



Development of a quantitative theory of polycondensation

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Abstract

This review presents the first systematic treatment of the voluminous literature on the theory of polycondensation. Processes for obtaining homo- and copolymers with linear and branched macromolecules are considered. Emphasis is on a thorough discussion of various polycondensation models, and the methods of their solution for the calculation of the statistical characteristics of the chemical structure of polymers. The effects on these characteristics of the process modes for thermodynamically and kinetically controlled regimes of a polycondensation are analyzed in detail.

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1. Introduction

The polycondensation method of polymer synthesis is one of the most widespread means of manufacturing high-molecular products. The ample potentialities of this method reside in both the impressive variety of monomers used and the wide range of chemical reactions resulting in the formation of macromolecules. In view of the utmost practical importance of polycondensation it has been extensively investigated in a wealth of experimental works.

A considerable body of experimental evidence on polycondensation has been accumulated by now. Its presentation and systematization can be found in monographs dealing with important classes of polycondensation polymers [1–3,10], or general regularities of polycondensation [4–10]. However, almost all these monographs focus on experimental results, whereas burning problems of quantitative theory are rather slightly covered. This deficiency is made up to a certain extent in sections of monographs [11,12] and reviews [13,14]. At the same time, when designing industrial processes, the choice of optimum performance conditions is of critical significance. Successful realization of this task suggests the availability of well-elaborated quantitative theory of these processes, to enable the development of adequate mathematical models

aimed at searching optimum technological regimes of polycondensation.

In this review theoretical work devoted to homophase polycondensation processes is critically surveyed. Major attention is focused on the discussion of the original postulates of the theory, the illustration of the potentialities of different methods of calculation and general problems of the modern quantitative theory of polycondensation.

To provide a comprehensive statistical description of the products of linear homopolycondensation, it is enough to determine their molecular-weight distribution (MWD). If a cyclization reaction is strongly pronounced for the process, it is necessary to additionally find the MWD of the cyclic molecules. Copolymer molecules are known to vary not only in the degree of polymerization (size), but also in the fractions of monomeric units of different types (composition). As a consequence, the inhomogeneity of the products of copolycondensation will be defined by the size-composition distribution (SCD). In addition, even copolymer macromolecules identical in size and composition may exhibit different microstructure, characterized by the pattern of arrangement of units in a polymer chain. When describing statistically branched polymers, the necessity arises to take into consideration that apart from the above mentioned characteristics macromolecules

differ also by their configurations. Specifically, they can vary in number and lengths of lateral branches and interjunction chains. Fortunately, for many practical purposes there is no need to differentiate all possible isomers.

The outlined statistical characteristics provide insight to the physico-chemical properties of polymers through the primary (i.e. configurational) structure of macromolecules, which carries information on possible conformations, and secondary supramolecular structures. Hence, the main objective of a quantitative theory of polycondensation consists in establishing dependencies of corresponding statistical parameters of the primary structure of a polymer sample on the composition of the initial monomer mixture, and on thermodynamic or kinetic parameters, i.e. on the constants of equilibrium or the rate of the reactions proceeding in the course of polymer synthesis. The solution of this problem is expected to furnish a means for a scientifically grounded choice of the optimum conditions for the synthesis of polycondensation polymers with desired service properties.

During a polycondensation process, several elementary reactions can proceed simultaneously. The main reaction for chain propagation implies the interaction of two functional groups belonging to different molecules, resulting in the formation of an intramolecular bond. Here, the combination of two reacting molecules (monomers, oligomers or polymers) results in the formation of one molecule, and is often (but not necessarily) accompanied by extraction of a low-molecular weight product. A common feature of polycondensation is the fact that in its course any two molecules containing interacting functional groups in a reaction mixture are able to enter into the condensation reaction. The reverse reaction with respect to propagation is the degradation of a polymer molecule. At sufficiently high values of the equilibrium constant k of this pair of elementary reactions degradation may be neglected, and polycondensation may be considered to be an irreversible process. Conversely, at moderate value of k the reversibility of the polycondensation becomes essential. While irreversible polycondensation is always nonequilibrium, reversible polycondensation may proceed under either equilibrium or nonequilibrium conditions. In order to perform polycondensation in

the equilibrium regime, it is necessary to remove low-molecular by-product from the reaction zone slowly enough to ensure for the system the possibility to be at every instant in a state of thermodynamic equilibrium, corresponding to the current concentration of the by-product. The rate of its removal from the reaction zone is responsible for the overall rate of such an equilibrium polycondensation. A reversible polycondensation will proceed under nonequilibrium regime when the rate of the by-product removal is comparable with that of its formation during the condensation reaction.

Along with the propagation and degradation of polymer molecules in the course of polycondensation, other elementary reactions are also possible, such as interchain exchange, termination and intramolecular cyclization. The interchain exchange reaction exerting no influence on the number average degree of polymerization can predetermine to a great extent both the MWD and SCD. There exist two types of exchange reactions. For the first of them an elementary act consists in the interaction of a terminal functional group with an intramolecular bond, whereas for the second one this role is played by mutual interaction of a couple of such bonds. When theoretically describing reversible polycondensation, in addition to the terminal functional groups (for instance, hydroxyl, carboxyl and amine groups), one should consider intramolecular bonds as 'internal' functional groups (e.g. ester or amide groups), because they participate in degradation and exchange elementary reactions. Termination reactions inherent in polycondensation consist of chemical deactivation of terminal functional groups. They are often caused by the interaction of these with monofunctional compounds, either introduced deliberately or present as impurities in the mixture. Under intramolecular cyclization, both of the reacting functional groups are on the same molecule. Consequently, such a reaction contributes to the consumption of these groups concentration, but does not lead to an increase of the polymer molecular weight. When carrying out practical calculations, not all elementary reactions should necessarily be taken into account, inasmuch as many of them proceed in such a moderate way under the conditions of particular process that they may be neglected for the construction of kinetic scheme of the process.

Treatments to compute the statistical characteristics of the primary structure of polycondensation products generally apply three principle approaches: kinetic, thermodynamic and statistical [11–14]. The first two consist in deriving and solving the material balance equations (kinetic approach) or chemical equilibrium equations (thermodynamic approach) for the concentrations of molecules involved in the process. Under the third approach, the fractions of molecules with specified configuration at fixed instant are calculated. This fraction is identified with the probability for a randomly chosen molecule to have the corresponding configuration. Different modifications of the statistical approach are in use for this calculation. Noteworthy, recourse can be made to several versions of the statistical approach for the quantitative description of even the same class of polycondensation processes. In the most convenient of these versions a macromolecule is regarded as an individual realization of a particular stochastic process of conventional progression, or movement, along a polymer molecule. These realizations can be calculated using the methods of the theory of the corresponding stochastic process.

The statistical method for the calculation of a polycondensation process was pioneered by Flory about half a century ago [11], and thereafter gained worldwide recognition as a quantitative description for a variety of both linear and branched polymers. An indisputable advantage of the statistical approach consists in its ability to provide an exhaustive and straightforward description of the configurational structure of macromolecules in terms of certain probability parameters. However, the choice of the stochastic process for the description of the products of a particular polycondensation system cannot be fulfilled in principle within the framework of the statistical method itself. The solution to this problem is provided only by kinetic and thermodynamic approaches, which enable simultaneous expression of the probability parameters of the stochastic process of interest through corresponding kinetic and equilibrium constants, the concentration of the reagents and other measurable quantities.

A key feature of the kinetic approach lays in the fact that its application implies the solution of an infinite set of material balance equations, due to infinitely large number of reagents. The fundamental

distinction from traditional chemical kinetics of low-molecular compounds resides in this circumstance. It is of prime importance that the kinetic equations of polycondensation are written down for the concentration of isomers varying in number of monomeric units and functional groups of different types, rather than for the concentrations of molecules of individual chemical compounds. The solution of these equations makes it possible to find the MWD or SCD, whose fit to those obtained by the statistical method testifies to the validity of the latter.

It is necessary to use the general principles of statistical physics and chemical thermodynamics, particularly, the detailed equilibrium principle, for a rigorous assessment of the applicability of a specific modification of the statistical approach to the description of the primary configurational structure of the equilibrium polycondensation products. Thus, the probability to find an arbitrary macromolecule in an equilibrium system is governed by the free energy alteration due to the formation of all its intramolecular bonds. In accordance with the detailed equilibrium principle, this probability does not depend on the sequence of the formation of these bonds, i.e. on the previous history of a system. Proceeding from general thermodynamic relationships, it is possible to express the free energy evolution during the formation of intramolecular bonds through the equilibrium constants of the respective elementary reactions corresponding to the stoichiometric scheme of the process in hand. The probability parameters employed in the statistical approach may then be determined in terms of these constants.

It is possible to clearly distinguish two stages for the evolution of the polycondensation theory. The first of them, originated by the fundamental work by Flory [11], only addressed systems which will be referred to as ideal. Furthermore, intramolecular reactions are neglected, whereas intermolecular reactions are assumed to obey the Flory principle. According to this basic principle, the reactivity of a functional group of specified type in every elementary reaction is the same, irrespective of the molecule to which this group belongs or its location in that molecule. The ideal polycondensation model, used extensively in the majority of published theoretical studies, has permitted calculation by different methods of a variety of statistical characteristics of the products of the most

general polycondensation processes with participation of any number of monomers of an arbitrary functionality, and with different type functional groups. The task of the elaboration of the theory of ideal polycondensation may be regarded as basically fulfilled. The next stage in the development of quantitative theory of polycondensation consists in the description of systems other than ideal ones. Attempts to describe such systems are generally concerned with overcoming difficulties of a fundamental nature. It is highly important that the dissimilarity of the factors contradicting the assumptions which underlay the ideal polycondensation model prevent a unified approach for the description of nonideal polycondensation. Hence, this stage of the theoretical development is presently far from complete.

Let us indicate the physical prerequisites underlying the original postulates of the model of ideal polycondensation systems, and reveal some of the reasons which can be responsible for the violation of those postulates. First, it should be stressed that polycondensation reactions in the liquid phase are comparatively slow, and are normally not diffusion-controlled. Intermolecular reactions are second order, whereas intramolecular ones are first order. This is conducive to the increase of the relative fraction of the latter via dilution of the reaction mixture by an inert solvent. The condition is readily achievable in which the cyclization reactions may be neglected for the description of the polycondensation kinetics. The probability in a unit of time that an arbitrarily chosen functional group of a macromolecule will enter into competing condensation reactions of inter- or intramolecular type equals, respectively, kC and k' , where k and k' represent the rate constants of bi- and monomolecular reactions, respectively, and C stands for the concentration of functional groups in the system. The quantity k' is proportional to the number of such conformations of the initial molecule for which in a close vicinity of the group chosen one more group belonging to this molecule is contained. In other words, the constant k' is proportional to the effective local concentration c , created in the vicinity of a chosen group by all the remaining groups of a polymer molecule due to its conformational rearrangements. Because the system is supposed to be in conformational equilibrium, the value of c

coincides with the concentration of corresponding conformers. If functional groups in a molecule are separated by sufficiently large number of intramolecular bonds the proportionality coefficient between k' and c is equal to k , since the probabilities of an elementary act of intra- and intermolecular reactions will be the same in that case. Consequently, the condition for neglecting intramolecular cyclization reactions, $k' \ll kc$, holds at $c \ll C$. The value of C decreases as the system is diluted, while c is defined by the configuration and segmental mobility (flexibility) of a polymer molecule, and in many systems is virtually unaffected by dilution. If the rates of inverse reactions are taken to be independent of conformational structure of molecules, all the above reasoning with respect to the rate constants of the reactions of condensation may be entirely transferred to the corresponding equilibrium constants k' and k . In particular, when the functional groups entering into the reaction are separated by many intramolecular bonds, the ratio k'/k is equal to the effective concentration c . Under equilibrium, the ratio c/C controls that contribution in the change of a macromolecule free energy at specified intramolecular reaction that is due to the decrease of the number of conformations of the molecule in the course of this reaction. Therefore, the value of c is unambiguously prescribed by the conformational entropy of a macromolecule, and may be calculated by thermodynamic methods.

By analogy with the conformational properties of macromolecules, conceivable reasons for the violation of the Flory principle may be divided into two classes: short- and long-range effects. Among the first, there are the so-called substitution effects due to steric, inductive or other kinds of the influence of reacted functional groups upon the reactivity of neighboring unreacted functional groups. Such effects are referred to as the first shell substitution effects (FSSE) provided a group reactivity is governed by the state of the functional groups involved exclusively in the monomeric unit which this group is attached to. Such an effect is peculiar to the polycondensation of many aromatic monomers. Sometimes allowance must be made for the possibility of higher order substitution effects when the group reactivity is acted upon by the states of the groups attached to neighboring units.

The calculation of polycondensation systems taking account of the substitution effect can be carried out using an extended Flory principle [12,13]. According to this principle, any functional group reactivity in a molecule can be controlled solely by the microstructure of neighboring fragments of the polymer molecule and can change during the process influenced by this microstructure evolution by the state of neighboring groups. In the FSSE model, the role of a kinetically independent fragment of a polymer molecule is played by a monomeric unit, with adjacent functional groups and chemical bonds connecting this unit with neighboring ones. The set of these bonds unambiguously specifies this fragment configuration, i.e. the type and kind of corresponding monad. Hence, under thermodynamic and kinetic approaches to the consideration of polycondensation of monomers with dependent functional groups, it would suffice to distinguish polymer molecules in the framework of the FSSE model by the number of monads of a given type and kind.

The long-range effects can be conditioned by the possible influence of the solvent on the spatial conformations of macromolecules and, as a consequence, on the reactivity of their functional groups. For example, shrinking of macromolecules occurring in passing from thermodynamically 'good' to 'poor' solvents may lead to a dramatic decrease in the accessibility of functional groups. Moreover, this effect can result in a total loss of the reactivity by these groups due to their intramolecular 'burying'. The account in the polycondensation theory of such long-range effects, where the accessibility of every individual group for its reactions with other groups is prescribed by conformational–configurational structure of an entire macromolecule, is a far more complicated problem as compared to that arising when describing the short-range effects.

A quantitative theory of polycondensation in which the long-range effects would be rigorously considered is virtually not available. The difficulties encountered in elaborating such a theory are due to the inapplicability of the Flory principle, even in its extended version. A theory of this kind calls for consideration of the conformational–configurational statistics of reacting the molecules. As for the intramolecular reactions, these latter unlike the intermolecular ones are, in principle, impossible to

calculate within the framework of a theory allowing for just short-range effects. This is obvious since the chemical interaction of any pair of functional groups belonging to a macromolecule depends essentially on their relative positions, as well as on the possible set of equilibrium conformations for this molecule. They are responsible for the probability that groups on a given molecule may draw close enough to ensure a chemical reaction.

An intrinsic peculiarity of ideal polycondensation systems ensues from the random character of the reactions proceeding in them. All of the statistical characteristics of the products of ideal polycondensation at every instant are independent of the previous history of the system. It is not essential whether the process proceeds under equilibrium conditions or not, nor whether destruction and transfer reactions take place or the process is completely irreversible. These characteristics are entirely controlled by the concentrations of functional groups and intramolecular bonds of each type at a particular time. This 'universality' principle when describing such systems by a statistical method provides a chance to choose the number of functional groups and bonds of each type in an arbitrary macromolecule as variables unambiguously setting its probability [12]. The fact that the state of a system in a nonequilibrium process does not depend on previous history (as in equilibrium) is exclusively due to the ideality of these processes. When the ideality is broken, the probability for the formation of a particular molecule in the course of nonequilibrium polycondensation is dependent on the sequence of the formation of bonds in that molecule. Hence, when invoking the statistical method for the description of the products of nonideal polycondensation processes in the absence of the equilibrium, the correctness of this method in the framework of the model chosen should be always verified by analysis of the solutions of corresponding kinetic equations.

The traditional examination of polycondensation is generally restricted to closed systems, in which neither input of monomers nor output of the reaction products takes place in the course of chemical transformations. The investigation of polycondensation in semi-open and continuous-flow reactor represents two limiting cases of open systems of special practical significance. In both, the input of monomers into the reactor is performed during

the polymerization. However, in the first case the rate of the output of polymers is zero, while in the second one it is equal to the rate of the input of the initial compounds. Both of these polycondensation processes exhibit a number of indisputable advantages compared to closed systems processes. This is especially true for the continuous-flow reactors extensively used in industry for many polymerizations [4]. It is worth emphasizing that the MWD, SCD and structure of molecules formed in the course of polycondensation are controlled, along with the stoichiometric, thermodynamic and kinetic parameters of a reaction system, by the way the process is conducted. Pronounced differences in the service properties of polymers synthesized in closed and continuous-flow systems are known to occur for the same values of the stoichiometric, thermodynamic and kinetic parameters.

Hereafter, we shall designate different monomers by a sequence of letters, the first of which, (R,S,...), will correspond to a monomeric unit, whereas each of the subsequent letters, (A,B,...), will define a particular type of functional groups in a monomer. If this monomer comprises several identical groups their number will be specified by a superscript appearing next to corresponding letter.

2. Linear polycondensation

2.1. Classification

Bifunctional monomers are generally used to prepare linear macromolecules. Homopolycondensation, heteropolycondensation and copolycondensation are distinguished, depending on the number and type of the monomers. The products of the first two processes are homopolymers with an elementary unit comprising, respectively, one or two monomeric units. The products of the third process are copolymers, with macromolecules varying in size, composition and microstructure. The processes of obtaining either polyamides from amino acids (initial monomer RAB, with only A and B interacting) or ethers from glycols (monomer RA²) are examples of a homopolycondensation. Under a heteropolycondensation the initial mixture is normally composed of two symmetric monomers, RA² and SB², with A and B

being different type groups. However, processes of a more general type are also plausible when the groups of the same type in each asymmetric monomer, RA₁A₂ and SB₁B₂, differ in reactivities. Among widespread heteropolycondensation processes are the formation of polyamides from diamines and dicarboxylic acids and the synthesis of esters from dicarboxylic acid chlorides and glycols. Their macromolecules contain regularly alternating monomeric units R and S, whose dyad RS plays the role of the elementary unit of the homopolymer being formed.

Except for the heteropolycondensation, all processes for which the number of monomers involved is more than one refer to a copolycondensation. The simplest cases of linear copolycondensation are bi- and interbipolycondensation. As an example of the first one a process can be mentioned, where at least one of the two initial monomers (e.g. amino acid) is able under given conditions to form the homopolymer. In the second process three monomers are simultaneously involved, for instance, S₁A₁², S₂A₂² and IB². Essentially the first two, termed comonomers, do not react one with another, while each of them is capable of entering into heteropolycondensation with the third component, referred to as an intermonomer. The reactivities of the functional groups of any of monomers may, generally speaking, be different. Such processes with an arbitrary number of comonomers are known as intercopolycondensation. In the following, heteropolycondensation and intercopolycondensation will refer to processes with using symmetric monomers unless otherwise specified.

2.2. Ideal homo- and heteropolycondensation

The first theoretical works dealing with linear polycondensation appeared in the late thirties [15,16]. Flory was the first [15] who managed to calculate the MWD of the products of homo- and heteropolycondensation by the statistical method, with the neglect of cyclization reactions, using his fundamental principle. The number average degree of polymerization, P_N , the weight function of the distribution $f_w(l)$ of molecules with degree of polymerization l , as well as the polydispersity coefficient K , defining the width of this MWD were

calculated [15] for homopolycondensation products:

$$P_N = (1 - p)^{-1}, \quad f_w(l) = (1 - p)^2 l p^{l-1}, \quad (1)$$

$$K = 1 + p$$

These statistical characteristics are controlled by the sole parameter p , equal to the functional group conversion. The same relationships are applicable for the description of the products of the heteropolycondensation of an equimolar mixture of monomers, while the corresponding formulas were also derived for the nonequimolar initial mixtures [15]. In the latter case, the formula $a_i b^l$ ($i = 1, 2, 3$) characterizes the MWD of each of the three kinds of molecules differing by the type of terminal functional groups, every kind having its individual value of parameters a_i . Such a distribution is identified as an extended Flory distribution. In order to calculate the distribution of polymer molecules for their molecular weight, rather than for their chemical size, it is necessary, to take account of the dependence of the statistical parameters a_i on the molecular weights of monomers [17,18].

Later on these relationships have been repeatedly rederived in a variety of ways. Thus, Schulz [16], proceeding from the principle of the detailed equilibrium calculated the MWD of the products of equilibrium homopolycondensation, found the theoretical dependence of the molecular weight of a polymer on the propagation reaction equilibrium constant. This problem was later solved independently by Elias [19]. Subsequently, Meggy [20] extended these results to an equilibrium heteropolycondensation. In the early 1940s, Flory [21] proposed two variants of the thermodynamic method to obtain the MWD in equilibrium systems. Various modifications of the statistical method have been employed for calculation of the most probable Flory distribution (1). In particular, they proceed from consideration of a one-dimensional process of a random walk [22] and a convolution integral [23]. The kinetic method has also been extensively applied when calculating the polymer MWD. The Flory distribution (1) was obtained by this method for products of irreversible [24] and reversible [25] polycondensation in closed system, as well as for reversible [26] and equilibrium [27] polycondensation, with allowance for the removal of a by-product from the reaction zone. An illustration of

the danger of mere speculation in the quantitative theory of polycondensation is the claim [28] that the Flory distribution (1) holds only for an irreversible polycondensation, whereas the account in the theory of the degradation reaction leads to MWD other than distribution equation (1). This assertion is erroneous [25,26,29], contradicting to the results of a rigorous kinetic consideration of reversible polycondensation [25,26].

Kinetic schemes adopted in papers [24–27] took no account of exchange reactions. The latter have been claimed [30] to be responsible for a considerable narrowing of the MWD as compared to the Flory distribution. However, this claim was found incorrect [31] upon simplified kinetic derivation of the MWD in a system where an exchange reaction (such as alcoholysis or acidolysis) proceeds, and the propagation and destruction of macromolecules is absent. The MWD of the polymer obtained in this equilibrium system was shown to be described by the distribution (1). Consideration of the general kinetic scheme of reversible homopolycondensation [32,33] with allowance for all the above-mentioned reactions discloses that the products of such a process at all its stages will be adequately characterized by the Flory distribution. Although an analogous general kinetic consideration has not been carried out for a heteropolycondensation, there are strong grounds for believing that with an equimolar mixture of initial monomers (this being the only possibility for high molecular products to be obtained), the MWD of a polymer prepared for an arbitrary reversible process will be defined by formula (1) as well. The proof of this statement for two opposite limiting cases, i.e. irreversible and equilibrium heteropolycondensation, supports this conjecture [12,13].

Theoretical analysis of the effects of the chain termination reaction on the polymer statistical characteristics was undertaken in papers [34–38]. The first to calculate the MWD and values of P_N and K for homo- and heteropolycondensation products was Case [34], using the statistical method. He established that the chain termination reaction does not affect the form of the polymer MWD, but controls the molecular weight. This inference was confirmed later by the kinetic method [35]. Sokolov et al. [36] have found the value of P_N analytically and numerically for different kinetic schemes and mechanisms of

the functional groups' deactivation. In particular, they examined the chain termination reaction by either impurities or a by-product released during the process. The chain of kinetic equations for the concentrations of macromolecules involved in an irreversible homopolycondensation has been written down [37,38], with allowance for the chain termination by the impurity. No exact solution of these equations has been reported by the authors, although some approximate results showing that the chain termination reaction may lead sometimes to a substantial narrowing of the MWD can be found in these papers.

There are statistical [34,39] and kinetic [40–42] considerations of heteropolycondensation of two monomers, one of which contains groups of different reactivity. It was revealed that the MWD of the products of such a process obeys an extended Flory distribution, which (at the same value of P_N) will be the wider the more strongly pronounced is the distinction in reactivity of the functional groups.

Mathematical modeling of a polycondensation can be highly efficient when developing new processes of a polymer synthesis, provided the theoretical results are grounded experimentally and realized as a computer program. An illustrative example of such a comprehensive approach is the series of publications by Costa and Villermaux [43–45], devoted to the investigation of polyesterification of adipic acid and triethyleneglycol.

Summing up the discussion of the quantitative theory of the ideal homo- and heteropolycondensation, it can be stated with reasonable confidence that no unsettled problems remain. However, many systems are known that are not amenable to description by an ideal model. The simplest criterion here is the value of the polydispersity coefficient K . Since for ideal systems its value must be close to two, any appreciable deviation from this value signals violation of the conditions of ideality. The treatment of the experimental data reported, for example, in reviews [46,47] points to the existence of nonideal systems, along with ideal ones. A polymer MWD in the former can prove wider, $K > 2$, or narrower, $K < 2$, as compared to the Flory distribution (1). The violation of the ideality of a kinetic model may happen because either the Flory principle no longer holds or a macrocyclization reaction is markedly pronounced.

Sections 2.3 and 2.4 discuss theoretical works taking account of each of these effects.

2.3. Models allowing for the violation of the Flory principle

Likely reasons for violations of the Flory principle may be attributed either to the long- or short-range effects. Among the first category are substitution effects due to steric and/or induction influence of the reacted functional groups on the reactivity of the neighboring unreacted groups. The simplest among the kinetic models taking such an influence into account is the FSSE model. According to this model, the reactivities of the functional groups of monomers differ from those of the rest of the molecules in the system, with any reactions between the latter presumed to obey the Flory principle. Monomers with a latent functionality like phthalic anhydride also can be considered as bifunctional monomers having kinetically dependent functional groups.

The specific polymeric nature of reagents is distinctly manifested in the long-range effects. The reactivity of a functional group positioned at the end of a polymer molecule is acted upon by fragments located over its entire length. A typical example is the intramolecular catalysis by active centers, that despite being separated from the terminal group by a large number of monomeric units, still fall within its vicinity as a result of conformational rearrangements of a polymer chain. When such long-range effects take place the reactivity of this group may be controlled by the number of units in a macromolecule [13].

2.3.1. The short-range effects

Almost all theoretical work accounting for short-range effects have been accomplished within the framework of the FSSE model. This model was introduced by Case [34] who presented the expressions for the MWD and its statistical moments for the products of a heteropolycondensation of two monomers. The first of them, RA^2 , has dependent groups, unlike the second monomer, SB^2 , for which the groups are independent. The MWD of polymers for this system is described by the extended Flory distribution, analogous to that obtained under an ideal heteropolycondensation of asymmetric RA_1A_2 and symmetric SB^2 monomers. Nonideal systems showing

such a property were called ‘quasi-ideal’ [48]. A rigorous kinetic substantiation of the foregoing expressions for the MWD that Case [34] presented using the statistical method, was carried out later [49] for the irreversible heteropolycondensation. An analogous substantiation evidently works for any reversible regime of a polycondensation in the quasi-ideal system due to the existence of an equivalent ideal system. The appearance of the MWD of the latter up to the values of the parameters of this distribution is invariant with respect to the presence of the degradation and exchange reactions. In papers [41, 49,50] the dependence is analyzed of the polydispersity coefficient on the conversion of functional groups as well as on the values of stoichiometric and kinetic parameters of an irreversible quasi-ideal heteropolycondensation. The quantity \tilde{K} that characterizes the polydispersity of the MWD of only the reaction products is best suited for such an analysis of systems described by the FSSE model. The exclusion of the monomer from the consideration in the framework of this model comes as no surprise because, unlike the case with an ideal polycondensation, the monomer plays a specific role as compared with other molecules in the reaction system. The value of the modified polydispersity coefficient \tilde{K} never exceeds two and is closer to this value the greater is P_N . For equimolar initial mixture of monomers, \tilde{K} does not deviate substantially from two, irrespective of the distinction in the reactivity of the first and the second groups of monomer RA^2 [41]. Some attempts have been made to rederive MWD expressions [51] presented in the literature [34,49].

An irreversible heteropolycondensation for which both monomers comprise dependent functional groups is considered in papers [52–54]. Sokolov et al. [52] calculated P_N at different values of four kinetic constants, which in the model chosen describe all plausible chain propagation reactions. The calculations disclosed that the greater the reactivity of the second group of monomers as compared to the first, the more high-molecular polymer can be obtained for a given conversion. When the above distinction in the reactivities becomes rather pronounced in both monomers, the polycondensation process exhibits the features inherent in a chain polymerization. The key feature is that high-molecular products can be obtained in a nonstoichiometric mixture of initial

monomers, and under incomplete conversion. Polycondensation systems of this kind have not been found experimentally. Case [53,54] managed to obtain the MWD of a polymer by the statistical method for the most general case of the irreversible heteropolycondensation, for which the groups of both monomers are not only dependent, but also differ in initial reactivity. This MWD is the extended Flory distribution, analogous to that derived for the heteropolycondensation of monomers with independent groups. However, a kinetic analysis indicates that the system examined by Case [53,54] is not quasi-ideal. In other words, the expressions he derived in these works for the MWD of the products of an irreversible polycondensation are erroneous. Moreover, even the heteropolycondensation of two symmetric monomers $RA^2 + SB^2$ does not exhibit the quasi-ideality property when both of them contain dependent functional groups [55,56]. That is why in such truly nonideal systems, unlike in quasi-ideal ones, it is reasonable to expect that, contrary to the Flory distribution, the expressions for the MWD will depend on the intensity of the degradation and exchange reactions, as well as on the regime of the process.

The simplest example of a truly nonideal system is the irreversible homopolycondensation of monomer RA^2 described by the FSSE model. This model is characterized by three kinetic parameters, k_0 , k_1 and k_2 . They are the rate constants of the reactions between functional groups of two monomers, monomer with polymer and two polymers, respectively. Using this example, Kuchanov [12,48] pointed for the first time to important peculiarities of such systems, qualitatively distinguishing them from a quasi-ideal ones. In particular, it was demonstrated that the Flory distribution describing the products of an equilibrium polycondensation in such a system does not satisfy the set of the kinetic equations of the irreversible polycondensation under any values of the kinetic parameters (apart from the trivial case corresponding to the absence of the substitution effect). Analytical and numerical examination of this set of equations [12,48] revealed that the character of the dependence of the modified polydispersity coefficient \tilde{K} on the polymer molecular weight may qualitatively differ from that under equilibrium polycondensation. For this regime, \tilde{K} always approaches two with increasing P_N . Conversely, under irreversible polycondensation,

when $P_N \rightarrow \infty$ there are kinetic parameters for a truly nonideal system for which the limiting value of \tilde{K} will be noticeably more than two.

Calculations of the time evolution of the number and weight average degrees of polymerization (unmodified and modified), as well as the MWD, has been reported [57–59] for an irreversible homopolycondensation in the framework of the simplified FSSE model. This model contains one kinetic parameter less than its general variant. Here, two different modifications of the simplified model were introduced. In the framework of the first of them [57,58], the rate constant of the reaction between two monomers was assumed to be distinct from that of the mutual interaction of all other pairs of molecules. In the second model [59], an analogous assumption was made with respect to the rate constant of the reaction of a monomer with any other molecule of an l -mer. Of special interest is the oscillating character of the MWD predicted by the theory for some values of kinetic parameters [58,59]. The period of these oscillations, for which the amplitude decreases with increasing conversion, is one monomeric unit. Further development of the theory of nonideal homopolycondensation described by the Gupta model [57] enabled Park [60] to obtain analytical expressions for the concentrations of monomers and dimers, as well as P_N and P_W of polymer products.

A more detailed analytical and numerical results on the investigation of the irreversible homopolycondensation of monomer RA^2 was published in which the kinetic method was invoked to theoretically analyze MWD in the framework of the FSSE model [61]. This in-depth analysis provided an answer to the centrally important problem of the applicability of the statistical method for the calculation of the MWD of the polymer molecules in the system under examination. The stochastic process of conventional movement along polymer chain considered under the statistical method has one regular and one absorbing state. The transition from one monomeric unit to the other and the abandoning the limits of a polymer molecule correspond, respectively, to the falling into the first and the second of these states. For an ideal model, the foregoing stochastic process is a Markov chain with probability p of transition into the regular state. As applied to the FSSE model this stochastic process was rigorously proved [61] to be non

Markovian since the probability of such a transition turns out to be predetermined by all preceding states. It is essential, however, that this dependence normally decays at scales n^* several monomeric units long. Hence, to numerically calculate the MWD of real polymers, one has to solve a set of about n^* differential equations, while under the straightforward kinetic method the number of equations to be solved is about $P_N \gg n^*$.

The main conclusions of the theoretical analysis of the FSSE model equations may be formulated as follows [61]. The distribution $f_W(l)$ of the polymer length l within the oligomer region, for which l is less than n^* , may vary in appearance depending on the values of the kinetic parameters $k = k_1/k_0$, $k' = k_2/k_0$, and the conversion p . In particular, this distribution can be either bimodal or oscillatory. In the second region, with l more than n^* , the MWD is described by the Flory distribution, such that the sole parameter in that distribution is specified by the values of k , k' and p . The same qualitative peculiarities seem to be inherent in the MWD calculated under consideration of a nonideal polycondensation in the framework of models allowing for the higher-order substitution effects.

More than a decade separates the publication [61] and papers by Irzhak et al. [62,63], in which the same FSSE homopolycondensation model was addressed. They reformulated the calculation of the MWD in terms of small fragments of polymer molecules, called 'bond blocks'. The authors found the distribution $f_W(l)$ by numerically solving the set of kinetic equations for these fragments. Using this approach, it became possible not only to reestablish an oscillating MWD, but also to formulate the conditions of the existence of such oscillations in terms of the kinetic parameters k and k' .

When considering the homopolycondensation described by the FSSE model, allowance for the effect of the degradation reaction leads to serious difficulties under analytical analysis of the equations for the l -mer concentrations. Here, their degradation as distinct from the ideal model may cause the change not only of the parameters of the MWD, but also its form as compared to that characterizing the products of an irreversible polycondensation. The difficulties arising are likely to be responsible for the absence of analytical results obtained in the framework of

the model. Indeed all theoretical results reported so far on the reversible homopolycondensation of a monomer with kinetically dependent functional groups were relevant only to numerical solution of the material balance equations for l -mers [64–66]. While Gupta et al. [64,65] proceeded from the simplified FSSE model with $k' = k$, Irzhak et al. [66] relaxed this constraint.

The quantitative theory of equilibrium polycondensation is far more simple than that of nonequilibrium polycondensation because of the applicability of fundamental thermodynamic laws. On their basis, a general algorithm was formulated [67] permitting one to calculate the MWD of the products of an equilibrium polycondensation described by the substitution effect model of arbitrary order, and to indicate the set of independent thermodynamic parameters for this model.

2.3.2. The long-range effects

In the papers discussed above, the role of the solvent and the impact of the long-range volume effects on statistical characteristics of polymers were totally ignored. Several attempts have been undertaken to take these effects into account in the theory of equilibrium polycondensation [68–73]. Thus, in papers [68–71] the equilibrium MWD of a polymer was calculated by minimizing the free energy of the polymer system. The expression for this was complemented by a term describing the interaction of polymer molecules with the solvent. The appearance of this term is prescribed by the particular model of such an interaction among those currently used in the theory of polymer solutions. So, for the concentrated solutions described by the Flory–Huggins lattice model it was shown [68–70] that the MWD of the products of the equilibrium polycondensation is characterized by the Flory distribution. Proceeding from other lattice models one may get other distributions [70]. The Flory distribution always describes the polydispersity of the products of the equilibrium polycondensation when the free energy of a macromolecule interacting with the solvent depends linearly on the number of its monomeric units. Only the Flory–Huggins model among all those considered in paper [70] meets this condition. The equilibrium MWD of a polymer was calculated [71–73] for dilute solutions, for which the interaction between the units

of different chains could be neglected. The lattice model seems to be the most suitable to determine the free energy of a system under theoretical consideration [71,72]. The MWD was found [71] to be narrower in a bad solvent and wider in a good one, in comparison with the Flory distribution. Besides, in a good solvent there exists a critical value of the number average degree of polymerization over which the MWD becomes bimodal [72]. The sophisticated methods of statistical physics were employed to consider a dilute polymer solution close to Θ -conditions [73]. Interestingly, the author of this work arrived at the conclusions opposite to those made in paper [71]. He found the equilibrium MWD of a polymer in a bad and a good solvent to be, respectively, wider and narrower than the Flory distribution. This contradiction, testifies, in particular to the existence of a number of issues to debate and problems to solve in quantitative investigation of the influence of the long-range effects and the solvent on the statistical characteristics of the products of an equilibrium polycondensation.

This conclusion applies more emphatically to nonequilibrium processes for which the thermodynamic approach is not applicable. Here, to develop a quantitative theory, one is supposed to determine the dependence of the kinetic constants of elementary reactions between functional groups on their location in macromolecules as well as on the number of their monomeric units. Then, it is necessary to calculate the statistical characteristics of a polymer proceeding from the solution of kinetic equations corresponding to the model chosen.

There are a number of publications [60,74–82] devoted to the calculation of the MWD of the products of an irreversible nonideal homopolycondensation using some empirical dependence of the constants of elementary reactions between polymer molecules on their lengths under the kinetic approach [60,74,75], or the analogous dependence of the probability parameters in case of the statistical approach [76–82]. So, for the constant of the reaction between polymer molecules whose lengths are i and j the empirical dependencies $k_0(ij)^{-\varepsilon}$ [76], $k_0[1 - \varepsilon(i + j)]$ [75] and $k_0[1 + \varepsilon(ij)]$ [60] were assumed. The authors of these publications did not manage to find analytical expressions for the MWD. Park [60] presented expressions for the fractions of monomers and dimers

as well as for P_N and K . As for the other two models, cumbersome approximate expressions for the fractions of di-, tri- and tetra-mers [74] as well as for P_N and K [75] valid only for $\varepsilon \ll 1$ were derived. Attempts were undertaken [75–82] to extend the statistical Flory approach to nonideal systems for the calculation of the MWD of the products of the ideal polycondensation. They were grounded on the same assumption implying that all ways of forming a macromolecule with a given degree of polymerization l are equiprobable. Under this assumption, the ‘history’ of its formation is of no importance. That is why analyzing the sequential addition of monomers one by one to the propagating chain the authors of publications [75–82] employed the formula $f_N = p(1)p(2) \cdot \dots \cdot p(l-1)[1-p(l)]$ for the number MWD of a polymer. Then having empirically taken two- or three-parametrical dependencies of the probability $p(l)$ of a bond formation on the degree of polymerization l of a molecule entering into the reaction they found the expression for the MWD of a polymer in terms of adjustable parameters $p(l)$.

It is pertinent to stress that for nonideal systems the equiprobability property of all conceivable ways of the formation of a molecule with fixed length has been rigorously substantiated only for systems under equilibrium [67]. Such a substantiation is not available for nonequilibrium processes. Moreover, systems are known (for instance, irreversible homopolycondensation of monomer RA^2 with kinetically dependent groups) for which this property does not hold. Consequently, the formal harnessing of the Flory statistical approach to calculate the MWD of nonequilibrium nonideal polycondensation products may lead to erroneous results. This reasoning equally applies to a derivation [76] of the MWD of the products formed during the above polycondensation process, in which the equiprobability property was used implicitly.

2.3.3. Macrocyclization reactions

The foundation was laid by Jacobson and Stockmayer in their classical work [83] presenting a quantitative consideration of linear polycondensation with allowance for intramolecular reactions. They calculated the MWDs and their statistical moments for linear and cyclic products of equilibrium homo- and heteropolycondensations. The calculations were

accomplished using the law of acting mass, with the equilibrium constant of the cyclization reaction found under the assumption that macromolecules are long and flexible enough to have a Gaussian end-to-end distance distribution. This means that the foregoing theory works only for the calculation of the concentrations of cyclic molecules with sufficiently large number of skeleton bonds n in the chain. Moreover, when considering the conformational statistics of macromolecules, the long-range effects may be neglected only under Θ -conditions. In this case Jacobson–Stockmayer’ theory being asymptotically exact when $n = ml \rightarrow \infty$ leads to dependence $k_l^c \sim l^{-2.5}$ of equilibrium constant k_l^c of the cycle-chain reaction on number l of a macromolecule. The proportionality coefficient in this dependence is controlled by the thermodynamic flexibility of the macromolecule and the number m of the skeleton bonds in a single monomeric unit. The rotational-isomeric conformation model [84–86] enables this coefficient to be calculated for a variety of widely used polymers. The results ensuing from the Jacobson–Stockmayer theory were later derived by statistical [87] and kinetic [88] methods.

Having analyzed the derivation of the expression for constant k_l^c reported in paper [83], Flory and Semlyen [89] noticed that one of the applicability conditions of this expression is the absence of correlations between the orientations of the terminal bonds under their approaching within the distance that allows the chemical interaction [86]. These correlations become stronger as l diminishes, and to take account of them Flory and co-workers [90] put forward a method for the calculation of k_l^c incorporating empirical observations on a number of polymers under Θ -conditions.

One more factor to be necessarily included in calculating k_l^c for oligomers with a small number of skeleton bonds is the violation of the Gaussian approximation for the distribution of the distance between a macromolecule ends. To calculate the cyclization constants for such oligomers proceeding from the rotational-isomeric model, recourse has been made to the matrix technique [90–96], straightforward enumeration of the conformers [97] as well as to computer simulation of chain conformations by the Monte Carlo method [98–101]. Along with these, there are similar papers dealing with the calculation of

the cyclization constant for a number of polymers in the framework of some conformational models [102–110]. The input parameters for such calculations are only the structure characteristics of polymer chains, such as valence angles, lengths of interatomic bonds, potentials of internal rotation around them. For some models, this set of parameters is complemented by the maximum value of the separation of terminal functional groups for their mutual diffusion that will permit the condensation reaction. The calculation of k_l^c is possible with limited use of adjustable empirical parameters since structural characteristics have been measured for a variety of polymers [86]. The values of k_l^c obtained for such calculations mostly show reasonable fit to those found experimentally via the analysis of the data on the MWD of the cyclic products of an equilibrium polycondensation obtained by the NMR technique. The results of such a comparison of the theory and experiment are reported for many equilibrium systems by Semlyen [102] as well as in some of the above cited papers.

Since the cyclization constant of a macromolecule is controlled by its equilibrium conformational set, it is reasonable to consider the problem of the statistical mechanical calculation of k_l^c [111–113]. This permits one to consistently include long-range volume effects in the calculation of the partition functions of a cyclic and linear macromolecule, the ratio of which is proportional to the probability of the cyclization. The literature abounds in publications addressing the calculation of the conformational characteristics of macromolecules using either lattice or continuous models, incorporating volume interactions of units positioned far apart from each other along a polymer chain. Inasmuch as the examination of the long-range effects is beyond the scope of this review, we will not dwell on the publications covering this matter, referring interested readers to reviews [114–117]. The general conclusion ensuing from the consideration of the results of theoretical study of conformational statistics of macromolecules performed both analytically and by means of computer simulations can be formulated as follows. Because of volume effects the exponent σ in asymptotic dependence $c_{\text{ef}} \sim l^{-\sigma}$ of effective local concentration c_{ef} of one terminal functional group in the vicinity of the other

exceeds the value $\sigma = 3/2$ typical for polymer chains under Θ -conditions.

Determination of the equilibrium MWD of linear and cyclic molecules with allowance for the long-range effects is of prime importance for the theory of equilibrium polycondensation. Erukhimovich [118] presented (omitting the derivation) an expression for the first of these distributions for the case of a dilute polymer solution in a thermodynamically good solvent. It follows from that expression that the products of an equilibrium polycondensation due to an excluded volume effect are expected to have a polydispersity coefficient $K = 1.85$, that is, a somewhat narrower number MWD than that for the Flory distribution. These distributions differ qualitatively in form, with the second of them showing its maximum at $l = 0$, and the first distribution attaining a maximum at $l > 0$.

For an equilibrium polycondensation, upon specifying the equilibrium constant k_l^c of the cyclization reaction for all l -mers, the MWDs and their statistical moments for linear and cyclic products have been calculated in a standard way using simple algebra [83]. By contrast, in the nonequilibrium regime to cope with this task, one is supposed to solve an infinite set of differential kinetic equations that describe the polycondensation, with the cyclization reactions incorporated into the kinetic scheme. Note, this set of equations is not closed, since the overall concentration of the linear molecules (occurring there as a coefficient) cannot be calculated independently, unlike the case for an ideal polycondensation. That is why it is necessary to make recourse to some assumption to truncate the set of equations for the concentrations of the linear l -mers. So, in considering the irreversible homopolycondensation, Moravetz and Goodman assumed that only monomer may enter the cyclization reaction [119]. They calculated the fraction of the monomer involved in cyclic molecules under complete conversion of all functional groups, depending on the sole dimensionless parameter of their model, equal to the ratio of c_{ef} to the initial monomer concentration. Gordon and Temple [120] numerically solved the equations of the irreversible heteropolycondensation with the cyclization employing the expression for the rate constant of this reaction derived proceeding from the Gaussian statistics of a polymer chain. Interestingly, to obtain a closed set of

equations, Gordon and Temple truncated it in an arbitrary way, retaining for the solution a system containing a certain number of equations, on the assumption that there exists some maximal degree of polymerization of macromolecule, beyond which they stop growing. Extending the Moravetz–Goodman model [119] the authors of paper [121] admitted for their calculations the possibility of the formation of cycles comprising up to twelve monomers. Calculating the concentrations of l -mers being formed in the course of an irreversible heteropolycondensation, Rolando and Macosko [122] abandoned the assumption concerning the Gaussian statistics of macromolecules [120], to vary the dependence of the cyclization constant k_l^c on the chain length l .

In developing a theory of nonideal polycondensation with cyclization, Irzhak et al. [123] did not restrict consideration to systems obeying the Flory principle. Unlike their predecessors [120,122], in calculating the irreversible heteropolycondensation they employed a model that took account of substitution effects, along with the formation of cyclic macromolecules. Kinetic equations were solved for a range of the kinetic parameters in the framework of the simplified FSSE model for the concentrations of l -mers. The dependence of the weight fraction of the cycles on conversion of functional groups was plotted [123], and the character of the MWD evolution during the synthesis was investigated [124] on the basis of these results. These curves feature a strongly pronounced plateau testifying to the dramatic decrease of the rate of the formation of cyclic molecules in the course of the synthesis. The MWD of such molecules formed during the irreversible heteropolycondensation over the whole range of conversions proved to be markedly narrower than the equilibrium distribution of cycles [124]. This assertion is also supported by comparison of the values of polydispersity coefficient K of macrocycles obtained in two limiting regimes of polycondensation.

In parallel with a straightforward solution of the set of kinetic equations for l -mer concentrations [119–124], a theory of nonideal heteropolycondensation made use of various modifications of the statistical method [125–127]. The key idea was to consider a small number of some small species, and to find their concentrations from the solution of a closed set of simultaneous differential equations, comprising

a much smaller set than required for the kinetic method. Given the concentrations of the small species, the statistical moments of the MWD of linear and cyclic polymers or the distribution itself may be determined using some probabilistic considerations. The main drawback of such statistical approaches is that the accuracy of the approximate results is unknown. In the ‘cascade theory’ [125] and the ‘rate theory’ [126], the role of the small species is played by monomeric units of types R and S distinguished by their kinds. The kind of a monomeric unit of given type is prescribed by the number of unreacted functional groups adjacent to it. There are three such kinds. Apart from them there is the ‘fourth’ one which every monomeric unit of given type involved in a cyclic macromolecule belongs to. Differing in the character of underlying probabilistic reasoning the ‘cascade theory’ [125] and the ‘rate theory’ [126] lead to distinct expressions for number fraction of ring molecules [128].

A variant of the statistical method radically different from those employed earlier [125,126] was advanced by Miller and co-workers [127]. They developed a combined kinetic–recursive approach for calculating the MWD of the products of an irreversible random heteropolycondensation, with allowance for cyclization. The major assumption of the model employed is the prohibition on the formation of cyclic molecules composed of more than a certain fixed number N of monomeric units. Under such an approach, along with the cycles and oligomer linear molecules with $l \leq N$ units, the small species were defined to include some auxiliary structures comprising one, two or three monomeric units, together with adjacent reacted and unreacted functional groups. A system of $4N + 3$ simultaneous kinetic equations was set up to describe the interconversion of these small species. After numerically solving this system, Miller et al. [127] used the auxiliary structures and the approximately recursive nature of the larger molecules to ‘build back’ the long chains. Later, these authors discussed [129] the main approximations underlying several approaches that have been used to model irreversible heteropolycondensations incorporating intramolecular reactions, and studied their range of validity. They found that some never give good results, while others may be used when cycle formation is low, and the better ones

may be applied with low to moderate levels of intramolecular reaction. None were satisfactory for a high degree of cycle formation.

The theoretical papers considered above [119–127] dealt with polycondensation systems for which the cyclization reaction is kinetically controlled. However, at sufficiently large value of the condensation reaction constant k , the rate of the formation of cyclic molecules is no longer dependent on k , and will be entirely controlled by the rate of macromolecule conformational rearrangements by which the terminal functional groups on a molecule approach in space. Since such an approach is due to their mutual diffusion, all analogous reactions are diffusion-controlled. The theory of such reactions was treated initially by Wilemski and Fixman [130]. In terms of the Rouse–Zimm model, their calculations predict a powerlaw dependence of the diffusion-controlled cyclization rate constant $k_l^c \sim l^{-\sigma}$ on chain length l . Excluded volume effects are neglected in this theory, and the magnitude of σ depends upon the extent of the hydrodynamic coupling associated with the polymer motion. For free draining chains, $\sigma = 2$, whereas for the more realistic nondraining description of polymers in dilute solution, $\sigma = 3/2$. Certain features of the theory have been examined in detail by Doi [131]. Perico and Cuniberti [132] have extended theory [130] to partially draining chains of finite length. Two extensive publications review both the theory and experiments associated with diffusion controlled polymer cyclization [133,134].

2.4. Linear copolycondensation

Molecules of linear heteropolymers are known to vary within a specimen in the numbers of their constituent units (size and composition), as well as in the pattern of arrangement of these units along the chain (structure). It should be emphasized that many problems arising for the statistical description of heteropolymers prepared by chain and step copolymerization differ substantially. Hence, in theories of radical copolymerization, one is inevitably faced with the task of finding the composition of the products formed. Conversely, in case of copolycondensation the above problem can emerge in closed reaction systems exclusively under a pronounced violation of the stoichiometric condition between functional

groups when oligomers are finite products. To get high-molecular polycondensates it is necessary to adhere to this condition by conducting the reaction up to nearly complete conversion. In that case, the copolymer average composition will be virtually the same as that of the initial monomer mixture and thus the problem of its determination ceases to be actual.

Another essential distinction between the products of copolycondensation and radical copolymerization is a marked configurational isomerism of the former. When at least one of the initial monomers has an asymmetric structure, a complementary type of structural isomerism arises due to the dissimilarity in the ways these monomers are added to the growing chain. Such a constitutional isomerism takes place even in macromolecules obtained for a homopolycondensation of an asymmetric monomer, with ‘head-to-tail’, ‘head-to-head’, or ‘tail-to-tail’ pattern of mutual arrangement of successive directed monomeric units. In the case of chain polymerization of most asymmetric vinyl monomers they add mainly by the ‘head-to-tail’ pattern, to form constitutionally regular polymers. For copolycondensates with asymmetric units fractions of different types of the above patterns of arrangement are normally comparable, so that constitutional isomerism must necessarily be taken into account for a statistical description of their configurational structure [135–139]. The methods of such a description of homopolymers exhibiting constitutional isomerism are similar to those traditionally employed to characterize an isomerism due to a distribution of different type units in copolymers [140,141]. Consequently, it seems reasonable to consider structural isomerism of homopolymers in this section.

2.4.1. Copolycondensation of symmetric monomers

The first classification of the processes of the linear copolycondensation may be that advanced by Shtraikhman [142], who derived an equation connecting the conversions of the functional groups of comonomers in an ideal irreversible interbipolycondensation. This equation was used to analyze the dependence of a copolymer composition on conversion at different stoichiometry of the initial monomers and their functional group reactivity [143]. A similar problem was also studied for a range of stoichiometric and kinetic parameters [144,145]. Expressions for

the composition of copolymer formed in the irreversible regime of the process are set up for an intercopolycondensation of an arbitrary number of comonomers [146,145] as well as for bipolycondensation of monomers RAC and SBC [147].

The foregoing publications utilized the ideal polycondensation model. Nikonov et al. [148] dismissed the Flory principle carrying out a calculation of the kinetics of the interbipolycondensation of monomers with dependent functional groups. On the basis of the simplified FSSE model allowing for the substitution effect for all three monomers, they wrote down a set of six material balance equations for the concentrations of the functional groups involved. Numerical solution of these equations at certain values of kinetic parameters permitted calculation of the composition of oligomer products formed under complete conversion of an intermonomer, present in the initial mixture with a molar fraction less than 1/2.

Expressions for different average molecular weights, MWD and size, composition and functionality (SCFD) of polycondensation copolymers were derived by the statistical method [34,149,150]. In particular, Case [34] obtained analytical relationships for the MWD, as well as weight average and number average molecular weights of the products of an ideal bipolycondensation, and the ratio of these was theoretically examined for copolymers synthesized by an ideal interbipolycondensation [149,150]. General expressions presented in monograph [12] and review paper [13] permit simple algebraic derivation of analytical expressions for the generating functions (gf) of the SCFD of an arbitrary ideal copolycondensation products. Given these expressions, it is possible to find the distributions and their statistical moments, resorting to the standard mathematical procedure. In the publications cited above, an algorithm was formulated of an analogous calculation of the SCFD for the products of a copolycondensation involving some monomers comprising kinetically dependent groups.

Different approaches to the statistical description of the chemical structure of condensation copolymers have been invoked. The most straightforward way to characterize the microstructure of such copolymers is to specify the fractions of all dyads of elementary units. In case of binary copolymer of a given composition these fractions are controlled only by

microheterogeneity coefficient K_M , which can be expressed through the fractions of different dyads of elementary units RI and SI as follows

$$K_M = \frac{P(RS)}{P(RS) + 2P(RR)} + \frac{P(SR)}{P(RS) + 2P(SS)} \quad (2)$$

For a mixture of two homopolymers $P(RS) = 0$ and, thereupon, $K_M = 0$. For a regularly alternating copolymer $P(RR) = P(SS) = 0$, and, consequently, $K_M = 2$. All conceivable values of coefficient K_M lay between these two extreme cases, corresponding to the ideally ordered arrangements of units in macromolecules. For example, $K_M = 1$ corresponds to a random (i.e. the most disordered) distribution of units. Thus, the degree of ordering of a copolymer microstructure can be quantified from the absolute value of the deviation K_M from unity. The sign of this deviation is indicative of the tendency of monomeric units' arrangement in chains either to regular alternation ($K_M > 1$) or to the formation of long blocks of both comonomers ($K_M < 1$). The challenge for a theory consists in expressing the fractions of dyads through kinetic (nonequilibrium processes) or thermodynamic (equilibrium processes) parameters, and to find, thereupon, the values of K_M (2).

The calculation of K_M has been carried out for the products of an irreversible interbipolycondensation [151–153] and a bipolycondensation [151]. It was demonstrated [151] that the sequence distribution in copolymer chains is necessarily random (i.e. Bernoullian) provided the intermonomer has independent functional groups. This result stems from the equality $K_M = 1$, which holds in this case irrespective of the values of the initial fractions of monomers, the reactivities of their functional groups, or the degree of their conversion. Besides, the effect of these factors on quantity K_M has been theoretically studied [151] for the opposite case when the comonomers have independent groups, unlike the intermonomer, for which the groups are dependent. In line with this model, the reactivity of an intermonomer second group positioned at the end of any polymer molecule does not depend on the type of a comonomer penultimate unit, though it differs in reactivity from the first group. Such a model is characterized by just four elementary reaction rate constants, i.e. by three dimensionless reactivity ratios of the functional groups. The number of these kinetic parameters

decreases to two when the reactivities of the first and the second groups of an intermonomer are presumed to be proportional in their reactions with the first and the second comonomer (following the authors of paper [148]). In the framework of such a simplified FSSE model, general regularities have been revealed of the dependence of K_M on stoichiometric and kinetic parameters, and simple analytical expressions for K_M have been derived at different limiting values of these parameters [151]. Analogous results have been reported [154] for the equilibrium regime of interbipolycondensation in which the independence of intermonomer groups was shown to be a sufficient condition for obtaining a random copolymer.

Theoretical analysis of the irreversible [151] and equilibrium [155,156] bipolycondensation revealed certain qualitative distinctions from the interbipolycondensation. Of prime importance among them is the fact that even for the ideal bipolycondensation model $RA_1B_1 + SA_2B_2$, the quantity K_M turns out, generally speaking, to differ from unity. A simple analytical expression for K_M was derived [151] for the particular case with $B_1 = B_2$.

The microheterogeneity coefficient is the best suited to characterize the chemical structure of copolymers whose molecules are made up of the elementary units of two types. If the number of such types exceeds two, the description of the sequence distribution in copolymer chains calls for several parameters similar to K_M . In this connection, a major problem facing a copolycondensation theory is an appropriate choice of the structure parameters for a particular system. Practical recommendations for such a choice have been suggested [157], with the general ideas exemplified by the copolycondensation of four monomers $R_1A_1^2 + R_2A_2^2 + S_1B_1^2 + S_2B_2^2$, whose functional groups of types A_i only react with groups of types B_i .

The second mode of description of the chemical structure of the macromolecules of linear copolymers consists in specifying the distributions for the length of blocks of different elementary units. The first calculations for the products of ideal intercopolycondensation of a stoichiometric mixture of monomers were made by Best [146]. Using the statistical method, he found that for each i th type of units the distribution is the Flory distribution with parameter $\alpha_i p_i^2$ depending on the initial mole fraction α_i of

a corresponding i th comonomer, $R_i A_i^2$, and the conversion p_i of its functional groups A_i . In contrast to this case, when the Bernoulli copolymer is formed a similar problem has been solved within the framework of a simplified FSSE model for the intermonomer [152]. The solution of corresponding kinetic equations gives the Flory distribution (as obtained earlier [146]) with a parameter, which being expressed through the concentrations of the dyads of the elementary units, reduces to $\alpha_i p_i^2$ only if the functional groups of the intermonomer are independent.

A statistical analysis of the distribution of blocks for length in the products of an ideal irreversible interbipolycondensation was carried out in papers [158–161]. The authors of the first two used the formalism of the Markov chains as applied to infinite [158] and finite [159] macromolecules. Gritsenko [160,161] conducted a qualitative theoretical study of the effect of the stoichiometry of the initial monomers and the reactivity of their functional groups on the character of distribution of units for a single- and two-step process mode. The latter case has been analyzed [162] to give the coefficient of polydispersity of the distribution of different type blocks for length, i.e. the ratio of the weight-average to the number-average block length of the i th comonomer as a function of the stoichiometry, conversion, as well as the reactivities of the first and second groups of the intermonomer. Various average block lengths have also been calculated [146,149,152,160,161].

The problem of finding the distribution of block lengths in macromolecules obtained for bipolycondensation of monomers with dependent groups was handled by Irzhak et al. [163] for the case with one of monomers incapable of forming a homopolymer. However, they failed to solve this problem, having restricted their calculations to the time-dependence of the fraction of triads.

An algorithm for the calculation of the probability of arbitrary sequence of units is needed for an exhaustive description of their distribution in a copolymer macromolecule. A very simple algorithm of this kind is available for linear copolymers with a Markovian configurational statistics. In this context, the finding that the sequence distribution in the products of an arbitrary homogeneous process of an ideal irreversible copolycondensation is described by

a Markov statistics is of general theoretical significance [164]. The Markov chain parameters are related to the constants of the elementary reactions and to the composition of the initial monomer mixture. A similar result was reported for an ideal equilibrium polycondensation [154]. The identity of the results for these two extreme process modes shows that any statistical characteristic of the chemical structure of the products may be calculated by the Markov chain formalism for any intermediate regime of an ideal copolycondensation. This fundamental property, referred to as ‘universality’ [12,13], is violated in systems not described by the ideal model. The sequence distribution in such systems proves to be predetermined to a considerable extent by the process regime.

When developing the quantitative theory of an equilibrium copolycondensation it was shown [154] that the extension of the model by incorporating any order ‘substitution effect’ does not disturb the Markovian character of the sequence distribution. The same authors employed different versions of the FSSE model to calculate the parameters of the corresponding Markov chain in the limiting case when the average length of a macromolecule P_N tends to infinity. A set of simple algebraic equations was derived to calculate these statistical parameters, and its analytical solution was found for interbipolycondensation. Expressions for the parameters of the Markov chain characterizing the chemical structure of macromolecules of finite length were presented for arbitrary P_N [165]. These expressions make it possible to perform calculations of the polycondensation processes used to obtain reactive oligomers important in the manufacturing of a variety of polymer materials. The above relationships are but a particular case of general expressions for the parameters of the Markov chain which describes the configurational statistics of the products of arbitrary equilibrium linear copolycondensation within the framework of the most general FSSE model [165].

A proof that the sequence distribution in macromolecules may be described by a Markov chain under the applicability of the same FSSE model, but in the course of a nonequilibrium copolycondensation, is missing. Moreover, it seems that such a proof is impossible to provide in principle for systems, which are not quasi-ideal. The quasi-ideality condition for

intercopolycondensation of any number of monomer types resides in the kinetic independence of functional groups, either of the intermonomer or of all comonomers. In the first case, even when the substitution effect takes place in the comonomers, the sequence distribution obeys Bernoulli statistics [166]. In the second case, it obeys first-order Markov chain [48,166]; the expressions for its parameters were derived first in a simplified FSSE model [166], and later in its full version [48].

Finding an unambiguous correspondence between the configurations of copolymer molecules and the realizations of a Markov chain made it possible to obtain simple asymptotic relationships at large P_N for the composition distribution of polycondensation copolymers [154,164,165]. In the case of interbipolycondensation, these distributions are Gaussian [154, 164,165], with parameters depending only on three quantities: P_N , the composition of the initial monomer mixture and K_M . An analysis of these dependencies reveals that the composition distribution becomes narrower as P_N grows or the average length of blocks in the copolymer decreases with increasing K_M .

The mathematical apparatus employed in the theory of Markov chains allows the calculation of any required statistical characteristics of the chemical structure of linear copolymers, including their MWD. Durand and Bruneau [167–171] derived the expressions for this distribution, describing copolycondensates obtained in various systems.

A resort to the method of computer simulation has been used for the solution of some problems of the theory of irreversible copolycondensation [158,159, 172–177]. This was employed to find the distribution of blocks for length, molecular weight distribution and some other statistical characteristics of the chemical structure of macromolecules obtained under the applicability of either the ideal model or FSSE model. Comparison of the results of the Monte Carlo simulations with those found via the numerical solution of the appropriate kinetic equations performed in some of the above cited papers revealed reasonable agreement.

2.4.2. Nonsymmetric monomers

Many monomers acting as the initial compounds for the synthesis of polycondensation polymers have a nonsymmetric chemical structure. It is possible to

designate such monomers by the symbol $A_1\bar{R}A_2$, conventionally distinguishing ‘head’ and ‘tail’ in the oriented monomeric units \bar{R} . Polymer molecules involving similar units will, obviously, show the constitutional isomerism due to their different mutual orientations. One of the major challenges to a quantitative theory of polycondensation with the participation of nonsymmetric monomers is revealing the dependence of the statistical characteristics of the microstructure of polymer products on the stoichiometric and kinetic parameters of the initial mixture. Evidently, this task resembles that discussed in Section 2.4.1. Just this analogy was exploited when studying the microstructure of chains formed in the course of the irreversible heteropolycondensation of nonsymmetric $A_1\bar{R}A_2$ and symmetric BSB monomers [178]. This paper was the first to report a theoretical analysis of the constitutional isomerism of polycondensates with nonsymmetric units, for which it was suggested that the microstructure could be characterized by a single parameter. This is analogous to K_M (2), with the sole distinction that the role of the triads of monomeric units, RIR, SIS and RIS is played here by $\bar{R}\bar{S}\bar{R}$, $\bar{R}\bar{S}\bar{R}$ and $\bar{R}\bar{S}\bar{R}$, respectively. This analogy motivates the adoption of all the theoretical conclusions obtained when considering interbipolycondensation of symmetric monomers for the analysis of heteropolycondensation $A_1\bar{R}A_2 + \text{BSB}$ [178]. Embarking on the study of more complicated polycondensation systems, it is preferable instead of K_M to use the structure parameter $K_O = 1 - K_M$, which can be called a ‘coefficient of orientation’. Its extreme values $K_O = -1$ and $K_O = +1$ correspond, respectively, to the limiting cases of the constitutional regularity, i.e. the head-to-tail and head-to-head/tail-to-tail arrangement of monomeric units.

An appreciable contribution to the theoretical investigation of the constitutional isomerism of condensation polymers was made by Suter and co-workers [138,179–181]. They began [179] by studying three polycondensation systems described by the ideal model. Among them there are homopolycondensation of nonsymmetric monomer $A_1\bar{R}A_2$ characterized by three constants of elementary reactions k_{11}, k_{12}, k_{22} between functional groups A_1 and A_2 , as well as the heteropolycondensation of nonsymmetric $A_1\bar{R}A_2$ and symmetric BSB monomers comprising two such constants, k_{1B} and k_{2B} . The parameter s

denoting the probability for two adjacent units to point in the same direction has been used to characterize the microstructure of homopolymers formed in these systems. In the limit $P_N \rightarrow \infty$ this parameter is related to the coefficient of orientation in a simple mode $K_O = 1 - 2s$. The theoretical dependence of s on the relative reactivities of functional groups has been presented for both the above systems. The third system taken in paper [179] is the heteropolycondensation of two nonsymmetric monomers $A_1\bar{R}A_2 + B_1\bar{S}B_2$. To describe the microstructure of polymer molecules involved in this system Suter et al. [179] used along with s , two additional structure parameters s_1 and s_2 . The latter two are controlled by the fractions of triads, unlike s , which is governed only by the fractions of dyads of nonsymmetric monomeric units. The parameters s_1 and s_2 are the probabilities that two nearest \bar{R} or \bar{S} units point in the same direction, respectively. When calculating structure parameters, use was made of the simplified variant of the ideal model [179], incorporating the assumption that the constants of elementary reactions are related by equation $k_{22}/k_{12} = k_{21}/k_{11}$. If so, the system is characterized by two reactivity ratios instead of the three, normally employed unless some simplifications are made. This assumption was subsequently abandoned by Gentile and Suter [180], who examined heteropolycondensation within the framework of the standard ideal model. In order to avoid the solution of the 38 kinetic equations of this model necessary for calculation of the structural parameters, they determined the fractions of dyads and triads by a Monte Carlo technique. Extending the theoretical study of the constitutional isomerism, Suter and co-workers [181] considered the heteropolycondensation of nonsymmetric and symmetric monomers, assuming that the functional groups of the latter are kinetically dependent. Having discarded the intention to examine the general kinetic model with five relative reactivities they restricted themselves to its simplified version involving a triple of such parameters.

Turning from homopolymers to theoretical analysis of copolymers with molecules containing nonsymmetric monomeric units, an additional isomerism comes into play, due to the difference in the arrangement of units along macromolecules. In this case, the problem of the choice of the structure parameters becomes nontrivial. The first question

a theory is supposed to answer concerns the number of parameters that should be specified to describe exhaustively the chemical structure of the chains formed during the linear copolycondensation of an arbitrary monomer mixture. Naturally, the answer is fully conditioned by the kinetic model of copolycondensation that is of interest. The second issue to be elucidated is the motivation for the choice of a particular set of structure parameters. In view of the ambiguity of such a choice, it would be advisable to make it for reasons of convenience of the application of these parameters for the treatment of experimental data on the microstructure of copolymers.

General approaches have been developed [137, 140, 141, 157] for the solution of the theoretical problems raised above, providing a comprehensive description of the chemical structure of the products of any ideal and quasi-ideal copolycondensation. Their configurational statistics is Markovian that permits finding any statistical characteristic of copolymers resorting to the mathematical apparatus of the theory of the Markov chains. The elaboration of such a theory involves two steps. The first consists in indicating the correspondence between the states of a Markov chain describing a particular system and fragments of polymer molecules. The second step involves the derivation of the expressions connecting the statistical parameters of this chain with the structural parameters of a copolymer and its composition. The approach advanced to carry out these procedures [137, 157] suggests the application of the universal Markov chain [137, 157]. The regular states of the above Markov chain correspond to directed chemical bonds of different kinetic types. Type (*ir*) of such a bond (e.g. an ester) is controlled by the types of groups A_i and A_r , which react to form the bond. The process of conventional movement along the macromolecule may be envisaged as a sequence of oriented bonds $\{ir\}$ ‘passing’ from the first index to the second one. The transition probabilities of the universal Markov chain are readily expressible through the relative fractions of pairs of states ($\{ri\}\{js\}$). Every such a pair represents monomeric unit R_α of a particular kind depending on with which groups A_r , A_s there have reacted groups A_i , A_j of monomer $A_i R_\alpha A_j$. The probability of the transition from state $\{ri\}$ into state $\{js\}$ of the universal Markov chain turns out to be proportional to the fraction $\lambda(\{ri\}\{js\})$ of units

of kind ($\{ri\}\{js\}$), i.e. to the fraction of the corresponding triads of oriented monomeric units. These triad probabilities are dependent, as they are related by a certain linear stoichiometric equations. Given the rank of the matrix of these equations, it is possible to unambiguously indicate how many among the probabilities of triads will be independent, in other words, to specify the number of structure parameters. The number of independent dyad parameters is obtained similarly.

The potential of this algorithm was demonstrated in a comprehensive theoretical study of the copolycondensation of four symmetric monomers [157] (see Section 2.4.1), and interbipolycondensation with one nonsymmetric comonomer involved [137]. The first of these systems is characterized by the dyad structure parameter, a coefficient of selectivity K_S , and four triad parameters, the microheterogeneity coefficients $K_M^{(i)}$, where $i = 1, 2, 3, 4$. The description of the microstructure for the second system requires three triad parameters, and it has been suggested that these be taken as K_M , a coefficient of direction, K_D , and a coefficient of orientation, K_O [137]. In the framework of a particular kinetic scheme of a copolycondensation process and given regime of its conducting it is an easy matter to find the dependence of the structure parameters on the rate or equilibrium constants of elementary chemical reactions between the functional groups of monomers as well as their initial fractions. It should be emphasized that these sets of structural parameters are intended to describe the configurational structure of the products of quasi-ideal copolycondensation when some of the monomers have kinetically dependent functional groups. If such monomers are absent, the number of independent structure parameters is reduced. For example, the microstructure of the products of ideal tetracopolycondensation is exhaustively described by a sole parameter K_S [157].

2.5. Special modes of polycondensation conducting

Up to this point the theoretical papers reviewed have dealt exclusively with polycondensation regimes under which the number of monomeric units remains unaltered throughout the whole process of the synthesis. However, alongside such closed (with respect to monomers) systems there exist others for

which the regime of polycondensation implies gradual addition or removal of some monomers, respectively, into or out of the reactor. Polymers in such semi-open systems are normally prepared in semi-batch reactors. Yet under the commercial manufacturing, preference is usually given to a continuous regime of condensation polymerization, in which monomer mixture is fed at constant rate into the reactor, and polymer products are steadily removed from the reactor. In these cases, it is known that the polydispersity is largely predetermined by the regime of hydrodynamic stirring in the reaction vessel. When studying open systems, the trend in chemical engineering science [182] is to distinguish macro- and micro-level of stirring, providing under mathematical modeling an explanation for such a distinction in terms of a 'continuous-flow stirred tank reactor' (CSTR). In the case of ideal stirring at both levels, a CSTR is said to be homogeneous. If this occurs only at the macroscopic level, one should take into account the effect of microscopic segregation in the theoretical analysis of chemical transformations in CSTR.

2.5.1. Semi-open systems

One of the important disadvantages of a batch polycondensation is that this mode virtually excludes any control over the polymer microstructure. Such an opportunity is, however, furnished when polymers are prepared in a semi-batch reactor. Here, by varying the types of monomers that are continuously fed into the reaction vessel, as well as the rate of their addition, it becomes possible to obtain macromolecules with a desired arrangement of their monomeric units.

There is a fundamental difference between irreversible and equilibrium polycondensation performed in such systems. To change statistical characteristics of chemical structure of polymer products obtained under these two limiting regimes, it is necessary in the first to add gradually monomers into the reactor, while in the second, conversely, to remove them from the reactor.

The influence of the rate of the monomer feed into the reaction vessel on the statistical characteristics of the products of an irreversible heteropolycondensation was theoretically explored using the kinetic method [183]. It was demonstrated that the MWD of the polymer is described by the Flory distribution, as in a closed system. However, unlike for the latter,

the polymer molecular weight may be rather high, even for a pronounced violation of the equimolarity condition of the initial compounds, provided the rate of the addition of the monomer present in excess is small enough. In this case, a simple expression has been derived enabling one to determine the rate constants of the condensation reaction, proceeding from the results of the measurements of the dependence of P_N on the feed rate.

Calculations for an ideal interbipolycondensation in semi-open system gave the dependence of the copolymer composition on stoichiometric and kinetic parameters and the rate of the addition of the comonomers [184]. The results showed that the compositions of the copolymer and monomer mixture can notably differ. Such a situation is impossible in principle for a polycondensation conducted in closed system.

The microstructure of the products of an irreversible interbipolycondensation in a semi-batch reactor was theoretically studied for the first time in work [152]. That study established the dependence of K_M on the reactivity ratios of the functional groups of monomers under their continuous addition, as well as under a variety of multistage modes of interbipolycondensation.

It is possible to obtain polymers with diverse microstructure with parameters governed by a reaction system parameters by changing the succession and the rate of monomer's addition into the semi-batch reactor. The most comprehensive theoretical examination of these dependencies in semi-opened systems was realized for irreversible heteropolycondensation of nonsymmetric and symmetric monomers [178,179,181]. Some of the general qualitative regularities established are of particular interest [138]. For example, the highest possible head-to-head/tail-to-tail regularity is achieved by a very slow addition of the symmetric monomer to a reaction mixture containing all of the nonsymmetric monomers. By contrast, a random polymer is invariably obtained under slow addition of a nonsymmetric monomer. Similar, though less detailed analysis of the structural regularity was accomplished for the case of an ideal heteropolycondensation of two nonsymmetric monomers [180]; the Monte Carlo technique was employed to find the dependence of three

structure parameters on the monomer feed rate for several particular values of reactivity ratios.

Degradation and rearrangement reactions of macromolecules are particularly important in many commercially significant polymer manufacturing processes. Among them is the production of poly(ethylene terephthalate) for which the macromolecules comprise alternating units of ethylene glycol R and terephthalic acids. However, in industry when synthesizing this polymer the common practice is to escape the direct heteropolycondensation of these monomers, $RA^2 + SB^2$ using some other method. They use the diester of ethylene glycol and terephthalic acid, ARSRA, as initial compounds, with the polycondensation conducted in a semi-batch reactor removing glycol as it is steadily released during pronounced interchain exchange reactions like alcoholysis and esterolysis. The first is the reaction between a hydroxyl group of one molecule and an ester linkage of any other molecule, whereas the second is the reaction between two ester linkages of different molecules. The set of equations for the concentrations of molecules C_l containing l units S was written out for reversible polyesterification proceeding in well-stirred semi-batch reactor [185, 186]. The kinetic scheme which underlies these equations incorporates only the alcoholysis reactions, distinguishing their three types



where A and A^g stand for hydroxyl groups belonging, respectively, to polymers and glycol, while Q and Q^t denote interior and terminal ester linkages of polymer molecules. Reaction $A^g + Q^t$ is excluded from the consideration because it does not alter the numbers of units in the reacting molecules. The model adopted for MWD calculations [185,186] presumed the reactivities of functional groups A, Q and Q^t to be independent of the polymer molecule in which they reside. However, we are likely to deal here with the FSSE model rather than with the ideal model of heteropolycondensation since external groups A and A^g as well as internal groups Q and Q^t are presumed to be kinetically distinguishable. The set of the material balance equations for concentration C_l corresponding to this model with three elementary reaction rate constants has the Flory distribution as its solution at all $l \geq 1$. This result was arrived at numerically [185]

and analytically [186]. Essentially, unlike for ideal heteropolycondensation here finding the value of the parameter of this distribution as well as the glycol concentration C_0 calls for special consideration that would take into account the equilibrium distribution of this glycol between liquid and vapor phases.

Two different diol esters of dibasic acids ARIRA and BSISB may be taken as the initial compounds in the synthesis of copolyesters by equilibrium interbipolycondensation. The synthesis should be conducted under conditions in which glycols ARA and BSB are continuously removed from the semi-batch reactor. Apart from finding the copolymer statistical characteristics, the theoretical examination of such processes [187–190] suggests the solution of a centrally important problem on establishing the equilibrium dependence between a copolymer composition and the fractions of intermonomers ARA and BSB in the vapor phase. Given this dependence it is possible to calculate the composition of the final products of the interbipolycondensation [187–190] which, generally speaking, will be other than that of the mixture of initial compounds. Such a distinction can be quite substantial, even for ideal interbipolycondensation, which is inconceivable when the synthesis is conducted in batch reactor.

2.5.2. Open systems

Theoretical investigation of polycondensation in open systems is of utmost importance for both the statistical chemistry of polymers and chemical engineering science [191,192]. Alongside indisputable technological advantages, a polycondensation process conducted under continuous regime features one material drawback. This is due to the considerable rise in polydispersity of macromolecules for their size and composition as compared to that for polymers obtained in a batch reactor. Because this may be responsible for a noticeable deterioration of the performance properties of polymer materials, the theoretical estimate of the above polydispersity depending on the parameters of the reaction system is of prime significance when developing new processes of the synthesis of polycondensates. In view of the complexity of such an estimate, theoretical papers have considered the general regularities of polycondensation in open system only for a CSTR or a series of such reactors.

The theoretical consideration of the irreversible homopolycondensation of monomer RA^2 in a CSTR [35,193–195] results in the following expressions for polymer MWD and its statistical characteristics

$$P_N = \frac{1}{1-p},$$

$$f_w(l) = \frac{(2l-2)!(1-p)}{[(l-1)!]^2(1+p)} \left[\frac{p}{(1+p)^2} \right]^{l-1}, \quad (4)$$

$$K = \frac{1+p^2}{1-p}$$

where p stands for the conversion of groups A. Expressions (4) as well as (1) remain true either for homopolycondensation of monomer RAB or heteropolycondensation of equimolar mixture of monomers $RA^2 + SB^2$. Comparison of the MWD in Eqs. (1) and (4) at the same value of P_N reveals that the second of them is markedly wider than the first one. This distinction is the more pronounced the higher is the polymer molecular weight. The value of the polydispersity coefficient K of the products of polycondensation prepared in a CSTR is $P_N \gg 1$ times larger than that of the products obtained in a batch reactor.

The polydispersity of the products of continuous polycondensation may be reduced if the process is conducted in a series of n CSTRs. The important problem of finding the theoretical dependence of the width of MWD on the number n of the reactors in a series was solved for the first time in paper [196]. An optimal polycondensation regime was found under which the products prepared show the lowest polydispersity at given number of reactors.

As distinct from studies of ideal homopolycondensation in a homogeneous CSTR [35,193–195], Tadmor and Biesenberger [197] examined the effects of microscopic segregation in a CSTR on the MWD of the polymers formed. Proceeding from the ideal model, they found substantial difference from results obtained by neglecting the segregation. A similar problem was solved in paper [196] for a cascade of n identical CSTRs. Gupta et al. [198] explored the influence of the ‘substitution effect’ on the MWD and its moments for a homopolycondensation of monomer RAB in a segregated CSTR.

Closing the section, it is pertinent to mention a pair of publications [199,200] in which equations describing the kinetics of cyclization in CSTR were numerically solved and analyzed. The dependence of the MWD of cyclic products on the kinetic and hydrodynamic parameters of a reaction system was found.

3. Branched polycondensation

3.1. Distinctive features

This section deals with branched and network polymers obtained in the course of polycondensation with participation of at least one monomer whose functionality is more than two. It should be stressed that although necessary for the synthesis of the above polymers, this condition is by no means sufficient. In real systems showing appreciable deviation from ideality, the involvement in the process of monomers with functionality more than two will not necessarily lead to the formation of a polymer network. For example, for the polycondensation of two four-functional monomers, pyromellitic dianhydride and *para*-phenilen diamine, the polymer formed is a cycloliner rather than of branched structure [201], owing to a strongly pronounced negative substitution effect. Thus, the reactivity of the carboxyl groups and unreacted hydrogen atom turns out to be too low to ensure that they take part in intermolecular reactions leading to branching. At the same time, due to the mutual configuration of these groups, favorable for the formation of the five-term imide cycle, the role of the effective local concentration of one of them in the vicinity of the other is high enough to induce an intramolecular imidization reaction. As a consequence, the consumption of functional groups occurs with the formation of imide cycles in the main chain.

The preceding example is one of two limiting cases of the polycondensation, for which intramolecular cyclization suppresses completely the tendency of macromolecules to branching. Ideal polycondensation represents another limiting case at which the cyclization reactions in molecules of finite size can be ignored completely. Real systems may be intermediate between these two limiting cases. The contribution of intramolecular reactions as compared to

intermolecular ones may be pronounced to different extent, depending on the conformational set of macromolecules, their flexibility and concentration in solution. Most of the experimental data on branched polycondensation in a melt or a concentrated solution indicate that for many systems, the majority of functional groups belonging to the sol fraction enter intermolecular reactions, rather than intramolecular ones. This enables one in the first approximation to ignore at all the reactions of cyclization in molecules of finite size when calculating the configurational characteristics of the polycondensation products in such systems, as it was suggested by Flory [11] in his model of ideal branched polycondensation. Later, more general models of this process have been developed, taking account of violations of ideality due to the substitution effects and intramolecular reactions before network formation.

The characteristic feature of branched polycondensation is gelation, i.e. the appearance of giant infusible and insoluble macromolecules having a three-dimensional spatial structure. They distinguish macro- or microgel depending on the relationship between the size of these structures and that of the reactor. In the first case, a three-dimensional polymer network pierces the entire reaction volume, while in the second one a microgel particles are found to be dispersed in it.

The physico-chemical factors such as chemical nature of a polymer, its affinity to the solvent, the intensity of the cyclization reaction prescribe the mechanisms of macrogel formation for branched polycondensation. The simplest among them is homogeneous gelation, in which a reaction system remains homogeneous during the synthesis up to the gel point, where this system instantly loses fluidity and solubility in response to macrogel formation. Other systems also exist in which macrogelation is preceded by microgelation. In the course of the latter a system undergoes phase microseparation, accompanied by the formation of colloidal particles, whose number and size can change with time. As a result of the subsequent crosslinking of the microgel particles, they integrate in a single macrogel network. This mechanism of gelation was put forward [202] to interpret experimental data on the solidification of alkyd resins. As for the quantitative theory of gelation all attempts of its elaboration have been undertaken

exclusively for homophase systems. An analogous theory of microgelation for branched polycondensation has not been reported.

Historically, starting with the fundamental work by Flory [11,203,204], various modifications of the statistical approach have been employed to calculate MWD, the average degree of polymerization and the critical conversion at the gel point. In parallel with straightforward combinatorial reasoning, a variety of the statistical methods found application based on the consideration of the probabilities of conventional movement along macromolecule. Some ideas and results of the theory of graphical enumeration and the theory of branching stochastic processes proved to be rather efficient under such a consideration. A characteristic feature of many works invoking the statistical approach is the absence of a rigorous substantiation of the results obtained. That is why the correctness of the final formulae of such publications may be predetermined to a great extent by the scientific intuition of their authors. This factor becomes insignificant when one uses the kinetic or thermodynamic methods of calculation as well as the approaches founded on general concepts of chemical kinetics, thermodynamics and statistical physics. The results achieved in such a way are rigorous within the kinetic models under examination and, consequently, can serve as a criterion of the validity of the expressions developed by the statistical methods.

As distinct from linear macromolecules, branched ones may vary in their topological configurational structure. In order to differentiate individual molecules obtained in the course of branched polycondensation, it is convenient to have them schematically represented as molecular graphs. (Mathematically speaking, a graph is a set of vertices connected by edges.) A graph is put to every molecule, in one-to-one correspondence, with a topological structure that correlates with the molecule configuration. For instance, to the products of ideal polycondensation there corresponds a 'forest' of molecular 'trees', i.e. graphs without cyclic fragments. The vertices of such a tree correspond to monomeric units and functional groups, while its edges correspond to chemical bonds.

The vertices corresponding to monomeric units are referred to as nodes (filled circles) while those corresponding to the functional groups are termed pending vertices (open circles). Any two nodes of

a molecular graph may be joined together with a broken line consisting of edges whose number controls the length of this path. To it there corresponds the linear fragment of a molecule connecting two monomeric units, known as a trail. In the case of tree-like molecules, any pair of units is linked by a single trail. A graph involving l nodes corresponds to an arbitrary homopolymer molecule with l monomeric units. The number of edges attached to each node of such a graph coincides with the functionality of the initial monomer. The molecules of an l -mer at given $l \geq 4$ can differ in topology (see Fig. 1). In order to differentiate the vertices of molecular graphs if several monomers are involved in the process, it is convenient to assign different colors to these vertices. Thus, when describing copolymers, colored graphs should be introduced.

The task of a comprehensive statistical calculation of a polymer configurational structure consists in finding the probabilities of the molecular graphs differing in the number of vertices and the topology. However at typical values of the degree of polymerization of statistically branched molecules, the number of their structural isomers is enormously large. In this case the description of the reagents commonly accepted in traditional organic chemistry by setting the concentrations of chemically individual compounds makes no sense even, for homopolymers. Instead, another approach may be recommended to characterize the topological structure of statistically branched polymers, based on introducing the hierarchy of probabilities $P(U_k)$ of different molecular fragments (U_k), termed k -ads, with progressively larger number k of monomeric units [205]. Obviously, the information on the configurational structure of

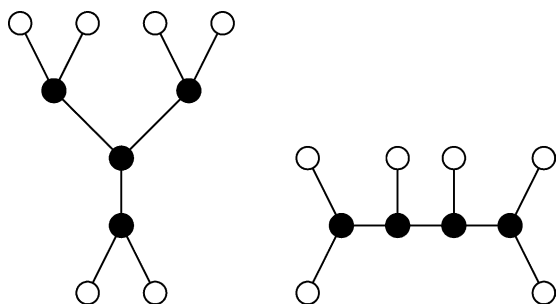


Fig. 1. Molecular trees of two structural isomers formed during homopolycondensation of monomer RA^3 .

such a polymer becomes increasingly detailed with the growth of k . An exhaustive description of this microstructure suggests the development of a constructive algorithm for the calculation of the probability of any fragment (U_k).

Key features of this approach are conveniently demonstrated by the simplest example of a tree-like homopolymer formed for the process of polycondensation of monomer RA^3 with three identical functional groups A in the approximation of the absence of intramolecular reactions. When characterizing branched polymers let us mean by k -ad (U_k) a molecular graph composed of k nodes and the edges incident to them. A part of these latter (internal edges) connect the nodes of a k -ad among themselves and with pendent vertices while the remaining (external edges) join these nodes with the other graph nodes situated outside this k -ad (see Fig. 2).

Branched homopolymers containing, by definition, only one type of units may be conventionally thought of, however, as heteropolymers since their molecules consist of units differing in kind, governed by the number i of chemical bonds connecting a given unit with others. For instance, the monads with i external

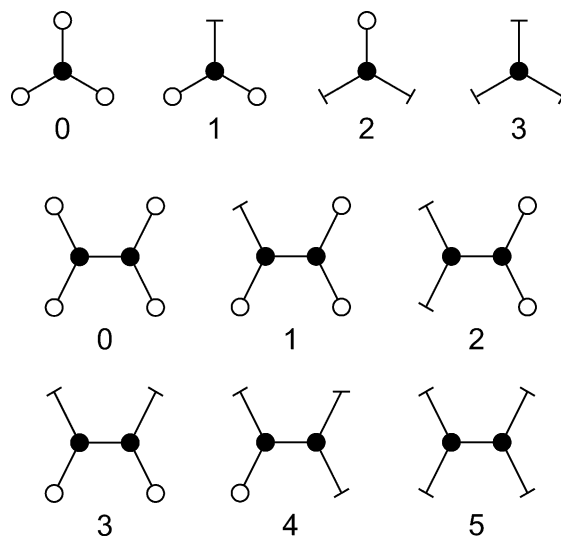


Fig. 2. Complete sets of acyclic monads U_{1q} ($q = 0-3$) and dyads U_{2q} ($q = 0-5$), which are fragments of molecules formed under homopolycondensation of monomer RA^3 . The black and white sites correspond to monomeric units R and functional groups A, respectively.

bonds depicted on Fig. 2 correspond to units of kind i . The simplest way to describe a polymer topological structure is to specify the fractions $\lambda_i = P(U_{1q})$ of units whose kind is $i = q$. Subsequent levels of the description of a microstructure detail consist in the indication of fractions $P(U_{2q}), P(U_{3q})$, etc. of different dyads (U_{2q}), triads (U_{3q}) and so on, arbitrarily indexed by q individually for each set of k -ads (U_{kq}) with given k . Knowledge of these quantities is of practical importance because they enter into expressions for the glass transition temperature and some structure–additive properties of branched polymers.

The general principles of the quantitative description of the chemical structure of branched homopolymers formulated above can be extended to heteropolymers. In order to characterize their molecules, it is necessary to distinguish by kinds monomeric units of every type. Under such a characterization, k -ads will additionally differ in number of units of different types. Unlike the case for homopolymers, here it is imperative to find the sol and gel composition.

As for polymer network formed after the gel point, apart from the calculation of the fractions of different k -ads describing its local topological structure, it is necessary to find some parameters which characterize the global topology of the molecular graph of the network. The most important among such parameters are the number per monomeric unit of elastically effective nodes μ and of elastically active chains ν connecting such nodes. (The effective nodes are those of an infinite graph of the gel, from which no fewer than three ways spring to infinity.) Evidently, μ and ν should be viewed as intensive variables. The significance of these parameters as well as of their difference $R = \nu - \mu$ is due to the fact that they govern the elasticity of a polymer network. The topological parameter R is the cyclic rank of its molecular graph. By definition, R is the least number of edges to be removed from the graph in order to convert it into a tree. The calculation of cyclic rank, the gel point, and the weight fraction of gel ω_g and its composition is one of the challenging problems of quantitative theory of a polymer network formation.

To find the statistical characteristics of the configurational structure of sol and gel molecules discussed above, an abstract graph should be put in correspondence to each of them. Such graphs provide

an exhaustive description of only the topological structure of a branched macromolecule, neglecting the positions of monomeric units in space. At this level of description, full information on the polymer is contained in its molecular-structure distribution, which sets the fractions of different structure-topological isomers. However, many physico-chemical characteristics of a polymer system (for instance, the average geometrical size of macromolecules or the intensity of the light scattering by its solution) are governed by conformation set of molecules constituting this system, along with configuration set. The calculation of such characteristics calls for averaging over both conformations and configurations of individual molecules of a polymer specimen. In this approach, a graph embedded in three-dimensional space should be put in correspondence to each macromolecule. Under such a description of a polymer specimen, the averaging is performed over the probability measure on the set of labeled graphs, i.e. such graphs every vertex of which is supplied by a label characterizing its location within the Euclidean space. This conformation probability measure is normally presumed to be specified by the equilibrium Gibbs distribution, because far away from the glass transition temperature of a polymer the characteristic time for conformational equilibrium to be established is markedly less than that of the chemical transformations in a reaction system.

The need for conformational averaging also arises under the theoretical consideration of intramolecular cyclization reactions inasmuch as the formation of cyclic fragment in a polymer molecule induced by a chemical reaction of any pair of its functional groups is preceded by their approaching each other in the three-dimensional space.

3.2. Ideal model of polycondensation

Flory pioneered the application of the ideal model for the calculation of branched polycondensation [203]. He provided a clear-cut definition of the gelation phenomenon and formulated its mathematical condition, which resides in the divergence of the polydispersity coefficient K characterizing the width of the MWD of the polycondensation products. Examining the statistics of trails in the course of a random walk along branched macromolecules, Flory

introduced the ‘probability of branching’ α , and connected its critical value at the gel point with the functionality of the branching monomer [203]. Using several simple polycondensation systems as examples, it was shown how α can be expressed through the conversions of functional groups and the stoichiometry of the initial monomer mixture [203], making it possible to find the critical value of conversion at the gel point. To find the MWD, Flory [203,204,206,207] invoked the statistical approach, calculating all of the necessary probabilities by means of direct combinatorial reasoning. In particular, the following expressions have been derived for the weight MWD, $f_w(l)$, of the products of the ideal homopolycondensation of monomer RA^f , as well as the number average P_N and weight average P_W degree of polymerization [202]:

$$f_w(l) = D(l)p^{l-1}(1-p)^{(f-2)l+2},$$

$$\text{where } D(l) = \frac{f[(f-1)l!]}{(l-1)![(f-2)l+2!]} \quad (5)$$

$$P_N = \frac{2}{2-pf}, \quad P_W = \frac{1+p}{1-p(f-1)} \quad (6)$$

The only parameter occurring in the above expressions is the conversion of the functional groups p . Although only some particular types of polycondensation systems were covered in these seminal papers [203,204,206,207], an indisputable merit of their author consists in laying the foundation of the theory for the ideal branched polycondensation.

The probabilistic approach advanced by Flory has been repeatedly employed, explicitly or implicitly, in various modifications by many researchers. Thus, the homopolycondensation of monomer $RAB_1 \cdots B_f$ was considered [208,209], where along with the MWD the distribution of molecules for number of different bonds was calculated as well. In a number of publications, the critical conversion was calculated for the polycondensation processes with several polyfunctional monomers, between the groups of which the only elementary reaction proceeds [210–216], and monofunctional compounds have also been taken into account [213–216]. The gel point for the polycondensation of different mixtures of mono-, bi- and polyfunctional monomers was calculated [217–222] for the systems with more than two

types of functional groups, and the effect of side reactions with involvement of the groups of bifunctional monomers on the gel point was also theoretically analyzed [223]. In the mid-1970s the statistical approach found further refinement in papers by American [224–228] and French [229–234] scientists. They proceeded from the recurrences for conditional probabilities to pass from one fragment of a macromolecule to another. The recursive method applied for the statistical treatment of several particular systems allowed them to derive expressions for a number of important statistical characteristics of the chemical structures of branched polymers. Among such characteristics are different average molecular weights [224,226,227,229–231,234], average functionalities [227,232], the gel point location [224–234], the weight fractions of sol and gel, the conversions of functional groups in each of them as well as the fractions of units of different types and kinds in a polymer network.

Application of the statistical approach discussed in the preceding entails rather cumbersome and non-trivial probabilistic reasoning for each system of interest. This is likely to be responsible for a number of mistakes committed by some researchers. For example, an erroneous relationship was derived for the critical conversion during homopolycondensation of a polyfunctional monomer with two types of functional groups [210]. The effect of monofunctional reagents on the location of the gel point was treated incorrectly [213,214], as later pointed out [215]. Considering irreversible polycondensation in systems with several types of groups and calculating probability parameters entering in formulas which they derived using statistical method the authors [221] failed to interpret the integrals obtained from the solution of kinetic equations. This led them to wrong conclusions on the limits of applicability of the Flory–Case statistical method employed. Among erroneous works paper [235] could be mentioned where an attempt was made to construct a probabilistic scheme of the process of ideal polycondensation distinct from the scheme introduced by Flory which resulted in other theoretical conclusions. Particularly, proceeding from this faulty scheme the divergence of P_N instead of P_W was claimed to be the condition of gelation. In the course of the discussion on this matter

[236–241] the source of errors in paper [235] was revealed.

A version of the statistical approach to the calculation of the gel point and MWD of the products of ideal polycondensation systems was proposed by Stockmayer [242–244]. The key ideas of this approach bear some resemblance to methods applied in statistical physics. Stockmayer took advantage of the fact that for an ideal system at fixed conversion of the functional groups, the probability of a particular distribution of molecules for number of monomeric units is proportional to the number Ω of ways in which all N monomeric units can be partitioned among the molecules with fixed MWD. Under the most probable distribution, Ω exhibits a sharp maximum and in systems with macroscopic N this distribution specifies the MWD of the polymer. Following the Stockmayer approach for the calculation of Ω it is necessary to solve the problem of enumeration of all equiprobable ways in which a molecular tree with given number of nodes may be formed. By using straightforward combinatorics, Stockmayer solved this problem for the products of the ideal polycondensation of an arbitrary number of monomers. However, his solution covered exclusively the case when every monomer comprised identical groups, and only one elementary reaction proceeded in the system [243,244]. However, his solution covered only the case when every monomer comprised identical groups, and with only one elementary reaction [243,244]. The results obtained exactly coincide with those derived by the Flory method, although this conclusion was questioned by some authors [216].

Rigorous substantiation of the Stockmayer statistical method as applied to the process of ideal equilibrium homopolycondensation of monomer RA^f was outlined in paper [245] in which the Mayer diagram technique extensively used in the theory of dense gases was employed. As a result it became possible to relate the MWD of the polymer obtained to the potentials of intermolecular interaction, and to calculate some thermodynamic parameters of the system. The equation of state obtained enabled the authors to draw an analogy between the gelation phenomenon occurring during polycondensation and gas–liquid phase transition under vapor condensation [245].

It must be admitted that the straightforward combinatorial technique put forward by Stockmayer

for the solution of the enumeration problem, as well as the Flory primitive probabilistic approach [11], look rather archaic today. To cope with this task it is far more convenient to resort to the graph enumeration method, which permits one to calculate any ideal system in a rather simple and universal way. Thus, the number of different ways of the construction of a molecular tree with fixed number of nodes is unambiguously prescribed by the symmetry of its configuration [246–248]. As a quantitative measure of this property of a graph, its combinatorial entropy, introduced by Gordon and Scantlebury [249], may be used. Gordon and co-workers devoted major attention [236,238,246–248,250–252] to the application of the graph theory concepts for the statistical description of the products of polycondensation, and some other processes, developing the so-called ‘chemical combinatorics’ [238,247,248]. Proceeding from the detailed equilibrium principle, they revealed the correlation between the constants of equilibrium of chemical reactions of branched molecules and the combinatorial entropy of the corresponding molecular graphs in case of ideal polycondensation.

In calculations of the combinatorial entropy, it is convenient to switch from molecular to rooted trees, in which one of the nodes, referred to as the ‘root’, is detached. All other nodes are connected to the root by a single path. The length of this path is equal to the generation number in which a given node is positioned in a genealogical tree corresponding to the given rooted tree. In a genealogical tree, the nodes pertaining to the same generation are situated on one horizontal line, along with all pendent vertices connected directly with the nodes of the preceding generation (see Fig. 3).

Two rooted trees may be thought of as identical only if the number and the order in which their vertices are arranged in every generation are the same. Choosing some node of a molecular tree as a root and varying the location of its vertices in every generation will give several different rooted trees with the topological structure of the initial molecular tree. Its combinatorial entropy was found to be related by a simple expression with the number of different rooted trees originated by the molecular tree [246]. Considerable progress has been made in the theory of graph enumeration in methods to find this number [253–257].

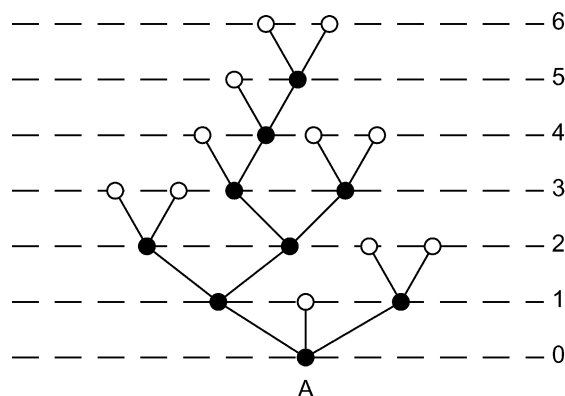


Fig. 3. One of the possible genealogical trees of the family generated by an ancestor A. The numbers correspond to generations of this family, whose representatives are denoted by filled circles.

The formalism of the theory of branching processes is more convenient for the calculation of the statistical characteristics of the molecular structure of randomly branched polycondensates. This formalism not only permits enumeration of all ordered rooted trees in a uniform manner, but also simultaneously gives the probability of each of them. In order to make use of the powerful mathematical apparatus of the theory of branching processes, it is necessary to establish a correspondence between the fragments of macromolecules and reproducing particles of a branching process as well as to specify correctly the probabilities of their reproduction. Gordon conjectured that the calculation of the statistical characteristics of randomly branched polymers can be performed by the methods of the theory of branching processes [258]. Then, Good noticed that this approach also allows determination of the average degrees of polymerization of molecules constituting the sol and its weight fraction [259]. Later, Gordon and co-workers showed how to proceed from known gf of a branching process to calculate different statistical characteristics of the products of ideal polycondensation of monomer RA^f [260] and some stoichiometric mixture of several monomers [261]. Monograph [262] comprises a special section devoted to the Gordon statistical method, abounding with examples which illustrate the potentialities of this method for the calculation of different statistical characteristics of branched polycondensation polymers.

The central ideas of the Gordon approach can be briefly formulated as follows. To each polymer molecule formed in the course of the ideal homopolycondensation of monomer RA^f corresponds a tree-like graph while the whole polymer specimen is associated with the ensemble of such trees, referred to as 'molecular forest'. This can be transformed into a clone, i.e. a forest of rooted trees obtained from molecular trees as a result of the selection of every node as a root. Such a transformation retains the probability measure, so the only thing to do is to find the distribution of rooted trees. Each of them may be viewed in its turn as a genealogical tree describing the history of a family, or as some realization of a stochastic branching process of the birth and death of particles. Thus, to the reproducing particles on Fig. 3 there correspond monomeric units R, presented by filled circles. Open circles denote functional groups A which are likely to take no part in reproduction, and thus can be excluded from the consideration under the construction of branching process. The history of the evolution of the population depicted on Fig. 3 is as follows. The particle-ancestor gives birth to two children-particles, the first of which produces two grandchildren-particles while the second one dies childless and so on. The complete set of such populations coincides with the set of all possible realizations of a branching process of conventional movement along randomly branched polymer molecules.

Knowing the algorithm to find the probability of an arbitrary realization of such branching process, it is possible to determine any statistical characteristic of a branched polymer described by this stochastic process. For instance, the weight MWD $f_w(l)$ is the probability that the overall number of the descendants in a population equals l . By means of the formalism of the theory of branching processes one can calculate the statistical characteristics of the products of branched polycondensation even after the gel point. In particular, the weight-fraction of sol equals the probability for a particle-ancestor to produce finite number of descendants, i.e. the population generated by this ancestor will eventually disappear.

Gordon was the first who anticipated that some polycondensation randomly branched polymers (hereafter mentioned as Gordonian) have the distribution of probabilities of rooted trees described by

the probability measure on the set of genealogical trees which are realizations of the Galton–Watson process. In every generation except the zeroth one, this branching process has the same distribution of probabilities for a particle to give birth to a certain number of descendants. The theory of the Galton–Watson branching processes being thoroughly elaborated enables one to express any statistical characteristic of the molecular structure of a Gordonian polymer through the probability parameters of the branching process describing this polymer. Further, it only remains to reveal the dependencies of these parameters on stoichiometric, kinetic or thermodynamic parameters of the ideal polycondensation which is a trivial problem.

Statistical parameters necessary for the calculation of any characteristic of the chemical structure of a Gordonian polymer are the probabilities for a particle to give birth to any number of children. For the products of the ideal homopolycondensation of monomer RA^f the role of such parameters will be performed by probabilities $a_i^{(0)}$ ($i = 0, \dots, f$) and a_i ($i = 0, \dots, f - 1$) of birth of i descendants by a particle in the zeroth generation and in all subsequent ones, respectively. Substituting the gf of these probabilities

$$F^{(0)}(s) \equiv \sum_{i=0}^f a_i^{(0)} s^i \quad (7)$$

$$F(s) \equiv \sum_{i=0}^{f-1} a_i s^i = \left. \frac{dF^{(0)}}{ds} / \frac{dF^{(0)}}{ds} \right|_{s=1}$$

into formulas of the Galton–Watson process for gf of the distribution of populations for overall number of particles in all generations

$$G_{\text{pop}}(s) = sF^{(0)}(u) \quad u = sF(u) \quad (8)$$

we will get the expressions for finding gf $G_W(s)$ of the weight MWD of the Gordonian homopolymer under consideration

$$G_{\text{pop}}(s) = G_W(s) \equiv \sum_{l=1}^{\infty} f_W(l) s^l \quad (9)$$

Making recourse to the expansion of implicitly given functions into a Taylor series, it is possible,

proceeding from Eqs. (8) and (9), to obtain formula

$$f_W(l) = \frac{1}{(l-1)!} \frac{d^{l-2}}{du^{l-2}} \left[\frac{dF^{(0)}}{du} F^{l-1} \right]_{u=0} \quad (l \geq 2), \quad (10)$$

$$f_W(1) = F^{(0)}(0)$$

which enables one to derive explicit analytical expressions for the MWD. Thus, for an ideal polycondensation where $a_i^{(0)}$ is described by binomial distribution we will have

$$F^{(0)}(s) = \sum_{i=0}^f \frac{f!}{i!(f-i)!} p^i (1-p)^{f-i} s^i \\ = (1-p+ps)^f \quad (11)$$

$$F(s) = (1-p+ps)^{f-1}$$

Substitution of these expressions into formula (10) will result in weight MWD (5) derived for the first time by Flory [203] via tedious combinatoric reasoning. Expression for the weight-average degree of polymerization (6) can be also easily derived, without explicit summation of MWD (5), by recourse to the formula

$$P_W = \sum_{l=1}^{\infty} l f_W(l) = \left. \frac{dG_W}{ds} \right|_{s=1} \\ = \left[1 + \frac{dF^{(0)}}{ds} \left(1 - \frac{dF}{ds} \right)^{-1} \right]_{s=1} \quad (12)$$

The essential drawback of the work cited above, and the succeeding similar publications [263–265], is the lack of rigorous proof of the correctness of the choice of particular branching process which properly describes the configurational statistics of macromolecules. Methods of the construction of the gf used under such an approach being intuitive may sometimes lead to wrong expressions for MWD and the gel point. The same refers to attempts at intuitive construction of the probability measure on the set of random graphs corresponding to the products of branched polycondensation [266–268].

The use of the kinetic method enables one to avoid the above mistakes in the calculation of the configurational statistics of a polymer formed during nonequilibrium polycondensation. For example, Stockmayer showed [242] by direct substitution that

the function MWD of the products of homopolycondensation of monomer RA^f which he derived by the statistical method is the solution of the corresponding kinetic equation describing the evolution of the concentrations of l -mers in the course of irreversible polycondensation. The kinetic method for the calculation of the distribution of branched molecules for the number of monomeric units and functional groups of different types was introduced in the early 1970s [269, 270]. Analytic solution was reported to this problem for arbitrary ideal copolycondensation for any number of types of monomers and functional groups [164]. A simple expression for the calculation of the gel point was also derived [12], including as particular cases the results of all papers devoted to this subject. The most general in terms of the model of ideal polycondensation expressions for number-average and weight-average degree of polymerization of macromolecules taking part in the reaction system, both before and after the gel point, are given in monograph [12].

Shortly after the appearance of papers [164, 269, 270] and monograph [12] publications [271, 272] were issued in which the kinetic method was employed to calculate the MWD and average degrees of polymerization of some particular systems. For example, Saito [271] wrote down kinetic equations for the concentrations of polymer molecules formed in the course of irreversible copolycondensation of monomers $RA^{f_1}B^{f_2} + SAB$, but did not present their solution, having merely integrated the equations for the statistical moments of the MWD. Stafford [272] commenced with the erroneous assumption that the solution of kinetic equations in case of homopolycondensation of monomer RA^f is also capable to describe the MWD of copolycondensation products, provided the symbol f denotes the mean functionality of initial monomers. The discussion of this mistake [273, 274] prompted Stafford to represent [275, 276] a derivation of the chemical size distribution of polycondensation systems that contain mixtures of monomers of different functionalities by a kinetic method, without artificial recourse to the ‘mean functionality’ assumption.

Employing the mathematical apparatus of the gf, Ziff calculated the MWD of the products of homopolycondensation of monomer SAB^2 and monomer RA^3 [277]. Examining the second of these systems, he obtained three distinct solutions for the MWD of

the sol, corresponding to the models put forward by Stockmayer, Flory and Ziff. For the first of these, reactions between sol and gel are assumed to be absent. In the second model, all functional groups have the same reactivity, irrespective of whether they belong to sol or gel. The third model differs from the second only by the absence of the intramolecular reactions in the gel. Recall, these reactions in sol are prohibited in all three models in line with the definition of an ideal polycondensation. Kinetic equations are presented for the concentrations of functional groups A pertaining either to sol or gel for each of these models [277]. Later Ziff and Stell [278] extended the results of paper [277] for the polycondensation of monomer RA^f with $f = 3$ to the case with arbitrary functionality f . Interestingly, for the Stockmayer model [242], they came to the hitherto reported conclusion [279, 280] about the invariance of the MWD of sol fraction during the gelation stage.

Two more works [281, 282] are worthy of mention where this distribution was calculated in the framework of the Flory model by the methods of the theory of branching processes [281] as well as by computer simulations [282]. In the latter case, an arbitrary pair of functional groups was presumed to have the same probability to enter into the reaction at any stage of polycondensation of monomer RA^f . It was shown that the MWD for macromolecules with large number of monomeric units was close to the distribution described by the theory of branching processes, either before or after the gel point. Besides, the dependence on conversion of the number of bonds in a network formed due to intramolecular cyclization reactions was calculated [282]. Computer simulations applied for the calculation of branched copolycondensation of some mixtures of monomers with two types of functional groups gave results [283, 284] which are in a good agreement with those of analytical calculations. The direct summation of the differential MWD was proposed to calculate its integral form [285] and average degrees of polymerization [286].

Theoretical investigation of ideal branched polycondensation was undertaken by Tang and co-workers [287–291]. When considering homopolycondensation of monomer RA^f they derived recurrences for the calculation of the dependence of statistical moments of MWD of arbitrary order on the conversion of functional groups A . In addition, they presented

asymptotical, i.e. scaling, expressions describing this dependence in the vicinity of the gel point. This approach was applied later to the copolycondensation of monomers $R_iA_i^f$ ($i = 1, \dots, m$) with monomers $S_jB_j^g$ ($j = 1, \dots, n$), where the reaction proceeds only between groups A_i and B_j [288]. In subsequent work [289], the recurrences for the statistical moments of the SCD were derived for the products of alternating copolycondensation of monomers $RA^f + SB^gC^h$, with functional groups that participate in two reactions $A + B$ and $A + C$. The expressions for the gel point, the weight fraction of sol and the equilibrium SCD of its molecules were also derived in this paper. Such a distribution is obtained by renormalization of the parameters of the SCD of the macromolecules present in the reaction system at the stage preceding gelation. The validity of this assertion, proved earlier for arbitrary ideal polycondensation [12], was reestablished many years later for particular cases of homopolycondensation of monomer RA^fB^g [290], as well as for copolycondensation of monomers $R_iA_i^f$ ($i = 1, \dots, m$) and $S_jB_j^g$ ($j = 1, \dots, n$) [291].

In applying the kinetic method for the calculation of MWD of branched polymers it sometimes proves advisable to invoke the analogy between polycondensation and coagulation [292–294]. Coagulation is the process of aggregation of colloid particles, resulting in the formation of new more large particles. It is conventional to describe the evolution of their weight distribution by an infinite set of ordinary differential equations put forward by Smolukhovski. Mathematically speaking this set may be viewed as an ordinary difference-differential equation bearing the name of Smolukhovski. This coincides with the kinetic equation of the ideal irreversible homopolycondensation of monomer RA^f in the limit $f \rightarrow \infty$, provided the probability of the coagulation of a pair of particles is proportional to the product of their weights. Such a coincidence seems to be quite reasonable, since polycondensation and coagulation in this case are described by the identical kinetic scheme of the aggregation of monomers and colloid particles, respectively. A wealth of work has been published in which this analogy is harnessed to apply the results of the coagulation theory to find the MWD of polycondensation polymers, as well as to describe gelation. Leaving aside the discussion of these works

let us note, however, that all results achieved in those which deal with ideal polycondensation are obtainable from the equations of the general theory [12,164] as particular cases.

The matter of coincidence of the equations for the configurational statistical characteristics of polymer obtained by a statistical method with those achieved by the kinetic or thermodynamic method is of critical significance in the theory of branched polycondensation. This coincidence was revealed for some of the simplest systems for the irreversible [295,296] and equilibrium [245–249] regimes of polycondensation, which testify to the validity of the statistical method employed. Such a conclusion was arrived at in monograph [12] as applied to the most general ideal polycondensation system. The proper branching process was constructed only upon rigorous examination of this system under each of these two regimes proceeding from kinetic [297] and thermodynamic [298] methods. It was found that the probabilities of the reproduction of particles for this branching process is controlled exclusively by the concentrations of terminal and internal (i.e. chemical bonds) functional groups. Given their values, the above probabilities are independent of the regime of polymer synthesis. This fundamental ‘universality’ property plays a key role in quantitative theory of polycondensation.

The idea to consider the change with time of the SCD of polymer molecules in terms of a Markov Stochastic Process (MSP) on the set of monomeric units [298] is particularly important for the theory of polycondensation. The state l of this stochastic process for homopolymerization corresponds to a unit entering into a l -mer molecule. The probability distribution of these states is, evidently, the weight MWD of polymer products. For copolycondensation, the state of the stochastic process is characterized by the type of the monomeric unit and the composition vector l of the molecule to which the particular unit belongs. The probability measure on the set of these states determines the weight SCD of the polymer. This distribution may be found from the solution of the Kolmogorov equations with matrix of coefficients (referred to as the generator of MSP), which is predetermined by this process peculiarities. Expressions for the generator for ideal polycondensation in systems RA^f , $R_1A^{f_1} + R_2A^{f_2}$, $RA^f + SB^g$,

$R_1A^fB^{g_1} + R_2A^fB^{g_2}$ were obtained by Faliagas through a certain probability reasoning [299]. For these systems, the Kolmogorov stochastic equations may be reduced to traditional material balance kinetic equations for concentrations of molecules with given composition vector \mathbf{l} . Instead of solving the latter it has been suggested that the solution of the former be found using the probability gf. This results in the expressions for MWD and SCD of polymers that strictly coincide with those distributions obtained earlier by kinetic and statistical methods.

3.2.1. Configurational and conformational characteristics of macromolecules

The foregoing discussion primarily concerned papers in which ensembles of polymer molecules were theoretically considered and their distributions for size and composition were found. However, the investigation of their configurational structure is equally important. Its exhaustive description suggests the construction of an algorithm to find the fractions of all fragments of the macromolecules. In terms of the graph theory, this means that instead of finding the probability measure on a set of molecular graphs, specifying MWD and SCD of a polymer specimen, it is necessary to determine the probability measure on a set of some subgraphs of these graphs [205].

For comprehensive analysis of the configurational structure of branched polymers, it has been suggested [298,300–302] that this be characterized by fractions of different k -ads, each representing a polymer molecule fragment composed of k monomeric units connected by chemical bonds. These fragments have been proposed to distinguish not only by types of monomeric units involved, but also by their kinds (see, for example, Fig. 2). The fractions of k -ads obey the equations of topological stoichiometry [300,302], which impose linear relations to some of them. These equations permit one to express fractions of subgraphs U_{k-1} through the fractions of subgraphs U_k . These relations prove to be rather useful in interpreting NMR-spectroscopy data for the experimental determination of the fractions of some of the k -ads.

To find them theoretically just the same methods can be invoked which are traditionally applied for deriving expressions for MWD or SCD of branched polymers. However, the statistical method is the best suited for an ideal polycondensation, because

a one-to-one correspondence is rigorously established between the probabilities of polymer molecules formed during the synthesis and the probabilities of the realizations of a stochastic branching process within the framework of the ideal model [297–298]. The general algorithm enabling one to derive the expression for the fraction of any k -ad by the statistical method was demonstrated for the products of homopolycondensation of monomer RA^f [301, 302]. The algorithm of the solution of the same problem by the kinetic method can be found in the textbook [33].

The statistical method allows the calculation of the probabilities not only of k -ads, but also those of any other fragments of polymer molecules [205]. Among them of prime importance are the trails, which are linear sequences of monomeric units. The fact is that the distribution of these trails for lengths enters into the expressions for the calculation of conformation-dependent characteristics of randomly branched polymers.

Among such characteristics, for example, are the mean geometric sizes and diffusion coefficients of the macromolecules, as well as the scattering intensity from their dilute solutions. The theoretical determination of these physico-chemical parameters necessarily requires the averaging over conformations and configurations of branched macromolecules. For the solution of this problem [303–319], it is assumed that every subchain (trail) connecting a pair of units in such molecules is freely jointed, and that chemical reactions do not break the conformational equilibrium. Such assumptions enable the averaging over all conformations of a macromolecule with an arbitrary configuration, so that just configurational averaging remains.

To this end, generally speaking, it is necessary to perform the averaging first over conformations of all topological isomers with fixed number of units, and second over SCD of the products of branched polycondensation. The number-average, weight-average or z -average values of characteristics of interest may be computed using the appropriate expressions for the selected distribution type (number, weight, etc.). In the latter case, the determination is substantially simplified. For example, it turns out possible to perform a single configurational averaging instead of double one in deriving the relationships for z -average

radius of gyration R_{gz} of macromolecules formed in an ideal branched polycondensation, and for the scattering factor from their dilute solution. This averaging, which is over the distributions of the trails for their length can be found from the recurrence relations [306,308,310,311,315,316,318,319]. The expressions have been derived for a variety of conformational–configurational characteristics of the products of the homopolycondensation of monomer RA^f [311,316,318], monomer $RA_1A_2A_3$ [306,308,310,315] and the copolycondensation of monomers $RA^f + SB^g$ [319], both before and after the gel point. Burchard et al. [308,315] came to the valid conclusion that the distribution of trails for length can be easily found provided every monomeric unit in a trail is supplied by a label. This label is assigned to a monomeric unit in accordance with the type of the reacted functional group attached to it, involved in the intramolecular bond connecting this unit with the preceding unit in the trail. Under homopolycondensation of monomer $RA_1A_2A_3$, there are three types of labeled units, R_1 , R_2 and R_3 , whose alternation in any trail is described by a Markov chain with three states, corresponding to every type R_α ($\alpha = 1, 2, 3$) of these units. The theory of Markov chains allows one to easily find the distribution for length of trails of labeled units, and then to erase the labels, joining three states in one. This procedure of ‘labeling–delabeling’ of monomeric units is rather efficient for the solution of many problems in the statistical chemistry of polymers [13]. The equivalence of the trails of the labeled units, and the realizations of a certain Markov chain revealed by Burchard et al. [308,315] for a particular system, was later rigorously proved for arbitrary polycondensation polymers synthesized under the condition of the applicability of the ideal model [298]. Furthermore, expressions for the elements of the transition matrix of this chain were derived, enabling one to find their dependence on kinetic or thermodynamic, as well as stoichiometric parameters of a reaction system. This provides a means to determine the probabilities of any trails and, consequently, to calculate configurational–conformational parameters of the products of an arbitrary ideal branched polycondensation.

The straightforward method for the evaluation of the probabilities of trails by means of the Markov chains is perfectly suited for the calculation of simple polycondensation systems. It has been suggested that

for more complicated systems ‘this technique becomes very difficult and nontransparent so that errors can scarcely be avoided’ [320], but this opinion can hardly be shared in the light of the results reported in paper [298]. The direct method of finding the z -average radius of gyration R_g of statistically branched macromolecules fails, however, for the calculation of either the number-average or weight-average R_g value. This is also true for any other configurational–conformational characteristic of the products of an ideal polycondensation. To cope with this problem the formalism of the theory of branching processes turns out to be rather convenient [260,261,303–305,307–309,312–314,317]. This technique makes it possible to obtain, among other things, explicit expressions for the elements of the transition matrix of the Markov chain occurring when the direct method is employed for the calculation of the trail probabilities. Following pioneer work by Gordon and co-workers [260–261] an original approach was put forward which used the path-weight gf to perform the averaging over configurations of randomly branched molecules [303–305]. The mathematical apparatus underlying this approach made possible a uniform derivation of the formulae for average gyration radii, the scattering factor, the diffusion coefficient and other analogous statistical characteristics of the branched polymers formed in the course of the polycondensation of monomers RA^f [303–305,316,318], $RA^f + SB^2$ [307,309], $RABC + SAB$ [312], and $RA^f + SB^g$ [319].

When calculating the characteristics described above, it is advisable to use an approach considering polymer molecules as graphs embedded in three-dimensional space [321–323,205]. The label r is assigned to every vertex of such a graph, characterizing the vertex position in this space. A graph with labeled vertices unambiguously sets not only the configuration of a macromolecule, but also its conformation. It is possible to find uniformly any statistical characteristic of the products of an ideal polycondensation having constructed the probability measure on the set of thus labeled graphs [205]. For such a consideration, results are formulated in terms of generating functionals (GF), which are a generalization of gf, widely used for finding the configurational characteristics of macromolecules considered as abstract graphs. For example, in the calculation of

the conformational characteristics of macromolecules it is of prime importance to obtain the distribution of the probability for a unit chosen at random at point r among the products of the ideal polycondensation of monomer RA^f to pertain to a molecule of an l -mer with a given conformation. The GF of this distribution is determined by the expression

$$G_W(\mathbf{r}; [s]) = s(\mathbf{r})\xi^f(\mathbf{r}), \quad (13)$$

$$\xi(\mathbf{r}) = 1 - p + p \int \lambda(\mathbf{r} - \mathbf{r}')U(\mathbf{r}'; [s])d\mathbf{r}'$$

where functional U is obtained from the solution of integral equation

$$U(\mathbf{r}; [s]) = s(\mathbf{r})\xi^{f-1}(\mathbf{r}) \quad (14)$$

Along with the conversion p of groups A relationships (13) and (14) comprise probability $\lambda(\mathbf{r} - \mathbf{r}')$ for a unit situated at point \mathbf{r}' to have a neighboring unit located at point \mathbf{r} . If the position of units in space is of no interest, then the function $s(\mathbf{r})$ should be put equal to a constant s . Then the functional U is no longer controlled by coordinate \mathbf{r} , and turns into gf $u(s)$. It is readily noticed that in this case Eqs. (13) and (14) are reduced to the well-known ones in Eq. (8) because the integral of function λ in the right-hand part of formula for $\xi(\mathbf{r})$ in Eq. (13) equals unity.

Under the approach introduced by Kuchanov and Korolev [205,321–323], a polymer molecule is characterized by a random function denoting their microscopic density $\rho^M(\mathbf{r})$, whereas under the traditional treatment such a molecule is characterized by random quantity l which is the number of its units. The GF of the distribution of the density $G_W(\mathbf{r}; [s])$ plays the same role that the gf Eq. (9) does in a traditional statistical approach. The statistical moments of random function $\rho^M(\mathbf{r})$, referred to as correlation functions, are found by variational differentiation of the functional $G_W(\mathbf{r}; [s])$ with respect to the argument $s(\mathbf{r})$. Of prime importance is the two-point correlator

$$\chi(\mathbf{r}' - \mathbf{r}'') \equiv \langle \rho^M(\mathbf{r}')\rho^M(\mathbf{r}'') \rangle = \rho s(\mathbf{r}'') \frac{\delta G_W(\mathbf{r}', [s])}{\delta s(\mathbf{r}'')} \quad (15)$$

where the angular brackets denote the averaging over all conformations and configurations of polymer

molecules and ρ stands for the overall density of units. Employing simple formulas connecting conformational–configurational characteristics of randomly branched polymers with the Fourier-transform of correlation function (15), it is an easy matter to find these characteristics. Noteworthy, such an approach provides the opportunity to determine not only their z -average values, but also number-average and weight-average values.

The expressions (13) and (14) for the GF derived from the Gibbs equilibrium distribution has a clear probabilistic meaning in terms of the general branching processes [324], describing both the reproduction of the particles and their diffusion in space. An ordinary branching process is completely characterized by the gfs of the probability distribution of a certain number of descendants which a particle can give birth to in each generation. As for a general branching process it is exhaustively characterized by analogous GFs carrying additional information on the probabilities of the random walk of the descendants in space during their lifetime. This universal approach works as well for the statistical description of the products of equilibrium ideal polycondensation when functional groups, bonds and units are acted upon by inhomogeneous external (e.g. electric) fields. Besides, this approach makes it possible to take into account the physical interactions among units and with the solvent [205].

Calculation of the statistical parameters of the topological structure of a polymer network formed under the conditions of the ideal model of polycondensation presents no fundamental difficulties. Once Scanlan [325] and Case [326] introduced the elastically active node and chain concepts, Dobson and Gordon [327] and later Hasa [328] demonstrated the potential of the application of the theory of branching processes for the calculation of these important topological parameters of a polymer network for the simplest polycondensation systems. The efficiency and simplicity of this approach ensured it a wide application under the theoretical prediction of the elasticity of polycondensation gels [329,330]. Equally successful is the recourse for this purpose to another variant of the statistical method based on the recursive probability analysis for the calculation of a polymer parameters by direct application of expectations and probabilities [331]. This method provides the opportunity to calculate the density of elastically active

nodes, fractions of elastically active and passive chains, as well as their number-average and weight-average lengths in polymer networks formed during homopolycondensation of monomer RA^f and alternating copolycondensation of monomers $RA^f + SB^2$ [225,227,228,233]. Later, the most general equation was derived to calculate the cyclic rank of a gel formed in the course of ideal polycondensation of an arbitrary mixture of monomers, with any number of functional groups types [332]. Costa and Dias [333] proposed to use a general kinetic analysis for the solution of such problems. The practical utility of their work is due to the fact that having started with comprehensive theoretical consideration of polycondensation processes, they completed their research by developing a computer program permitting the calculation of many statistical characteristics of sol and gel.

3.2.2. Continuous processes of polycondensation

Theoretical consideration of a linear homopolycondensation (see Section 2.5.2) leads to the conclusion that the transition from closed systems to open ones might be responsible for a perceptible growth of the polydispersity of the products. Moreover, the MWD form in asymptotic limit $l \rightarrow \infty$ was found to change. A sophisticated theoretical treatment of the ideal polycondensation of monomer RA^f in a CSTR revealed an analogous situation for a branched polycondensation [196]. Thus, if the polycondensation of this monomer is conducted in a batch reactor, i.e. in a closed system, the asymptotic formula for MWD at $l \gg 1$ reads

$$f_N(l) \sim \frac{\delta^l}{l^{5/2}}, \quad (16)$$

$$\text{where } \delta = \frac{(f-1)^{f-1}}{(f-2)^{f-2}} p(1-p)^{f-2}$$

At $p = p^* = (f-1)^{-1}$ the value of δ is unity, and at this gel point the character of the MWD decay with the growth of l changes qualitatively. Consequently, prior to gelation ($p < p^*$) the weight MWD statistical moments of all orders have finite values, whereas at $p = p^*$ they all become infinite. As the gel point is approached an unlimited rise of the polydispersity

coefficient is observed

$$K \equiv \frac{P_W}{P_N} = \frac{(2-fp)(1+p)}{2[1-(f-1)p]} \quad (17)$$

Expressions (16) and (17) are applicable, evidently, for the description of the polydispersity of products of continuous polycondensation of monomer RA^f obtained in a plug-flow continuous reactor.

The comparison of relationships (16) and (17) with those derived for polycondensation in CSTR [196]

$$f_N(l) \sim \frac{1}{l^\nu}, \quad \text{where } \nu = \frac{3 - \sqrt{\kappa}}{1 - \sqrt{\kappa}}, \quad (18)$$

$$\kappa = 1 - \frac{4(f-2)p}{(1-p)^2} = 1 - \frac{\gamma^*}{\gamma}$$

$$K = \frac{(2-fp)}{(f-2)} \left[\frac{f(1-p)}{1-p + \sqrt{(1-p)^2 - 4(f-2)p}} - 1 \right] \quad (19)$$

is indicative of their qualitative distinction. The polydispersity coefficient K given by Eq. (19) is valid for $p \leq p^*$, where $p^* = (\sqrt{f-1} - \sqrt{f-2})^2$, with K approaching $(2-fp^*)(f-1)/(f-2)$ as p becomes arbitrarily close to p^* . This occurs for a value of the Damkeholder parameter γ equal to $\gamma^* = 4(f-2)$ [182,191]. If $\gamma < \gamma^*$, the reactor will necessarily contain gel. Two different stationary regimes of branched polycondensation are possible for γ larger than the critical value γ^* . Gelation occurs only under one of these regimes. Which of them is realized in a CSTR depends, apart from γ , on the value of a parameter α , equal to the ratio of the initial molar concentration of a monomer in the reactor to its concentration in the input flow. A prerequisite to the realization of the second regime, in which only finite sol molecules with a MWD given by Eq. (18) are formed, is the following inequality $\alpha < 2/(1 - \sqrt{\kappa})$. If the inverse inequality $\alpha > 2/(1 - \sqrt{\kappa})$ holds, the reactor will attain the first stationary regime after some time, with the polycondensation products containing gel particles.

The comparison of the asymptotic expressions Eqs. (16) and (18) for the MWD shows that the first of these decays markedly faster than the second as $l \rightarrow \infty$. In other words, switching from a batch reactor to a CSTR inevitably results in increased polydispersity of the branched polymers, as also takes place for

a linear polycondensation (see Section 2.5.2). This inference is also supported by the comparison of K calculated by formulas (17) and (19) at identical values of monomer functionality f and conversion p . In particular, the critical value p^* of p for the polycondensation of monomer RA^3 in a batch reactor and CSTR is equal to 0.50 and 0.18, respectively. Attention should be paid to one more qualitative distinction between distributions (16) and (18). This lies in the fact that at the gel point all statistical moments of the first of these MWDs with order two and more turn simultaneously to infinity, whereas the statistical moments of the second MWD of order three and more already are infinite as p approaches its critical value p^* . Theoretical analysis of the polycondensation conducted in a cascade of several CSTRs enabled investigation [196] of the effects of hydrodynamic stirring in a reaction system on the polydispersity of the homopolymer formed, as well as on the value of the critical conversion at the gel point.

3.2.3. Multistage processes

Many commercial condensation polymers are currently manufactured in two stages, in which reactive oligomers synthesized first are subsequently crosslinked due to the reactions between the functional groups unreacted in the first stage [334]. Examples are epoxy resins and amine hardeners, prereacted in the first stage and later cured in the second stage. Since prepolymers may be manufactured in more than one stage, theoretical consideration of multistage polycondensation is a challenging task. The first attempts of such an examination have been undertaken nearly simultaneously by Kuchanov [335] and Dusek et al. [336] who used, respectively, kinetic and statistical approaches.

The general principles of the calculation of the statistical characteristics of the polymers obtained by the crosslinking of oligomers are outlined in the first of the papers cited above, studying the one-stage evolution of the distribution of polymer molecules for size, composition and functionality (SCFD) [335]. The results reported in this work make it possible to consider theoretically the curing stage of oligomer resin with an arbitrary SCFD. Taking this distribution as initial for the crosslinking stage and using the expressions derived in paper [335], it is an easy matter to find the SCFD of the products of curing.

The theoretical analysis yielded important general conclusions concerning an ideal multistage polycondensation [335]. If the SCFD of polymers obtained for the first stage is the ‘most probable’ then the SCFD of those prepared in the second stage will belong to the same class of distributions, but with other probability parameters. The latter are expressed through the stoichiometric parameters of the crosslinked polymer and the concentrations of intramolecular bonds in its molecules, easily obtained from the solution of the kinetic equations for the concentration of functional groups. Otherwise stated, the products prepared by crosslinking any Gordonian polymer are also Gordonian polymers. This fundamental ‘invariance property’ is an intrinsic feature of an ideal polycondensation, and shows up in homogeneous processes carried out in any number of stages. This property is retained even if the temperature and/or a catalyst concentration arbitrarily changes in the course of polycondensation. It is highly important that the SCFD of the final polymer being controlled exclusively by the parameters of its microstructure in no way depends on the parameters for the prepolymers at intermediate stages. This reduces the calculation of the statistical characteristics of the products of crosslinking of oligomers with a most probable SCFD to ordinary problems of the ideal polycondensation theory.

Under theoretical treatment of branched multistage polycondensation, recourse was also made to the statistical approach employing the theory of the branching processes [336–338]. General ideas of the transformation of the probability gfs, enabling one to relate the statistical characteristics of the polymer at the beginning and end of every polycondensation stage, were exemplified for some systems [336]. In particular, a multicomponent system was studied in which monomers are converted into a final network in several consecutive stages. For simplicity, the authors [336] assumed that reactions possible at stage i are no longer possible at stage $(i + 1)$. Then the process was examined for a network formation in six-component, three-stage process [337–338]. Two different modifications of the statistical method were applied. In the first, the whole molecules obtained for each stage were used as the building units for the subsequent stage. In another modification, the system was treated as a quasi-one-stage process

and the original monomers were used as building units, irrespective of the stage at which they react. The two approaches give analytically identical results, but along completely distinct derivations. This is an argument in favor of the correctness of the results achieved, important because a rigorous kinetic substantiation of the statistical approach employed is missing in papers [336–338].

3.3. Models incorporating the substitution effects

3.3.1. Peculiarities of nonrandom polycondensation

The substitution effect inherent in a branched polycondensation can be responsible for pronounced discrepancy in the reactivity of isomers with identical degrees of polymerization. This discrepancy is easier to exemplify with the FSSE model for which the reactivity of an arbitrary functional group is governed solely by the number and the position of each type reacted groups attached to the same monomeric unit. Here, the reactivity of a polymer molecule is fully prescribed by the number of its constituent monomeric units with different configurations. In view of this, in terms of this model the molecules should be differentiated solely by this attribute. The model for the Second Shell Substitution Effect (SSSE) distinguishes polymer molecules by the number of pairs of neighboring monomeric units with different configuration. In treating nonrandom polycondensation it is customary to resort to the slightly modified methods usually applied with ideal systems.

Gordon and Scantlebury [249] were the first to calculate the configurational statistics of the branched polycondensation products in the framework of the FSSE model, using homopolycondensation of a monomer RA^f as an example. They proceeded from certain branching process, but put forward a way (other than that employed for ideal systems) to set the probabilities for the reproduction of particles. This approach suggests that the probability for each particle to give birth to certain number of descendants is controlled by the kind of a monomeric unit corresponding to the particle. The theory was designed to describe an arbitrary polycondensation regime provided the probability parameters of the branching process were related in an appropriate way to the kinetic or thermodynamic parameters of the system. They determined this relation for either

equilibrium or irreversible polycondensation, and expressed the number-average and the weight-average molecular weights of a polymer and the conversion at the gel point through the above parameters. Later the statistical approach was applied for this system to calculate some characteristics of the sol-fraction [260], gel-fraction [339] and distribution of polymer molecules for the number of different kind monomeric units [340]. Such a system was suggested to describe [262] by a branching process with the same propagating particles as in paper [249], but with other probabilities of their birth and death. In some treatments, authors investigating a model of irreversible copolycondensation of various monomer mixtures formally resorted to either a direct probabilistic examination [217,218,341–347] or to the formalism of the theory of branching processes [261,265,339,348]. To verify results achieved by the statistical method, it is necessary to compare them with those obtained using kinetic calculations.

Application of the kinetic method for the calculation of the distribution for size, composition and functionality of the products of branched polycondensation of monomers with kinetically dependent groups was pioneered in paper [49]. A general algorithm formulated there enables derivation of the corresponding kinetic equations for the distribution described above. Analysis of the solution of these equations for the homopolycondensation of monomer RA^f revealed that the configurational statistics of some systems in the framework of the FSSE model may not be amenable to description by any branching process [12,48,349]. Systems for which the traditional statistical method commonly employed for the calculations of an ideal polycondensation does not work are referred to as truly nonideal systems. Along with these, there exist quasi-ideal systems, for which the traditional method can yield correct results. Unfortunately, consistent criteria to judge whether a system described by the FSSE model belongs to quasi-ideal are missing.

Rigorous thermodynamic examination shows that polycondensation of an arbitrary monomer mixture performed under equilibrium conditions is always quasi-ideal [350]. An algorithm has also been presented for the construction of a corresponding branching process to describe the configurational

statistics of a polymer molecule for any such a system [350]. Upon the kinetic consideration of nonequilibrium polycondensation for a wide range of monomer mixtures it was conjectured [48] that a sufficient condition for a system to be quasi-ideal is that in any molecule every unit of a monomer with dependent functional groups is connected exclusively with the units containing independent groups. For example, this condition is met in systems for which the groups of one of the monomers are independent [265,341–345], but is not met for the homopolycondensation of monomer RA^f or the copolycondensation of monomers $RA^f + SB^2$ if both of them have dependent groups [339,346–348]. The applicability of the statistical methods for the description of polymers synthesized by nonequilibrium polycondensation was also covered in papers [295,351–352]. Authors pointing out the analogy between the models of a polycondensation and the build-up of biological macromolecules arrived at virtually the same condition [351–353] as that put forward in paper [48].

3.3.2. Equilibrium polycondensation

The elaboration of a quantitative theory of equilibrium polycondensation in the framework of the FSSE model is just slightly more complicated than that for ideal systems. Thus, in the simplest case of homopolycondensation of monomer RA^f , Gordon et al. [249,260], seeking to find MWD of the products of the reactions by the statistical method, recommended to make use of the Eqs. (7)–(10) and (12) of the ideal model, with probability parameters $a_i^{(0)}$ differing from those that occur in expression (11). These parameters, coinciding with molar fractions λ_i of monomeric units of kind i , are governed only by the equilibrium constants of the elementary reactions between functional groups attached to units of different kinds. The gf of the weight MWD in Eq. (9) can be calculated by formula

$$G_W(s) = sF^{(0)}(u), \text{ where } F^{(0)}(u) = \sum_{i=0}^f \lambda_i(t)u^i \quad (20)$$

where the dependence of function u on the dummy variable s is obtained from the solution of

the algebraic equation

$$u = sF(u),$$

$$\text{where } F(u) = \left. \frac{dF^{(0)}(u)}{du} / \frac{dF^{(0)}(u)}{du} \right|_{u=1} \quad (21)$$

The weight fraction $\omega_s = G_W(1)$ of sol may be calculated from expressions

$$\omega_s = F^{(0)}(u^*), \quad u^* = F(u^*) \quad (22)$$

where u^* stands for the least positive root of Eq. (22).

Among theoretical publications dealing with the description of the products of the equilibrium FSSE polycondensation, the quite elegant works by Whittle merit special mention [354,355]. On the basis of an original approach [356], he derived rather general equations that permit the calculation of the MWD and SCD, as well as the critical conversion at the gel point. These results coincide with those ensuing from the theory of branching processes for the homopolycondensation of monomer RA^f [249]. It remains an open question whether the relations reported [354,355] are suitable for more complicated systems. The fact is their derivation is based on the assessment of the coefficients of certain kinetic equations, although only equilibrium systems are addressed. Naturally, the kinetic restriction used in papers [354,355] implying that substitution effects are absent under degradation reactions, is not necessarily presumed to be imposed for these systems.

The thermodynamic method invoked [67,249,357,358] to calculate the probability parameters of branching processes describing the configurational statistics of branched polymers is free from these superfluous restrictions. As already noted in the foregoing, the most general and rigorous solution of this problem for an arbitrary equilibrium FSSE polycondensation system has been provided [350], in an algorithm for the construction of the corresponding branching process, as well as that of the calculation of its probability parameters. The reported results embrace as particular cases all the systems considered earlier, including the copolycondensation of two monomers $RA^f + SB^g$, each having independent functional groups. Dusek presented without derivation the expressions for the gfs of the corresponding branching process for this system,

and calculated from them the gel point position and other parameters of the polymer network [359].

Mention should be also made of paper in which the methods of the theory of random graphs are recruited for the calculation of the configurational statistics of the assembly of macromolecules formed in the course of the build-up reactions of inorganic polymers [360]. With slight modifications, the results might be employed to calculate the products of the equilibrium polycondensation, with allowance for the different order substitution effects.

The substitution effects of order $m > 1$ were studied at $m = 2$ for homopolycondensation of monomer RA^f [301,358,361]. Having introduced this SSSE model, Gordon and Parker [361] advanced the idea to resort to some branching process for the description of the MWD in terms of this model. However, since they provided no rigorous substantiation for the system quasi-ideality, the meaning of the probability parameters of this process and their relation to the constants of the elementary reactions of the model employed remains vague. Such a relation was revealed for an equilibrium regime of polycondensation, and the number of the independent thermodynamic parameters of this model was also indicated [301,358].

The field theoretic formalism is the most efficient method for the calculation of conformational characteristics of the products of nonrandom equilibrium polycondensation [205,321,362]. This makes possible to extend the traditional statistical approach and to formulate thermodynamic and scattering problems in terms of a stochastic branching process, for which the particles along with reproducing are also involved in diffusion in three-dimensional space. Elaborated for the description of the products of ideal polycondensation, after minor modifications [322] this approach can be applied to an equilibrium polycondensation of monomers showing FSSE.

3.3.3. Irreversible polycondensation

Unlike the configurational statistics of polymers synthesized by ideal polycondensation, the statistics of the products of nonrandom polycondensation are dependent, generally speaking, on the regime of the process performance. Qualitative distinctions in the statistical characteristics of the molecular structure of polymers prepared under equilibrium and

nonequilibrium regimes may show up if the polycondensation system is truly nonideal.

The simplest among these is the irreversible homopolycondensation of monomer RA^f with kinetically dependent groups. Consideration of this system within the framework of the FSSE model was undertaken by a theoretical analysis proceeding directly from the kinetic scheme of the reactions between macromolecules [363–369], unlike several other studies on this system [249,260,339,340,346,347]. In line with the general concepts of the statistical chemistry of polymers, it was recommended [12] that monomeric units of different kinds be selected as kinetically independent units, rather than functional groups, as for an ideal polycondensation. Under this approach, every polymer molecule was characterized by a vector \mathbf{I} , with components l_i ($i = 0, \dots, f$) equal to the numbers of such units [48]. Recourse to the extended Flory principle [12,13] permits one to derive the equation for the distribution of the concentration of molecules with a given value of vector \mathbf{I} , and reduce it to the partial differential equation for the gf of this distribution [48]. Unlike the case for an ideal polycondensation, its exact analytical solution is hardly obtainable. However it is an easy matter to derive the ordinary differential equations for the statistical moments of the MWD of polymer products from this equation. The conversion p^* at the gelation moment can be calculated from the condition of the divergence of these moments with order two. An alternative independent approach based on the bifurcation condition of the solution of the kinetic equation at the gel point has been employed to calculate p^* . Comparison of the results obtained in these two procedures revealed their nearly complete agreement for a variety of kinetic parameters, within a wide range of their values [363].

Monte Carlo computer simulations provide another method for the gel point determination. Using this method, Mikes and Dusek [364] found values p^* for the polycondensation of monomer RA^3 in the framework of the simplified version of the FSSE model, for which the constant of elementary reaction k_{ij} between groups attached to monomeric units of kinds i and j , is known to factorize as $k_{ij} = k_i k_j$. Besides the dependencies of the polydispersity coefficient and the weight fraction of the gel on conversion were found

at some values of the kinetic parameters k_i . The authors compared the results of their Monte Carlo simulations with those obtained by Gordon's approach [249] (empirical for this truly nonideal system), concluding that the values of the statistical characteristics found in two ways are almost identical except for a very few special cases. However, this conclusion should be viewed with caution for two reasons. On the one hand the authors [364] restricted themselves to a monomer functionality f equal to three, on the other the simulations were performed exclusively in the framework of the simplified FSSE model.

Kinetic equations have been presented under the same restrictions for the concentrations of polymer molecules with fixed numbers of units of different kinds [365–367]. These equations are nothing but a particular case of those derived earlier [48] in the framework of the general kinetic theory of irreversible FSSE polycondensation of monomer RA^f . Comparison of the gel point position, as well as dependence of number-average and z -average degree of polymerization on conversion calculated by kinetic and statistical methods shows minor discrepancy [366] for several sets of the values of the elementary reactions' constants.

The acceptability of the statistical method for the calculation of critical conversion p^* , for the formation of a polymer network in the course of nonrandom polycondensation of monomer RA^f , was scrutinized by Kuchanov and Kholostiakov [368]. They implemented the idea [301,369] formulated formerly of the construction of a hierarchy of branching processes for the approximate description of the configurational statistics of polymers formed during a truly nonideal polycondensation. The first in this hierarchy is the ordinary branching Galton–Watson process, in which all particles reproduce independently [249]. The second approximation is the nontraditional branching process, with a probability for a particle to have a given number of 'children' depending on the number of its 'brothers'. The probability parameters of the first and the second branching process are controlled, respectively, by the fractions of monads and dyads presented in Fig. 2, obtainable from the solution of closed sets of ordinary differential equations. A set of such equations was written down to describe the microstructure of

the products of polycondensation of monomer RA^f with arbitrary functionality f in the framework of the complete FSSE model. The solution of this set at different values of kinetic parameters resulted in several conclusions about the applicability of the Gordon statistical approach to the description of the polycondensation system in hand. The following are among the conclusions of prime importance [368]. There is an ample range of the reactivity ratios for which this statistical method leads to values of p^* markedly differing from the exact ones. In some cases such a distinction can be substantially lessened by switching from the monad branching process to the dyad one, but systems have been revealed for which even this approximation produces error in p^* that is too large.

Given the solution of differential equations for monads and dyads reported in paper [368], it is possible to find the dependence on conversion of all probability parameters of the dyad branching process approximating the nonideal polycondensation of monomer RA^f . Since the expression for the gf of this stochastic process is known (see Eq. (20) in Ref. [301]), it is an easy matter to calculate not only p^* in this approximation, but any statistical characteristic of the chemical structure of a polymer as well. Such calculations have, in particular, been carried out for the MWD of oligomer products being prepared for the polycondensation of monomer RA^3 [370]. The authors of this work, having rederived equations for the particular case $f = 3$ of the more general dyad branching process reported earlier [301,368], appear to consider them as exact in the framework of the FSSE model, as no mention was made of the approximate character of their equations.

The kinetic equations for the fractions of dyads being formed in the course of the irreversible RA^3 polycondensation described by the FSSE model were presented first in the Appendix to a paper by Macosko et al. [371]. An algorithm has been put forward by them intended to modify recursive relations traditionally employed in the framework of the Miller–Macosko statistical approach [224–227,331] for the description of a polycondensation processes. The results obtained on the basis of this algorithm (referred to by the authors as the 'bond distribution model') coincide with those achieved in the framework of the dyad branching process. Hence, both of

these approximations prove to be fully equivalent for the calculation of the statistical characteristics of branched polymers. Paying tribute to the valuable contribution of paper [371] to the statistical theory of polycondensation, it is hardly possible to agree with their opinion that the dyad approximation is only a marginal improvement over the monad approximation. Such a conclusion certainly ensues from comparison of the values of the critical conversion at the gel point p^* calculated by them for several sets of kinetic parameters of the simplified FSSE model. However, even in the framework of this model, there are values of these parameters for which switching from the monad to the dyad approximation one can reduce the error of calculated value p^* tenfold [368].

Of crucial importance is the answer to the question concerning the existence of a branching process capable of providing an exact statistical description of the chemical structure of the products of truly nonideal polycondensation. A positive answer makes it possible to easily calculate the topological characteristics of a polymer network controlling its elasticity properties. The rigorous prove of the existence of such a branching process for the description of a nonrandom homopolycondensation of monomer RA^f is provided only by the kinetic method. Its application provides an expression for the gf of the weight MWD of polymer molecules [61] that reads [13,372]

$$G_W(s) = s\mathcal{F}^{(0)}[\mathbf{u}],$$

$$u_i(\tau) = s \sum_{j=0}^{f-1} \pi_{ij}(\tau) \mathcal{F}_j(\tau, [\mathbf{u}]) \quad (23)$$

where the following designations are used

$$\mathcal{F}^{(0)}[\mathbf{u}] = \sum_{i=0}^f \int \cdots \int P_i(t; \tau_0, \dots, \tau_{i-1}) \prod_{j=0}^{i-1} u_j(\tau_j) d\tau_j \quad (24)$$

$$\mathcal{F}_i(\tau, [\mathbf{u}]) = \left. \frac{\delta \mathcal{F}^{(0)}[\mathbf{u}]}{\delta u_i(\tau)} \right|_{\mathbf{u}(\tau)=1} \quad (25)$$

$$\frac{d\lambda_i}{dt} = \varphi_{i-1} \lambda_{i-1} - \varphi_i \lambda_i, \quad \lambda_i(0) = \delta_{i0} \quad (26)$$

$$\pi_{ij}(\tau) = \frac{\tilde{k}_{ij} \lambda_j(\tau)}{\varphi_i(\tau)}, \quad \varphi_i(\tau) = M \sum_{j=0}^{f-1} \tilde{k}_{ij} \lambda_j(\tau),$$

$$\tilde{k}_{ij} = (f-i)(f-j)k_{ij}$$

Here \tilde{k}_{ij} denotes the rate constant of the elementary reaction between monads of kinds i and j while k_{ij} is that of the reaction between functional groups entering in this monads. The comparison of expressions (23)–(26) and (20) and (21) points to a certain similarity between them. If the FSSE polycondensation proceeds under an equilibrium regime, it is described by a branching process exhaustively characterized by the gf $F^{(0)}(u)$ of distribution $\lambda_i(t)$ of monads for number i of their chemical bonds. For the irreversible polycondensation the role of gf is played by Generating Functional (GF) $\mathcal{F}^{(0)}[\mathbf{u}]$ of the density of the distribution $P_i(t; \{\tau_j\})$ of monads supplied with labels $\{\tau_j\} = (\tau_0, \dots, \tau_{i-1})$ that indicate the instant for the formation of these bonds. Expression (25) relating GF \mathcal{F}_i with $\mathcal{F}^{(0)}$ looks like Eq. (21), which relates gf F with $F^{(0)}$. The distinction is that the role of the ordinary derivative in Eq. (21) is played by a functional derivative in Eq. (25). To get the gf of a polymer weight MWD, it is necessary first to find the solution of the set of the integral equation (23) for functions $u_0(\tau), \dots, u_{f-1}(\tau)$, and to subsequently substitute this solution into the expression for functional $\mathcal{F}^{(0)}[u]$ in Eq. (24).¹ The weight fraction of sol $\omega_s = G_W(1)$ equals GF (24) taken at functions $0 \leq u_i^*(\tau) < 1$ ($i = 0, \dots, f-1$) that are the solution of the set of nonlinear integral equations

$$u_i^*(\tau) = \sum_{j=0}^{f-1} \pi_{ij}(\tau) \mathcal{F}_j(\tau, [u^*]) \quad (27)$$

Such a solution is always unique, and is easy to determine by an iteration method. The calculation of the dependence of the weight fraction of gel $\omega_g = 1 - \omega_s$ on conversion has been first exemplified by two particular systems [13].

A thorough theoretical analysis has been performed of the effect of the FSSE model kinetic parameters on the character of the dependence on conversion not only of the gel-fraction ω_g , but also of the fraction ω_{ge} of elastically effective material and the cyclic rank R of the polymer network [372]. Special attention was paid to the study of responsible

¹ Review [13] comprises integral equations (23) written down erroneously due to an unfortunate misprint at the stage of the manuscript preparation. The results of the calculations reported in this review are certainly correct since these were obtained from the solution of the undistorted set of Eqs. (23).

gels which have a very small fraction of branching monomeric units. They, being capable of absorbing and retaining a great amount of solvent, find an ever increasing application. Such critically branched networks are formed at conversions just slightly exceeding the critical one p^* . Asymptotic methods were found to be especially efficient in theoretical examination of such networks synthesized in the very vicinity of the gel point [372].

Relationships (23)–(25) admit an illustrative probabilistic interpretation in terms of a branching process giving a detailed account of the populations of particles of two kinds [372]. A particle of every kind is characterized here by two attributes, namely, by its type i and label τ . The first of these variables is discrete, with values $0, 1, \dots, f - 1$, while the second is a continuous variable, with values in the interval 0 to t . The first kind particle with type i and label τ being incapable of reproducing becomes, in the next generation, an active particle retaining the same label. The conditional probability for this particle of the second kind to belong to type j is $\pi_{ij}(\tau)$. The latter can give birth to 0 to $f - 1$ particles of the first kind, each being characterized by its own type and label. The density of the probability of various sets of these labeled particles has a GF given by Eq. (25). Further, the branching process follows the scenario described above. Because generations of passive and active particles regularly alternate when considering a population propagation, it is reasonable to focus exclusively on either even or odd generations. Such a treatment leads to a reduced branching process with particles of a single kind. Expressions (23) describe this process of the development of the populations of passive particles. It was found that there is no need to distinguish them by types, provided the simplified FSSE model is used. In such a model the constants of elementary reactions factorize, $k_{ij} = k_i k_j$, so that the probability $\pi_{ij}(\tau)$ (26) is independent of the first index. In this case the set of f Eq. (23) for the components $u_i(\tau)$ of vector-function $\mathbf{u}(\tau)$ reduces to the single equation for scalar function $u(\tau)$.

The results discussed, obtained for the first time in papers [13,372], enabled a rigorous justification of the statistical method for the calculation of sol and gel being formed in the course of the irreversible FSSE homopolycondensation of monomer RA^f . In this connection, the remarkable paper by Sarmoria and

Miller [373] extending the probability recursive approach [331] to the description of the above system is worthy of attention. This variant of the statistical method, with origins in the Combined Kinetic–Markovian (CKM) analysis, implies that the molecules of the polycondensation products may be viewed as built out of some superspecies. By this term are meant certain small fragments of these polymer molecules that characterize their microstructure [373]. In accordance with the CKM analysis, they considered a conventional two-stage process to obtain polymer molecules. Having found the fractions of superspecies by solving the corresponding kinetic equations in the first stage, the authors [373] combine these building blocks at random during the second stage to get the true final product, referring to the random combination in the second modeling stage as ‘Markovian’. To analyze the Markovian structure statistically, they suggested using the probabilistic recursive technique [331] discretizing the conversion into a number of small intervals.

Sarmoria and Miller [373] proposed to take chemical bonds as superspecies, distinguishing them by the moment of their formation, as well as by the kinds of functional groups which for their reaction formed the intramolecular bond under examination. (The kind of a functional group coincides with that of a monomeric unit to which this group is attached). Having chosen these superspecies, these researchers claimed that their CKM version of the statistical method ensured an exact description of the FSSE homopolymerization of monomer RA^f . Their only argument lending support to this claim was the negligibility of the deviation of the values they obtained for the conversion at the gel point from those found earlier by their predecessors by both the rigorous kinetic examination [366] and the Monte Carlo method [364]. This argument hardly seems able to replace a rigorous substantiation of the equivalence of the CKM and the kinetic approaches. This concern is not unreasonable, especially bearing in mind that comparison of values p^* calculated using these approaches was only accomplished for the polycondensation of three-functional monomer and, moreover, was done only in the framework of the simplified FSSE model. However, there are strong grounds to believe that the variant of the stochastic method which Sarmoria and Miller [373] put forward

from intuitive reasoning is correct. Its comparison with the other variant of the statistical method [13,372] employing the formalism of the theory of branching processes reveals two drawbacks of the former. Among these is the conversion discretization procedure and the difficulties that might emerge when extending this approach to the copolycondensation of several monomers. The second variant of the statistical approach, being free of these shortcomings, enables the extension of the results of publications [13, 372] to the general case of irreversible FSSE polycondensation of an arbitrary monomer mixture [374].

Turning from homopolycondensation to copolycondensation it is worth noting that only a limited number of publications are devoted to the theoretical study of truly nonideal systems. Among them mention should be made of work by Galina et al. [366,375,376, 463], who explored the possibilities to employ the traditional Gordon's statistical approach in the calculation of the gel point for an alternating copolycondensation of three-functional and bifunctional monomers, each having kinetically dependent functional groups. Both of the systems $RA^3 + SB^2$ [375] and $RA_1^2A_2 + SB^2$ [366,376], were calculated only in the framework of the simplified FSSE model. That is why it comes as no surprise that the values of the critical conversion at the gel point found by the Gordon statistical method and from the solution of kinetic equations for the second order moments of MWD turn out to be very close. Nevertheless, by analogy with homopolymerization [368] there is serious reason to expect that the transition from the simplified FSSE model to the normal one will appreciably extend the range of the kinetic parameters over which the traditional statistical approach is a poor approximation for the calculation of the gel point.

This approach, referred to by different names [294, 331,368,377,378], is strictly valid for the alternating copolycondensation of two monomers, provided the functional groups of at least one of them are kinetically independent. The best-studied among such quasi-ideal systems is the curing of diepoxides with diamines [330], for which the functional groups of the diepoxides are presumed to be independent [379–393]. A diamine molecule comprises a pair of amino-groups, each involving two primary amino hydrogens. When one of them reacts with diepoxide,

the reactivity of the remaining hydrogen changes markedly [379–381]. This substitution effect can be termed local, since taking account of the distinctions between primary and secondary amino hydrogens, it does not embrace another amino group attached to the monomeric unit. Formally, this curing process may be viewed as copolycondensation of monomers $RA^2 + SB^2B^2$, characterized by two kinetic parameters that are the constants k_1 and k_2 of the reaction of primary and secondary amine hydrogens with an oxirane A. Theoretical treatment of such a quasi-ideal system has been carried out by both statistical [382] and kinetic [383,384] methods. In the first case, use was made of the theory of branching processes, whereas in the second case the solution was found for the difference-differential equation for molar concentrations of molecules $C(i,j,k)$ formed from i tetrafunctional monomeric units S and j bifunctional chain links R that contain k unreacted primary amine hydrogens.

The simple kinetic model of the synthesis of amine cured epoxy resins given above suffers from the shortcoming that it disregards polyetherification reaction normally occurring in the course of a curing process [380,381]. Bokare and Gandhi [385] seem to be the first who incorporated this reaction in the kinetic scheme of amine-epoxy network formation. Later, a number of theoretical works appeared [386–392] in which, along with the substitution effect in diamine, allowance was also made for competing amidization and etherization reactions. The severity of the problem of the quantitative description of such a system is that whereas the first of these reactions proceeds by the stepwise mechanism, the second one goes by a chainwise mechanism. This may be one of the reasons for the variety of models, leading sometimes to results differing by several hundred percent. A critical analysis of five of such models brought Gupta and Macosko [393] to the conclusion that only one of them is exact, the 'combined model' [385]. They also elucidated the nature of the approximation in Dusek's model [387], and extended the combined model to postgel analysis.

A variant of the kinetic approach put forward by Cheng and Chiu can be used to calculate the average molecular weight of the products of curing reactions of epoxy resins with amines [394]. This approach is rather general, and even claims to cover systems with

multistage processes. Its authors resorted to the formalism they developed earlier to treat the polycondensation of epoxy resins with primary amines, taking into account the substitution effect and etherification reaction [395]. The dependence of P_N and P_W on epoxy conversion as well as its critical value at the gel point found theoretically agree well with those determined by other methods and measured experimentally. Later, the extent to which these statistical characteristics are influenced by a monoepoxide added in the reaction system was studied theoretically [396].

A specific process in which the substitution effect plays a central part is the step-growth catalytic polymerization of tetraethylorthosilicate (TEOS) conducted in a water–ethanol solution [397]. The initial monomer here is RB^4 , where R is a silicon atom and B is an epoxy group. Its functional groups B transform due to the hydrolysis into hydroxyl groups A, which later enter into the condensation reaction $A + A$ to form ether bonds. To describe such a polycondensation in the framework of the FSSE model, Macosko et al. [397] suggested the use of monads Q_i^j differing in numbers of reacted i and unreacted j hydroxyl groups as kinetically independent fragments. The concentrations of these 15 superspecies satisfy a closed set of kinetic equations, written down with allowance for reversible hydrolysis and irreversible condensation elementary reactions. No analytic results are reported in paper [397] since it entirely deals with the elaboration of an algorithm for the Monte Carlo solution to the kinetic equations for the monads.

3.4. Cyclization in processes of branched polycondensation

Intramolecular reactions known to proceed in the course of branched polycondensation give rise to the formation of macromolecules with a number of different cycles. Molecular graphs corresponding to them are also supposed to contain cyclic fragments. The task of the identification of such cyclic graphs is far more involved than that for the case of trees. Nevertheless, its fulfillment is absolutely indispensable to furnish a comprehensive, physically adequate description of intramolecular reactions, inasmuch as the long-range effects should necessarily be taken into

account for the calculation, unlike the case for ideal systems (as pointed out in Section 1).

First, let us dwell briefly on the factors capable of exerting influence on the course of intramolecular reactions during a branched polycondensation, and then indicate possible approaches to their quantitative description, as well as make an attempt to analyze the premises underlying currently available models for the calculation of the products of corresponding processes. This is an especially intriguing subject, bearing in mind that the physico-chemical substantiation of the models discussed above was not the matter of prime concern to their authors. In spite of the fact that among all conceivable intramolecular transformations we will entirely focus for simplicity on condensation reactions in a homopolymer, the consideration of analogous reactions in copolymers or intramolecular exchange reactions does not qualitatively change the general picture of a process.

3.4.1. Theoretical problems

The elementary act of an intramolecular condensation reaction consists in the chemical interaction of two terminal groups of a molecule, with subsequent formation of a cyclic fragment. The probability of such an interaction is prescribed by mutual spatial arrangement of the reacting groups involved in the reaction, which in turn is controlled by the conformational–configurational structure of the molecule. Depending on which pair of functional groups reacts, one or another configurational isomer of the initial molecule will form. Generally speaking, the interaction constants for every pair will be different. That is why mutual transitions between isomers due to intramolecular reactions have different probabilities. On the other hand, proceeding from the configurational structures of the initial and terminal isomers, one can unambiguously reveal the reacted pair of functional groups and, thus, determine the rate constant of the corresponding intramolecular reaction (or corresponding constant of equilibrium if that is the case). Consequently, in order to elaborate a rigorous theory of branched polycondensation involving cyclization it is imperative, first, to identify in some way all isomers and, second, to specify the probabilities of mutual transitions between them. However, this problem can hardly be solved in such a general formulation.

Hence, it would apparently be advisable to adhere to a strategy implying the construction of less general models, where the character of simplifying assumptions is associated, however, with particular physico-chemical peculiarities of the system under examination. Just these peculiarities are supposed to condition a particular choice of the values of the constants of interaction between all possible pairs of functional groups in every molecule. Owing to such model assumptions, either the number of transitions between configurational isomers due to intramolecular reactions may drastically decrease, or many such transitions will become equilibrium.

Let us consider some of the factors concerning the possible choice of these constants. Irrespective of whether polycondensation is carried out under equilibrium conditions or not, the probability of the interaction of a pair of functional groups, e.g. i th and j th, pertaining to a macromolecule of specified configurational structure σ is prescribed by the effective concentration c_{ij}^{σ} created by one of them in the immediate vicinity of the other under different conformation rearrangements of a macromolecule they are involved in. One of the quantities characterizing the mutual conformation of an arbitrary pair of groups in a molecule is the number of chains joining these groups. In a tree-like molecule any two functional groups are connected by only one chain. If the relative fraction of bonds involved in cyclic fragments of a molecule (cyclic bonds) is small, then the majority of its functional groups exhibit this property. It is reasonable to assume that in this case for every pair of such groups the value of c_{ij}^{σ} is entirely dependent on the statistics of possible conformations of the chain which connects them. To have this statistics determined one may resort, as in case of linear molecules, either to the freely jointed chain model or to the corresponding rotational isomeric state model. Such an approximation means that only short-range effects should be allowed for in the calculation of a conformational structure, whereas long-range (excluded volume) effects may be neglected. With a growing number of cyclic bonds, the fraction of functional groups connected by two and more chains increases, and the calculation of the values of their effective concentrations becomes far more intricate. On the one hand, owing to the presence of cycles corresponding macromolecular fragments

contract and become more condensed, which inevitably results in the growth of c_{ij}^{σ} . On the other hand, these macromolecule fragments prove to be more rigid due to the emergence of network structures (skeleton) that prevents the formation of conformers which favor the proceeding of intramolecular reactions. In addition, the possibility of the occurrence of loops and knots should also be taken into account.

3.4.2. Quantitative approaches

A rigorous quantitative theory of branched polycondensation with simultaneous cyclization is not yet available. Several dozen publications are available which attack the corresponding problem using a variety of arbitrary assumptions. However, these assumptions provide the possibility to obviate mathematical difficulties arising for the calculations, rather than to adequately reflect physical picture of the process of interest. Yet, any scientifically grounded model is expected to a certain extent to take into account physico-chemical peculiarities of a system.

Various approaches are used in theoretical considerations of branched polycondensation. Along with the distinction in the character of the assumptions underlying models of the polycondensation systems, authors of different papers used a variety of theoretical methods. For example, Harris [398] and Hoeve [399] took Stockmayer's statistical method [242] as a basis, while Kilb [400] and Stepto et al. [401,402] proceeded from the Flory probabilistic approach [11]. The formalism of the theory of branching processes has been suggested for the description of cyclization [125, 249,360,348,403–409]. Further impetus for theoretical progress has been fertilized by the ideas of statistical physics and field theory [205,300, 410–413].

The kinetic method has also been employed to calculate polycondensation systems undergoing intramolecular reactions. Since no exact analytical solutions are achievable, approximate solutions are normally obtained, resorting to either asymptotic [269] or computational methods [414]. 'Rate theory' [415–418], a variation of the kinetic method, permits the formation of cycles of only minimal size. This idea, consisting in the rigorous account of the smallest size cycles, with neglect of cycles of all other sizes, has been harnessed in papers [127,419–421].

An original statistical-kinetic approach to the consideration of branched polycondensation was put forward by Whittle [355,356,422–424]. Like Harris [398], he applied the Flory principle to the description of intramolecular reactions. Nevertheless, unlike Harris, Whittle developed a quantitative theory, without vague mathematical assumptions. Despite the indisputably high mathematical level of Whittle's work, due to the formal nature of physico-chemical model used, the results are of limited practical value.

Another statistical approach was proposed for use in the theory of branched polycondensation. According to this, the gelation phenomenon is considered as a percolation transition in the context of the theory of critical phenomena and phase transitions [425–430]. Under this approach, emphasis is placed on finding the so-called 'critical indices' characterizing the dependence of some macroscopic quantities on the degree of proximity $\Delta p = p - p^*$ of the conversion p to the gel point p^* , rather than on the calculation of the gel point itself. Detailed discussion of the percolation approach to the description of branched polycondensation can be found in reviews [429,205].

3.4.3. Models incorporating cyclization

The discussion of the physico-chemical peculiarities of cyclization reactions in Section 3.4.1 introduced the important characteristic c_{ij}^σ , the effective concentration produced by one of the two reacting functional groups of a molecule with configuration σ in the vicinity of another group. In this section, we utilize c_{ij}^σ to discuss the principal models available in the literature for the quantitative description of the products of branched polycondensation involving cyclization. Specifying the conditions to be imposed on possible values of c_{ij}^σ in a particular model will enable us to determine initial prerequisites underlying each of them. First of all it should be stressed that on setting $c_{ij}^\sigma = 0$ for all functional groups we will arrive at the ideal polycondensation model provided, of course, the Flory principle holds for intermolecular reactions. This will be implicit in what follows.

To calculate an irreversible polycondensation of monomer RA^f with regard for intramolecular reactions, Hovee [399] extended the statistical method introduced by Stockmayer [242], assuming that no monomeric unit is involved in more than one cycle. In line with this, homopolymer molecules differ not only in the degree of

polymerization, as in Stockmayer's case [242], but also by the fraction of monomeric units in cycles of different size. The solution of the corresponding combinatorial enumeration problem by Hovee permitted him to find the MWD up to the gel point and the critical conversion p^* . The supposition that no monomeric unit is in more than one cycle is equivalent to the condition $c_{ij}^\sigma = 0$ for all functional groups connected by two and more chains. This condition is not expected to perceptibly affect the results of the calculations provided the number of such groups is comparatively small, i.e. under moderate relative fraction of cyclic bonds. However, recourse to a statistical method may be substantiated only for equilibrium conditions of the process mode. At the same time, for such a model the statistical characteristics of the configurational structure of polymers for any functionality f of the monomer will differ, depending on whether they were obtained under equilibrium or its absence. Thus, the results arrived at in paper [399] for irreversible process turn out to be erroneous. Proceeding from these results it is possible to conclude that in equilibrium the critical conversion p^* decreases as compared to its value for corresponding ideal system. This decrease is the more pronounced the smaller is the concentration of monomeric units, i.e. the reaction system is more dilute.

In order to reveal initial premises of other models, it is convenient to consider the effective concentration c_i^σ induced in the vicinity of a specific functional group i of a macromolecule by all its other groups. The value of c_i^σ prescribes the probability for a group i to enter into any intramolecular cyclization reaction, being dependent in general not only on the rigidity of a molecule and its configuration σ , but also on the position of group i in the molecule.

The system addressed above [399] has also been treated [269] by the kinetic method, and under other model assumptions. When setting up the corresponding kinetic equations for the concentrations of macromolecules, the authors assumed that the probability for a molecule functional group to enter into a cyclization reaction is proportional to the overall number of groups in the molecule. The results did not admit the gel point in its classical definition. Rather, for a sufficiently low value of the parameter ε (equal to the ratio of the probabilities for a functional group to enter intra- or intermolecular reactions, respectively), gel formation is defined mathematically not

as a point, but as a narrow interval of conversions. Within this interval, which is the narrower the smaller is ε , a dramatic change of the weight average degree of polymerization occurs, although the latter nowhere becomes infinite [269]. Such a model corresponds to the assumption that the effective concentration c_{ij}^σ for any pair of functional groups in the reaction mixture is identical irrespective, for example, of the number of the chains connecting them and their lengths. Consequently, this assumption completely ignores the conformational structure of molecules. Important, that the value of c_i^σ for all functional groups of every macromolecule is not controlled by i , but rather is proportional to the overall number of these groups in a molecule.

Under an analogous model assumption this same system, but under equilibrium, was studied by Whittle [355,356] and Harris [398]. (In paper [398] one more model was put forward which will be addressed later.) The second of these publications used the statistical Stockmayer method [242], with the only distinction being that the molecules were distinguished not only by the number l of monomeric units, but also by the number s in them of intramolecular bonds, so that the probability of any molecule was governed by the values of numbers l and s . An arbitrary group was deemed capable of forming without any restrictions an intramolecular bond, including a cyclic one, with any group of the system, i.e. no limitations on the set of the configurations in hand were imposed. The calculation reported by Whittle [355,356,422–424] was accomplished by virtue of the detailed equilibrium principle with the elements of a graph enumeration theory. The weight average degree of polymerization of the products was found to diverge at arbitrarily small conversion, which qualitatively disagrees with the corresponding result [269] for a irreversible process. The absurdity of the value $p^* = 0$ was obvious to the authors [355,398], and was apparently due to the total neglect of differences in the conformational–configurational structure of molecules. The probability for any molecule with particular values of l and s is proportional to the number of all conceivable spatial configurations with the given values of these quantities. This number increases dramatically with the growth of l and s , and for macromolecules having high a degree of polymerization becomes so high that the probability of a gel

macroscopic molecule is equal to zero at arbitrarily small conversions.

Another model for the calculation of the products of polycondensation of monomer RA^f has been put forward [407]. Here an intramolecular reaction was considered as one possible variant of the chain termination process, in the course of which any functional group may, regardless of the other groups, enter into a cyclization reaction with a specified probability, losing thereby the possibility of further involvement in the process. In accordance with that assumption, the calculation is supposed to be performed by virtue of a special branching process. To take account of intramolecular reactions proceeding for this process, an additional type of particle was virtually introduced, incapable of reproduction and corresponding to the groups which had already reacted with the formation of cyclic bonds. Such a model corresponds to an ideal polycondensation of the initial monomer in the presence of monofunctional admixture, where a chain termination reaction proceeds, thus, enabling one to calculate the statistical characteristics of a polymer. Along with conversion, among the parameters of this model is the probability of cyclization, i.e. the probability for a reacted group to enter into a cyclic bond. The critical conversion p^* calculated in such a way, increases with the growth of this parameter. An attempt was made to calculate this parameter, as well as to substantiate the model advanced for the case when only groups connected by a single chain are capable of entering into an intramolecular reaction [408,409]. To this end, the probability of the cyclization of an arbitrary group should be thought of as a sum of probabilities for it to enter into the reaction in order to form cycles of all conceivable sizes. Calculation of these probabilities generally resort to the conformational statistics of freely jointed chain, as well as to the assumption that the size of every cycle formed in the course of the interaction of two groups equals the difference in the number of the generations of the genealogical tree (see Fig. 3) in which they are involved. However, such an attempt to calculate the probability parameters within the framework of the statistical method itself is doomed to failure, inasmuch as two functional groups belonging even to the same generation can be joined together by an arbitrary length chain and, consequently, the size of the cycle formed for their reaction

may be arbitrary as well. In fact, the model proposed by the authors [407–409] is based on the premise that the effective concentration c_i^σ for any functional group of the reaction system in every instant is independent of the molecule to which this group pertains, and its position on that molecule. Since this is equivalent to application of the Flory principle for intramolecular reactions, it follows that the statistical characteristics of the products (the critical conversion being among them) do not depend like in the case of ideal polycondensation on whether the process is conducted under equilibrium conditions or not.

In essence, similar supposition served as the basis of an earlier publication by Kilb [400], in which the critical conversions were calculated for the systems $RA^2 + SB^f$ and $RA^2 + S_1B^2 + S_2B^f$, with condensation reactions proceeding exclusively between groups of different types. Noteworthy, Kilb managed to perform calculation only for the first system. Unlike the preceding authors, he made use of the Flory statistical method, which is rather cumbersome and inconvenient for calculations. He extended it to the case for which every functional group is capable with some probability of participating in a cyclization reaction. Despite being far more involved technically than methods employed in the papers discussed above [407–409] (causing the underlying assumptions to be less apparent), the final results for the two schemes are entirely equivalent. Thus, all the conclusions and remarks made above with respect to the initial premises of the model introduced by the authors [407–409], including those related to the calculation of the probability of cyclization may be fully applied to the results of work [400].

Stepo and co-workers [401,402] improved the Kilb approach [400], freeing it from some of its shortcomings. They presented an equation to determine the gel point for a copolycondensation $RA^2 + SB^f$ [401], later refining their theoretical treatment by extending it to copolycondensation in the following systems [402]:

$$\sum_{\alpha=1}^m R_\alpha A^{f_\alpha} + \sum_{\beta=1}^n S_\beta B^{g_\beta} \quad \sum_{\alpha=1}^m R_\alpha A^{f_\alpha}$$

The functionalities $\{f_\alpha\}$ and $\{g_\beta\}$ of monomers, as well as numbers of their types, m and n , may have any

values. A considerable shortcoming of these treatments developed to take into account the cyclization consists in the absence of a rigorous substantiation of the approximations employed. This shortcoming, however, seems to be significantly redeemed by the simplicity of the final formulas, an indisputable advantage when using them for the treatment of experimental data. Their comparison with theoretical results for a variety of particular polycondensation systems can be found in review articles by Stepto [128,416,431–437].

Another model for the calculation of equilibrium polycondensation of monomer RA^f with cyclization, with similar initial assumptions to those discussed in the preceding, was put forward by Harris [398], in order to obtain more plausible results than those ensuing from his first model. Again he made a recourse to the Stockmayer method, differentiating molecules by the degree of polymerization and the number of bonds, although this time he substantially restricted the number of allowed spatial configurations. To this end, Harris assumed each functional group of a molecule exhibiting a configurational tree-like structure to be capable of forming a cyclic bond with specified number of other groups of the molecule (not with all of them, as in the first model), not controlled by its degree of polymerization. As the number of cyclic bonds in a molecule increases, the number of the groups remaining in it decreases, and the number of groups capable of forming a bond with the given one diminishes proportionally. Proceeding from such suppositions, Harris managed to calculate completely only the system gel point, finding it to increase with dilution of the reaction system, until a dilution is reached beyond which gel formation is no longer possible. The initial assumptions of the Harris model are as follows: the Flory principle is valid for intramolecular reactions of functional groups of the tree-like molecules, i.e. for them the concentrations c_i^σ are not controlled by i and σ ; and for groups of other molecules, the values of c_i^σ are governed only by σ and decrease with increasing number of cyclic bonds, in proportion to the number of terminal groups remaining in molecules.

Finally, let us address the calculation scheme proposed by Gordon and co-workers [125,249,357,403,406]. This scheme provides the possibility to calculate statistical characteristics of the products of

polycondensation with cyclization of one or several monomers. Moreover, it permits one to determine them either before or after the gel point, and to find the critical conversion even in the presence of the substitution effect. With this aim in view, the authors [125,249,357,403,406] suggested resort to a branching process, with an additional type of particles corresponding to functional groups already reacted to form cyclic bonds. However, as distinct from the treatments [407–409], Gordon and Scantlebury presumed [249] that the probability for an arbitrary particle to give birth to a particular number of other particles in the subsequent generation is prescribed, as in the case of the FSSE model only, by the number of the reacted functional groups involved in a monomeric unit corresponding to the particle. Gordon et al. were of the opinion that their calculation scheme would provide a plausible picture of any branched polycondensation with intramolecular reactions, regardless of whether or not it is conducted under equilibrium conditions, provided the probability parameters of corresponding branching process are properly set [125, 249,357,403,406]. They also endeavored to substantiate their model for the case when only functional groups connected by a single chain may enter into cyclization reaction, so that every bond of a molecular graph may be involved in not more than one cycle. Conventionally, cutting any bond in every cycle it is possible to reduce the set of such cyclic graphs to corresponding set of trees. Such a procedure underlies the ‘spanning-tree’ model, which owes its name to the graph theory for which trees obtained in such a way are referred to as spanning trees. For this procedure, one more type of pending sites is added, known as cyclic ones, appearing in pairs as a result of every cutting. These trees, depicted as root trees, are presumed to be realizations of a branching process.

However, such an interpretation, not substantiated kinetically, can hardly be accepted as correct. In fact, let us admit that cutting a certain bond results in the appearance of two cyclic sites divided by a length n trail. If one of them belongs to some generation of the genealogical tree, the other should necessarily be involved in one of the nearest n generations. But the point is that such a mandatory appearance of particles of a specified type can, in principle, be described by no branching process for which particles independently give birth to other particles in every generation.

The ‘spanning-tree’ model utilizes the assumption that the value of c_i^g of an arbitrary functional group is controlled solely by the number of groups on the same monomeric unit already reacted, and is proportional to this number, i.e. this model proves to be based on one of the modifications of the extended Flory principle for cyclization reactions. However the relevance of this principle is by no means justified in this particular case, unlike its application with the FSSE model.

Despite its formal character, the spanning-tree approximation model looks rather appealing to theorists as a means to furnish a quantitative description of branched polycondensation with intramolecular reactions, regardless of the size of the rings formed. Recently, Sarmoria and Miller [438] presented a modification of such a model that uses more accurate internal estimates of the probabilities of cyclization. This requires limited Monte Carlo simulations of some molecular structures, resulting in a hybrid probability approach, combining analytic and Monte Carlo approaches. They suggested three possible extensions of the spanning-tree model of varying degrees of complexity, and calculated for the RA^f homopolycondensation such characteristics as intramolecular conversion, the gel point, the fraction of the sol, and weight-average molecular weight of its molecules.

Recourse to the kinetic–recursive approach [224, 331] turns out to be highly efficient for a quantitative description of the polycondensation for which the formation of the smallest possible rings is prevalent. Using that formalism, a rigorous theoretical consideration has been performed of systems $(RA^3 + SB^2)$ [127], $(RA_1^2A_2 + SB^2)$ and $(RA^3 + SB_1B_2)$ [421], in which the formation of only those cycles is admissible that involve just two monomeric units. The gel point has been calculated in the framework of this approximation, as well as the dependence on conversion of the average degree of polymerization and weight fractions of gel, elastically effective material and pendant material of a polymer network. These characteristics have been calculated by the statistical-recursive method, proceeding from equations whose probability parameters are determined through the fractions of superspecies comprising one or several monomer fragments. The evolution of their concentrations has been found from the solution of kinetic equations derived under the Flory principle. It is worth noting that all the results reported in papers

[127,421] are fully accurate for the physico-chemical model of polycondensation employed.

Models of this sort are, apparently, most appropriate for the description of condensation processes of the formation of inorganic polymer networks. The sol–gel polymerization of Si-based materials has been among the most studied, and has been shown to be highly nonideal [439]. Evidence of this nonideality is, for example, the extraordinarily high conversion at the gel point ($p^* \approx 0.8$) for tetraethoxysilane (TEOS), compared with the ideal value $p^* \approx 0.33$. Such a pronounced difference in value of p^* cannot be accounted for in the FSSE model because the maximum gel conversion does not exceed 0.50 for polycondensation of monomer RA^4 described by this model [397]. The value $p^* = 0.375$ predicted from the percolation model signals that the random cyclization leads only to a slight increase in gel conversion as compared to the ideal model (even with allowance for the long range excluded volume effect) [440]. To resolve the large difference between theory and experimental observation, it has been proposed to describe the sol–gel polymerization of TEOS by means of models where cyclization reaction between silicon sites separated by only several siloxane bridges is considered as preferred [440]. This type of cyclization is evidently not amenable to description by a percolation theory, in which loops of various sizes are formed randomly. Macosko et al. [441,371] harnessed one such ‘preferred cyclization’ (PC) model, for which loops can only form as the result of an intramolecular reaction in trimers and linear tetramers. In parallel with cyclization, FSSE for the simplified kinetic model (with factorable constants of elementary reactions of condensation) was also taken into account. The dependence of P_w on conversion up to the gel point has been calculated in the monad approximation of the FSSE model, using the kinetic–recursive approach.

The model employed in papers [441,371], demonstrating that the combined effects of PC and FSSE can have a significant impact on the gel conversion, fails, however, to quantitatively describe the acid-catalyzed sol–gel polymerization of TEOS. This conclusion ensues, for instance, from the fact that at values of the rate constants of TEOS polymerization, the theory predicts a gel conversion $p^* = 0.51$. Hence, the limited cyclization allowed in these papers is completely

insufficient to explain the value $p^* = 0.83 \pm 0.02$ experimentally observed for a wide range of reagent concentrations. This circumstance points to a highly nonrandom character of cyclization reactions, as well as to the presence in the reaction system of compact three-dimensional cagelike intermediates [440]. These form in the course of the first (rapid) stage of the TEOS polymerization, to connect with each other as new precursors, eventually forming a gel during the second (slow) stage. A diversity of experimental data supports the plausibility of such a scenario, for which primary units of nanometer length scale (cubes, prismatic hexamers, etc.) are first formed by nonrandom cyclization, to be involved later in gelation as ‘monomers’. Assuming the second stage to be described by the ideal model, one can easily estimate a value of p^* , which turns out equal to 0.75–0.80 [440]. Quantitative theoretical consideration of the moderate negative substitution effect, observed for the TEOS polycondensation [371], will certainly provide a good fit of the conversion calculated at the gel point with the $p^* = 0.83$ found experimentally. This fit is a necessary, but not sufficient, condition for a physico-chemical model to be adequate for providing an exhaustive quantitative description of alkoxysilane polycondensation. Such a model is supposed to describe correctly the kinetic peculiarities of this process, as well as molecular-weight and structure characteristics of polymer products formed. A paper [442] whose authors took a first step toward unified modeling of the kinetics and structure of silica gelation merits special mention. They developed dynamic Monte Carlo simulations, incorporating such well-established kinetic trends as hydrolysis, FSSE and nonrandom cyclization. As distinct from earlier simulations [371], the new ones allowed unlimited formation of three-site rings. Though the majority are not found in real silicates (where four-site rings dominate), the basic qualitative features of sol and gel structures are most likely to be captured properly by the model used in paper [442]. It predicts a broader range of gelation behavior than prior kinetic models, as well as the feasibility of a polycondensation regime in which gelation is preceded by the formation of an assembly of different three-dimensional cagelike cyclic molecules, each comprising several Si units.

In closing this section it is possible to make the following conclusions. Despite a variety of models

put forward, a rigorous quantitative description of the processes of branched polycondensation with allowance for intramolecular reactions is not available. Almost all currently available mathematical models are based on arbitrary assumptions, which in our opinion, are not related to the physico-chemical peculiarities of the systems of interest. Specifically, the application of the Flory principle for intramolecular reactions, unlike for intermolecular ones, has not provided an adequate physico-chemical substantiation. The only means enabling a researcher to verify the adequacy of some of the models discussed in the foregoing is comparison of the results of calculations with experimental data obtained for a particular process. However, the available body of experimental findings does not provide sufficient information to guide a solution for the majority of the systems considered in the papers cited above. As a rule, the extent to which intramolecular reactions contribute to the deviation of these systems from the ideal ones remains unclear.

3.5. Hyperbranched polymers

One of the major challenges for macromolecular chemistry is the synthesis of polymers with well-controlled and novel architectures. Dendrimers, which are highly symmetric and monodisperse branched polymers, perform leading role among them [443,444]. They are an assembly of identical perfect macromolecules, with chains emanating from a central core, and with a branch point at each repeat monomeric unit. Their content in each successive level (generation) of such units with degree of branching $f+1$ is f times more than that in the preceding generation. Although dendrimers show some valuable properties, unusual for other polymers, their synthesis is normally quite a long and tedious multistage procedure. The search for simpler methods to prepare dendrimer-like polymers resulted in the design of hyperbranched polymers [443,445–448]. Unlike dendrimers, they are polydisperse in molecular weight and degree of branching, but contrary to dendrimers, hyperbranched polymers can be prepared in a one-pot reaction.

Polycondensation is one of the most widespread methods for the synthesis of hyperbranched polymers. The processes of their preparation, being amenable to

all regularities of a branched polycondensation, exhibit, however, a number of special features, the most important of which are described in the following. An infinite polymer network cannot develop at any level of functional groups conversion. Molecules formed during the synthesis are either of tree-like architecture or contain a single cycle. The above peculiarities substantially facilitate the theoretical consideration of hyperbranched polymers in comparison with other condensation polymers, that makes it appropriate to address them in a separate section.

In the field of statistical chemistry of hyperbranched polymers Flory [207] was the first to derive by a statistical method an expression for the MWD and its statistical moments for the products of ideal homopolycondensation of monomer RAB^f , where only groups of different types may react. All arborescent molecules formed here contain a single A group at the root of a tree. Such dendrimer molecules are distinct in both the number of generations and number of units in each of them. Erlander and French [208] extended Flory's results [207], theoretically considering the homopolycondensation of monomer $RAB_1B_2 \cdots B_f$, for which all B-type groups differ in reactivity. A particular case of this process at $f=2$ has been independently examined by Allen [209]. Proceeding from the ideal model of polycondensation, the authors of both papers [208] and [209] derived expressions for MWD and the distribution of molecules for the number of chemical bonds $\{b_i\}$ formed as a result of the reaction between groups A and B_i . The kinetic method was also employed to find the MWD of ideal polycondensation of monomer RAB^2 [277,449]. Given the statistical moments of the MWD, it is possible to calculate the number average P_N , weight average P_W and z -average P_Z degree of polymerization of macromolecules, expressions for which are derived in the above cited works.

It is common practice to estimate the inhomogeneity of molecules of hyperbranched polymers (as well as that of any other homopolymers) using the polydispersity coefficient $K = P_W/P_N$. The closer this is to unity, the closer is the polymer to a dendrimer, for which $K = 1$.

Molecules of hyperbranched polymers differ not only in the number of constituent monomeric units but also in pattern of their arrangement. This circumstance

stipulates the existence of a variety topological isomers similar to those depicted in Fig. 1. The easiest way to characterize these isomers is by the numbers of their different monads, i.e. monomeric units of different kinds. In the simplest case of polycondensation of monomer RAB^2 there will be five such kinds. Two of them, corresponding to monomer and rooted unit, might well be ruled out of consideration since their fraction in the products of high-conversion polycondensation is small. Only the remaining three kinds of monads are actually interesting, because molecules formed at low conversions are oligomers, consisting basically of few units. Thus, ignoring units with unreacted groups A, they normally consider units of only three kinds, i.e. terminal, linear and dendritic. These units with 2, 1 and 0 groups B attached correspond, respectively, to monads of kinds 1, 2 and 3 in Fig. 2. The fractions of these monads, $T = \lambda_1$, $L = \lambda_2$, $D = \lambda_3$, can be found by NMR-spectroscopy, permitting an evaluation of the degree of branching of the polymers. Its quantitative characterization can be performed by means of different parameters, the simplest of which, $DB = (T + D)/(T + L + D)$ [450]. The larger is DB, the less pronounced is the distinction between a sample of hyperbranched polymer and perfect dendrimer, for which $DB = 1$. This parameter has been employed by several researchers to evaluate the degree of branching from NMR-spectroscopy data. Later, another definition of the degree of branching $DB = 2D/(2D + L)$ was suggested for use as more appropriate for the description of low-molecular weight polymers [451]. As the molecular weight increases the difference between these two definitions of DB disappears because the difference between the values of quantities D and L becomes progressively less pronounced. For the description of the microstructure of hyperbranched molecules one more parameter, ANB = $D/(D + L)$ (Average Number of Branches deviated from linear direction per nonterminal unit), was defined [451]. This parameter is convenient when comparing the degree of branching of polymers obtained by polycondensation of monomers RAB^f with an arbitrary number f of groups B. Since the number of types of different monads in molecules of such polymers can exceed three, the characterization of their microstructure in terms of T , L and D turns out to be insufficient. This motivates the extension [451] of the definition of structure

parameters DB and ANB. As the topological structure of molecules changes from linear to perfectly branched, these parameters grow from 0 to 1 for DB and to $(f - 1)$ for ANB. For example, their limiting values at $P_N \rightarrow \infty$ for the ideal model of polycondensation of monomers RAB^f are as follows [451]:

$$DB = \left(\frac{f-1}{f}\right)^{f-1}$$

$$ANB = \left[\left(\frac{f}{f-1}\right)^f - 1\right]^{-1}$$
(28)

With functionality of a monomer increasing from $f=2$ to ∞ the first of these parameters decreases from $1/2$ to $1/e \approx 0.37$, whereas the second one grows from $1/3 \approx 0.33$ to $1/(e-1) \approx 0.58$. The dependence of parameters DB and ANB on the conversion of groups A was calculated for values $f=2, \dots, 6$ [452].

A more detailed description of the configuration structure of hyperbranched polymers was realized by Moller et al. [453]. They have calculated the distribution function of molecules for the number of different monads D for products of the ideal polycondensation of monomer RAB^2 , and have compared DB values obtained for the two definitions put forward in earlier work [450] and [451].

One way to increase DB of the random polycondensation products is to employ perfectly branched dendrons instead of monomers. The formula for DB derived in this case [452] provides a limiting value that substantially exceeds that which may be obtained from expression (28).

Another option to increase parameter DB is the use of a monomer RAB^2 with kinetically dependent groups B. All theoretical papers excluding [454] addressed only the simplified FSSE model of polycondensation, for which the reactivity of any B-group is the same, irrespective of whether it is a constituent of a monomer or polymer. This model comprises just two parameters, k_T and k_L , equal to the rate constants of the elementary reactions of group A with group B, which enters into monads T and L , respectively. Evidently, as the reactivity ratio $x = k_L/k_T$ increases, the formation of hyperbranched molecules will take place with a lower fraction of monads L than obtained from the random one-pot polycondensation, thus leading to higher than $1/2$ values for DB. Holter

and Frey [452] substantiated this conclusion quantitatively, calculating the theoretical dependence of parameters DB and ANB on conversion p_A for A groups at various x , as well as the dependence on x at $p_A = 1$. Subsequently, the profiles of P_N, K and DB with the conversion p_A were calculated for the same system [455,456]. An increase of parameter x leading to the growth of DB value was found to be simultaneously responsible for widening of the MWD of the polycondensation products.

To authors' knowledge, the kinetics of the formation of hyperbranched polymers has been considered in the framework of the complete FSSE model in only one paper [454], marking that as particularly important for the theory of the process. The most thorough theoretical analysis in this respect was performed for polycondensation of monomer RAB^2 characterized, in the model by 12 constants of elementary reactions, between six kinds of different monads. A set of differential equations for their fractions was suggested in a matrix form, making it possible to easily extend this treatment to other systems. Analysis of the solutions of these equations shows [454] that the 'substitution effect' might sometimes be responsible for an appreciable distinction in microstructure exhibited by hyperbranched polymers and those synthesized by an ideal polycondensation. In an attempt to describe this microstructure in more detail, authors calculated the fractions of various dyads [454]. However, instead of finding them from the solution of kinetic equations, they proceeded from the arbitrary assumption that the probability of a dyad is proportional to the product of probabilities of the constituent monads. An elegant algorithm for deriving a set of kinetic equations for monads was also employed in the consideration of homopolycondensation of monomer RAB^3 , as well as that of monomer $RABC$, with groups B and C that do not react one with each other.

All of the kinetic models discussed above for the synthesis of hyperbranched polymers ignore intramolecular reactions. Accounting for them makes the theoretical consideration more complicated, though not to the same extent as for the processes of polymer network formation. The reason is that no hyperbranched polymer molecule can contain more than one cyclic fragment. Nevertheless, even here the problem of finding the rate constant $k^c(l)$ of

the cyclization reaction for molecules with l monomeric units remains unsolved. This constant is equal to the product of the rate constant k of elementary reaction between groups A and B and effective local concentration $c_{AB}(l)$ of groups B in the vicinity of group A in an l -mer. In order to find an expression for $c_{AB}(l)$, it is necessary to average over all configurations σ of rooted molecular trees with l units. Instead of such an averaging, Dusek et al. [457] suggested to take as effective concentration $c_{AB}(l)$ the arithmetic mean of the values of the effective concentration $c_{AB}^{lin}(l)$ and $c_{AB}^{den}(l)$ in l -mers which have linear and dendritic configurations, respectively. The accuracy of the results obtained under such an assumption remains uncertain. This uncertainty is even greater for treatments such as those [449,456] in which $c_{AB}(l)$ is assumed to be proportional to the number of groups B present in a molecule of an l -mer. In this model, $c_{AB}(l) = (l + 1)\lambda$, with volume $1/\lambda$ of a polymer molecule that proves to be independent of number of its units. Such an assumption is, obviously, physically inconsistent and, consequently, appears to be incorrect. Moreover, this model, being physically senseless, is hardly appropriate for practical calculations leading to an unclosed set of equations for statistical moments of the MWD [449,456]. Just the same deficiency is inherent in the kinetic model proposed in paper [457].

One of the main distinctions of hyperbranched polymers from dendrimers is their more pronounced polydispersity. It might be substantially reduced if polycondensation of monomer RAB^f is conducted in the presence of a certain amount of multifunctional core molecules SC^g whose functional groups C react exclusively with group A. The theoretical examination of such polycondensation systems is undertaken in several recent publications [452,458–461]. The limiting values of the degree of branching of polymers formed turn out to be the same (28) as in the absence of core molecules [452], but the MWD of these polymers becomes noticeably narrower when a compound SC^g is involved.

Yan and Zhou [458] studied the ideal polycondensation of monomer RAB^2 in the presence of molecules SB^g with an arbitrary number g of groups B. They wrote down a set of kinetic equations for the concentrations of l -mers of different architectures present in the reaction system. This attribute was

chosen to distinguish molecules having the topology of free tree with A-group as a root and the topology of a core molecule with $n = 1, \dots, g$ trees growing from it. The exact analytical solution of the kinetic equations provides explicit expressions for the distribution for number of units in molecules of any mentioned topological structure, as well as the MWD and its statistical moments [458]. As ensues from these equations, in the course of the polycondensation the MWD first broadens, and then abruptly narrows as the reaction approaches completion. The greater the number g of groups in the core moiety, the narrower the final MWD of the hyperbranched polymer. These conclusions remain true when monomers of an arbitrary functionality are employed [459]. Theoretical consideration of ideal polycondensation $RAB^f + SB^g$ revealed [459] that when the process approaches completion, the MWD of the resultant polymers is found to broaden with increasing f and becomes more narrow with increasing g .

Since the reactivity of functional groups C in a core molecule is, generally speaking, different from those B in the monomer, it is of specific interest to examine the effect of this distinction on the polydispersity of hyperbranched polymers. With this in mind Cheng and Young [460] considered the ideal polycondensation $RAB^2 + SC^3$ theoretically. Unlike their precursors [458,459] they failed to obtain analytic expressions for the MWD and its statistical moments. However, they succeeded in deriving differential equations for the calculation of the dependence on conversion (or time) of such statistical characteristics as P_N , K and DP . The solution of these equations enabled them to investigate the effect of stoichiometric and kinetic parameters of the system on molecular weight, polydispersity and the degree of branching [460]. These parameters are the ratio of molar fractions of core molecules and monomers and the ratio of the reactivities of functional groups C and B in their reaction with A groups.

In an effort to elucidate the effects of violation of the Flory principle on the statistical characteristics of hyperbranched polymers synthesized in the presence of core molecules, Galina et al. [461] studied the polycondensation $RAB^2 + SB^3$ in the framework of the simplified FSSE model. This follows from the complete FSSE model under two assumptions: first, that the B group reactivity is exclusively dependent on

how many neighboring B groups have reacted, and is unaffected by whether or not a neighboring A group has reacted; and second, that the substitution effect is identical in both molecules, RAB^2 and SB^3 . Such a kinetic model of polycondensation is completely specified by the three rate constants of elementary reactions between a group A and groups B belonging to molecule SB^3 , monad T , or monad L . When using the kinetic method, every molecule in the reaction system may be characterized by its number of monads T and L . Ordinary differential equations have been derived [461] for the statistical moments of the two-dimensional distribution of molecules for these numbers. The numerical solution of these equations enabled the authors of this paper to compute P_N , K and DP versus group A conversion, which they presented graphically for different values of the parameters of the kinetic model.

Evidently, the positive substitution effect (when group B reactivities in a monad of monomer RAB^2 increases as soon as neighboring B group enters the reaction) leads to an increase in DB . The same effect may be achieved if to the solution of core molecules one adds the monomer with the rate markedly lesser than that of the reaction between functional groups. When the ratio of these rates tends to zero the reaction of single RAB^2 monomer with T or L monad of polymer molecule remains the only reaction occurring in the system. In this limiting case, the reaction between monomers might be, obviously, neglected because their concentration tends to zero. The number of polymer molecules under this approximation coincides with the number of core molecules, whereas the process of the formation of hyperbranched polymers resembles a 'living' chain polymerization more than a step-growth one. In such a regime of ideal polycondensation of monomer RAB^2 the limiting values of parameters DB and ANB will be, respectively, $2/3$ and $1/2$, markedly larger than their values $1/2$ and $1/3$ for the same polymer prepared under a traditional regime. This inference remains true for polycondensation of monomer RAB^f with an arbitrary functionality f . This ensues from the comparison of the expressions [452]

$$DB = \frac{f}{2f - 1} \quad ANB = \frac{f - 1}{f} \quad (29)$$

for the structure parameters of a polymer synthesized in semi-open system with slow monomer feeding, with

expression (28) for the same parameters for the products of polycondensation obtained in a closed system.

Hyperbranched polymer with microstructure most closely resembling that peculiar to dendrimers can be synthesized by slowly adding to core molecules the monomer RAB^2 with kinetically dependent functional groups showing a positive substitution effect. In this case expressions for structure parameters look as follows [452]

$$\begin{aligned} \text{DB} &= 4 \left(3 + \sqrt{\frac{x+8}{x}} \right)^{-1} \\ \text{ANB} &= 2 \left(1 + \sqrt{\frac{x+8}{x}} \right)^{-1} \end{aligned} \quad (30)$$

where $x = k_L/k_T$ represents the ratio of the constants of elementary reactions of condensation of group A with B group, constituent of monads L and T. It is clear from formulas (30) that by increasing the value of the reactivity ratio x , one can synthesize hyperbranched polymers whose structure parameters will differ to progressively smaller extent from those characterizing dendrimers.

Calculation of the geometric sizes of the molecules and the scattering behavior of their solutions has a particular place in the theory of hyperbranched polymers. To solve these problems, it is necessary to perform averaging over both the configurations and conformations of the polymer molecules. The mathematical apparatus of the theory of branching stochastic processes is normally employed for this purpose [320]. Using this approach, Burchard derived expressions for the average square radius of gyration of molecules and scattering factor for hyperbranched polymers obtained for processes of ideal homopolycondensation of monomers RAB^2 [306] and RABC [311]. Interestingly, the curves of angular dependencies of the amplitude of scattering of these two polymers have qualitatively distinct appearance, differing from the analogous curve that describes the products of a random polycondensation of monomer RA^3 .

Concluding this section, let us note that the theory of hyperbranched condensation polymers containing monomeric units of several types is virtually missing. To the authors' knowledge, only one paper [462] has

been published on this subject, in which the degree of branching of copolymers obtained by ideal polycondensation of monomers $\text{RAB}^f + \text{SAB}^g$ was theoretically scrutinized. Extending their approach introduced earlier for homopolymers [451,452] to copolymers, the authors presented expressions for parameters DB and ANB at different values of the functionality f and g of monomers of interest.

4. Conclusion

The material outlined in this review portrays the progress in the theoretical approaches commonly applied for the quantitative description of polycondensation processes. Preparing this publication, the authors sought to embrace a voluminous literature on this subject, reflected in an impressive list of references. When discussing each of the papers surveyed, particular attention was given to the following aspects.

1. Type of a polycondensation system considered
2. Polymer statistical characteristics being calculated
3. Kinetic model chosen for the description of the system in hand
4. Theoretical methods being used
5. The results achieved.

Summarizing the results reported in the reviewed papers it is possible to make the following general conclusions about the current state of the quantitative theory of polycondensation. The theory is complete for systems described by the ideal model. General relationships have been derived for such systems that enable one to find any configurational or conformational characteristics of the products of a polycondensation, provided the stoichiometric and kinetic parameters of the model are known. Using these relationships it is possible to calculate any statistical characteristic for the products of polycondensation of an arbitrary mixture of monomers, each having an arbitrary set of functional groups. Consequently, there is, obviously, no need to rederive each time the theoretical equations, provided a particular system is examined in the framework of the ideal model.

The quantitative theory of nonideal polycondensation is far short of completion. Such a theory has

progressed substantially only for the systems for which cyclization is negligible and the violation of the Flory principle is exclusively due to short-range effects. These systems, according to contemporary concepts, can be exhaustively described theoretically provided use is made of a more general version of the Flory principle, rather than the traditional version. In the extended Flory principle, the reactivity of a functional group in a polymer molecule is supposed to be governed exclusively by the microstructure of adjacent fragment of the molecule. It is assumed that the reactivity of a given group alters in the course of the process, as this fragment undergoes changes caused by the reactions of neighboring groups. In the framework of models allowing for this 'substitution effect', kinetically independent units are not functional groups (as for the ideal model), but small fragments of a polymer molecule comprising several such groups. Rigorous analysis proved the applicability of the statistical method in calculating the characteristics of the chemical structure of the products of nonideal polycondensation obeying the extended Flory principle. Though, unlike for ideal polycondensation, general expressions for such calculations have not been derived so far, the algorithm of their performance is perfectly clear for any particular system. This means that today there are no fundamental difficulties for creating the comprehensive quantitative theory of polycondensation taking into account 'substitution effects'.

A correct account of cyclization reactions in the theory of polycondensation is a far more complicated task than that for substitution effects. The reason has to do with the necessity to consider along with configurations of molecules, their conformations as well. Hence, under a rigorous theoretical approach, the description of a polycondensation in the framework of any kinetic model admitting intramolecular reactions a need generally arises for a double averaging over both conformations and configurations of polymer molecules. The only exception here is a linear polycondensation, for which the necessity of the second averaging falls away. In condensation processes of the synthesis of hyperbranched polymers, the algorithm of configurational averaging is simple enough, because macromolecules of such polymers can not contain more than one cycle, which is the trivial one (with a cyclic rank of unity).

Evaluating the prospects of the elaboration of a general theory of the branched polycondensation allowing for intramolecular reactions in molecules of finite sizes, one must admit that they are rather vague. In this respect, more realistic theoretical approaches are based on some approximation suggesting the formation of only selected cyclic fragments. Two such approaches are presently the best known. The first admits any cycles of small size, whereas the second permits cycles of any size, provided they have the simplest topology, with minimal cyclic rank.

Closer inspection of a vast literature on the quantitative theory of polycondensation inevitably has brought us to the conclusion that many papers have independently rederived equations already reported in literature. The reason, apparently, is that these authors were not properly familiar with preceding publications. The authors of this review hope that it might contribute to making up this deficiency.

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