01$) and accelerating ($\kappa = 100$) FSSE, respectively. For the determination of the degree of the accuracy of the monad approximation as applied to these systems we employed the methodology used above to analyze the factorisable model. Our results (see Figs. 4 and 5) indicate that the error of the Gordon approach when going from the factorisable model to the nonfactorisable one markedly increases only for the system with accelerating FSSE. Conversely, for those with retardative FSSE such an increase is not pronounced. This inference is in qualitative agreement with that made earlier[21] on the basis of the analysis of the critical conversion p^* value.
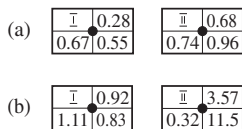

Fig. 4. Estimate of the accuracy of monad approximation by the first (a) and the second (b) criteria for kinetic model (52) with retardative ($\kappa = 0.01$, system I) and accelerating ($\kappa = 100$, system II) FSSE. The procedures of the evaluation by each of these criteria and the designations inside the rectangles are the same as in Figs. 1 and 2, respectively.
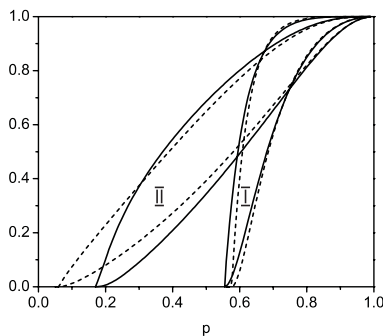
Fig. 5. Dependencies of the gel-fraction ω_g and of the fraction of elastically effective material ω_{ge} for the systems I and II (see caption to Fig. 4) on conversion. Curves are designated here in the same manner as in Fig. 3.

6. CONCLUSIONS

In this work we have theoretically examined the irreversible branched homopolycondensation of a monomer comprising an arbitrary number of identical functional groups. Their reactivity does not remain unaltered in the course of the synthesis, as it takes place under a random polycondensation, changing with the entry into the reaction of neighboring groups in a monomeric unit. This system described by the FSSE kinetic model is the simplest one among those where the stepwise polymerization is of cooperative character. The model in hand presuming the absence of the cyclization reactions in finite size polymer molecules is nowadays one of the most extensively used in polymer chemistry.[7, 23] More than 20 years ago it was established[14–16] that the employment of the traditional statistical approach for the description of this non-random polycondensation of monomer RA^f leads to the results other than those obtained from the solution of the kinetic equations of the FSSE model. In this connection it has been speculated[18, 20] that the statistical methods based on the formalism of the theory of branching processes are not appropriate to deal with some non-random polycondensation systems. This viewpoint was questioned by Sarmoria and Miller[22] who put forward a recursive probabilistic approach that provided, on their opinion, an exact description of this process in the framework of the FSSE model. Which of these two standpoints is correct can not be decided unless the recourse to the kinetic method is made.

The analysis of the kinetic equations carried out in this paper has allowed us to provide a rigorously substantiated answer to the above question that is under discussion in literature up to now. It was shown that the calculation of the MWD of sol molecules as well as the characteristics of the topological structure of a gel can be performed using the formalism of

the theory of branching processes where the role of the reproducing particles (as in the case of random polycondensation) is played by reacted functional groups. However, now these should be distinguished by "color" i and label τ. So, symbol $\bar{A}_i(\tau)$ denotes reacted group $\bar{A}$ formed at moment τ from group A attached to a monomeric unit with i reacted groups. For the probability parameters of this branching process with colored labeled particles equations are derived that describe the dependence of these parameters on conversion. Given these parameters one can calculate the statistical characteristics of the products of the non-random polycondensation invoking the mathematical apparatus of the theory of general branching processes.[30, 31] Similar stochastic processes with labeled particles found their application, for instance, under the theoretical consideration of biological populations, neutron nuclear reactions and cosmic rays.[30, 31]

The statistical method, whose rigorous substantiation is presented in this paper, is particularly efficient in calculating the parameters of the topological structure of a network being formed for the polycondensation. Among them are fractions of monomeric units of gel involved either in pendant or elastically active material, the number of elastically effective nodes and elastically active chains as well as average length of these latter. We calculated these network structure parameters at different values of conversion of functional groups and compared their values with those obtained from the equations of the Gordon approximate statistical approach. Such a comparison gave us an opportunity to estimate quantitatively the accuracy of this approximation for different domains of the kinetic parameters of the FSSE model. We performed just the same estimate as applied to critically branched polymer networks formed within the region of conversion p close to the gel-point p^*. In case of such networks asymptotic expressions have been derived for their structure parameters, which are the more accurate the lesser is the quantity $\varepsilon' = p - p^*$. In this work we presented results of these parameters' calculations for critically branched networks.

The statistical method we have introduced above to describe non-random polycondensation differs from that advanced earlier by Sarmoria and Miller[22] at least in two peculiar features. Firstly, our method has a rigorous kinetic substantiation and, secondly, it makes use of the thoroughly developed mathematical apparatus of general theory of branching processes. The last circumstance enables one in a straightforward manner to cope with the task of the description of sol and gel escaping some artificial tricks employed in paper[22] like the discretization of time of a polycondensation process and the consideration of virtual crosslinking of superspecieces. Incorporation of these tricks for the calculation of the statistical characteristics of gel is, apparently, conducive to substantial

difficulties. These seem to be responsible for the fact that no results on the calculation of the above network characteristics were reported by Sarmoria and Miller.[22] The algorithm of the calculation of such characteristics by means of our original statistical method admits the extension to the processes of non-random irreversible polycondensation of an arbitrary monomer mixture described by the FSSE model.[13]

This paper addresses one particular model of non-random polycondensation. The underlying assumption for this FSSE model, commonly accepted nowadays in polymer chemistry, is that the reactivity of a functional group is controlled exclusively by number of reacted neighboring groups. Here the violation of the Flory principle is due to the short-range effects,[7] i.e., to the influence on the reactivity of molecule fragments situated in the vicinity of the reaction centre. If such an influence is from all units of a polymer molecule they speak about long-range effects.[7] To the authors' knowledge a rigorous quantitative polycondensation theory taking account of these effects is missing so far. However, it is possible to comment on how such effects could influence the gelation process provided the reactivity of a group in a polymer molecule is presumed to be controlled by number of units l in this molecule rather than by its configuration. Under such an assumption the problem of finding the distribution of molecules for size l reduces to the solution of the Smoluchowski equation. The kernel of the integral operator in this equation is the rate constant $K(l', l'')$ of the condensation reaction with participation of molecules comprising l' and l'' units. The character of the behaviour of function $K(l', l'')$ in asymptotic limit $l' \to \infty, l'' \to \infty$ is critical for the analysis of gelation. Of particular interest is the model with kernel $K(l', l'') \sim (l'l'')^{\omega}$ describing ideal polycondensation (when $\omega = 1$) and polycondensation where only those groups react that are located at the surface of molecules (when $\omega = 2/3$). For this model with the decrease of the exponent ω from 1 to $1/2$ the gel point moves towards higher conversions to make the polymer network formation absolutely impossible at $\omega < 1/2$.[33–35]

REFERENCES

1. *Kinetics of Aggregation and Gelation*, F. Family and D. P. Landau, eds. (Elsevier Science Publishers, Amsterdam, 1984).
2. M. H. Ernst, in *Nonequilibrium Phenomena. I. Boltzmann Equation*, J. L. Lebowitz and E. W. Montroll, eds. (Elsevier Science Publishers, Amsterdam, 1983), chap. 3.
3. R. M. Ziff, in *Kinetics of Aggregation and Gelation*, F. Family and D. P. Landau, eds. (Elsevier Science Publishers, Amsterdam, 1984), pp. 191–199.
4. M. H. Ernst, in *Fundamental Problems in Statistical Mechanics*, Vol. 6, E. G. D. Cohen, ed. (Elsevier Science Publishers, Amsterdam, 1985), pp. 329–364.

5. M. Ernst, in *Fractals in Physics*, L. Pietronero and E. Tossati, eds. (Elsevier Science Publishers, Amsterdam, 1986), chap. 6.

6. S. I. Kuchanov, *Methods of Kinetic Calculation in Polymer Chemistry* (Khimia, Moscow, 1978).

7. S. I. Kuchanov, *Adv. Polym. Sci.* **152**:157 (2000).

8. M. Gordon and G. R. Scantlebury, *Trans. Faraday Society* **60**:604 (1964).

9. G. Dobson and M. Gordon, *J. Chem. Phys.* **41**:2389 (1964).

10. K. Dusek, *Discuss. Faraday Chem. Soc.* **57**:101 (1974).

11. P. Luby, *J. Chem. Phys.* **78**:1083 (1974).

12. D. P. Kochetov, *Vysokomol. Soedin. Ser. B* **26**:756 (1984).

13. S. I. Kuchanov, (to be published).

14. S. I. Kuchanov, in *Abstracts of Papers Presented on IUPAC Symposium on Macromolecular Chemistry, Tashkent, USSR, 1978*, Vol. 3 (Nauka, Moscow, 1978), p. 50.

15. S. I. Kuchanov, *Dok. Akad. Nauk SSSR* **249**:899 (1979).

16. S. I. Kuchanov and E. S. Povolotskaya, *Vysokomol. Soedin. Ser. A* **24**:2190 (1982).

17. H. Galina, *Europhys. Lett.* **3**:1155 (1987).

18. H. Galina and A. Szustalewicz, *Macromolecules* **22**:3124 (1989).

19. H. Galina, *Makromol. Chem., Macromol. Symposia* **40**:45 (1990).

20. J. Mikes and K. Dusek, *Macromolecules* **15**:93 (1982).

21. S. I. Kuchanov and A. G. Kholostyakov, *J. Polym. Sci. Ser. A* **37**:2145 (1999).

22. C. Sarmoria and D. R. Miller, *Macromolecules* **24**:1833 (1991).

23. D. R. Miller and C. Sarmoria, *Polym. Eng. Sci.* **38**:535 (1998).

24. O. E. Philippova, *Polymer Science Ser. C* **42(2)**:208 (2000).

25. *Responsive Gels 1, 2. Adv. Polym. Sci.*, Vols. 109–110 (1993).

26. *Polymer Gels and Networks*, Y. Osada and A. R. Khokhlov, eds. (Marcel Dekker, New York, Basel, 2002).

27. M. Gordon and M. Judd, *Nature* **234**:96 (1971).

28. *Numerical Solution of Integral Equations*, L. M. Delves and J. Walsh, eds. (Clarendon Press, Oxford, 1974).

29. *Numerical Recipes*, http://www.nr.com.

30. T. E. Harris, *Theory of Branching Process* (Springer, Berlin, 1963).

31. A. T. Bharucha-Reid, *Elements of the Theory of Markov Processes and Their Applications* (McGraw–Hill, N.-Y., Toronto, London, 1960).

32. R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, N.-Y., London, 1953).

33. F. Leyvraz and H. R. Tschudi, *J. Phys. Ser. A* **14**:3389 (1981).

34. F. Leyvraz and H. R. Tschudi, *J. Phys. Ser. A* **15**:1951 (1982).

35. M. Ziff, E. M. Hendricks, and M. H. Ernst, *Phys. Rev. Lett.* **49**:593 (1982).