CHAPTER 4

Principles of Statistical Chemistry as Applied to Kinetic Modeling of Polymer-Obtaining Processes

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Contents

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Advances in Chemical Engineering, Volume 39
ISSN: 0065-2377, DOI 10.1016/S0065-2377(10)39004-1

Abstract The subject matter of statistical chemistry of polymers consists in revealing quantitative theoretical dependencies of the characteristics of chemical structure of polymers on the conditions of their obtaining. The fundamental concepts of this branch of macromolecular science are outlined in simple language, bypassing any mathematics. A classification is presented of the kinetic models of macromolecular reactions currently used under mathematical modeling of diverse processes of the synthesis and chemical modification of polymers. A comparative analysis is carried out of theoretical methods engaged in calculations of both the kinetics of such processes and the composition and chemical structure of macromolecules formed. The efficiency of application of general approaches of statistical chemistry is illustrated using the processes of polycondensation, radical polymerization, and chemical modification of polymers as example. A special section is devoted to the discussion of the peculiarities of the effect of hydrodynamic stirring in a reactor on chemical inhomogeneity of obtained polymer products.

1. INTRODUCTION

Kinetic modeling plays an ever-increasing role in the design and optimization of the processes of polymer manufacturing. The efficiency of this method as applied to chemical engineering is predetermined to a great extent by the choice of an appropriate kinetic model underlying the modeling of a particular process. Such a model is supposed to correctly take into account the main physicochemical peculiarities proceeding from the current level of knowledge in polymer science. Only then the model chosen can be used for an extrapolation procedure, ensuring thus a scientifically based employment of the results of the kinetic laboratory research for the optimization of industrial reactors.

When choosing the kinetic model of a particular polymerization process an engineer-researcher inevitably faces the necessity to proceed from two opposite considerations. On the one hand, he is interested in the maximal simplicity of this model bearing in mind the analysis of the results obtained on the basis of such a model and the subsequent solution of optimization problems. On the other hand, he is perfectly aware of the impossibility for too oversimplified a model to correctly predict the performance properties of polymer products, which results in essentially reduced efficiency of the application of mathematical modeling. Hence, the question is to which extent a kinetic model may be simplified to retain the ability to properly predict the physical and mechanical properties of the polymers obtained. The answer depends on a number of factors, among which are the reliability of the knowledge on the kinetics and mechanism of the process of the synthesis of polymer, experimental possibilities for its characterization, and other factors. Their appropriate allowance predetermines an optimal strategy of the choice of the kinetic model and necessary extent of its detailing. The present review aims at formulating the general principles of such a choice based on the knowledge of current state of art in polymer science. Here there is no discussion of particular works, and the list of references, not pretending to be complete, contains just some key publications.

Choosing a kinetic model of a polymer-obtaining process, one is supposed to take into account some specific features absent under modeling of chemical processes in which only low molecular weight compounds are involved. Among such features, the most important is the polydispersity of the products of synthesis and chemical modification of polymers. As a rule, a great variety of macromolecules differing in molecular weight, composition, and chemical structure are simultaneously present in a reactor at any time. Clearly, an exhaustive description of such a reaction system suggests the recourse to statistical approaches. The Nobel Prize winner Paul Flory (1953) was the first who introduced these approaches in polymer chemistry. Later, his ideas gained wide recognition in the theoretical description of many processes of polymer obtaining.

The problem of crucial importance here is revealing the relation between the process mode and the chemical structure of polymer products obtained for this process. The elaboration of general approaches to the solution of this fundamental problem falls within the realm of the statistical chemistry of polymers (see, for example, Kuchanov, 1978, 2000), whose mathematical apparatus is based on the employment of some fields of the applied mathematics. Among them, for instance, is the theory of random processes, the graph theory, the theory of dynamic systems, and some other mathematical disciplines. Their application in modeling of polymerization processes is perfectly indispensable to provide a complete description of polymer products formed. Regretfully, such level of the description of polymers has not been properly addressed so far in the literature devoted to polymerization engineering and polymerization process modeling (Asua, 2007; Beisenberger and Sebastian, 1983; Dotson et al., 1996; Gupta and Kumar, 1987; Meyer Keurentjes, 2005; Rudin, 1982; Seavey and Liu, 2008). This circumstance substantially restricts the possibilities of theoretical prediction of some of their important service properties, especially when polymer products are polydisperse specimens composed of macromolecules varying in chemical composition and topological structure. Success in a quantitative description of the molecular structure of any such specimen and, consequently, the efficiency of the prediction of its properties are predetermined to a great extent by an appropriate choice of the kinetic model of polymer-obtaining process. In this brief review an attempt is undertaken to discuss in the context of the statistical chemistry of macromolecular reactions the strategy of the choice of such a model keeping in mind its employment under mathematical modeling of polymerization processes.

2. MAIN PECULIARITIES OF THE DESCRIPTION OF POLYMERS

Polymer products formed in the course of the synthesis and chemical modification represent an ensemble of individual chemical compounds, the number of types of which is virtually infinite. Macromolecules of these products can differ in the degree of polymerization, tacticity, the lengths and number of branchings, as well as in other characteristics describing the configuration of a macromolecule. In case of copolymers, their macromolecules vary also in composition and the pattern of arrangement of different types of monomeric units. A complete quantitative description of such a system specifying the concentration of all individual compounds of a particular chemical (i.e., primary) structure is mostly impossible. However, for many practical purposes, it is often enough to know only partial distributions of molecules in some of their principal characteristics, such as molecular weight or composition, neglecting a more detailed description of their chemical structure. In other cases, the character of the structure of polymer chains essentially governs some of their physicochemical properties. Here the determination of quantitative characteristics of primary structure of macromolecules becomes indispensable. Generally speaking, the more minute is the quantitative description of a polymer system due to increased number of attributes responsible for the difference between individual macromolecules, the larger is the number of macroscopic properties of this system that can be theoretically predicted. This is because the chemical structure of macromolecules characterized by their composition and configuration carries a specific information on their possible conformations, secondary and supermolecular structures, and, consequently, their physical properties. Finding of quantitative correlations between these properties and the characteristics of the primary structure of macromolecules belongs to the area of the statistical physics of polymers and constitutes one of the three central problems whose solution is indispensable to provide a scientifically grounded prediction for obtaining polymers with desired set of properties. The second problem relevant to the chemical kinetics of macromolecular reactions consists in ascertaining their mechanism and determining the constants of elementary reactions of the processes of polymer obtaining and transformation. Once this problem has been solved, one should choose an appropriate kinetic model of the process. Based on this model, one can calculate the quantitative dependencies of the statistical characteristics of the primary structure of macromolecules on the reactivities of the species involved and the process mode. This review discusses just this, the third problem, which is typical for the statistical chemistry of polymers.

Let us first address linear polymers, whose topological structure is the simplest. Depending on the number m of types of monomeric units, homopolymers ($m = 1$) and copolymers ($m \geq 1$) are distinguished. In the most trivial case, homopolymers' molecules are identified only by number l of constituent monomeric units, whereas the composition of a copolymer macromolecule is characterized by vector $\mathbf{l}$, whose components $l_1,\ldots,l_\alpha,\ldots,l_m$ are equal to the numbers of units of each type. Having identical composition, these molecules can vary in microstructure characterized by the pattern of arrangement of different units along a copolymer chain. Since typical values of the degree of polymerization $l = l_1 + \ldots + l_m$ in synthetic copolymers are 10^2–10^4, the number of possible types of isomers differing in microstructure is considered to be virtually infinite. Evidently, a quantitative description of any such polymer specimen consisting of macromolecules with enormous number of configurations is feasible only through statistical methods.

2.1 Statistical approach

In the framework of a statistical approach, every macromolecule of such a specimen can be unambiguously associated with a certain realization of the stochastic process of conventional movement along the copolymer chain. This movement can be thought of as a succession of stochastic transitions from a unit of the chain to the neighboring one. The type of monomeric unit on each step is determined therewith in accordance with the statistics of the stochastic process describing the polymer specimen of interest. In order to consider the set of the trajectories associated with realizations of infinite length, it is convenient to believe that after the terminal unit of a molecule a trajectory falls into absorbing state to remain there forever. Therefore, to any particular specimen of linear copolymer with m types of units there corresponds a certain stochastic process with discrete time, m regular states, and one absorbing state. In mathematics such a stochastic process is referred to as a chain. The best known among them are the Markov chains (Lowry, 1970), for which the probability $\nu_{\alpha\beta}$ to reach at any step a β-type state is controlled exclusively by type α of the state at the preceding step.

When the attempt to formulate the algorithm of finding the probability of any trajectory of the above-mentioned stochastic process is a success, a statistical description of a copolymer specimen will be exhaustive. For those of them in molecules of which the alteration of units is described by a Markov chain, such an algorithm is trivial. It enables one proceeding from the general theory of these chains to immediately find any statistical characteristics of the Markovian copolymers in terms of elements $\nu_{\alpha\beta}$ of the transition matrix of the corresponding Markov chain. In this case, the peculiar features of particular processes of the synthesis of such copolymers are taken into account only when finding the dependencies of matrix elements $\nu_{\alpha\beta}$ on time, stoichiometric, and kinetic parameters of a reaction system. Hence, mathematical modeling of the products of the synthesis of copolymers with Markovian statistics of units' alteration is trivial. That is why when choosing an appropriate kinetic model of a particular process of obtaining a copolymer, an engineer-researcher should know whether this copolymer is Markovian or not. This question is answered for many practically significant cases (Kuchanov, 1978, 2000).

What is the strategy of the mathematical modeling for non-Markovian copolymers, where the attempt to formulate a general algorithm of the construction of the probability of any individual macromolecule fails? Here the necessity arises to find the statistical characteristics of the chemical structure of a polymer specimen in the framework of a chosen kinetic model for each particular manner of its synthesis. These characteristics can be divided into two groups. Those belonging to the first group describe macromolecules' inhomogeneity in the degree of polymerization l (chemical size) and composition, while the characteristics pertaining to the second group describe their chemical structure.

Among the characteristics constituting the first group is the size–composition distribution (SCD) function $f(\mathbf{l})$, which is equal to the probability that a unit chosen at random pertains to the macromolecule with fixed value of vector $\mathbf{l}$. This distribution is indispensable for constructing a phase diagram of solution or melt of a copolymer (Kuchanov and Panyukov, 1996). This is of crucial importance for the prediction of some of its properties, for example, the transparency. Its loss in the course of the synthesis of polymers can occur as a result of the phase separation in a reaction system induced by chemical transformations. Such a transformation is due to increasingly more pronounced composition inhomogeneity of the copolymer being formed. This assertion is rigorously theoretically substantiated (Kuchanov and Panyukov, 1996, 1998) and ensues from the formula relating the heat of mixing of a copolymer solution with the elements of the covariance matrix of composition distribution (CD). The latter can be measured by chromatographic methods (Glockner, 1991) and compared with the distribution calculated in the framework of the model chosen.

Statistical characteristics belonging to the second group describe the microstructure of copolymer molecules. If these are linear, such characteristics are fractions $P\{U_k\}$ (probabilities) of sequences $\{U_k\}$ involving k monomeric units (Koenig, 1980). The simplest here are dyads $\{U_2\}$, the overall set of which for a binary copolymer comprises four pairs of units $M_1M_1, M_1M_2, M_2M_1, M_2M_2$. The number of k-ad types in chains of m-component copolymer grows exponentially as m^k, so that in practice a researcher has to confine his consideration to sequences $\{U_k\}$ with small values of k. Their calculation is highly useful under mathematical modeling of any processes of copolymer obtaining by two reasons: Firstly, some of their important service characteristics are expressed through the fractions of these sequences. So, it is a common practice to use semiempirical relationships connecting the glass transition temperature of copolymers with the fractions of dyads in their macromolecules (Guillot and Emelie, 1991). Secondly, probabilities $P\{U_k\}$ can be determined for $k=2$–4 by spectroscopic methods with high degree of accuracy (Tonelli, 1989). The comparison of these experimental data with the results of mathematical modeling calculated in the framework of the kinetic model permits judging its adequacy for the description of the process under consideration.

Along with the isomerism of linear copolymers due to various distributions of different monomeric units in their chains, other kinds of isomerisms are known. They can appear even in homopolymer molecules, provided several fashions exist for a monomer to enter in the polymer chain in the course of the synthesis. So, asymmetric monomeric units can be coupled in macromolecules according to "head-to-tail" or "head-to-head"—"tail-to-tail" type of arrangement. Apart from such a constitutional isomerism, stereoisomerism can be also inherent to some of the polymers. Isomers can sometimes substantially vary in performance properties that should be taken into account when choosing the kinetic model. The principal types of such an account are analogous to those considered in the foregoing. The only distinction consists in more extended definition of possible states of a stochastic process of conventional movement along a polymer chain.

2.2 Microstructure parameters

The microstructure of polymer chains is frequently more convenient to characterize by parameters representing some combinations of probabilities $P\{U_k\}$, rather than by such probabilities themselves. As an example, considering a binary linear copolymer it is convenient to use as such a parameter the coefficient of microheterogeneity K_M. For copolymers consisting of long blocks, the value of K_M is close to zero, whereas for regularly alternating copolymer $K_M=2$. Between these two extreme cases corresponding to a perfectly ordered distribution of monomeric units in copolymer macromolecules, there fall all possible values of the coefficient of microheterogeneity. Value $K_M = 1$ corresponds to the most disordered (random) sequence distribution, described by the Bernoullian stochastic process. Consequently, the modulus of the deviation of K_M from unity allows one to quantitatively estimate the degree of ordering of the sequence distribution in chains of a binary copolymer. Essentially, the sign of this deviation testifies to the inclination of units either to regular alternation (if $K_M > 1$) or to the formation of long blocks of both types of units (if $K_M < 1$).

The coefficient of microheterogeneity has been introduced for the description of the microstructure of binary copolymers with symmetric units (Korshak et al., 1976). At larger number of types of units and/or when the structure isomerism is taken into account, the role of K_M will be played by other analogous parameters. A general strategy of the choice of these latter is developed in detail (Korolev and Kuchanov, 1986), while their values are measured by the nuclear magnetic resonance (NMR) spectroscopy technique for a number of polycondensation polymers (Vasnev et al., 1997).

It should be emphasized that for the Markovian copolymers, the knowledge of these structure parameters will suffice for finding the probabilities of any sequences $\{U_k\}$, i.e., for a comprehensive description of the structure of the chains of such copolymers at their given average composition. As for the CD of the Markovian copolymers, for any fraction of l-mers it is described at $l \gg 1$ by the normal Gaussian distribution with covariance matrix, which is controlled along with l only by the values of structure parameters (Lowry, 1970). The calculation of their dependence on time and on the kinetic parameters of a reaction system enables a complete statistical description of the chemical structure of a Markovian copolymer. It is obvious therewith to which extent a mathematical modeling of the processes of the synthesis of linear copolymers becomes simpler when the sequence of units in their macromolecules is known to obey Markov statistics.

2.3 Chemical correlators

Along with the traditional manner of the description of the chemical structure of linear copolymers by means of the hierarchy of probabilities $P\{U_k\}$ of sequences of units $U_k (k = 1,2,\ldots)$, there is one more mode of the description of this structure. It is based on the consideration of the hierarchy of chemical correlation functions (so-called *chemical correlators*) (Kuchanov, 1978, 2000). The simplest among them, $Y_{\alpha\beta}(k)$, has the meaning of probability to find two randomly chosen monomer units of types α and β divided along a macromolecule by any sequence U_k consisting of k units. This two-point correlator is of the utmost importance because its generating function enters into the expression for spinodal (Kuchanov, 1992), where the spatially homogeneous state of a polymer liquid becomes absolutely unstable. An arbitrary representer of the hierarchy is the n-point chemical correlator $Y_{\alpha_1}\ldots\alpha_2(k_1,\ldots,k_{n-1})$, which equals the probability of finding in a macromolecule n monomeric units whose types are α_1, $\ldots,\alpha_n$ divided by $(n-1)$ sequences $U_{k_1},\ldots,U_{k_{n-1}}$ comprising $k_1,\ldots,k_{n-1}$ units, respectively (Panyukov and Kuchanov, 1992). Generating functions of such correlators play a key role in the theory of microphase separation in solutions and blends of block copolymers (Kuchanov, 2007). Therefore, the approach commonly accepted in statistical chemistry, which rests on the consideration of chemical correlators, permits a theoretical prediction of the dependence of the phase behavior of heteropolymer liquids on chemical structure of their macromolecules.

3. SPECIFICITY OF THE DESCRIPTION OF BRANCHED POLYMERS

Only polymers of linear structure have been discussed in the foregoing. Nevertheless, a variety of polymers exist with other topological configurations of macromolecules. The most commonly encountered among them are comblike, starlike, treelike, and network polymers. The feature peculiar to all of them is the presence of branching units and adjoining polymer chains. Any molecule of such a polymer can be schematically presented as a molecular graph with vertices and edges corresponding to branching units and polymer chains, respectively. If these latter consist of monomeric units of a single type, they can be marked by ascribing to each edge the number equal to the length of corresponding chain. Every macromolecule of branched or cross-linked homopolymer is associated with a marked molecular graph, whereas a set of such graphs corresponds to a particular macroscopic specimen. Its exhaustive statistical description is performed by specifying the probability measure on the set of all marked graphs. For starlike and comblike polymers, the finding of the above-mentioned probability distribution involves no difficulties of principal character, since the topology of their molecules is fixed unlike the statistically branched treelike and cross-linked network polymers with random topology of molecules. When calculating average geometric sizes of macromolecules of such polymers, their optical properties, viscosity, and some other characteristics, the necessity arises to make an averaging procedure over topological configurations of macromolecules.

3.1 Stochastic branching process

The probability measure on the set of such configurations can be constructed for some classes of statistically branched polymers whose molecules do not contain cycles. Each of them is associated with the molecular graph referred to as tree, while to the whole polymer specimen the set of such trees, termed molecular forest, corresponds. The latter can be transformed into the forest of rooted trees which are obtained from molecular trees by sequential sampling of each of their vertex as a root. Such a transformation retains the probability measure, so that the probability distribution of rooted trees is the only thing which remains to be found. Each of them can be viewed, in turn, as a genealogical tree describing the history of some family. Besides, a rooted tree can be associated with some realization of stochastic branching process describing "birth and death" of particles. The simplest among them is the Galton–Watson process, in which the distribution of the probability for a particle to give birth to a fixed number of "children" particles is the same in every generation, being independent of other particles (Harris, 1963). Gordon (1962) was the first who discovered that for some polycondensation branched polymers (which below will be referred to as Gordonian polymers) the probability distribution of the rooted trees is described by the probability measure on the set of genealogical trees representing the realizations of the Galton–Watson branching process. The theory of these stochastic processes has been thoroughly developed (Harris, 1963), which makes it possible in a relatively simple manner to express any statistical characteristics of a Gordonian polymer in terms of the probability parameters of the corresponding branching process (Kuchanov, 1978, 2000). The only thing which remains to be done consists in establishing the dependencies of these parameters on time, constants of elementary reactions, and composition of the initial monomer mixture. The equations for finding the above dependencies have been derived for a variety of Gordonian polymers (Kuchanov, 1978). Clearly, a special role of the latter among randomly branched polymers resembles that of Markovian copolymers among linear ones.

A simple algorithm (Kuchanov et al., 1988) enables one to determine the probability of any fragments of macromolecules of the Gordonian polymers. Their comparison with the NMR spectroscopy data permits estimating the adequacy of the chosen kinetic model of the process of synthesis of a particular polymer specimen. These probabilities also enter in the expressions for the glass transition temperature and some structure-additive properties of randomly branched polymers (Chompff, 1971).

3.2 Gelation

A special feature of a process of branched polymer formation is the possibility of the appearance in the reactor of a macroscopic structure whose size is comparable with that of the reactor. The main peculiarity of such a phenomenon, known as gelation, is that the range of conversions at which an abrupt increase of the viscosity occurs is rather narrow. That is why gelation can be regarded as a phenomenon proceeding at a certain moment, referred to as gel point. After this moment, the increase of the weight fraction of gel ω_G in the course of the process is accompanied by the decrease of the weight fraction ω_S of sol molecules. The prime objectives of the mathematical modeling of branched polymerization and polycondensation as well as of the processes of cross-linking of macromolecules are the calculation of the gel point and the determination of the dependence of $\omega_G = 1 - \omega_S$ on conversion. If monomeric units of several types are involved, analogous dependencies for compositions of sol and gel should be additionally calculated. The gel is a polymer network normally exhibiting elastic properties. According to the theory (Flory, 1976), the elasticity modulus of this network is governed by the cyclic rank of its molecular graph. This characteristic of a graph is equal, by definition, to the minimal number of its edges to be deleted in order to transform this cyclic graph into treelike one. Obviously, calculation of the cyclic rank, pertaining to the most essential characteristics of the topological structure of a polymer network, is among the most challenging problems of the mathematical modeling of network polymers. Its solution, along with that of the abovementioned problems of calculation of the statistical characteristics of the Gordonian polymers, can be found by means of the mathematical apparatus of the theory of branching processes.

4. KINETIC MODELS OF MACROMOLECULAR REACTIONS

When deriving a material balance equation, the rate of transformation of each component in a reactor is normally governed by the mass action law. However, unlike for the reactions in which only low molecular weight substances are involved, the number of such components in a polymer system and, consequently, the number of the corresponding kinetic equations describing their evolution are enormous. The same can be said about the number of the rate constants of the reactions between individual components. The calculation of such a system becomes feasible because certain general principle can be invoked under the description of the kinetics of the majority of macromolecular reactions. Let us discuss this principle in detail.

4.1 Ideal kinetic model

The processes of the formation and transformation of polymer molecules proceed as a result of chemical reactions of their active centers, whose role can be played by functional groups, free valences in radicals, double bonds, and so on. Often, it may be suggested that the reactivity of the active center in a polymer molecule is controlled neither by its configuration (i.e., molecular weight, composition, structure) nor by the location of this center in the molecule. This fundamental principle, advanced first by Flory (1953) and bearing his name, permits considering the rate constant of the elementary reaction of any active centers of given types as being the same. That is why the number of such elementary reactions in a particular process is usually small enough, which enables it to be characterized just by a few kinetic constants. So, the process of radical polymerization is described by the rate constants of elementary reactions of initiation, propagation, and termination of a chain.

The Flory principle makes it possible in a simple way to relate the rate constants of the reactions of macromolecules (whose number is infinite) with the corresponding rate constants of elementary reactions. Since according to this principle all chemically identical active centers are kinetically indistinguishable, the rate constant of the reaction between any two molecules is proportional to the rate constant of the reaction between their active centers and numbers of these centers in reacting molecules. Therefore, only a few rate constants of elementary reactions will enter in the material balance equations as kinetic parameters.

The Flory principle is one of two main assumptions underlying the *ideal* kinetic model of any processes of synthesis and chemical modification of polymers. The second assumption is the neglect of the reaction between any active centers belonging to the same molecule. Clearly, in the absence of such intramolecular reactions, molecular graphs of all components of a reaction system will not contain cycles. The last affirmation applies just to sol molecules. As for the gel, in the framework of the ideal model, the cyclization reaction is admissible.

4.2 Models allowing for the deviations from ideality

The Flory principle, whose validity has been established for a wide range of polyreactions, is rather good approximation for the description of the kinetics of many processes of polymer obtaining. However, a considerable body of experimental results is currently available concerning a number of macromolecular reactions where this principle is deliberately violated. Possible reasons for the deviations from this principle can be attributed to the short- or long-range effects (Kuchanov, 2000).

Among the first of them are the so-called substitution effects due to steric, induction, catalytic, or some other types of influence of the reacted active centers on the reactivity of neighboring unreacted centers. In order to take account of such short-range effects it has been suggested (Kuchanov, 1978) to use under mathematical modeling an *extended* Flory principle. In line with this principle, the reactivity of any active center of a molecule is supposed to be controlled exclusively by local chemical structure of the fragment involving this center and changes in the course of the process due to the alteration of the local structure caused by the entry in the reaction of the neighboring active centers. The effect of other factors on the reactivity therewith may well be neglected. In the framework of the models of such a kind, the fragments of molecules comprising the active centers should be chosen as kinetically independent elements rather than these centers themselves, as it is normally done in case of the ideal model. Under such an approach employed for the mathematical modeling of the processes of copolymerization, co-polycondensation, and polymer-analogous transformations, the number of kinetic parameters characterizing the model chosen is rather small.

The polymer nature of reagents is the most strongly pronounced in the long-range effects at which the reactivity of the active center of a macromolecule is acted upon by the fragments situated in all its parts. An example is intramolecular catalysis by functional groups spaced apart from the active center in a macromolecule but falling in the vicinity of this center as a result of spatial conformational rearrangements of the polymer chain (Plate et al., 1995). In the presence of such effects, the reactivity of its terminal active center can be controlled by the degree of polymerization of this macromolecule and the distribution along polymer chain of units containing catalytic groups. In case of fast reactions, like recombination of macroradicals, the dependence of the rate constant on their lengths owes its existence to the diffusion factors (Allen and Patrick, 1974). Sometimes thermodynamic reasons can be responsible for the appearance of the long-range effects in the course of macromolecular reactions. An example is the appearance at the initial stages of copolymerization of the dependence of the rate of the growth of a macroradical on its length and composition. The origin of this phenomenon is connected with the fact that the monomer mixture composition differs inside and outside a macroradical due to the preferential sorption of monomers of different types (Harwood, 1987; Semchikov, 1996). The allowance for long-range effects in choosing a kinetic model of the processes of polymer synthesis, complicating to certain extent the calculations, proves to be sometimes indispensable for the treatment of experimental data.

5. METHODS OF CALCULATIONS

Calculating the statistical characteristics of the primary structure of macromolecules, a researcher usually faces the problems of finding their average molecular weight, composition, molecular weight distribution (MWD), and SCD, as well as the characteristics of their chemical structure. To tackle these problems, two different approaches, namely, kinetic and statistical, are generally invoked. The first consists in deriving and solving the material balance equations for the concentrations of molecules of all types involved in the process under consideration. Under the second approach, the most general formulation of which has been proposed in a monograph by Kuchanov (1978), every macromolecule is conceived as an individual realization of a particular stochastic process of conventional movement along polymer chain. The probability of this realization is equal to the fraction of corresponding molecules in the reactor. In the framework of such a method, for the calculation of the statistical characteristics of polymers the averaging procedure is performed over realizations of the corresponding stochastic process instead of averaging over macromolecules. Methods of such an averaging for some of these processes are perfectly developed, which makes it possible to find the required characteristics of the Markovian and Gordonian polymers in a relatively simple way.

5.1 Statistical method

Both statistical and kinetic methods of calculation of the parameters of a polymer's primary structure naturally have advantages as well as shortcomings. Nobel Prize winner Paul Flory was the first who, as early as in late 1930s, proposed (Flory, 1953) to resort to the statistical method for the calculation of the kinetics of the reactions with participation of macromolecules. This method has found an extensive application in the quantitative description of a variety of particular processes of obtaining and chemical modification of polymers. An indisputable advantage of the statistical method is its ability to exhaustively describe in a straightforward manner a detailed structure of macromolecules in terms of few probability parameters. However, the issue of specifying appropriate stochastic processes for the quantitative description of the products of a particular process cannot in principle be settled in the framework of the statistical method itself, whose application in all its modifications is, in essence, of a formal character. Expressions for the statistical characteristics of polymers therewith are traditionally obtained by speculative probabilistic reasoning, whose correctness is predetermined to a great extent by the author's intuition. Naturally, adhering to such a formal statistical approach, a scientist cannot rigorously establish a strict correspondence between the kinetic model of the process of polymer synthesis and the type of the stochastic process adequately describing the statistical characteristics of macromolecules formed. This, generally speaking, makes the issue of the areas of applicability of the statistical method an open question. Only the kinetic approach provides an answer to this question, enabling one to simultaneously express the probability parameters of this stochastic process through kinetic constants, reagents' concentrations, and other variables describing the process at hand.

With this in mind, a general strategy has been developed (Kuchanov, 1978, 2000) implying a rigorous (in the framework of the models generally accepted today in polymer chemistry) substantiation of the statistical method for the calculation of different classes of polymerization processes proceeding from their kinetic consideration. Expressions for the distribution of macromolecules in size and composition, arrived at as a result of such a consideration, are compared with the analogous expressions derived in the framework of the theory of stochastic processes. The coincidence of corresponding distributions argues for the applicability of the chosen variant of the statistical approach. Under such a comparison, the dependencies of the probability parameters of the stochastic process on stoichiometric and kinetic parameters of a reaction system are simultaneously revealed. At the next stage, the possibility appears to calculate in the framework of the statistical approach necessary statistical characteristics controlled by the chemical structure of polymer molecules. This general strategy has been successfully applied under mathematical modeling of different polymers obtained by free-radical copolymerization (Kuchanov, 1992, 2000), polycondensation (Kuchanov, 2000; Kuchanov et al., 2004), and chemical modification of macromolecules (Kuchanov, 1996, 2000).

5.2 Kinetic method

The kinetic method turns out to be especially efficient in the mathematical modeling of the processes of obtaining of polymers describable by the ideal kinetic model. In this case, the material balance equations for the concentrations of polymer molecules containing fixed numbers of monomeric units and active centers often can be integrated analytically using the method of generating functions (Kuchanov, 1978). Such a function is completely equivalent to the distribution of concentrations of molecules in size, composition, and functionality (SCF distribution), which can be obtained as coefficients of the series expansion of the generating function. This proves to be especially convenient for the calculation of the statistical moments of the SCF distribution, which are expressed through the derivatives of the generating function at a single point when the values of all its arguments are unity. An infinite set of ordinary differential equations for the distribution of concentrations of polymer molecules in case of the *ideal* kinetic model is reduced to one equation for the generating function. It will be ordinary differential equation or the first-order partial differential equation, depending on whether linear or branched polymers are formed in the course of the process of interest. Along with the rate constants of elementary reactions, the coefficients of this equation are controlled by average concentrations of the active centers and low molecular weight reagents. They can be found from the solution of a set of differential equations, which is always closed under the applicability of the ideal kinetic model since the elementary reactions can be considered in its framework separately from polymeric reactions. In many cases of practical importance, a partial differential equation for the generating function is possible to integrate analytically using the method of characteristics.

When the statistical moments of the distribution of macromolecules in size and composition (SC distribution) are supposed to be found rather than the distribution itself, the problem is substantially simplified. The fact is that for the processes of synthesis of polymers describable by the ideal kinetic model, the set of the statistical moments is always closed. The same closure property is peculiar to a set of differential equations for the probability of arbitrary sequences $\{U_k\}$ in linear copolymers and analogous fragments in branched polymers. Therefore, the kinetic method permits finding any statistical characteristics of loopless polymers, provided the Flory principle works for all chemical reactions of their synthesis. This assertion rests on the fact that linear and branched polymers being formed under the applicability of the ideal kinetic model are Markovian and Gordonian polymers, respectively.

5.3 Extension of statistical and kinetic methods

These important properties are not peculiar to polymers synthesized in reaction systems, which are describable by *nonideal* kinetic models. Nevertheless, for some of them, in which the deviations from ideality are due to the short-range effects, the modern approaches of the statistical chemistry permit formulating a rather general algorithm by means of which any characteristics of the chemical structure of such polymers can be calculated. Underlying to this algorithm is the Flory principle in its extended formulation that makes possible to write down kinetic equations for the reagents in closed form. Using these equations it is usually possible to substantiate rigorously the correctness of the recourse to a particular version of the statistical method in order to provide an exhaustive description of the chemical structure of polymer products. Noteworthy, the stochastic processes engaged in such a description are characterized by the states having some additional attributes in comparison with those peculiar to the states of Markovian or Gordonian polymers.

For example, under kinetic modeling of “living” anionic copolymerization in the framework of the terminal model, a macromolecule is associated with the realization of a certain stochastic process. Its states (α,τ) are monomeric units, each being characterized along with chemical type α and also by some label τ. This random quantity equals the moment when this monomeric unit entered in a polymer chain as a result of the addition of α-type monomer to the terminal active center. It has been rigorously shown (Kuchanov et al., 2002) that a stochastic process of conventional movement along macromolecules whose units are labeled in such a way is Markovian. Besides, the expressions for the transition probabilities between successive states of this process have also been derived there. This makes possible in principle to find any statistical characteristics of the chemical structure of macromolecules with labeled units. Once these characteristics are found, they should be averaged over the probability distribution of random quantity τ, which can be formally interpreted as "erasing" of labels. As a result, statistical characteristics of real copolymers with non-Markovian statistics of the succession of units in macromolecules can be found (Kuchanov et al., 2002).

The above-described "labeling-erasing" procedure is in common use in statistical chemistry of polymers (Kuchanov, 2000). It gives a chance to obtain a number of important theoretical results under kinetic modeling of polymerization and polycondensation processes, where the deviation from their description in terms of the ideal kinetic model is due to the short-range effects.

A different situation arises when in the kinetic model any long-range effects should be taken into account. As a rule, no results can be achieved here analytically. As for the equations for the statistical moments of SC distribution and for the fractions of the fragments of macromolecules, they are not closed as it takes place for the ideal model. Hence, finding of these statistical characteristics implies the necessity of a numerical solution of the material balance equations for concentrations of molecules with fixed numbers of monomeric units and active centers. Here the problem of the solution of an infinite set of equations arises. To escape this problem one is supposed to switch from discrete variables characterizing the size and composition of macromolecules to continuous variables. Under such a transition, the mathematical problem is reduced to the solution of a single integro-differential equation containing partial derivatives.

Of considerable promise for mathematical modeling of macromolecular reaction is the Monte Carlo method (Lowry, 1970). It consists in modeling the dynamics of any particular process of polymers' obtaining by means of statistical tests, which obey the probability laws corresponding to the kinetic model chosen. Subsequent averaging over all computer-simulated realizations of this stochastic process enables one, in principle, to find any statistical characteristics of synthesized polymers. The Monte Carlo method is particularly effective when polymers are not Markovian or Gordonian. This method makes possible a direct computer simulation of particular macromolecular reactions, avoiding thus the derivation and solution of corresponding kinetic equations which can be either too complicated or even cannot be derived at all. The method of computer simulations has already found its application for calculations of the statistical characteristics of the products of some processes of polymer synthesis and chemical modification (Lowry, 1970; Motoc and O'Driscoll, 1981; Plate et al., 1995). However, its potentialities in this area are still far from being exhausted.

6. SOME GENERAL THEORETICAL RESULTS

In this section, some general results are reported of the theoretical consideration of the main processes of polymer synthesis in the framework of different kinetic models. This information could be of assistance to an engineer-researcher in making a scientifically grounded choice of such a model.

6.1 Polycondensation

Functional groups play here the role of active centers. If their number in each monomer is two, only linear macromolecules will be obtained as a result of the synthesis. In order to prepare branched and network polymers, among monomers involved those having three and more functional groups should be present.

The quantitative theory of polycondensation processes describable by the ideal kinetic model may be thought of as completed (Kuchanov et al., 2004). So, it has been found (Kuchanov, 1976) that the sequence distribution in the products of joint polycondensation of any set of bifunctional monomers is described by a certain Markov chain. Its parameters are related in a known way with the reactivity of the functional groups and the initial stoichiometry of monomers. As for branched polymers, a branching process has been developed and rigorously kinetically substantiated (Korolev et al., 1981; Kuchanov, 1978) to describe the products of co-polycondensation of arbitrary mixture of monomers, each comprising any numbers of functional groups of arbitrary types. Every type of reproducing particles of this branching process is associated with a particular type of reacted functional groups. These results have been extended (Kuchanov, 1987) to arbitrary multistage processes in the course of which the reactive oligomers first form, cross-linking then to generate a network polymer. Here the statistical characteristics of both intermediate and final products turn out to be describable by the formulas of branching process with properly chosen probability parameters. Being universal, this fundamental property manifests itself in polycondensation processes conducted in any number of steps with possible arbitrary alteration of temperature and/or catalyst's concentration during the cross-linking stage (Kuchanov et al., 2004, 1987).

Many service properties of the products of cross-linking of reactive oligomers are essentially controlled by their distribution in functionality types (Entelis et al., 1989). This important statistical characteristic of forepolymers obtained in the first stage can be found for polycondensation of any monomer mixture by known formulas (Korolev et al., 1981; Kuchanov, 1976).

The statistical method allows a mathematical modeling of branched polycondensation describable by the ideal kinetic model not only before the gel point but also after it. A complete statistical description of sol molecules is performed by the same branching process as before the gelation point but with the values of the probability parameters renormalized in a certain way (Korolev et al., 1981; Kuchanov, 1978). As for gel, not only local characteristics of its topological structure can be calculated but also global ones. Among these latter is the cyclic rank of the molecular graph of polymer network, whose value controls its elasticity properties (Kuchanov, 1987). The quantitative theory of branched polycondensation enables one, in particular, to predict the moment of gelation, to describe the evolution of compositions of sol and gel, as well as to calculate in each of them the conversions of functional groups of all types (Korolev et al., 1981).

The above reasoning allows a conclusion that once a researcher has decided upon the particular ideal kinetic model of polycondensation, he or she will be able to readily calculate any statistical characteristics of its products. The only thing he or she is supposed to do is to find the solution of a set of several ordinary differential equations for the concentrations of functional groups, using then the expressions known from literature.

Addressing now nonideal kinetic models, it should be emphasized that for those of them which allow for the short-range effects, the quantitative theory of polycondensation is developed reasonably well (Kuchanov et al., 2004). The most typical manifestation of such effects is the change in the reactivity of the second functional group in a bifunctional monomer caused by the entry in the reaction of the first group. This “substitution effect” is known to be peculiar to many aromatic monomers (Allen, 1988; Sokolov, 1979). It has been theoretically established (Kuchanov, 1979) that the participation of such monomers in linear co-polycondensation can result in the formation of non-Markovian copolymers. A criterion has been formulated (Kuchanov, 1979) for deciding whether the substitution effect in some monomers violates the Markovian statistics of the succession of units along polymer chains. An analogous criterion has been suggested (Kuchanov, 1979) for mathematical modeling of a branched polycondensation. It permits specifying the conditions under which the polymers formed will be Gordonian despite the involvement of monomers with kinetically dependent groups. Mathematical modeling in this case is performed in such a simple manner as that for the ideal model.

Somewhat more complicated is the modeling of a branched polycondensation of monomers with kinetically dependent groups, the products of which represent Gordonian polymers (Kuchanov et al., 2004). Their chemical structure can be exhaustively described by means of the “labeling-erasing” procedure based on the results of work by Kuchanov and Zharnikov (2003). Those authors, when writing down the material balance equations for polymer molecules in line with the extended Flory principle, have chosen the monads (i.e., monomeric units with adjacent functional groups) as kinetically independent elements. At such a level of detail, a polymer molecule is completely characterized by the numbers of constituting monads of different kinds. The analysis of the equation for the generating function of distribution of molecules in a number of monads brought Kuchanov and Zharnikov (2003) to the conclusion about the existence of a general branching process (Harris, 1963), which permits finding any characteristics of the products of a polycondensation of monomers with kinetically dependent groups. Reproducing particles of this process is associated with the reacted functional groups, each being supplied by a pair of labels, discrete and continuous ones. The first of them denotes the kind of a monad incorporating the functional group under consideration before its entry into a condensation reaction. The second label designates a moment at which this reaction occurred. Having performed these labels’ “erasing,” one can find, in particular, the dependence of statistical characteristics of the polymer network of a gel responsible for its elasticity properties on the conversion of functional groups (Kuchanov and Zharnikov, 2003).

Further progress of a general theory of branched polycondensation of monomers with kinetically dependent groups is connected with allowance for the effect of monomer configuration on the change of their reactivity due to the entry of the neighboring groups into a reaction. An account of this factor, first realized in Kuchanov et al. (2006), calls for the extension of the traditional kinetic model of the “substitution effect.” In this publication, the validity of the statistical method for the complete description of the chemical structure of the products of branched polycondensation proceeding under the applicability of the above-mentioned model has been rigorously substantiated. The recourse to this method enables the allowance for the configurational effects when calculating any statistical characteristics of sol and gel (Kuchanov et al., 2006).

6.2 Conventional free-radical copolymerization

The active centers in this process are free radicals, whose reaction with double bonds of monomers leads to the growth of a polymer chain. In the framework of the ideal kinetic model, the reactivity of a macroradical is exclusively governed by the type of its terminal unit. According to this model, the sequence distribution in macromolecules formed at any moment is described by the Markov chain with elements controlled by the instantaneous composition of the monomer mixture in the reactor as well as by the reactivity ratios whose values were tabulated for hundreds of particular monomeric pairs (Eastmond and Smith, 1976; Greenley, 1980). Since the above composition changes during the synthesis, the final products certainly will not be Markovian copolymers representing a mixture of such copolymers formed at different moments of this process. The quantitative theory of copolymerization of an arbitrary number of monomers, describable by the ideal model, is thoroughly elaborated (Kuchanov, 1992). It has been shown (Kuchanov, 1992; Kuchanov et al., 1989; Yakovlev and Kuchanov, 2000) how its application provides the possibility to predict by means of mathematical modeling the transparency and thermostability of industrial terpolymers.

The allowance for the short-range effects has been carried out in two types of kinetic models (Kuchanov, 1992). In the first of them, the reactivity of a macroradical is presumed to be dependent on the types of n monomeric units preceding the terminal one. Here the mathematical formalism differs from that used in the case of the ideal model only in one point. The states of the Markov chain are associated in the framework of these models with monomeric units, each supplied by the label specifying the type of sequence $\{U_n\}$ of units acting upon the reactivity of the active center.

The second type of nonideal models takes into account the possible formation of donor–acceptor complexes between monomers. Essentially, along with individual entry of these latter into a polymer chain, the possibility arises for their addition to this chain as a binary complex. A theoretical analysis of copolymerization in the framework of this model revealed (Korolev and Kuchanov, 1982) that the statistics of the succession of units in macromolecules is not Markovian even at fixed monomer mixture composition in a reactor. Nevertheless, an approach based on the "labeling-erasing" procedure has been developed (Kuchanov et al., 1984), enabling the calculation of any statistical characteristics of such non-Markovian copolymers.

Under copolymerization of some monomers, a number of anomalies have been experimentally revealed (Semchikov et al., 1990a, 1990b, 1996) which cannot be explained in the framework of the above-discussed traditional kinetic models. Among such anomalies are the dependence of a copolymer composition on its molecular weight as well as a strongly pronounced intramolecular inhomogeneity of polymer chains. In order to provide an explanation for these anomalies, a new model taking into account the phenomenon of the preferential sorption of monomers by growing macroradicals has been put forward (Kuchanov and Russo, 1997). Evidently, the monomer mixture composition inside each of them differs, generally speaking, from its value in bulk of the reactor because of the physical interactions of monomers with monomeric units of a polymer chain. That is why the monomer mixture composition inside a macroradical will be controlled by its composition, i.e., the rate of the monomers' addition to the active center will be predetermined not only by its neighboring units but also by all units of a polymer chain. The allowance for such long-range effects in the kinetic model of copolymerization permits the explanation of the anomalies observed and, in particular, the intramolecular inhomogeneity of polymer products (Kuchanov and Pogodin, 2008; Kuchanov and Russo, 1997).

It should be emphasized that performing mathematical modeling of a copolymerization in systems where the preferential sorption of monomers plays a decisive role, it is not enough to confine the consideration to the kinetic equations describing the growth of macroradicals. They should be complemented with thermodynamic expressions establishing the dependence of monomers' concentrations in the vicinity of the active center of a macroradical on its chemical size and composition, as well as on concentrations of monomers in bulk of the reactor. The joint solution of the equations of chemical kinetics and interphase equilibrium provides the possibility to calculate both the rate of polymerization and the characteristics of the molecular structure of the copolymer. The results of such a calculation (Kuchanov and Pogodin, 2008; Kuchanov and Russo, 1997) testify to the efficiency of combining the approaches of statistical chemistry and thermodynamics of polymers to tackle the problems of utmost practical importance.

6.3 Chemical modification of polymers

Potentialities of the statistical chemistry for the description of such processes can be illustrated by consideration of polymer-analogous reactions (PARs) of a linear homopolymer (Plate et al., 1995) whose macromolecules comprise in each monomeric unit A a reactive functional group. Its reaction with a low molecular weight compound results in transformation of unit A into unit B. Successive transformations of such a kind lead to the formation in a reaction system of heteropolymer macromolecules varying in composition and in pattern of arrangement of A and B units. As an example of PARs, we might mention the esterification of polymethacrylic acid and saponification of polyvinyl acetate. In the course of the first of these reactions, carboxyl groups transform into ester ones, whereas for the second reaction acetate groups transform into hydroxyl ones.

If the rate constant k of the elementary reaction of transformation $A \rightarrow B$ is supposed to be the same for all groups, the pattern of arrangement of units in macromolecules will be perfectly random. However, such an ideal kinetic model is not appropriate for a vast majority of real polymers because of the necessity to take into consideration under mathematical modeling of PARs proceeding in their macromolecules the short-range and long-range effects. The easiest way to take account of the first of them is to resort to the "neighboring-group" (NG) model (Kuchanov, 1978; Plate et al., 1995), according to which the rate constant of an elementary reaction of an arbitrary functional group depends solely on the types of two adjacent monomeric units. This model is characterized by three rate constants k_0,k_1,k_2 of elementary reaction of the groups in unit A whose nearest neighbors are, respectively, 0,1,2 units B. Kinetically independent fragments here are triads of units. Surprisingly, even such simplest model invokes for its solution a rather sophisticated mathematical apparatus (Kuchanov, 1996). Difficulties emerging thereby originate from the non-Markovian character of the distribution of monomeric units along macromolecules. However, these difficulties have been successfully overcome, which made possible to solve rigorously in the framework of the NG model the problems of finding both the CD of heteropolymers formed in the course of PAR (Brun et al., 1982; Flory, 1953; Kuchanov and Brun, 1976, 1983) and the structure of their macromolecules (Brun and Kuchanov, 1977; Flory, 1953; Kuchanov and Aliev, 1997; Noa et al., 1973; Plate et al., 1974). A detailed description of the quantitative theory of PAR is presented in the review articles (Ewans, 1993; Kuchanov, 1996).

The statistical characteristics of the products of PAR are significantly affected by the thermodynamic quality of the solvent with respect to the polymer. This influence is especially strongly pronounced in dilute solutions, where every macromolecule can be considered individually. The above-outlined theory of PAR is relevant to the case of a thermodynamically good solvent, when macromolecules are in coil-conformational state (Grossberg and Khokhlov, 1994). Here the concentration of a low molecular weight reagent z in the vicinity of reactive centers (i.e., functional groups) coincides with the concentration of this reagent throughout the reactor.

A completely different situation takes place when PAR proceeds in moderately poor solvent. In such systems, macromolecules are in a conformational state of globules inside which the density of units is not high enough to hamper the diffusion of reagent z into the globular nanoreactor. At the same time, this density appreciably exceeds the density of units in the polymer coil. This can be responsible for the strongly pronounced influence of preferential sorption of reagent z on the kinetics of PAR (Kuchanov et al., 2008). As the thermodynamic quality of the solvent deteriorates, the density of monomeric units in a globule increases, leading to hindering of the diffusion of low molecular weight reagent inside nanoreactors. This density can become so high in a poor solvent that PAR will proceed in the diffusion-controlled regime instead of a kinetically controlled one. In line with theoretical analysis (Kuchanov and Khokhlov, 2003; Kuchanov et al., 2003), the chemical structure of macromolecules obtained in nanoreactors in these two regimes of PAR will substantially differ even under the applicability of the ideal kinetic model. Thus, the chemical structure of heteropolymers formed in a diffusion-controlled regime is described by a rather sophisticated stochastic process of conventional movement along macromolecules, which resembles in a manner that describing the chemical structure of some biological macromolecules (Kuchanov and Khokhlov, 2003).

7. EFFECT OF HYDRODYNAMIC STIRRING IN A REACTOR ON SOME SERVICE PROPERTIES OF POLYMER PRODUCTS

7.1 General discussion

It has been experimentally established that the mechanical and physicochemical properties of the products of the synthesis or chemical modification of polymers obtained by batch and continuous methods can markedly differ despite the similarity of temperature and hydrodynamic regimes. Essentially, the character of hydrodynamic stirring in a continuous reactor can substantially affect the service properties of polymer products prepared. That is why designing continuous polymer processes an engineer is supposed to perform an in-depth examination of the dependence of polymer product quality on the regime of stirring in a reactor. The reason is that the properties of commercial polymers can essentially differ from those of polymers synthesized on the laboratory scale. This section is devoted to the consideration of some general aspects of the above problem as applied to three main classes of the processes of obtaining of polymeric synthetic materials, i.e., polymerization, polycondensation, and chemical modification of polymers. The kinetic peculiarities of macromolecular reactions in open systems controlling the above-mentioned dependencies are still not sufficiently studied. It especially concerns two last classes of the processes. In the meantime, the importance of the investigation of the kinetics of the reactions in open systems for chemical technology has been outlined (see, for instance, Beisenberger and Sebastian, 1983; Dotson et al., 1996; Emanuel, 1979; Meyer and Keurentjes, 2005).

As noted in the foregoing, any grade of synthetic polymer represents practically an infinite set of different individual compounds whose macromolecules can vary in the degree of polymerization (chemical size) l, composition, and chemical structure (Kuchanov, 1978, 2000). Therefore the performance parameters governing the quality of a polymer specimen are always determined as a result of certain averaging of some statistical characteristics of macromolecules over this set. The probability measure over which this averaging is performed depends on the preparation conditions of given polymer specimen being controlled by kinetic, diffusion, hydrodynamic, and other factors exerting influence on macrokinetic conditions in a reactor. Thus, in order to connect them with the quality of polymer obtained, one should do the following. First, it is necessary to reveal the correlation between the performance parameters characterizing the quality and corresponding statistical characteristics of a specimen, and, second, using kinetic calculations to express these characteristics through the parameters of a reaction system.

In the present state of the art of polymer physics, an exhaustive solution of the first of these two problems has not been found so far, although some attempts in this direction have been undertaken. At the same time, an intensive development of production of polymers puts forward demands of the prediction of their properties. To cope with this task chemical engineers generally use in practice some simple semi-empirical correlations. In doing so, they resort to certain qualitative theoretical approaches to treat the available experimental data. According to the most reputable adherent of this method, van Krevelen, such semi-empirical correlations are highly effective and provide rather reliable results in most practically important cases (van Krevelen and te Nijenhuis, 2009). However, even in the framework of the above approach, considerable difficulties are encountered, because often there is no clear idea about which specific statistical characteristics of a polymer are responsible for a particular mechanical and physicochemical property. It especially concerns copolymers because the number of their characteristics of such a kind is larger than that for homopolymers.

Evidently, it would be pertinent to discuss the hierarchy of different statistical characteristics of a polymer proceeding from the degree of their influence on each of its properties. Belonging to the first hierarchy level are such characteristics as average degree of polymerization and (in case of copolymers) average composition of a polymer specimen. On the next hierarchy level, the subject of consideration is the effect on the properties of the manner of distribution of macromolecules in a specimen in their chemical size and (for copolymers) in composition at fixed average values of such quantities. It is precisely this factor that plays a key role in the prediction of the quality of a polymer when switching from batch to continuous process of its production. Indeed, by varying the conditions of polymerization (reagent concentrations, temperature, catalyst, and so on), it is possible to select the regimes under which the average characteristics of the products will be identical in both processes. Nevertheless, the character of MWD in homopolymers, as well as the CD of macromolecules of copolymers in their composition can essentially differ for the above-discussed two methods, depending on the regime of hydrodynamic stirring in a reactor. Changing this regime, for example, by varying the number of steps of stirring by means of the apparatus sectioning or by switching to a cascade reactor, an engineer is able to control the quality of polymer products retaining unaltered their average characteristics.

All commercial specimens of synthetic polymers are characterized by a certain degree of inhomogeneity of macromolecules in size and composition, which predetermines the quality of a polymer. That is why it is necessary to analyze the factors responsible for the inhomogeneity of a specimen appearing in the course of its synthesis. These factors are largely controlled by the type of chemical reactions, the process mode, the character of hydrodynamic stirring, and (in case of heterophase systems) also by macrokinetic parameters. The analysis of heterophase systems is a far more complex issue because no general regularities exist for their modeling, and, consequently, every particular case calls for a special theoretical consideration. Therefore, it is expedient to invoke a structure multilevel approach by which, at every hierarchy level, the factors are revealed responsible for the degree of molecular inhomogeneity of a polymer. Having realized a sequential estimation of the contribution of each level to the overall inhomogeneity of a specimen, one can specify by calculations the main factors, leaving apart those of less importance. An example of practical implementation of such an approach for the mathematical modeling of the commercial process of chlorination of polyethylene with allowance for the quality of the product obtained is the investigation reported by Brun and Kuchanov (1980). However, as the analysis of macrokinetic factors is beyond the scope of this chapter, the subsequent consideration of the continuous process will be focused mainly on homogeneous systems.

The commonly known advantages of continuous commercial processes over batch processes are basically peculiar to the polymer-obtaining technology as well, although some specific problems arise in the latter case. One of the most important of them is the effect of hydrodynamic stirring on the quality of polymers.

In a plug flow reactor (PFR), where there is no stirring at all, the regularities of a periodic process with the same residence time θ are realized. Another limiting hydrodynamic regime takes place in a continuous stirred tank reactor (CSTR), characterized by exponential distribution function of the residence time. In any real apparatus, which is intermediate between these two extreme types of reactors, the degree of hydrodynamic stirring is normally characterized by the number of steps of ideal stirring, n, in a cell model or by the values of the effective Peclet number Pe^* in the framework of the diffusion model. If the degree of stirring is low enough, both these models yield the same results at $n = Pe^*/2 \gg 1$ (Aris, 1961). It turns out that even slightly pronounced stirring in a reactor can be responsible for a dramatic change of polymer's inhomogeneity. This should be necessarily taken into account when switching from periodic processes to continuous ones.

The pioneer investigator of polymerization in continuous-flow systems was Denbigh (1947). He formulated (Denbigh, 1951) the conditions enabling one to distinguish two limiting types of systems differing in character of the effect of the regime of hydrodynamic stirring on the MWD of the polymer formed. Belonging to the first type are systems in which the characteristic time of the formation of a macromolecule t_f being in active state is large enough as compared to its average residence time θ in a reactor. The values of these two quantities are controlled by different factors, namely t_f depending on kinetics while θ being governed by hydrodynamic stirring, so that the ratio between them can be arbitrary. A typical example of the first type of systems is living anionic polymerization, characterized by fast initiation and sufficiently slow chain termination. For such a polymerization, inequality $t_f \gg \theta$ holds. In systems of the second type, for example, in conventional radical polymerization, opposite ratio between the rates of chain initiation and chain termination takes place, so that inequality $t_f \ll \theta$ is true. These two types of systems are characterized by qualitatively different effects of hydrodynamic stirring in a reactor on the width of MWD of the polymer synthesized. In the first type of systems, on going from PFR to CSTR, the MWD widening occurs, unlike in the second type of systems, where the MWD narrowing happens. In this case, a very narrow Poisson distribution of the products of living anionic polymerization with the value of polydispersity coefficient K close to unity is replaced by the exponential Flory distribution with $K=2$. Conversely, under the same change of the regime of hydrodynamic stirring, the rather wide MWD of a polymer with K essentially larger than 2 formed at high conversions during radical polymerization switches to narrower distribution with the polydispersity coefficient in the interval between 1.5 and 2. Quantity K is found in this case by formula $K=0.5(1+\lambda)(3-\lambda)$, where λ and$(1-\lambda)$ are, respectively, fractions of radicals, terminating by disproportionation and recombination mechanisms.

The reason for increase in the polydispersity of the products of living anionic polymerization conducted in the perfect stirring regime instead of the plug flow regime is the variation in the residence time of macromolecules in a reactor. The wider is the distribution of the residence time (DRT) of macromolecules, the larger is the dispersion of MWD of a polymer. Besides, since for living anionic polymerization, the contribution to polydispersity connected with the random character of the monomer addition is negligible, the appearance of MWD of macromolecules obtained in a reactor will be exactly described by the function of DRT of this reactor.

7.2 Radical polymerization

Quite different factors exert an influence on the polydispersity of the products of radical polymerization, where the formation of any macromolecule is so fast that it practically has no time for moving in space over a distance sufficient for a considerable change in monomer concentration M.

So, it is conceivable that in analogous second type of systems, in each elementary reactor's volume dV with particular value of M, the formation occurs of macroscopic number dN of polymer molecules with some local MWD. The resulting MWD of final products represents the superposition of such local distributions of macromolecules formed all over the reaction volume which leave the reactor simultaneously. If there is certain distribution of concentration of monomer M along PFR, macromolecules leaving the reactor at every instant are formed at different values of M at different points of the reactor. This can lead to an essential polydispersity of a product. In case of CSTR, the gradient of monomer concentration in the reactor is absent; therefore, all polymer molecules are formed under the same conditions. This circumstance enables the exclusion of one of the reasons of the appearance of polydispersity due to the inhomogeneity of the formation conditions. In this case coefficient K drops to value $K = 0.5 (1+\lambda)(3-\lambda)$ which is minimal for given mechanism of the reaction.

Sometimes, for technology reasons, a radical polymerization should be conducted in PFR. However, this option inevitably entails a pronounced polydispersity of the products, for avoiding which it is necessary to find the ways for increasing time t_f of the formation of macromolecules. This can be realized by performing a polymerization, for example, in the presence of polyfunctional initiators whose molecules comprise several peroxide groups. A distinctive feature of the mechanism of polymerization in the presence of such polyinitiators is the appearance of macromolecules containing peroxide groups in the main chain in the course of the process. Under the cleavage of these groups, macromolecules transform in macroradicals capable of further propagation to form subsequently new macromolecules as a result of mutual recombination. Under repeatedly occurring acts of cleavage and recombination, the formation of inactive macromolecule will be completed only when it contains no peroxide group. The corresponding characteristic time t_f is prescribed here by the half-decay period of a peroxide group, rather than by the lifetime of a radical as in the case of a regular polymerization in the presence of monofunctional initiators. As the scales of these times can differ by several orders, the conditions are conceivable when inequality $t_f \ll \theta$, indicative of the belonging of a system to the second type; however, it does not hold because of the large value of t_f. Kinetic calculations show (Kuchanov, 2007) that in such systems a certain narrowing of MWD can be expected in CSTR when switching from monofunctional initiators to polyfunctional initiators.

One more option for increasing time scale t_f of the formation of macromolecules in the processes of radical polymerization is the employment of nontraditional initiators, such, as iniferters. The term "iniferter," introduced by Otsu and Yoshida (1982), is a result of the fusion of three words: *ini*tiator, trans*fer* agent, and *ter*minator. A special feature of an iniferter is its participation in each of the three reactions mentioned.

What all iniferters have in common is that despite possible essential differences in structural formulas, their molecules contain labile interatomic bonds, capable of cleavage in the course of synthesis resulting in the formation of a pair of primary radicals. At least one of them does not turn into polymer radical, although it does take part in the chain termination reaction. This reaction leads to the formation of a macromolecule with labile terminal bond, able to decay under the action of heat or light. As the consequence of such a decay, the macromolecule decomposes into two components. One of them is the active macroradical, whereas another one is the small radical which is stable enough to avoid the initiation of a new polymer chain. In its turn, the macroradical after its propagation recombines with stable small radical to become eventually a polymer molecule of macroiniferter. The latter decomposes again into a pair of radicals dramatically differing in their reactivity, and so on. According to this kinetic scheme of stepwise polymerization, every polymer chain can successively be in two states: alive (as a macroradical) and dormant (as a macromolecule). Because a polymer chain lives for a rather short time in comparison with the time of its inactive state, macromolecule growth is believed to occur by separate steps. At every such step, the length of polymer chain increases by just one length of elementary chain, whose number in macromolecules can be large enough. In this case, polymerization products will be characterized by narrow MWD and high molecular weight.

Polymerization with participation of iniferters represents just one of the conceivable ways of performing “living” radical polymerization (LRP). A comprehensive description of its kinetics and mechanism is presented in voluminous literature (see, for example, Davis and Matyjaszewski, 2002; Goto and Fukuda, 2004; Matyjaszewski, 2003,). A common trait of any LRP is the ability of a polymer chain for alternating its active and nonactive states. As far as the mechanism is concerned, LRP holds an intermediate position between conventional free-radical polymerization and living anionic polymerization. In the first of them, macromolecules are incapable of activating in principle, contrary to the second one, where being constantly in active state they retain their ability to growth. As noted above, each of these two limit cases of LRP calls for a particular limit regime of hydrodynamic stirring in a reactor, the most appropriate for carrying out a continuous process of polymerization. So, the best-suited candidates for conducting conventional free-radical polymerization and living anionic polymerization are PFR and CSTR, respectively. What can be recommended to an engineer designing a continuous LRP process with regard to optimum choice of hydrodynamic stirring? To answer this question one is supposed to compare average time of a polymer chain being in dormant state t_f with its average residence time θ in a reactor. If the values of t_f and θ are comparable, LRP products will be macromolecules consisting, on average, of few elementary chains, and thus differing noticeably in chemical size and composition. With this in mind, when designing a continuous LRP process, preference should be given to reactors in which the regime of hydrodynamic stirring is as close as possible to the ideal mixing. The products of such polymerization can be expected to have rather low polydispersity. The opposite recommendation to an engineer choosing the type of continuous reactor can be given when inequality $t_f \ll \theta$ holds. Under such conditions, PFR is preferable in which polymer specimens close to monodisperse ones will be formed. The explanation is that macromolecules in this specimen are characterized by large values of average number m of elementary chains involved. Upon turning number m to infinity and average length of the elementary chain to zero, we will arrive at this limit at living anionic polymerization.

7.3 Polycondensation

Among typical systems of the first type are polycondensation processes. Here the lifetime t_f of a macromolecule during which its formation occurs in the absence of impurities or deliberately added chain terminators is practically infinite. The reason is that at any growth step, a macromolecule remains active because it comprises reactive functional groups. As with any system belonging to the first type, there are two reasons responsible for the polydispersity of the products of continuous polycondensation. The first of them is due to the statistical nature of chemical transformations in the course of polycondensation, whereas the second one owes its origin to the dispersion of the residence time of molecules in the reactor. If the reactor operates in the plug flow regime, the second reason is excluded, so that the inhomogeneity of a polymer specimen obtained in such a reactor (in comparison with any other reactor at the same conversion) will be minimal. Obviously, hydrodynamic stirring in the apparatus providing residence time distribution (RTD) with nonzero dispersion is always the factor causing an additional increase of polydispersity of the products. The comparison of two polymer specimens obtained in PFR and CSTR at the same value of conversion p and number average degree of polymerization $P_N = (1-p)^{-1}$ shows that MWD of the second specimen turns out to be essentially wider than MWD of the first one. This distinction is especially strongly pronounced in the most important region of conversions close to unity, where $P_N \gg 1$. Here the value of polydispersity coefficient of the products prepared in CSTR is $P_N \gg 1$ times larger than K of the polymer with the same value of P_N but synthesized in PFR. As typical values of P_N for commercial polycondensation polymers are close to 100, the distinction in polydispersity of the specimens synthesized in PFR and CSTR is tremendous, exceeding considerably the analogous distinction in the same characteristic of the polymerization products. In a search for ways to reduce the polydispersity of the products of continuous polycondensation, it is possible to increase the number of steps of hydrodynamic stirring in a system by apparatus sectioning or by employment of a cascade consisting of *n* successive CSTRs. The problem of calculation of the dependence of the width of MWD on number *n* has been solved earlier (Kuchanov, 1981). The results of this work allow a general conclusion about the advisability of conducting a continuous polycondensation in hydrodynamic regime which is as close to plug flow regime as possible. This recommendation is essential because even a minor deviation from this regime substantially decreases the apparatus capacity, increasing simultaneously undesirable polydispersity of the products of continuous polycondensation.

7.4 Effect of stirring on composition inhomogeneity

Hydrodynamic stirring evidently exerts an influence on the inhomogeneity of macromolecules not only in chemical size but also in composition. Analysis of the factors affecting this inhomogeneity shows that the regularities outlined above for the consideration of polydispersity remain in force exclusively for the second type of systems. In these systems, the composition inhomogeneity of copolymer specimens (characterized by dispersion σ^2 of CD of macromolecules) synthesized in CSTR is markedly less than the inhomogeneity of a copolymer obtained in PFR. So, the products of radical copolymerization prepared in CSTR have the minimal possible value of σ^2 (as compared to the reactor of any other type), which is controlled only by the stochastic character of chemical reactions. Quantity σ^2 in this case is inversely proportional to number average degree of polymerization P_N, whereas proportionality coefficient D is of order 10^{-1} being governed by kinetic parameters and monomer mixture composition. Inasmuch as the typical value of P_N for radical copolymerization is 10^{-3}–10^{-4}, corresponding values of σ^2 are equal to 10^{-4}–10^{-5}. Due to their smallness they are out-of-experimental accuracy. Therefore, it is possible to neglect in practice this contribution to the composition inhomogeneity in comparison with the contribution originated by the spatial inhomogeneity of monomer concentrations inside a reactor. The existence of gradients of these concentrations in PFR can lead to substantially larger values of σ^2 as compared to the dispersion of copolymers synthesized in CSTR, which affects some macroscopic properties of the copolymers formed. Because of poor compatibility of the majority of different polymers, even relatively slight composition inhomogeneity of a copolymer induces phase separation of a reaction mixture accompanied by a dramatic deterioration of the service properties. A characteristic attribute of such a phenomenon is the appearance at certain monomers' conversion of the opalescence of this mixture with subsequent complete loss of its transparency. The final product of this process is heterophase turbid copolymer, whose poor performance properties make it normally improper for practical applications.

It is clear from the above how important for practice is the investigation of the conditions at which a reaction mixture undergoes in the course of copolymerization the phase transition to heterophase state accompanied by the loss of its transparency. In this connection, the fundamental research by Slocombe (Slocombe, 1957), who studied about 43 component systems, deserves special attention. He analyzed the dependence of the transparency of terpolymers obtained at high conversions in a batch reactor on the initial monomer mixture composition. This analysis enabled Slocombe to establish some empirical rules which later have been theoretically substantiated (Brun and Kuchanov, 1977). Using as examples particular copolymers, the authors of this paper found quantitative correlations between the dispersion σ^2 of CD of a copolymer and its transparency. They showed that limit value of dispersion, σ_{cr}^2, exists for each copolymer. If dispersion σ^2 of any copolymer specimen exceeds σ_{cr}^2, this specimen loses its transparency due to the pronounced inhomogeneity of its macromolecules in composition. If the parameters of the kinetic model of copolymerization are known, dispersion σ^2 can be theoretically calculated for any model of hydrodynamic stirring. Therefore, the approach put forward in work (Brun and Kuchanov, 1977) enables an engineer to make the choice of the conditions of conducting industrial processes of obtaining transparent copolymers scientifically grounded.

7.5 Polymer-analogous reactions

Unlike for radical copolymerization, where the ideal mixing regime is preferable for preparing compositionally homogeneous specimens, it is recommended to conduct the reactions of chemical modification of polymers by their polymer-analogous transformations in a regime which is as close as possible to the plug flow regime. Such reactions as chlorination of polyethylene and polyvinylchloride or the synthesis of polyvinyl alcohol by the hydrolysis of polyvinyl acetate pertain to the first type of reactions. This conclusion ensues from the fact that the period of the formation t_f of polymer products in these reactions is rather prolonged, being predetermined by the time of complete transformation of all functional groups belonging to a particular macromolecule. The most practically important products of the processes of such a kind are copolymers in which the above-mentioned transformation is realized only partially. Theoretical analysis of the dependence of σ^2 on number n of steps of stirring showed (Brun and Kuchanov, 1980) that at low values of n the composition inhomogeneity of these copolymers is very pronounced, whereas at $n \gg 1$ the dispersion decreases proportionally to n^{-1} until n becomes comparable with the average degree of polymerization of macromolecules. This means that the number of steps ($10^3 - 10^4$) should be very large in order for the degree of composition inhomogeneity of the products of polymer-analogous transformations in a continuous process to be comparable with that taking place in a periodic process.

7.6 Microsegregation

As the overall kinetic order of the reactions of the synthesis and chemical modification of polymers is generally larger than unity, the products' inhomogeneity in size and composition depends not only on the distribution of the residence time in a reactor but also on the degree of micromixing in this apparatus. This factor has been theoretically investigated for homopolymerization and homo-polycondensation (Kuchanov, 1981; Tadmor and Biensenberger, 1966) as well as for radical copolymerization (O'Driscoll and Knorr, 1969; Szabo and Nauman, 1969) by comparing the results of calculation of the inhomogeneity in two limit cases, namely complete mixing at microlevel and complete segregation. The effect of micromixing in a reactor is most pronounced in the case of polycondensation products, where the transition from the first limit case to the second one is accompanied by an appreciable rise in the productive capacity of the reactor with concurrent decrease of the products' polydispersity.

ACKNOWLEDGMENTS

The author owes sincere gratitude to his wife, Natasha, for her help and patience. He is also very indebted to Prof. Yablonsky, a co-editor of this volume, for the kind suggestion to contribute a chapter to the present work.

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