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The Present State of the Quantitative Theory of Polycondensation Processes

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The computational and theoretical studies in the field of homogeneous polycondensation are subjected to a critical analysis on the basis of the universal classification of the kinetic and thermodynamic models used in this field. The limits of the applicability of the models are discussed from the standpoint of the physicochemical characteristics of the processes which they describe and the parameters calculated on their basis are compared with the corresponding experimental data. The fundamental problems awaiting solution by the quantitative theory of polycondensation in the present stage of its development are formulated.
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I. INTRODUCTION

The polycondensation method for the synthesis of polymers is at present one of the most widely used procedures for the formation of synthetic high-molecular-weight products. The extensive scope of this method is associated with the wide variety of monomers employed as well as the chemical reactions leading to the formation of macromolecules. In view of the practical importance of polycondensation it has been the subject of an enormous number of experimental studies. Here mention should be made of the great contribution made by V. V. Korshak and his School to the development of ideas about polycondensation processes. These studies made it possible to understand many important features of polycondensation and to obtain new polymers with valuable practical properties.

An enormous amount of experimental data on polycondensation has now accumulated. They have been surveyed and arranged systematically in monographs devoted both to individual important classes of polycondensation polymers[1-5] and to general characteristics of polycondensation[6-10]. However, in all these monographs, except Flory's familiar book[11], mainly experimental data are quoted and very little space is devoted to the quantitative theory and computational studies. At the same time, in planning industrial manufacturing processes one of the most important tasks is that of selecting the optimum conditions for polycondensation processes. The successful solution of this problem requires a well developed quantitative theory of such processes[12], which would make it possible to devise for them adequate mathematical models and to seek with the aid of a computer the optimum technological polycondensation régimes in terms of such models.

The present review presents a critical analysis of published computational and theoretical studies devoted to homogeneous polycondensation processes. Attention has been concentrated on the discussion of the initial postulates of the theory, the illustration of the possibilities of various computational methods, and the general problems of the modern quantitative polycondensation theory. Certain results arising from the theory of heterophase polycondensation are quoted in the review of Sokolov and Nikonov[13].

For a detailed statistical description of the products of linear homopolycondensation, it is sufficient to determine their molecular weight distribution (MWD). If cyclisation reactions proceed to an appreciable extent during the process, it is necessary to find also the MWD of the cyclic molecules. The copolymer molecules differ not only in the degree of polymerisation (size) but also in the fractions of units of different types (composition). The inhomogeneity of the copolycondensation products will therefore be described in terms of a size–composition distribution function (SCD). Furthermore, copolymer molecules having the same size and composition can have completely different microstructures characterised by the way in which the units are distributed in the chain. On passing from linear to branched polymers, it is necessary to take into account in their statistical description the fact that, apart from the above characteristics, macromolecules differ also in their steric configurations, particularly in the number and lengths of branches and intermodal chains, although for many practical purposes there is no need to distinguish all possible isomers in the description of the process.

The statistical characteristics enumerated above determine the primary, i.e. the configurational, structure of macromolecules which carries definite information about their possible conformations and secondary supermolecular structures and hence also about the physicochemical properties of polymers. Thus the main task of the quantitative polycondensation theory is the establishment of computational relations corresponding to the statistical parameters of the primary structure of the polymeric specimen as a function of the composition of the initial monomeric mixture and thermodynamic or kinetic parameters, i.e. as a function of the equilibrium constants or rate constants for reactions occurring during the synthesis of the polymer. The solution of this problem will permit an approach on a sound scientific basis towards the selection of the optimum polycondensation conditions in order to obtain polymers with a specified set of practical properties.

In the course of polycondensation there is a possibility of the simultaneous occurrence of different types of elementary reactions. The main one of these is chain

propagation—the interaction of two functional groups in different molecules to form the corresponding linkage between them, which will henceforth be referred to as the "intramolecular bond". This involves the joining together of two reacting molecules of monomers, oligomers, or polymers into a single entity which is frequently (but not necessarily) accompanied by the liberation of a molecule of a low-molecular-weight product. A common feature of polycondensation is [14] that during its course any two molecules of the initial or intermediate product in the reaction mixture, containing interacting functional groups, can be involved in a condensation reaction with one another. The reverse reaction in relation to chain propagation is chain degradation. For fairly high equilibrium constants k corresponding to this pair of elementary reactions, degradation in the course of polycondensation can nevertheless be neglected and their polycondensation can be regarded as an irreversible process. On the other hand, if k is small, the reversibility of polycondensation becomes significant. Whereas irreversible polycondensation is always a non-equilibrium process, reversible polycondensation can proceed under both equilibrium and non-equilibrium conditions. In order to achieve the equilibrium régime, it is necessary to remove the low-molecular-weight side product from the reaction zone at a fairly low rate, so that at each instant the system is in a state of thermodynamic equilibrium corresponding to the current concentration of the side product. The rate of this removal from the reaction zone evidently determines the overall rate of such equilibrium polycondensation. On the other hand, if the rate of removal of the side product is comparable to the rate of its formation in the condensation reaction, then reversible polycondensation will proceed in a non-equilibrium régime.

Apart from the growth and degradation of polymeric chains, elementary reactions involving interchain exchange, chain termination and intramolecular cyclisation are possible in the course of polycondensation. Without influencing the number-average degree of polymerisation, interchain exchange reactions can to a large extent determine the form of the MWD and the SCD for the polymer. Exchange reactions may be of two types. The elementary step in the first type involves the interaction of the terminal functional groups with an intermolecular bond, while in the second type it involves the interaction of two such bonds with one another. Apart from terminal functional groups (for example hydroxy-, carboxy-, or amino-groups), in calculations on reversible polycondensation it is necessary to treat intramolecular bonds [for example, ester(ether) or amide bonds] as "internal" functional groups, because they are involved in elementary degradation and interchain exchange reactions. Chain termination reactions in polycondensation, which consists in chemical deactivation of terminal functional groups, frequently takes place as a result of the interaction of the latter with monofunctional compounds, which are either specially introduced or are present in the system as impurities. In intramolecular cyclisation both reacting functional groups belong to the same molecule so that this type of reaction, which increases the degree of conversion of the group, does not lead to the growth of the molecular weight of the polymer†. In practical calculations there is usually no need to take into account all the elementary reactions, since, under the conditions of a specific process, many of them take place to such an insignificant extent that they can be neglected in setting up a kinetic scheme.

In the calculation of the statistical characteristics of the primary structure of polycondensation products two approaches are used: kinetic and statistical. The first consists in setting up and solving material balance equations for the concentrations of all types of molecules participating in the given process. In the second process the fractions of molecules with specified configurations, among others in reaction mixture, are calculated. These fractions are identified with the probability that a molecule selected at random has the corresponding configuration. There exist various versions of the statistical approach to the calculations of the above probabilities for molecules and even within the same class of processes it is possible to use several of them simultaneously. In the most convenient approach each macromolecule is represented as an individual occurrence of a definite random process involving conventional motion along the polymer chain and the probability of such occurrence is calculated with the aid of the theory of the corresponding process.

The statistical approach to calculations on polycondensation processes was first proposed by Flory as early as the end of the 1930s [11] and has found the widest applications in the quantitative description of many polymers, both linear and branched. The principal advantage of the statistical approach is that it makes it possible to describe exhaustively and at the same time comparatively simply the detailed configurational structure of macromolecules in terms of several probability parameters. However, the problem of the selection of the type of random process for a description of the products of a specific polycondensation system cannot be solved, in principle, within the framework of the statistical method alone. An answer is provided by the kinetic approach, which makes it possible to express simultaneously the corresponding probability parameters of the random process in terms of kinetic constants, reactant concentrations, and other measurable quantities. In order to prove rigorously the applicability of a particular modification of the statistical approach to the description of the primary configurational structure of the products of equilibrium polycondensation, the general principles of statistical physics and chemical thermodynamics, particularly the principle of detailed balancing, are used. Thus at equilibrium the probability of observing an arbitrary molecule in the system is determined by the free energies of formation of all its intramolecular bonds and, according to the principle of detailed balancing, is independent of the order in which the bonds appear, i.e. of the previous history of the system. On the basis of general thermodynamic relations, it is possible to express the free energy of formation of intramolecular bonds in terms of the equilibrium constants of the elementary reactions corresponding to the stoichiometric scheme for the given process. This makes it possible to determine in terms of these quantities the probability parameters used in the statistical approach.

In the course of the development of a quantitative theory of polycondensation two stages may be traced. In the first stage, which originated from Flory's fundamental work [11], only systems which we shall henceforth call ideal are considered. They do not involve intramolecular reactions and Flory's principle applies to the intermolecular reactions. According to this fundamental principle, the activity of any functional group of a particular type in each elementary reaction is the same regardless of which molecule the given group belongs to and in which part of the

†In the present review we are not considering polycondensation processes where only functional groups adjoining the chain can take part in the cyclisation reaction.

molecule it is located. The model of ideal polycondensation systems, to the development of which most published theoretical studies have been devoted, permitted the calculation by various methods of the necessary statistical characteristics of the products of the most general polycondensation processes with participation of many monomers of arbitrary functionality and with functional groups of various types. The problem of devising a theory of ideal polycondensation can now be regarded as largely solved[12]. The next stage consisted in a quantitative description of non-ideal systems. The attempts at calculations on such systems are usually associated with the overcoming of fundamental difficulties and the wide variety of factors tending to cause a departure from ideality precludes the use of a particular single approach. This stage of the development of the theory is therefore still far from complete.

We shall note the physical principles underlying the initial postulates of the model of ideal polycondensation systems and shall point out certain causes which may lead to the breakdown of these postulates. In the first place one should note that polycondensation reactions are comparatively slow and therefore occur under liquid phase conditions in such a way that their rate is not as a rule limited by diffusion factors. Intermolecular reactions are of second order, while intramolecular reactions are of first order, which leads to an increase of the proportion of the latter as the reaction mixture is diluted by an inert solvent. It is easy to achieve a condition where cyclisation reactions may be neglected in the description of the process kinetics. The probabilities, per unit time, that an arbitrary selected functional group of a macromolecule is involved in competing condensation reactions of the intermolecular and intramolecular type are respectively kC and k', where k and k' are the rate constants for bimolecular and unimolecular reactions and C is the concentration of the functional groups in the system. The quantity k' is proportional to the number of conformations of the initial molecule for which another group of this molecule is in the immediate vicinity of the selected group, i.e. is proportional to the effective local concentration c, which all the remaining groups of the molecule set up near the selected group as a result of the conformational rearrangements of the molecule. Since conformational equilibrium is assumed in the system, c is identical with the concentration of the corresponding conformers. If the functional groups in the molecule are separated by a fairly large number of intramolecular bonds, the proportionality coefficient between k' and c is equal to k, because the probabilities of the elementary step in the intramolecular and intermolecular reactions are in this case identical. Consequently $k' \ll kc$ and it is legitimate to neglect intramolecular reactions when $c \ll C$. The quantity C diminishes in proportion to the dilution of the system and c is determined by the configuration and segmental mobility (flexibility) of the polymer chains and is almost independent of the degree of dilution, although it may change on passing from one solvent to another. If it is supposed that the rates of the reverse reactions are independent of the conformational structure of the molecule, the foregoing statements concerning the rate constants for condensation reactions are fully applicable also to the corresponding equilibrium constants k' and k. In particular, if the functional groups involved in the reaction are separated by a large number of intramolecular bonds, the ratio k'/k is equal to the effective concentration c. At equilibrium the ratio c/C determines the contribution to the free energy change of the macromolecule in a given intramolecular reaction associated with the decrease in its course of the number of possible conformations of this molecule. Consequently c is unambiguously determined by the conformational entropy of the macromolecule and can be calculated by thermodynamic methods.

The possible causes of the deviations from Flory's principle can be divided into two classes, by analogy with the conformational properties of macromolecules: the short- and long-range effects. The former include the so called substitution effects associated with steric, inductive, or other types of influence of functional groups which have reacted on the activities of the neighbouring functional groups which have not. One speaks of a first-order substitution effect if the reactivity of the group depends on the state of the functional group only in the same monomer unit. Sometimes it is necessary to take into account also the possibility of higher-order substitution effects where the reactivity of the given group is influenced by the state of the groups in neighbouring units. Long-range order effects are determined by the possible influence of the solvent on the steric conformational structure of macromolecules and hence on the activity of the functional groups contained in them. For example, on passing from "good" to "poor" solvents, there is a possibility of the contraction of the reacting macromolecules accompanied by a reduction of the accessibility of the functional groups and actually resulting in the limit in the complete loss of reactivity by these groups owing to their intramolecular "protection". Such long-range order effects, where the accessibility of each individual group for reaction with other groups is determined by the conformational-configurational structure of the entire macromolecule, are significantly more difficult to take into account in the polycondensation theory than the short-range order effects. In the latter case calculations on polycondensation systems taking into account the substitution effect are carried out using the generalised Flory principle[12], according to which the activity of any functional group in the molecule can depend only on the microstructure of the neighbouring sections of the polymer chain and varies during the process owing to the changes in its microstructure associated with the reaction of neighbouring groups.

There is at present virtually no quantitative theory of polycondensation in which long-range order effects are rigorously taken into account. The difficulties in devising such a theory are due to the inapplicability in this instance of the Flory principle even in its generalised formulation. Such a theory requires the consideration of the conformational-configurational statistics of the reacting molecules. In contrast to intermolecular reactions, calculations on intramolecular reactions within the framework of the theory taking into account only the short-range order effect cannot be made at all. This is reasonable, because the interaction of any pair of functional groups within a single molecule depends significantly on their relative positions in the molecule and possibly on the choice of equilibrium conformations of the molecule, which determine the probability of the steric approach of the given groups to a distance necessary for the chemical reaction step.

An important property of ideal polycondensation systems, associated with the random nature of the reactions occurring in them, should be noted. Any statistical characteristics of the products of ideal polycondensation are independent at any instant of the previous history of the system, i.e. of whether the process takes place under equilibrium or non-equilibrium conditions, whether

degradative or exchange reactions occur, or whether the process is fully irreversible. They are fully determined by the concentrations of the terminal functional groups and the intramolecular bonds of each type at a given instant. In calculations on such systems by any statistical method this makes it possible to choose the numbers of functional groups and bonds of each type in an arbitrary molecule as parameters which unambiguously specify its probability. Thus in non-equilibrium processes the state of the system is independent (as at equilibrium) of its previous history, is associated with the ideality of these processes, and may break down on deviation from the latter; the probability of the appearance of a particular molecule in the absence of equilibrium can then depend also on the order in which its bonds have been formed. In the description by the statistical method of products of non-ideal polycondensation processes in the absence of equilibrium it is therefore always necessary to test the method for the adequacy of the chosen model by means of the corresponding kinetic equations.

Next we shall denote various monomers by a sequence of letters, the first of which (R,S,...) corresponds to the monomer unit and each of the latter (A,B,...) corresponds to a definite type of functional group in the monomer. If the monomer contains several identical groups, their number will be designated by a superscript to the corresponding letter.

II. LINEAR POLYCONDENSATION

In order to obtain macromolecules with a linear structure, bifunctional monomers are used. Depending on their number and type, homopolycondensation, heteropolycondensation, and copolycondensation are distinguished. The products of the first two processes are homopolymers, the elementary units of which consist of one or two monomeric units respectively, while the products of the third process are copolymers whose macromolecules differ in size, composition, and microstructure within the limits of a single specimen. Examples of homopolycondensation are provided by processes involving the formation of polyamides from aminoacids (the initial monomer is RAB and there are reactions only between A and B) and polyethers from glycols (RA^2 monomer). In heteropolycondensation the initial mixture usually consists of two symmetrical monomers RA^2 and SB^2 with groups A and B of different types, although there is a possibility of more general processes involving the reaction between RA_1A_2 and SB_1B_2, where groups of the same type in each asymmetric monomer have different reactivities. The heteropolycondensation products ~RSRSR~, typical examples of which are the formation of polyamides from diamines and dicarboxylic acids or the synthesis of polyesters from dicarboxylic acid chlorides and glycols, consist of rigorously alternating monomeric units R and S, i.e. the elementary unit of the homopolymers formed is in this case RS. With the exception of heteropolycondensation, all the processes involving more than one monomer are copolycondensation processes. The simplest characteristic instances of linear copolycondensation are bipolycondensation and interbipolycondensation. An example of the former process is a reaction where at least one of the initial monomers (for example, an aminoacid or a hydroxyacid) is capable of undergoing homopolycondensation under the given conditions. In the second process three monomers, for example $S_1A_1^2 + S_2A_2 + IB^2$, are involved simultaneously, the first two of which, called comonomers, do not react with one another but each is capable of undergoing heteropolycondensation with the third component (the intermonomer). The reactivities of two functional groups of any monomer can be in general different. Processes of this type with an arbitrary number of comonomers are called intercopolycondensation. Furthermore, unless a special stipulation is made, heteropolycondensation and intercopolycondensation imply processes with participation of symmetrical monomers.

1. Ideal Homopolycondensation and Heteropolycondensation

The first computational and theoretical studies on linear polycondensation were published as early as the end of the 1930s.[15,16] In his fundamental investigation[15] Flory calculated for the first time by a statistical method, on the basis of his principle, the MWD of the products of homopolycondensation and heteropolycondensation on the assumption that there is no cyclisation reaction. The number-average degree of polymerisation P_N, the weight distribution function $f_W(l)$ for molecules in terms of the degree of polymerisation l (MWD), and the polydispersity coefficient K_p characterising its width, which Flory[15] calculated for homopolycondensation, are given by the expressions

$$P_N = (1-p)^{-1},\ f_W(l) = (1-p)^2 l p^{l-1},\ K_P = 1+p \qquad (1)$$

and are determined by a single parameter p, which is equal to the conversion of the functional groups. The same formulae describe the products of the heteropolycondensation of an equimolar mixture of monomers and the corresponding formulae have been derived also for non-equimolar initial mixtures[15]. In the latter case the the formula $a_i b^l$ (where $i = 1, 2, 3$) describes the MWD for each of three types of molecules, differing in the type of terminal functional groups, and each has its own value of a_i. Distributions of this kind can be called generalised Flory distributions.

Subsequently these relations were frequently rederived in several different ways. Thus, using the principle of detailed balance, Schulz[16] calculated the MWD for the products of equilibrium homopolycondensation and derived a theoretical relation between the molecular weight of the polymer and the equilibrium constant of the reaction. Subsequently, Meggy[17] extended these results to equilibrium heteropolycondensation. At the beginning of the 1940s Flory[18,52] proposed two thermodynamic methods for the derivation of MWD in equilibrium systems. In the calculation of the most probable Flory distribution [Eqn.(1)] various modifications of the statistical method were used, in particular the treatment was based on a random migration process along a straight line[19] and the convolution integral[20]. The kinetic method has also been widely used in calculations of MWD for a polymer. The Flory distribution [Eqn.(1)] was derived by this method for the products of irreversible[21] and reversible[22] polycondensation in a closed system and also for equilibrium polycondensation[23], taking into account the possible removal of the side product from the reaction zone. In the kinetic schemes adopted[21-23] no account was taken of exchange reactions. It was suggested[24] that their occurrence leads to a narrowing of the MWD compared with the Flory law. However, the simplified kinetic calculation of the MWD in a system where an exchange reaction of the type of alcoholysis or acidolysis takes place and there is no

growth or degradation of macromolecules leads to equilibrium in the distribution defined by Eqn. (1).[25] Examination of the general kinetic scheme for reversible homopolycondensation[26] with allowance for all the reactions mentioned above shows that the products of this process can be described by the Flory distribution at all its stages. Although this type of general kinetic calculation has not been made for heteropolycondensation, there is every reason to believe that, for an equimolar mixture of the initial monomers (only then is there a possibility of the formation of high-molecular-weight products), the MWD for a polymer obtained in an arbitrary reversible process is also determined by Eqn. (1), because the latter has been proved rigorously for two opposite limiting cases: irreversible and equilibrium heteropolycondensation.

A number of studies have been devoted to the theoretical investigation of the influence of the chain termination reaction on the statistical characteristics of the polymer[27-30]. The MWD and the corresponding values of P_N and K_p for the products of homopolycondensation and heteropolycondensation were first calculated by Case[27] using a statistical method. Sokolov et al.[28] calculated analytically and numerically on a computer the values of P_N for a polymer corresponding to different kinetic schemes and mechanisms of the deactivation of functional groups. In particular, they examined termination both by impurities and by a side product formed in the course of the process. An infinite chain of kinetic equations for concentrations of different individual products of irreversible homopolycondensation has been formulated[29,30] with allowance for chain termination by an impurity. The authors did not find an exact solution for this system; certain approximate results are quoted, showing that the chain termination reaction can lead in certain cases to an appreciable narrowing of the MWD.

Statistical[27,31] and kinetic[32] calculations have been made on the heteropolycondensation of two monomers, one of which contains groups having different reactivities. It was shown that the MWD of the products of such a process is described by the generalised Flory distribution, which (for the same value of P_N) is wider the greater the difference between the reactivities of groups of the same type.

The problem of the influence of the rate of supply of one of the monomers to the reaction zone on the statistical characteristics of the products of irreversible heteropolycondensation was investigated by a computational method[33]. Using the kinetic method, the authors showed that the MWD of the polymer is described by the Flory law and the value of P_N may be large even when the condition of the equimolarity of the initial compounds is appreciably infringed, provided that the rate of supply of the monomer taken in excess is sufficiently low. A simple formula was derived in this case, which makes it possible to determine the rate constant for the condensation reaction from the measurements of the dependence of P_N on the rate of supply.

Attention has been drawn to the fact[34] that, in calculations on polycondensation kinetics, account must be taken of the decrease in the volume of the system during the process. The error arising when this fact is ignored reaches several tens per cent according to the author[34].

2. Non-Ideal Systems

Since the MWD of a polymer under the conditions of ideal polycondensation should be described by the Flory distribution with a polydispersity coefficient K_p close to two, any deviation from this value is associated with the breakdown of the ideality of the system. Analysis of experimental data quoted, for example, in Howard's review[35] shows that, together with ideal polycondensation systems, there are also systems which are not consistent with this model. Their MWD is described by broader ($K_p > 2$) or (and this is observed more frequently) narrower ($K_p < 2$) distributions than the Flory distribution. We shall consider further polycondensation models in which account was taken of particular deviations of the system from ideality.

The simplest of these is the model based on the first-order "substitution effect", according to which the reactivities of the functional group of the monomers differ from those of the remaining groups for which the validity of the Flory principle is postulated. Statistical[27] and kinetic[36] calculations have shown that the MWD of the products of irreversible heteropolycondensation of two symmetrical monomers, $RA^2 + SB^2$, the first of which has dependent groups and the second independent groups, is described by the generalised Flory law. Its statistical parameters are expressed in terms of the conversion p, the initial fractions of the monomers, and the relative reactivity κ of the first reacting group of the monomer relative to the remaining second group which has not reacted. Systems with $\kappa \geqslant 0.5$ have the same width of the MWD of the polymer ($K_p = 2$) as if they were ideal and systems with an appreciable accelerating substitution effect, where $\kappa < 0.5$, are characterised by an appreciably greater polydispersity ($2 < K_p < 4$). It is of interest that the formulae for the MWD of the polymer in this system do not differ in their forms from those for the MWD of the polycondensation products in the $RA_1A_2 + SB^2$ monomer system with independent but different groups in one of them. Irreversible heteropolycondensation, where both monomers contain dependent functional groups, has been examined within the framework of the first-order "substitution effect" model[37,38]. Sokolov et al.[37] evaluated numerically on a computer the values of P_N for a polymer corresponding to four different kinetic constants describing all the possible chain propagation reactions in the selected model. The calculations showed that the greater the reactivity of the second groups of the monomers compared with the first, the higher the molecular weight of the polymer obtained for the same conversion. When the difference between the reactivities becomes sufficiently large in both monomers, the process acquires features characteristic of polymerisation, because high-molecular-weight products can be formed for a non-stoichiometric ratio of the initial monomers and an incomplete conversion. Polycondensation systems of this type have not so far been observed experimentally. Case[38] obtained by a statistical method the MWD function for a polymer in the most general case of irreversible heteropolycondensation, where both monomers not only have dependent groups but also groups with different initial reactivities. This function constitutes a generalised Flory distribution analogous to that derived for the heteropolycondensation of monomers with independent groups. However, since a kinetic justification of this result is lacking, the problem of its validity still remains open. For an equilibrium process, this result can be rigorously justified[39] on the basis of fundamental thermodynamic principles. A general algorithm for the calculation of the MWD of equilibrium polycondensation products has been devised[39] for a model based on the "substitution effect" of arbitrary order and the number of independent thermodynamic parameters of this model was indicated.

There is now no doubt that the approximation assuming ideality does not hold for many polycondensation systems and substitution effects must be taken into account in the calculation[6]. In particular, this applies to the polycondensation of aromatic monomers, which frequently have dependent functional groups. In order to justify the "substitution effect" model and determine its parameters, the kinetics of the reactions of bifunctional monomers with the corresponding monofunctional compounds are usually studied under conditions close to those in polycondensation.

Such studies on model systems[40-42,43-47] made it possible to estimate quantitatively the relative reactivity κ of the first or second groups of monomers (bisphenols, dicarboxylic acid dichlorides, aromatic diamines) participating in acceptor-catalytic polyesterification and polyamidaton processes. The results of these investigations[40-47] have shown that $\kappa > 1$ for the majority of the monomers investigated and the first group can be several times more reactive than the second. A combined approach[46,48], which makes it possible to determine the suitability of the "neighbour effect" model for the description of specific non-equilibrium heteropolycondensation processes and at the same time to determine its parameters, is extremely interesting. On the basis of correlations obtained for reaction series of monofunctional compounds, a correlation equation has been derived[46,48] and has been used to calculate four kinetic constants in both the first and second groups for each of twenty different aromatic diamine + dicarboxylic acid dichloride pairs of monomers. These constants were then substituted in the four kinetic equations for the functional groups, which were next solved on a computer. Comparison of the solutions with the experimental data for the kinetics of the initial polycondensation stage showed[46,48] that the agreement is satisfactory in all the twenty systems investigated. A convincing experimental demonstration of the suitability of the "substitution effect" model for the description of equilibrium polycondensation was apparently achieved for the first time by Challa[49-51] in relation to the synthesis of poly(ethylene terephthalate).

In the above studies the influence of the solvent and long-range volume effects on the statistical characteristics of the polymer was completely ignored. Several attempts were made to take these effects into account in the theory of equilibrium polycondensation[52-57]. The equilibrium MWD of the polymer has been calculated[52-55] by minimising the free energy of the system. A term describing the interaction of the polymer molecules with the solvent was added to the expression for the energy. The form of this term was determined by the choice of the specific model of such interaction among those available in the theory of polymeric solutions. First it has been shown for concentrated solutions[52-54] that, for the Flory–Huggins lattice model, the MWD of the equilibrium polycondensation products is described by the Flory law. If other lattice models are used, it is possible to obtain other distributions[54]. It is easy to show[106] that the Flory distribution is obtained when the free energy of the macromolecule varies linearly with the degree of its polymerisation if account is taken of the interaction with the solvent. Among the models considered[54], this condition is satisfied by the Flory–Huggins model alone. The equilibrium MWD of the polymer in dilute solutions, where interactions between the segments of the different chains may be neglected, has been calculated[55-57]. In order to determine the free energy of this system, a number of workers[55,56] also used the lattice model. It was found[55] that in a poor solvent the MWD obtained are narrower, while in effective solvents they are broader than the Flory distribution. Furthermore, in a good solvent there exists a critical number-average degree of polymerisation above which the MWD becomes bimodal[56]. A fairly dilute solution has been examined[57] with the aid of special statistical physical methods, but only in systems close to θ-conditions. The author[57] arrived at results directly opposed to those of Berlin et al.[55]; in a poor solvent the equilibrium MWD of the polymer broadens, while in an effective solvent it becomes narrower compared to the Flory distribution. This contradiction shows, in particular, that in a quantitative study of the influence of long-range order and solvent effects on the statistical characteristics of the products of even equilibrium polycondensation processes, there are still many controversial questions and unsolved problems.

This applies particularly to non-equilibrium processes where the thermodynamic approach is inapplicable. In order to devise a quantitative theory, it is necessary to determine the dependence of the kinetic constants for the elementary reactions between the functional groups on their location in the macromolecules and on the degree of polymerisation of the latter and then to evaluate the statistical characteristics of the polymer from the solution of the corresponding kinetic equations.

There have been several theoretical studies[58-65] whose authors attempted to calculate the MWD of the products of irreversible polycondensation, specifying several empirical relations between the elementary reaction constants and the degree of polymerisation in the kinetic approach[58,59] or between the probability parameters and the degree of polymerisation in the statistical approach[60-65]. Thus the arbitrary relations $k_0(ij)^{-\epsilon}$ [58] and $k_0[1 - \epsilon(i + j)]$ [59] were adopted for the interaction constants of molecules with degrees of polymerisation i and j; the MWD was not calculated but only approximate (for $\epsilon \ll 1$) and cumbersome expressions were found for the concentrations of dimers, trimers, and tetramers[58] or the formulae for P_N and K_p.[59] In an attempt to extend to non-ideal systems Flory's statistical approach to the calculation of the MWD of ideal polycondensation products, a number of workers[60-65] began with the assumption that all ways leading to the formation of a macromolecule with a given degree of polymerisation l are equally probable. The "history" of the formation of the macromolecule is then unimportant; by considering the successive addition of the monomers to one of the growing chains, the authors therefore obtained the formula $f_N = p(1)p(2)\ldots p(l-1)[1 - p(l)]$ for the numerical MWD of the polymer. The investigators[60-65] then selected empirically two- and three-parameter relations between the probability of the formation of the bond $p(l)$ and the degree of polymerisation l of the reacting molecule and found relations between different molecular weights of the polymer and the parameters of the functions $p(l)$.

It is noteworthy that the assumption of equal probabilities of all ways leading to the formation of a molecule with a fixed length is rigorously justified for non-ideal systems only under the conditions of equilibrium[39]. For non-equilibrium processes, there is no such justification and one can actually quote systems (for example, the irreversible homopolycondensation of a monomer RH^2 with dependent groups) where this assumption is invalid. Consequently the formal application of Flory's statistical method to the calculation of the MWD of the products of non-equilibrium non-ideal polycondensation can lead to erroneous results. All the foregoing considerations apply equally to a study[60] where the assumption of equal

probabilities was effectively also used in the derivation of MWD for this process.

Unfortunately there are at present no experimental data whereby one could establish even for a single system a quantitative relation between the chain propagation rate constant and the length of the reacting macromolecules over the entire necessary range of variation of these quantities. For oligomeric molecules, this problem has been studied experimentally in detail on model systems by comparing the rates of reaction of a hydroxy-group with carboxy- [66,67] and isocyanate [68,69] groups in homologous series of compounds differing from one another solely by their molecular weight. It has been shown that, in all the systems investigated, the functional groups of the molecules separated by a bridge with a length corresponding to more than 2–3 methylene units may be regarded as independent and their reactivities may be regarded as identical regardless of the size of the oligomers containing these groups. Consequently in the absence of the substitution effect, i.e. when the above bridge is sufficiently long, Flory's principle holds in reactions between oligomeric molecules. On passing to high-molecular-weight reactants, there is a possibility of deviations from this principle associated with the macromolecular nature of the reactants, i.e. with long-range order effects. The study [70] whose authors investigated for model systems the dependence of the rate constant for the formation of aromatic polycarbonates on the length of the reacting molecules and the nature of the solvent is therefore of interest. In the range of molecular weights investigated (from 6000 to 28 000) it was shown that the reactivity of the functional groups k_θ is independent of the chain length in the θ-solvent and depends only slightly on the length in an effective solvent, where it diminishes to a constant value k_{eff}. The values of k_θ and k_{eff} are close to the polycondensation rate constants in the corresponding solvents and differ from one another approximately by an order of magnitude. The authors [70] attribute this difference to the difference between the densities of the macromolecular coils and hence to the accessibility of the functional groups, depending on the thermodynamic affinity of the polymer and the solvent.

3. Macrocyclisation Reactions

Linear polycondensation processes are frequently accompanied by the formation of cyclic molecules of different sizes. This usually occurs as a result of the condensation of different terminal groups in the same linear molecule, which has assumed a cyclic conformation as a result of the random motion of its segments. There is also a possibility of attack by one of the terminal groups on an internal bond in the same molecule (for example, intramolecular alcoholysis). In all cases the rate constant (or equilibrium constant when equilibrium has been attained) for the corresponding unimolecular reaction is determined by the effective local concentration c established by one of the groups participating in the reaction in the immediate vicinity of another as a result of various conformational rearrangements of the macromolecule containing them. An important feature of intramolecular reactions, which constitutes a fundamental difference between them and intermolecular reactions, is therefore the dependence of their kinetics on the conformational structure of the macromolecules, i.e. on the possible set (taking into account their probabilities) of steric conformations of the molecules. Examination of conformational statistics shows that, even in the absence of the substitution effect, the cyclisation reaction rate constants depend on the degree of polymerisation of the molecule, the only parameter characterising the configurational structure of the homopolymer. This leads to different types of MWD of the products of equilibrium and non-equilibrium processes. Different approaches are therefore required for a quantitative description of processes in these two classes.

It is usually assumed that the rate of intramolecular polycondensation reactions is not limited by the conformational rearrangement of molecular units, because the characteristic times of these reactions as a rule greatly exceed the time required for the attainment of conformational equilibrium. The effective concentration c therefore agrees with the concentration of the corresponding cyclic conformers of linear molecules. Hence information about the size distribution of the cyclic compounds formed, which may be obtained by gas–liquid and gel permeation chromatography [71], can yield useful data about the equilibrium conformational structure of linear chains, provided that an appropriate theory is available. Calculations on equilibrium polycondensation taking into account cyclisation reactions are based on the thermodynamic principle of detailed balancing [72,73]. Thus the Law of Mass Action for condensation and cyclisation reactions, which are respectively reactions of the exchange type and reactions between terminal groups,

$$C_l + C_m \overset{2k}{\rightleftarrows} C_{l+m} + Z,\ C_{l+m} \overset{k_l}{\rightleftarrows} \tilde{C}_l + C_m,\ C_l \overset{k_l'}{\rightleftarrows} \tilde{C}_l + Z \qquad (2)$$

makes it possible to determine the equilibrium concentrations of linear (C_l) and cyclic ($\tilde{C}_l$) l-mers and to relate the equilibrium constants of these reactions:

$$C_l = Z\nu^l/k,\ \tilde{C}_l = k_l\nu^l,\ k_l' = kk_l. \qquad (3)$$

where Z is the concentration of the side product and the parameter ν is determined from the constancy of the total number of monomeric units in the system. It follows from Eqns. (3) that the MWD of linear chains is described by the Flory law but including a parameter ν which is in general not identical with the conversion. In order to determine the MWD for cyclic species and the parameter ν, it is necessary to know the dependence of the equilibrium constant of the second reaction (2) on l. In conformity with thermodynamics, it is determined by the free energy of this reaction. For fairly large values of l, whereupon the heat of this reaction, i.e. the strain in the corresponding ring, is small, k_l is determined solely by the statistics of the steric conformations of linear molecules and may serve as a measure of their flexibility.

In a theoretical study of these conformations, it is usually assumed that the process takes place in a θ-solvent, neglecting, in particular, the long-range volume effects (i.e. the excluded volume effect) and either the statistics of a freely jointed chain or the more realistic rotational isomer model [75,76], whose parameters are known for many systems [76], are used [72–74]. Both these models lead to a normal (Guassian) distribution of the distances between the ends of a chain with l units and hence to an asymmetric behaviour of $k_l \propto l^{-2.5}$, provided that l is large. The rotational isomer model makes it possible to calculate the proportionality coefficient in this formula for many real chains, which depends on the rigidity [76]. Calculation of k_l for low values of l, when it is necessary to take into account the correlations between the directions of the terminal bonds of linear chains assuming cyclic conformations [73,77] as well as deviations from the normal approximation, can be carried out within the framework of the rotational isomer model, or with the aid of a matrix technique [77–83], or by simulating the conformations of the

chain on a computer by the Monte Carlo method[84-87]. Thus the theoretical treatment in the above studies makes it possible to calculate the equilibrium constants k_l, taking into account the above assumptions for the models selected in the relevant studies and then to evaluate the MWD for the reaction products by Eqns. (2) and (3). Here the initial parameters are only the structural characteristics of the polymer chains: valence angles, interatomic bond lengths, and internal rotation potentials. They have been measured independently for a whole series of polymers[76], which permits calculations without using adjustable empirical parameters.

We shall now formulate certain results obtained within the framework of the above theory. The MWD for cyclic molecules is wider compared with the Flory distribution. For a fairly high degree of polymerisation of linear chains, the concentration of rings is independent of the dilution of the system and depends on temperature to only a very slight extent. On the other hand, the weight fractions of all the cyclic molecules in equilibrium depend significantly on the polymer concentration in solution. Thus there exists a critical value of the latter, below which the polycondensation products are virtually only cyclic species[72-74].

The above theoretical conclusions and results, including the values of k_l calculated on the basis of the corresponding rotational isomer models, were tested by studying (by chromatographic methods) the MWD for cyclic products in a large number of equilibrium systems: polyethers[88], polyesters[89-93], polyamides[94-96], polymeric alkylsiloxanes[97], and polysiloxanes[73,78-81,98-105]. In all the systems investigated, the calculated and experimental values of the constants k_l are in good agreement, with the exception of instances corresponding to very low values of l. Cyclic oligomeric dimethylsiloxanes have been studied both experimentally and theoretically in greatest detail[73,78-81,98-101,104,105]. It was found that the experimental values of k_l obtained when the process is carried out in bulk[79,80,104], agree satisfactorily with the values calculated on the basis of the rotational isomer model in the region $8 \leqslant l \leqslant 200$ [80,81,104] (for long rings, fractionation was not carried out), and the Gaussian approximation is valid (Fig. 1) for $l \geqslant 20$. On the other hand, for low values of l ($4 \leqslant l \leqslant 7$) the experimental data are appreciably higher than the theoretical results[79-81,104]. There is no temperature dependence in the region $4 \leqslant l \leqslant 40$ (the process was not investigated for large values of l). Very similar values of k_l were obtained also when the process was carried out in a poor solvent in the vicinity of the θ-point (diethylene glycol at 333 K).[104] A different behaviour was observed in effective solvents. Thus in toluene the experimental data are described satisfactorily by the rotational isomer model only in the region $8 \leqslant l \leqslant 40$ (Fig. 1), while in xylene the values of k_l are independent of the solvent concentration only when $11 \leqslant l \leqslant 40$ and increase with increasing dilution in the region $4 \leqslant l \leqslant 10$.[80,101] Measurements of the weight fraction of cyclic species at different polymer concentrations[80] confirmed the existence of the critical dilution, predicted by the theory[72,74], which is independent of temperature and above which the system consists solely of cyclic molecules. However, the critical concentrations of the polymer proved to be somewhat higher than the theoretical value[80]. Unduly high observed values of k_l for low values of l are usually attributed to the strain in small rings[106] or to the neglect of correlations between the directions of the terminal bonds in short linear chains which have assumed cyclic conformations[73,77]. However, it has been shown for cyclic polydimethylsiloxanes[107,108] that, for $l \geqslant 4$, the ring strain is virtually zero. Correct allowance for correlations between the directions of terminal bonds within the framework of the rotational isomer model also failed to yield a result for $4 \leqslant l \leqslant 7$.[105] The possible cause of the discrepancy with experiment can therefore be the inapplicability of the model to the description of the statistics of the conformations of such small rings. The unduly low theoretical critical dilution of the polymer, starting from which the latter consists of cyclic molecules, is in all probability associated with an incorrect allowance for small rings. The differences between the theoretical and experimental values of k_l for high values of l in an effective solvent (Fig. 1) can be accounted for by long-range volume effects[71,104]. Thus allowance for the excluded volume effect by means of simulation on a computer[109-112] or analytically[113-115] leads to the relation $k_l \propto l^{-2.8 \pm 0.1}$ or a similar relation[109], which agrees fairly well with the experimental values $k_l \propto l^{-2.86}$ and $k_l \propto l^{-2.69}$ obtained by Brown and Slusarczuk[99] and Wright[104] respectively.

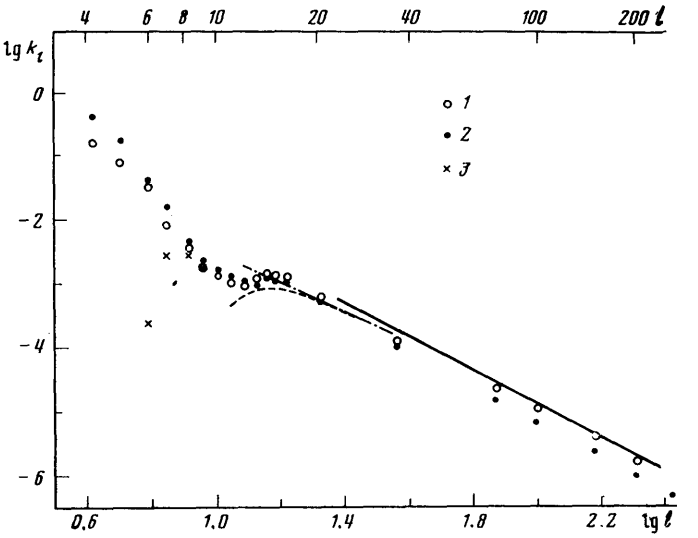


Figure 1. Variation of the equilibrium constants for polydimethylsiloxanes with the degree of polymerisation l. The experimental points were obtained[104] in the absence of a solvent (*1*) and in toluene (*2*) at 383 K. The calculation was performed with the aid of the rotational isomer model in different investigations: continuous line—by Flory and Semlyen[73] (Gaussian approximation); dashed and dot–dash lines—by Suter et al.[105]; 3) by Semlyen and Wright[80].

An important problem is the determination of the relation between the MWD parameters of polymers and their physicochemical properties. An example of this type of study for equilibrium polydimethylsiloxanes is provided by the investigation of Dodgson and Semlyen[116]. Products obtained when the polycondensation was carried out in three different solvents were fractionated to give linear and cyclic components, after which the intrinsic viscosities corresponding to different molecular weights were measured in both fractions. It was found that the relations obtained in a θ-solvent (butanol at 293 K) are very well correlated with the theoretical calculations

predicted previously[117-119]. For example, the ratio of the intrinsic viscosities of the cyclic and linear fractions for identical molecular weights is 0.67, while the theoretical value at the θ-point is 0.662.[116,118,119]

The combined theoretical and experimental studies illustrated above for products of the equilibrium polycondensation of polydimethylsiloxanes make it possible to solve one of the fundamental problems in polymer chemistry: the physicochemical properties of molecules can be determined from their microstructural quantum-mechanical characteristics at least in a θ-solvent. Such studies have been partly carried out also for certain other linear equilibrium polycondensation systems in which cyclisation takes place[71].

The results obtained for irreversible linear polycondensation processes in the presence of intramolecular reactions are much more modest. The MWD for the products of such processes can be calculated only by solving the corresponding kinetic equations, whose form depends on the specific kinetic process mechanism, for example, on whether intramolecular exchange reactions take place or whether cyclisation occurs solely via reactions between terminal functional groups. The rate constant for the reaction between the functional groups of the molecule depends both on its size and on the segmental mobility. As a result of this, even the MWD of linear molecules is not described by the Flory formula in the absence of the substitution effect, which can be readily tested by substituting it in the corresponding kinetic equations.

No general studies have so far been made in order to solve such equations with the aim of investigating the behaviour of the MWD for the products of irreversible polycondensation processes under different conditions, as has been done under equilibrium conditions[72-74]. Solutions of the kinetic equations, derived on the assumption that there are no exchange reactions and no substitution effect, in the interpretation of a specific kinetic experiment[122,123], have been found[120,121]. The kinetics of the formation of lactones from ω-hydroxy acids of the type $HO-(CH_2)l-COOH$ with l between 5 and 24 have been studied[122]. Comparison of the results of this experiment with the solutions of the corresponding kinetic equations made it possible to determine the rate constants for the cyclisation reactions corresponding to different values of l.[120] Sisido[83] showed subsequently that these values are in good agreement with constants which he calculated on the basis of the rotational isomer model for the methylene chain.

The number-average fraction of cyclic polyurethanes, obtained in the reaction of hexamethylene di-isocyanate with poly(ethylene glycols) $HO-(CH_2CH_2O)_{4.5}-OH$ in bulk and in benzene for different dilutions and initial compositions of the monomer mixture, has been measured[123]. By comparing the theoretical expressions with experimental data[123], Gordon and Temple[121] determined the dependence of the cyclisation constants kl on dilution. However, the absence of a rotational isomer model for such chains and the lack of experimental data for the separation of cyclic molecules in terms of their lengths preclude an unambiguous conclusion concerning the applicability of the given theoretical models to the description of the test system.

4. Joint Polycondensation

The molecules of linear copolymers differ, within the limits of the same specimen, by the number of different units (size and composition) and the way in which they alternate in the chain (structure). The equation for the average composition of the products of ideal irreversible interbipolycondensation was obtained independently by Shtraikhman[124] and Beste[125] and the dependence of copolymer composition on conversion for different activities and proportions of the initial monomers was analysed[126] on its basis. If the monomers have dependent functional groups, then in the general case it is not possible to obtain analytical formulae for the composition and the latter must be calculated on a computer[127]. However, it is noteworthy that the problem of calculating the composition of the products of the above process when the initial compounds are supplied simultaneously arises only when their proportions are non-equimolar or when the final reaction products are oligomers. In order to obtain high-molecular-weight products, it is necessary to carry out the reaction between rigorously equimolar amounts of monomers up to nearly 100% conversion. The composition of the copolymer is then always the same as the composition of the initial monomer mixture and the problem of its calculation does not arise.

The first attempt at a quantitative description of the structure of the chains of polycondensation copolymers was undertaken by Beste[125] who calculated the distribution function with respect to length for blocks of various monomeric units in products of ideal intercopolycondensation of a stoichiometric mixture of monomers. For units of the ith type, this function is identical with the Flory distribution having the parameter $b_i = \alpha_i p_i^2$, which depends on the initial fraction of the ith comonomer α_i and the conversion p_i of its groups. It was shown subsequently in relation to interbipolycondensation[128] that this distribution is also obtained in the more general case of an intercomponent with dependent groups, but the parameter b_i is then more complex and is found by numerical calculations on a computer.

A characteristic of the structure of the chains of binary copolymers, which is simple and convenient for theoretical and experimental determination, is the microheterogeneity coefficient K_M, which is expressed in terms of the fractions of different diads of RI and SI elementary units (or triads of monomeric units) by means of the relation

$$K_M = \frac{P(RS)}{P(RS) + 2P(RR)} + \frac{P(RS)}{P(RS) + 2P(SS)}. \qquad (4)$$

For a mixture of two homopolymers, $P(RS) = 0$ and correspondingly $K_M = 0$, while for a regularly alternating copolymer $P(RR) = P(SS) = 0$, to which corresponds $K_M = 2$. Between these two extreme cases, corresponding to an ideally ordered arrangement of units in macromolecules, lie all possible values of K_M, $K_M = 1$ corresponding to the fully statistical (i.e. the most disordered) distribution of units. Consequently the degree of order in the copolymer microstructure may be deduced quantitatively from the absolute magnitude of the deviation of K_M from unity, while the tendency of monomeric units towards either a regular alternation in the chains ($K_M > 1$) or (when $K_M < 1$) towards the formation of long blocks of both comonomers can be inferred from the direction of this deviation. The theoretical problem is to express the fraction of the diads in terms of kinetic (for non-equilibrium processes) or thermodynamic (for equilibrium processes) parameters of the system and to find K_M from Eqn. (4).

The kinetic calculation of K_M, carried out for products of irreversible interbipolycondensation[129], showed that the nature of the chain microstructure is determined mainly by the reciprocal relation between the reactivities of the functional groups in the intercomponent. If they are independent, then, according to the theory, $K_M = 1$ and the

distribution of units for any conversion, comonomer ratio, and the activities of the comonomers is always fully statistical. A general correspondence has been established[129], within the framework of a simplified "substitution effect" model, between the nature of the change in the reactivity of the functional groups in the intercomponent in the course of their reaction with the comonomers and the nature of the distribution of the units in the copolymer. If the activity of the second groups of the intercomponent diminishes when the first groups react, a tendency by the chain units to alternate ($K_M > 1$) should be observed; in the opposite case an increase of the reactivity of the second groups should entail the appearance of a tendency towards the formation of blocks ($K_M < 1$). For the same intercomponent with dependent groups, the degree of order in the copolymer microstructure increases with increasing difference between the reactivities of the comonomers. Certain qualitative conclusions concerning the relation between the microstructure of copolymers, the reactivities of the monomers, and the conditions of non-equilibrium interbipolycondensation were reached by Gritsenko[130-132] on the basis of statistical considerations. However, this approach does not make it possible to follow the dynamics of the changes in the microstructure during the process and to relate K_M to the kinetic parameters of the system.

An attempt at a quantitative description of the chain structure in binary copolymers obtained by equilibrium copolycondensation was undertaken by Sawada[133,134], who expressed the fractions of different diads in terms of the thermodynamic parameters of the RR, RS, and SS bonds. K_M for this process was calculated[135] taking into account the non-equimolarity of the initial mixture of monomers.

The use of high-resolution NMR, which makes it possible to determine with a fairly high accuracy (to within ~5%) the fractions of diads of elementary units in the specimen, gives rise to a considerable scope for the investigation of the composition and structure of polycondensation copolymers. The products of both equilibrium and non-equilibrium copolycondensation have been investigated by this method in many specific systems[136,137]. The method has been particularly successful in the latter case, where its use enabled Korshak and coworkers to discover many general features of non-equilibrium interbipolycondensation in relation to acceptor-catalytic copolyesterification[137]. Comparison of the calculated and experimental values of K_M for this case showed that the quantitative agreement between them for different reactivities of the initial compounds and different process conditions was satisfactory[42].

It is noteworthy that the concept of K_M has significance only for copolymers with two types of elementary units, but even in this case K_M does not in general permit an exhaustive description of the copolymer microstructure, i.e. it does not enable one to find the probability of any given sequence of units in it. For arbitrary copolymers, obtained via a polymerisation mechanism, the general problem of the calculation of the microstructure was solved by Price[138], who showed that the molecules of such copolymers may be regarded as individual manifestations of a Markov chain. The mathematical theory of these chains has been thoroughly developed[139], which makes it possible to express the probabilities of any sequences of units in the copolymer in terms of the parameters of the corresponding Markov chain using standard rules and simple algebraic transformations. Kuchanov's study[140], where it was established that the products of an arbitrary homogeneous joint irreversible ideal polycondensation process are described by Markov's chain whose parameters are related in a known manner to the constants of the elementary reactions and the ratios of the initial monomers, is therefore of general importance for the quantitative theory. An analogous result for equilibrium copolycondensation was obtained by Kuchanov and Brun[135], who showed that allowance for arbitrary order in the theory of "substitution effects" does not infringe the Markov nature of the distribution of units in the copolymer. There is no proof that the products of an arbitrary non-equilibrium process have such a property, although it has been obtained[141] for the copolymers formed in the intercopolycondensation of comonomers having independent groups with an intermonomer whose functional groups are dependent.

The problem of the quantitative description of the inhomogeneity of polycondensation copolymers was first considered by Case[27], who calculated by a statistical procedure the distribution function for the molecules with respect to size and composition (SCD) for products of the ideal bipolycondensation of $S_1A_1B_1 + S_2A_2B_2$ monomers. A complete solution of this problem was obtained by Kuchanov[140,141], who proposed a kinetically justified general algorithm for the analytical calculation of the SCD for an arbitrary irreversible ideal copolycondensation, and who derived, as an example, an expression for such distribution in intercopolycondensation. An analogous algorithm for equilibrium processes was devised by Kuchanov and Brun[135]. The demonstration of an unambiguous correspondence between the configurations of the copolymer molecules and the occurrence of a Markov chain enabled the authors[135,140,141] to obtain simple asymptotic formulae for large values of P_N for SCD and the distribution of polycondensation copolymers with respect to composition. For interbipolycondensation, which was considered by the above workers[135,140,141], the above distributions depend solely on the values of three parameters: P_N, the composition of the initial monomer mixtures, and K_M. Analysis of these relations showed that the distribution with respect to composition becomes narrower with increase of P_N and as the block structure of the copolymer becomes more pronounced with increase of K_M.

The study of Korshak and coworkers[142] devoted to the theoretical and experimental investigation of the homopolymers formed in the course of non-equilibrium heteropolycondensation of monomers with an asymmetric distribution of functional groups has a significant bearing on polycondensation theory. In such polymers there is a possibility of the addition of monomers to the chain in two ways—of the "head to head" and "tail to tail" type, on the one hand, and of the "head to tail" type, on the other, as in the homopolymerisation of asymmetric vinyl monomers. It has been shown[142] that a statistical description of such polymers, taking into account the type of addition of their units, can be achieved on the basis of the formulae of copolycondensation theory.

Proceeding now to the consideration of processes involving the formation of block copolymers, the difference between the mechanisms of their formation in equilibrium and non-equilibrium polycondensation reactions is noteworthy. Thus, in the former case, when the mixture of two homopolymers is heated, exchange reactions begin and lead to a redistribution of the monomeric units in the molecules and the formation of block copolymers[6,7]. A quantitative theory of such a process has been developed by Kotlyar[143], who calculated the distribution of blocks with respect to lengths and the content of residual homopolymers in the system. In non-equilibrium interbipoly-

condensation, even of comonomers with markedly different reactivities, statistical copolymers are formed for the simultaneous introduction of all the initial compounds[42,129]. Block copolymers are obtained in such a process when the intermonomer is introduced gradually and fairly slowly into the reaction zone[42,144]. Under these conditions, the average length of the blocks increases to a limit with decrease of the rate of introduction of the intermonomer, the limit being greater the more pronounced the difference between the reactivities of the comonomers. This conclusion and other experimental relations of the parameters of the microstructure of the copolymers and the kinetic constants and methods of introduction of the initial compounds, obtained in non-equilibrium interbipolycondensation, carried out in different ways, are satisfactorily correlated with calculated data[128,136,137].

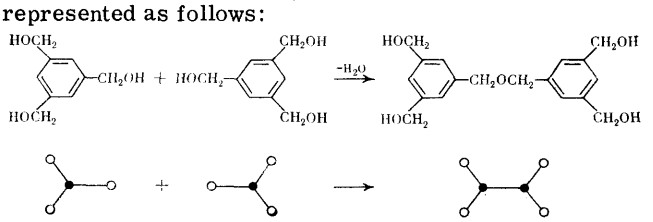
One of the ways of synthesising linear homopolymers and copolymers, widely used in industry, consists of the following steps. An intermediate product is obtained initially in the form of reactive oligomers having terminal functional groups, which are then cross-linked by the polycondensation procedure. The main task of the theory is in this case the determination of quantitative relations between the statistical characteristics of the oligomers, on the one hand, and the polymers formed from them, on the other. In fact, the calculation on such a system is analogous to the calculation on ideal polycondensation. However, in contrast to the latter, the initial compounds can contain different numbers of monomeric units. This problem was considered for the first time by Case[145,146], who calculated by a statistical method the distributions of macromolecules with respect to the degree of polymerisation and the number of oligomeric chains incorporated in them. Bearing in mind that the intermediate oligomers can be obtained both by polycondensation and by ionic and radical polymerisation, Case specified appropriately the MWD for these oligomers. The calculated MWD for the polymer usually differs little from the Flory distribution (1). Only when the cross-linking agent contains functional groups with markedly different reactivities can the MWD for the polymer be significantly narrower[145]. In subsequent studies[21,147,148] an analogous problem was solved for different systems by the kinetic method.

It is noteworthy that molecules with different numbers of useful functional groups (i.e. capable of involvement in further polycondensation) can be formed in the synthesis of the intermediate oligomers. Consequently the concept of "functionality" for such an intermediate has a statistical significance and its quantitative description requires the introduction of a distribution function with respect to the types of functionality (DTF), which determines the number-average and weight-average functionalities of the oligomers[149]. The review of Entelis et al.[149] discusses in detail the possible methods for the determination of DTF for specific oligomers. Systematic experimental studies, permitting a quantitative test of the computational relations established in the studies quoted above, are apparently lacking. We can only note a recent investigation[150], where the influence of the DTF of the initial oligomers on the MWD of the polyurethanes obtained as a result of the cross-linking by di-isocyanates of oligomeric isoprene–butadiene block copolymers with terminal OH groups is the only one that can be mentioned.

III. BRANCHED POLYCONDENSATION

In contrast to linear macromolecules, branched macromolecules can have different steric configurational structures. In order to distinguish individual products of branched polycondensation, it is convenient to represent them schematically by molecular graphs.

(In mathematics a graph is defined[151] as a set of vertices joined by edges.) Each molecule is associated in a one-to-one correspondence with a graph whose topological structure corresponds to the configuration of the given molecule. For example, molecular "trees", i.e. graphs without cyclic fragments, correspond to the products of ideal polycondensation. Chemical bonds are usually associated with the edges of the graph and monomeric units and functional groups are associated with its vertices. Thus the formation of a dimer from two monomeric molecules of a trihydric aromatic alcohol can be represented as follows:



The vertices corresponding to the monomeric units are called nodes (filled circles) and those corresponding to functional groups are referred to as pendant vertices (open circles). Any two nodes of a molecular graph can be connected by a broken line (trail) consisting of edges whose number defines the length of the trail. A linear molecular fragment connecting two monomeric units, called a chain, corresponds to this trail. In the case of trees any pair of nodes is joined by one trail. A definite graph with l nodes corresponds to an arbitrary homopolymer molecule with a degree of polymerisation l (an l-mer) and the number of edges originating from each node of the graph is equal to the functionality of the initial monomer. If several monomers are involved in the process, then the vertices of the graphs corresponding to them are distinguished by colouring the vertices in different ways so that coloured graphs are used for the description of copolymers. The problem of a detailed statistical calculation of the configurational structure of the polymer involves the calculation of the probabilities of various molecular graphs.

An important characteristic of branched polycondensation is gel formation, i.e. the appearance in the system of enormous infusible and insoluble macromolecules having a three-dimensional steric structure‡. Here one can speak of a macrogel or a microgel depending on whether the dimensions of these structures are comparable to those of the reaction apparatus. In the former case, the three-dimensional polymer network occupies the entire reaction volume, while in the latter particles of the microgel are dispersed in it.

Depending on many physicochemical factors (the chemical nature of the polymer formed, its affinity for the solvent, the rate of the cyclisation reaction, etc.) different ways of forming the microgel in branched polycondensation are possible[152]. The simplest involves "homogeneous" gel formation in which the reaction system remains homogeneous during the process up to a certain instant, referred to as the gel point, where it loses fluidity and solubility

‡Only gels formed as a result of a network of covalent bonds and belonging to the first type in Papkov's specification[154] are considered in the present review. Gels of the second or mixed type are disregarded, because of the lack of a quantitative theory of gel formation applicable to them.

almost instantaneously owing to the formation of the macrogel. Together with systems of this kind (we shall henceforth refer to them as classical), there are also others in which the macrogel formation is preceded by the microgel formation stage [153]. In the course of the latter microlayer formation occurs in the system accompanied by the formation of colloid particles whose number and dimensions may vary with time. As a result of the subsequent cross-linking of the microgel particles, they are combined into a single macrogel network. This gel formation mechanism was proposed by Bobalek et al. [153] to account for data concerning the hardening of alkyd resins and was then convincingly demonstrated experimentally in relation to the formation of cross-linked polyurethanes. All attempts at establishing a quantitative theory of gel formation refer solely to classical systems, and an analogous theory for branched polycondensation accompanied by microgel formation is not available.

1. Ideal Systems

In calculations on ideal branched polycondensation various modifications of the statistical approach were used. Together with direct combinatorial considerations use was made of computational methods taken from statistical physics as well as the modern mathematical theory of the enumeration of graphs and of random branching processes. Initially we shall consider in detail studies where calculations were made by these methods of the statistical characteristics of polymers obtained before the onset of gel formation. Next we shall discuss the existing approaches to the description of the process beyond the gel point, and finally we shall illustrate the possibilities of the quantitative theory of branched polycondensation in relation to a specific ideal polycondensation system, investigated in detail by a number of workers both theoretically and experimentally.

Flory [156] was the first to employ a statistical approach to ideal branched systems, having calculated for this purpose all the necessary probabilities (including the probability of an infinitely large molecule, the instant of the appearance of which indicates the onset of gel formation) by means of direct combinatorial procedures. He showed theoretically that gel formation does indeed have pronounced "explosive" properties and is accompanied by an infinite growth of the weight-average molecular weight of the polymer. The conversion of the functional groups p^* at the gel point (the critical conversion) is then independent of temperature, catalyst, dilution, and other process conditions and is determined solely by the functionality of the initial monomers and their fractions. Flory himself considered theoretically only a few specific polycondensation systems [11,156-159] in which not more than one polyfunctional monomer was present, but the computational method which he proposed was later applied to systems which were more complex mathematically. Thus the polycondensation of a polyfunctional monomer with different functional groups, which all react with only one group, has been considered [160,161]. Apart from the MWD, also the distribution function for molecules with respect to different bonds has been calculated. The critical conversion in polycondensation involving several polyfunctional monomers, between which only one elementary reaction takes place, has been calculated in a number of studies [162-167]. In some investigations [165,166] account was taken also of monofunctional additives. Some workers [168-173] calculated the gel point in the polycondensation of various mixtures of mono-, bi-, and poly-functional monomers.

Thus one of the variants of the statistical method, proposed by Flory, has been used until recently in ideal polycondensation systems. However, the corresponding procedure for the calculation of probabilities requires in each specific instance fairly cumbersome and non-evident steps, which was in all probability the reason for the errors made by some investigators using this approach. Thus an incorrect formula has been obtained [162] for the critical conversion in the polycondensation of a polyfunctional monomer with two types of functional groups. Other workers [165,166] incorrectly took into account the influence of monofunctional impurities on the degree of reaction at the gel point [167], while others [172] were unable to attribute the correct statistical significance to the integrals obtained by solving kinetic equations. Finally an attempt has actually been made [174] to construct a statistical scheme for the process, different from that of Flory, on the basis of the same initial postulates, which led to a revision of Flory's fundamental results, including his relation between the critical conversion and the functionality of the initial monomers. However, it was later shown [175-179] that this new scheme is erroneous.

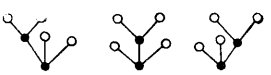
Another variant of the statistical approach to the calculation of the gel point and the MWD (SCD) for the products in ideal polycondensation systems, similar to methods in statistical physics, was proposed by Stockmayer [180-182], who used the fact that, for a fixed conversion, the total number of ways Ω in which all the N monomeric units may be shared between molecules for a given distribution of the latter with respect to the degree of polymerisation in an ideal system is a measure of the probability of the occurrence of such a distribution. For the most probable distribution, Ω has a maximum and in systems with a macroscopic value of N this distribution determines the MWD for the polymer. In order to calculate Ω, it is necessary to solve the problem of the enumeration of all equally probable ways in which the molecular tree with the given number of nodes can be formed. Stockmayer solved this problem by a direct combinatorial calculation for the products of the ideal polycondensation of an arbitrary number of monomers, but only in the case where each monomer has identical groups and only one elementary reaction takes place in the system [181,182].

The application of Stockmayer's statistical method to ideal equilibrium polycondensation has been justified rigorously in a study [183], where Mayer's diagram method [184], well known from the theory of dense gases, was used in succession. As a result it was possible to relate the MWD of the polymer directly to the intramolecular and intermolecular interaction potentials and to calculate various thermodynamic system parameters. The equation of state obtained by Cohen et al. [183] made it possible to draw an analogy between the gel formation phenomenon in polycondensation and the gas–liquid phase transition in the condensation of vapours. Furthermore, the above study threw light on the physical significance of Flory's initial principle and is therefore particularly valuable.

The direct combinatorial method proposed by Stockmayer for the solution of the enumeration problem as well as the corresponding computational scheme proposed by Flory [11,156] are nowadays considered obsolete. It is much more convenient to use for this purpose the methods of graph theory [175,185-195] or the theory of branching processes [196-201], which permit fairly simple and

general calculations on any ideal branched system. Thus the number of different ways in which a molecular tree with a specified number of nodes can be formed is unambiguously related to the symmetry of its configuration, investigated in the theory of graphs [186,187]. The combinatorial entropy of the graph, introduced for the first time by Gordon and Temple [187], can serve as a quantitative measure of this property of the graph. It is noteworthy that Gordon and coworkers [175,186-189] have developed systematically theoretical graph concepts for the description of the products of polycondensation and certain other processes—the so called chemical combinatorial procedure. On the basis of the principle of detailed balancing, they established, for example, a relation between the equilibrium constants of the chemical reactions of branched macromolecules and the combinatorial entropy of the corresponding molecular graphs in ideal polycondensation.

In order to calculate the combinatorial entropy, it is convenient to replace molecular trees by rooted trees. A rooted tree is understood to be one where one of the nodes is distinguished and called the root of the tree [151]. A number equal to the length of the trail connecting any other node with the root is assigned to the given node. This number is called the number of the generation in which the given node is located. A rooted tree is usually represented by a genealogical tree in which all the nodes of a single generation are distributed on a single horizontal line together with all the pendant vertices connected directly to the nodes of the preceding generation. All the possible rooted trees with two trifunctional nodes are represented below:



Evidently two rooted trees can be regarded as identical only if the number and sequence of their vertices (including pendant vertices) in each generation are the same. Having chosen as the root a particular node of the molecular tree and having arranged its vertices in different ways in each generation, we obtain several different rooted trees with the topological structure of the initial molecular tree. It is found [186] that the combinatorial entropy of the latter is related by a simple formula to the number of different rooted trees obtained from it. This number is defined in a standard way in the theory of the enumeration of graphs.

However, the simplest and most universal method of enumerating rooted (genealogical) trees is provided by the theory of random branching processes or more precisely by the Galton-Watson model for such processes [196,197], developed by Good and Otter [198-201]. The formalism corresponding to this theory permits not only a unique enumeration of all such trees but also allows one to determine the probability of each of them. A branching process is one involving the random generation and destruction of particles arranged in the generations of the genealogical tree starting from its root K (Fig. 2) and each particle can reproduce, independently of others, a particular number of new particles (descendants) in the next generation with a specified probability. In the description of branched polycondensation processes either the nodes or the edges between them can be arbitrarily chosen as the particles. The rooted tree represented in Fig. 2 corresponds to one of the individual products of the polycondensation of a trifunctional monomer, the nodes of the tree having been chosen as the particles. The root particle reproduces all others in the first generation; the left-hand particle gives rise in its turn to two particles, while the right-hand particle gives rise to none at all, etc. In the ideal joint polycondensation of several monomers the corresponding molecular and rooted trees contain nodes of different types (a specific colour is assigned to each monomer). The branching process describing such systems must therefore also involve several types of particles, each with its own probabilities of giving rise to a particular number of descendants.

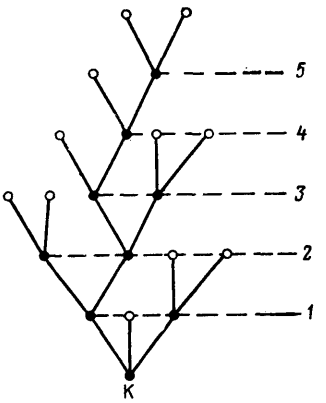


Figure 2. Genealogical tree which is one of the manifestations of a branching process for the ideal polycondensation of a monomer RA^3. The dashed lines connect all the particles of a single generation, whose number is designated by a numeral; K—the root of the tree.

Gordon [202] was the first to suggest that the method of the theory of branching processes be used in calculations on products of ideal branched polycondensation, which led to significant progress in the quantitative description of such systems. Thus the use of a branching process with several types of particles made it possible to calculate [203] fairly simply and uniquely the critical conversions and SCD of a polymer for most general ideal polycondensation systems. Analogous results were obtained independently in some instances by other workers [204,205], who also used for this purpose the theory of branching processes. A rigorous mathematical proof of the applicability of this theory to equilibrium ideal polycondensation processes has been given by Gordon et al. [188]

Another possible approach, which makes it possible to calculate the statistical characteristics of the polymer, consists in the derivation and solution of kinetic equations for the concentrations of various components in a polycondensation process [140,206,207]. When such equations are derived for ideal systems, it is sufficient to distinguish macromolecules solely in terms of the number of functional groups and intramolecular bonds of different types, which significantly facilitates their solution. The results obtained by Kuchanov [140] describe the general irreversible ideal polycondensation process involving an arbitrary number of monomers with any number of types of functional group in each. The SCD of the polymer, found from the solution of the corresponding kinetic equations, agrees

with that calculated with the aid of the theory of branching processes. This confirms that any statistical characteristics of the products of ideal polycondensation processes with specified concentrations of the end groups and intramolecular bonds of all types are independent of whether or not the process takes place under equilibrium conditions. Thus, the critical conversion, MWD, and SCD of the products of ideal branched polycondensation can be calculated in the most general form by both statistical and kinetic methods.

A convenient procedure for the experimental test of the ideality of specific polycondensation systems involves the measurement of the degree of reaction at the gel point, which can be usually done fairly accurately on the basis of the sharp increase of the viscosity of the reaction mixture. The critical conversion has been determined by this method for a fairly large number of systems. When the polycondensation of many of these was carried out in bulk, the experimental values proved to be fairly close to the calculated results obtained by the methods described above. Some of these systems are presented in the Table. The slight discrepancy between theory and experiment can be explained[156] by the occurrence of intramolecular reactions leading to some increase of the critical conversion.

Comparison of the theoretical and experimental conversions at the gel point for certain systems.

System	Monomers			Molar proportions of monomers	p^*_{theor}	p^*_{exp}	Refs.
1	Tricarballylic acid	Adipic acid	Diethylene glycol	0.195:0.707:1	0.88	0.91	156
2	Ditto	Succinic acid	Ditto	0.129:0.806:1	0.92	0.94	156
3	"	Ditto	"	0.270:0.597:1	0.84	0.89	156
4	Benzene-1,3,5-triacetic acid	———	———	———	0.50	0.52	220
5	———	———	1,3,5-Tris-(hydroxymethyl) benzene	———	0.50	0.51	220
6	Benzene-1,3,5-triacetic acid	———	Decamethylene glycol	0.667:1	0.71	0.72	220
7	Tridecanoic acid	———	Pentaerythritol	1.333:1	0.577	0.55	220
8	Lauric acid	Adipic acid	Tris(hydroxymethyl)ethane	1.000:1.000:1	0.866	0.908	166
9	Ditto	Isophthalic acid	Pentaerythritol	1.250:1.375:1	0.696	0.760	166

The statistical characteristics of the products of polycondensation processes examined above do not by themselves yield complete information about the properties of the polymer obtained. Thus many physicochemical parameters of branched macromolecules in solution (average size, intrinsic viscosity, intensity of light scattering, and hydrodynamic Stokes radius) are determined by their conformational and configurational structures. The problem therefore arises of the calculation of the corresponding statistical characteristics of macromolecules by averaging with respect to all their conformations and configurations. In the solution of this problem it is usually assumed[203,208-212] that each chain in the branched macromolecule is freely jointed and is at the same time capable of assuming different conformations regardless of the positions of other parts of the macromolecule. In addition it is postulated that chemical reactions do not affect the conformational equilibrium. These assumptions permit averaging with respect to all the conformations of the molecule with an arbitrary configurational structure and the problem reduces to the calculation of the probabilities of different configurations. In ideal systems methods of the theory of branching processes are again the most suitable for this process. The average dimensions of branched macromolecules formed in the ideal polycondensation of a monomer RA^f [208] and in the polycondensation of several monomers[203] were calculated for the first time with their aid. The theory of branching processes has been applied most logically and fully to the study of the configurational statistics of polycondensation polymers[209-212]. As a result, all the physicochemical parameters enumerated above were calculated by a single method for any ideal branched polycondensation processes, including multicomponent processes[212]. This greatly extends the scope of the experimental test of the theory of such systems. However, one should note the complete neglect in the above calculations of the excluded volume effect, which may play an even greater role in branched polymers than in linear polymers.

So far our discussion of ideal systems was restricted to the purely homogeneous stage of the polycondensation process, up to the gel point. It is important to determine the properties of a classical polycondensation system after the onset of gel formation during the period of the so called hardening when the reaction mixture contains two fractions: the insoluble gel and the dissolved low-molecular-weight sol, the proportion of which decreases with increase of conversion. If the initial postulates of the theory of ideal systems are formally adopted, it is necessary to "prohibit" all intramolecular reactions, including those in the macroscopic gel molecule. The corresponding model was proposed first by Stockmayer[180] and was later developed in detail by Whittle[213]. Here the complete conversion of functional groups cannot exceed a limiting value (equal to $2/f$ for the polycondensation of a monomer RA^f) and the MWD of the sol fraction as well as its average degree of polymerisation remain constant throughout the "hardening" process[213,214] (Fig. 3*a*). The hypotheses underlying this model correspond to virtually infinite rigidity of the gel molecule, as a result of which the effective local concentrations of its end groups in the vicinity of each of them, which determine the rate of the intramolecular reaction, may remain much smaller than their average concentration in the reaction mixture. It is noteworthy that classical systems obeying such rules are not known at the present time[214].

A more realistic model for the calculation of the statistical characteristics of the polymer beyond the gel point was proposed by Flory[156,215]. Here intramolecular reactions are prohibited only in molecules of the sol fraction and Flory's principle of equal activity is assumed to be valid for all the remaining polycondensation reactions, including the cyclisation reactions in the gel. Hence it is assumed that the intramolecular reactions between the functional groups of the gel fraction proceed, like the intermolecular reactions, in conformity with the Law of Mass Action. With these assumptions, all the statistical characteristics of the sol fraction, including the proportion by weight, as for ideal systems up to the onset of gel formation, and the average degree of polymerisation of the molecules beyond the gel point[217] can be calculated by methods of the theory of branching processes for both polycondensation[205,208,216] and copolycondensation systems[203,212]. The results of some of these calculations

for the polycondensation of a trifunctional monomer are presented in Fig. 3*b*. It is noteworthy that the hypothesis of the validity of the Law of Mass Action for reactions between functional groups belonging to the same macroscopic network is not entirely correct even for infinite flexibility of its chains, because here too the motion of its functional groups is not absolutely free and hence absolutely random. Nevertheless, this model gives a much better description than the previous one of the products of real polycondensation processes, which is confirmed by the experimental values of the statistical and physicochemical characteristics of the sol fraction[212,218].

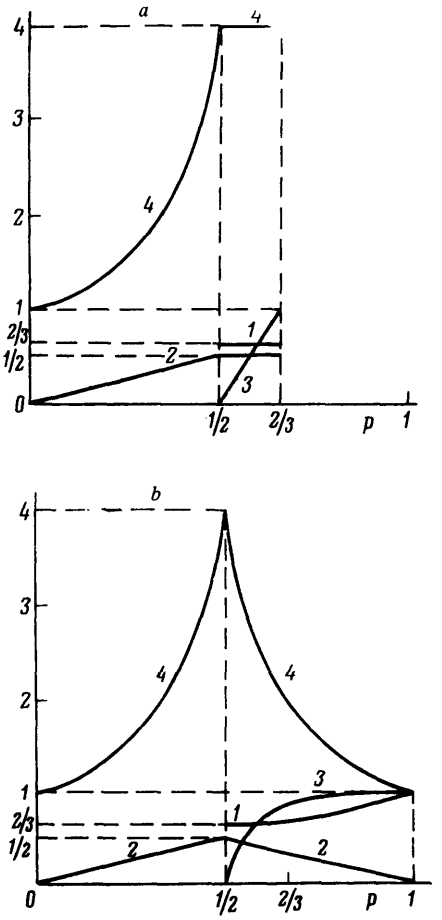


Figure 3. Calculated relations between certain statistical characteristics of the polymer and the conversion of the functional groups in the ideal polycondensation of a monomer RA^3 for the Stockmayer[180] (*a*) and Flory[156] (*b*) models: 1) conversion of the functional groups of the gel fraction; 2) ditto for the sol fraction; 3) proportion by weight of the gel fraction; 4) number-average degree of polymerisation of the sol fraction.

Various theories of the viscoelasticity and swelling of polymer gels[219-221] include as a parameter the number N_e of elastically active chains (EAC)§ of the network. For example, the modulus of elasticity and hence the strain on extension are proportional to N_e.[220] The theory of branching processes makes it possible to calculate N_e and the average length L_e of the EAC in gels formed in ideal polycondensation for the second of the two models discussed above[225]. However, the results obtained can apparently be used only during the initial period of gel formation even in ideal systems. This is because this type of treatment, based on the theory of branching processes, suffers from internal contradictions. On the one hand, a branching process can only be represented by trees, which applies entirely also to the configurational structure of the macroscopic gel molecule. On the other hand, intramolecular reactions in the gel, which are bound to occur beyond the gel point in the model employed, lead to the formation of cyclic fragments. This contradiction entails the so called paradox of "Malthus packing"[214,226,227], consisting in the fact that rooted trees, which are manifestations of the branching process, cannot be accommodated ("packed") in the three-dimensional space beyond the gel point in such a way that the average density of their nodes does not increase without limit as the generation number increases. This follows from the fact that, when $p > p^*$, the average number of particles in each generation, calculated with the aid of the branching process, increases exponentially as $(p/p^*)^n$ with the number n of the generation, whereas the volume in which they must be distributed is proportional to n^3. Only in the immediate vicinity of the gel point ($p/p^* \simeq 1$), where the number of rings in the gel is still relatively small, can one expect the theory to be adequate. Some studies[220,228-230] have demonstrated a satisfactory agreement between the theory and experiment in weakly structured polycondensation gels (Figs. 4 and 5).

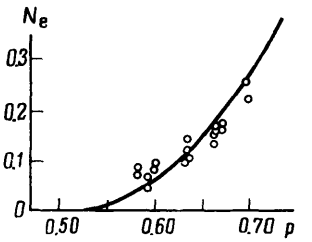


Figure 4. Dependence of the EAC concentration on the conversion determined experimentally from the equilibrium swelling of a phenol-formaldehyde resin[229]. Continuous line—theoretical curve calculated for the corresponding ideal system[220,229].

§This is the name given to any chain bounded by two nodes, each of which has at least three bonds directed to the boundary of the network and containing no other nodes of this kind within it[222-224].

It is noteworthy that the polycondensation reaction in a strongly cross-linked gel cannot proceed under kinetic conditions at all owing to the considerable diffusion-dependent hindrance to the motion of functional groups, which makes it still more difficult to construct an appropriate theory.

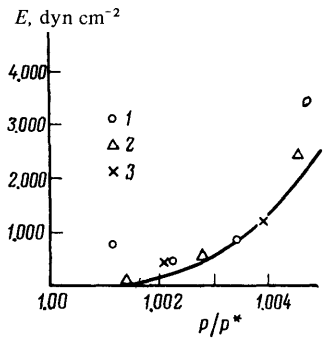


Figure 5. Dependence of the modulus of elasticity E on the conversion of the functional groups for the products of the joint polycondensation of a stoichiometric mixture of decamethylene glycol and benzene-1,3,5-triacetic acid in the melt at 423 K, obtained in three independent experiments (*1–3*) in the "critically branched region" [230]. Continuous line—theoretical curve calculated [230] with the aid of the classical theory of viscoelasticity in which the EAC concentration is evaluated from the formulae for the corresponding ideal system.

Summarising, we may thus say that the theory of ideal branched polycondensation processes is virtually complete only in the field of pre-critical conversions and permits the calculation of the statistical parameters of the reaction products in the immediate vicinity of the gel point. On the other hand, theoretical study of the polymer for higher conversions, particularly of the structure of highly cross-linked gels, constitutes a problem which is still far from being solved. Its solution within the framework of the model of ideal polycondensation is in principle impossible.

The above theoretical results permit the calculation from the known kinetic or thermodynamic parameters of a specific polycondensation system of various statistical characteristics of a polymer obtained for different conversions (both before and after the onset of gel formation) and thus one can obtain extensive information about its structure and about the associated physicochemical and mechanical properties of the products. Combined experimental studies make it possible to establish the adequacy of the ideal model in the process investigated. The initial monomers should then be as far as possible rigid and should have functional groups at a fairly large distance from one another in order to avoid cyclisation and substitution effects. Examples of such monomers have been published [231].

This type of combined study has been recently carried out by Gordon and coworkers [212,218,230,232–236] for the copolycondensation in bulk of a stoichiometric mixture of decamethylene glycol and benzene-1,3,5-triacetic acid. Kinetic measurements established [212] that this reaction is described by a third-order kinetic curve and that its rate is independent of temperature in the range 413–443 K. The weight fractions of both monomers and the dimer, throughout the region up to the gel point, were measured [232] with the aid of gel permeation chromatography and it was possible to compare them with the theoretical values for an ideal system (Fig. 6). The so called critically branched polymer [218], i.e. specimens obtained in the range of conversions directly adjoining the critical conversion both on the left-hand side ($p < p^*$) and on the right-hand side ($p > p^*$), has been studied in particular detail [218]. Thus the value $p^* = 0.720 \pm 0.006$ has been determined with a high accuracy from the measured viscosities of the system in the pre-critical region [230,233] (Fig. 7), which agrees fairly well with the theoretical value $p^* = 1/\sqrt{2} \simeq 0.707$. Hence it was concluded that a "critically branched polymer" contains virtually no rings (not more than one ring bond in one hundred [218]). The modulus of elasticity E was measured by the method developed previously [237] immediately beyond the gel point for different conversions [220,230,233]. Its values also agreed satisfactorily with the calculated results (Fig. 5).

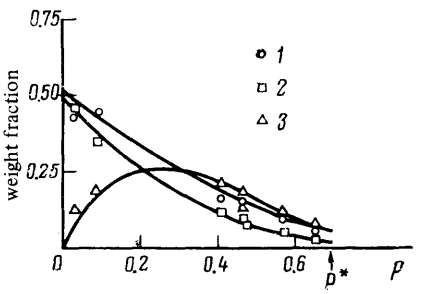


Figure 6. Variation of the weight fractions of decamethylene glycol (*1*), benzene-1,3,5-triacetic acid (*2*), and the corresponding dimer (*3*) with increased conversion of the functional groups in the joint polycondensation of these monomers in the melt at 423 K. The experimental points were obtained [232] by gel permeation chromatography. Continuous lines—theoretical curves for the ideal system [232].

In addition, the following further experiments were performed on the system considered. Specimens of a "critically branched polymer", taken both before the gel point and after it (sol fraction), were stabilised by the addition of monofunctional compounds in order to bind the residual functional groups [234]. The specimens were then dissolved in butanol [236] or ethyl methyl ketone [212,235] at 298 K. The average square of the macromolecular radius z was measured by the light scattering method [212,236] and the sedimentation and diffusion coefficients were determined with the aid of an ultracentrifuge [235] in the solutions thus obtained. The calculation [212,218], carried out with the aid of the theory described above for ideal systems, made it possible to evaluate from these data the weight-average molecular weights of the specimens, which proved to be close to the corresponding values obtained from kinetic and viscometric experiments. In addition, the average distance between the monomeric units in the molecules was calculated. The values of the latter quantity agreed

almost fully for pre-gel and post-gel specimens and were found to be almost independent of the molecular weight[212,218], which also confirms the validity of the theory used in the calculation. Thus extensive experimental and theoretical studies demonstrated the virtually complete adequacy of the ideal polycondensation model for the system under consideration, which gives rise to the hope that the model may be used widely in the investigation of the properties of the products of various branched polycondensation processes.

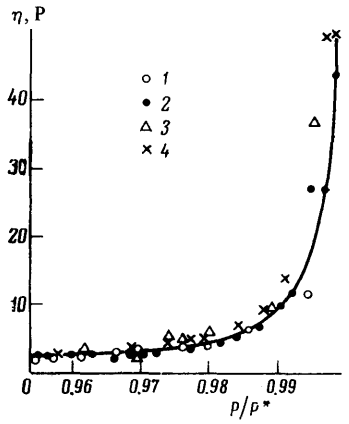


Figure 7. Variation of the viscosity η with the conversion of the functional groups in the "critically branched region" for the same system as in Fig. 5, measured in four independent experiments (*1–4*).[230] The continuous line is described by the theoretical relation between η and the weight-average molecular weight calculated from the formulae for the ideal system [232].

2. The Substitution Effect

As a result of the substitution effect in branched polycondensation, the reactivities of isomers with the same degree of polymerisation may be different. For example, in the first-order substitution effect model, where the activity of an arbitrary functional group depends on the number and positions of groups of each type which have reacted and which are attached to the monomeric unit containing the given group, the reactivity of the molecule is determined by the numbers of its monomeric units with different configurations. It is therefore necessary to distinguish molecules in this model in terms of this feature. Correspondingly, in second-, third-, and higher-order substitution effect models all the molecules are distinguished in terms of the different configurations of pairs, sets of three, etc. adjacent monomeric units present in them. In calculations on the corresponding processes the same methods were used[226,238–246] as for ideal systems but with certain modifications.

The first calculation on a branched polycondensation process taking into account the first-order substitution effect was carried out by Gordon and Scantlebury[238] in the polycondensation of a monomer RA^f. In all the studies published to date, with two exceptions[226,239], the substitution effect was taken into account only within the framework of this model, which will be henceforth assumed to be understood and will no longer be stipulated. Gordon and Scantlebury[238] used the methods of the theory of branching processes in their calculation, but proposed a method for specifying the probabilities of the multiplication of particles different to that in ideal systems. They suggest that the probability that a particle generates a particular number of descendants depends on the configurational structure of the unit corresponding to the particle. Gordon and coworkers believed that their theory describes any polycondensation of a monomer RA^f and they calculate the parameters of the model for two extreme cases: equilibrium and irreversible processes [238]. Gordon and Scantlebury[238] obtained the dependences of the number-average and weight-average molecular weights and of the conversion at the gel point on these parameters, while Dobson and Gordon[208] extended these results to the calculation of the statistical characteristics of the sol fraction of the polymer beyond the gel point. Using a similar computational method, Luby[240] later calculated the distribution of the polymer molecules with respect to the numbers of their monomeric units containing different numbers of groups which have reacted. Gordon and coworkers[238,241] believe that the products of both equilibrium and non-equilibrium polycondensation of any number of arbitrary monomers may be described with the aid of a branching process, taking into account the substitution effect in the monomers, by analogy with ideal systems. In particular, such a process has been indicated[241] for the $RA^2 + SB^f$ system (only groups of different types react) with the substitution effect in both monomers. Since the mathematical apparatus for branching processes makes it possible to calculate all the necessary statistical characteristics of the polymer, Gordon and coworkers thus regard the theory of branched polycondensation with the substitution effect as complete in principle[226].

However, this view is open to objection for several reasons. In the first place the applicability of the methods of the theory of branching processes to calculations on the systems considered was not proved[226,238,241]. The necessity for such proof becomes clear even from an examination of the simplest of these sytems: the polycondensation of a monomer RA^f with allowance for the substitution effect. Analysis showed[239] that the products of the corresponding equilibrium process can indeed be described by methods of this theory. On the other hand, the MWD of the polymer obtained in irreversible polycondensation with the substitution effect does not agree with the formulae of the theory of branching processes. This can be tested by substituting them in the corresponding kinetic equations[12]. Consequently the question of the applicability of the theory of branching processes, like that of any statistical method, to the calculation on each specific polycondensation system with the substitution effect requires separate analysis.

Another statistical approach to the description of the products of equilibrium polycondensation with the substitution effect was proposed by Whittle[242,243]. This method is based on the application of the principle of detailed balancing to specific equilibrium reactions occurring in the system, using in the calculation elements of graph theory. Whittle examined theoretically the polycondensation of both a single monomer RA^f [242] and of several types of monomers $R_iA_i^{fi}$, but only for the case where the reactions take place between the functional groups of different monomers[243]. His method makes it

possible to calculate the statistical characteristics of the polymer before the onset of gel formation and to calculate the critical conversion at the gel point. For a single monomer, Whittle's results agreed[242] with the corresponding values which follow from the theory of branching processes[238]. For copolycondensation processes, Whittle's study did not reach the stage of computational formulae. Some workers[168,169,244,245] calculated the gel point in specific branched polycondensation processes with the substitution effect by Flory's statistical method having extended it to the case where one of the monomers involved in the process has dependent groups. In these studies[168,169,244] the substitution effect was taken into account only for groups of bifunctional monomers and in that of Durand and Bruneau[245] only for a trifunctional monomer. The study of Kuchanov and Pis'men[246] is the only one where a calculation was performed on the branched polycondensation of monomers with dependent groups by a kinetic method. They proposed a general approach, which makes it possible to derive the corresponding kinetic equations for polycondensation processes in which the substitution effect is significant.

The second-order substitution effect was considered theoretically for the first time by Gordon and Parker[226] for the polycondensation of a monomer RA^f. They suggested that the MWD of the products of the corresponding reactions be described in terms of a branching process. However, as noted above, even in the first-order substitution effect model the statistical characteristics of the products of non-equilibrium polycondensation in such a system cannot be described with the aid of any branching process. This also applies to the second-order substitution effect model. The applicability of the method of the theory of branching processes to the calculation of the products of equilibrium polycondensation within the framework of this model was proved by Brun and Kuchanov[239], who also established a relation between the statistical parameters of the branching process and the thermodynamic parameters of the system. In the formal approach used by Gordon and Parker[226] this relation was not established, which significantly restricted the possibilities for the interpretation of the experiment.

The presence of the substitution effect in branched polycondensation processes was tested in the synthesis of polyesters[241,245,247], polyurethanes[248], and phenol-, melamine-, and urea-formaldehyde resins.[249,250] In particular, a small positive substitution effect, where the bonds formed accelerate the reaction of the terminal groups adjoining the monomeric unit, was established for pentaerythritol, tris(hydroxymethyl)ethane, and tris-(hydroxymethyl)propane in their esterification by adipic or lauric acids[241,247,249]. On the other hand, in the formation of polyurethanes a negative substitution effect was observed[248]. The study of Durand and Bruneau[245] merits most attention among the available experimental investigations. In relation to the polycondensation of tris(hydroxymethyl)propane (SB^3) with adipic (R_1A^2) and lauric (R_2A) acids in the melt, they proposed a general method for testing the adequacy of the substitution model in a specific process and a procedure for determining the parameters of this model. For this purpose, they esterified tris(hydroxymethyl)propane with lauric acid in a preliminary step under the same conditions. The products of this reaction were analysed on a chromatograph and the results were used to determine the fractions of tris-(hydroxymethyl)propane which failed to react and of its mono-, di-, and tri-esters for different conversions. The kinetic constants for the esterification of the functional groups of the same monomers, whose ratios characterise the substitution effect in the triol, were evaluated by comparison with the calculated relations. The conversion at the gel point for the initial process was then calculated from the observed kinetic parameters and was compared with the corresponding value obtained from an independent experiment.

3. Cyclisation in Polycondensation Processes

The intramolecular reactions occurring in the course of branched polycondensation lead to the formation of macromolecules with a particular number of different rings. The corresponding molecular graphs should also contain cyclic fragments. The problem of the identification of such cyclic graphs is much more complex than the corresponding problem for trees. However, its solution is necessary for a complete physically adequate description of intramolecular reactions, because, as already mentioned in the introduction, in contrast to ideal systems the calculation requires allowance for long-range effects in this instance. A rigorous quantitative theory of branched polycondensation accompanied by cyclisation is lacking at the present time, although there have been individual studies[190,206,243,251-261], whose authors attempted to solve the corresponding problem by means of various arbitrary assumptions. However, the latter are more likely to obviate the mathematical difficulties arising in the calculations than to reflect the physical picture of the process. At the same time any scientifically well founded model must take into account to some extent the physicochemical features of the system.

We shall next consider briefly the factors which may influence the course of intramolecular reactions in branched polycondensation and shall point out the possible approaches to their quantitative description. An attempt will also be made to analyse the initial postulates underlying the available models, which permit calculations on the products of the corresponding processes. This is of interest because the authors of the models themselves were not concerned with problems of their physicochemical justification. Although, for the sake of simplicity, we shall discuss only condensation reactions in a homopolymer among all the possible intramolecular transformations, the consideration of analogous reactions in copolymers and also of intramolecular exchange reactions does not alter the qualitative picture of the process.

The elementary step in the intramolecular condensation reaction consists in the interaction of two terminal groups of one molecule with formation of a cyclic fragment in the latter. The probability of such interaction is determined by the relative steric positions of the reacting groups, which depend on the conformational-configurational structure of the molecule. Depending on which pair of functional groups react, particular configurational isomers of the initial molecule will be obtained. Here it is significant that the interaction constants are generally speaking different for each pair. The interconversions of isomers associated with intramolecular reactions therefore have different probabilities. On the other hand, the pair of functional groups which have reacted can be deduced unambiguously from the configurational structures of the initial and final isomers and hence the rate constant for the corresponding unimolecular reaction can be determined (or the corresponding equilibrium constant, if equilibrium is established). Thus, in order to construct

a rigorous theory of branched polycondensation with cyclisation, it is, firstly, necessary to identify in some way all isomers and, secondly, to specify the probabilities of their interconversions. However, the problem can hardly be solved in this general formulation. It is therefore apparently necessary to construct less general models in which the nature of the simplifying assumptions is associated with specific physicochemical characteristics of the system under consideration. These characteristics must determine a particular set of values of constants for the interaction between possible pairs of functional groups in each molecule. By virtue of such model assumptions, there is a possibility of either a significant decrease of the number of transitions between configurational isomers which can occur as a result of intramolecular reactions or many such transitions can become equally probable.

We shall now quote certain considerations concerning the possible selection of these constants. Regardless of whether or not polycondensation is carried out under equilibrium conditions, the probability of the interaction of any two functional groups, say the ith and jth groups, belonging to a macromolecule with a specific configurational structure σ is determined by the effective concentration c_{ij}^{σ} established by one of them in the immediate vicinity of the other for different conformational rearrangements of the molecule in which they are contained. One of the quantities characterising the relative positions of an arbitrary pair of groups in the molecule is the number of chains connecting these groups with one another. In a tree-like molecule, any two functional groups are joined by a single chain. If the fraction of bonds present in cyclic fragments of the molecule (cyclic bonds) is small, a greater proportion of its functional groups possesses this property. It is reasonable to suppose that in this case c_{ij}^{σ} for each pair of such groups depends only on the statistics of the possible conformations of the chain connecting them, which can be determined, as for linear molecules, either by means of the model of a freely jointed chain or the corresponding rotational isomer model. This approximation implies that, in the calculation of the conformational structure, account must be taken only of short-range order effects; the long-range order effects (excluded volume) are neglected. With increase of the number of cyclic bonds, there is an increase of the fraction of functional groups connected by two and more chains. Calculation of the effective concentrations of these groups becomes significantly more complicated. On the one hand, because of the presence of cyclic fragments the corresponding sections of micromolecules contract and become denser, which should lead to an increase of c_{ij}^{σ} and, on the other hand, these sections become more rigid as a result of the appearance of cross-linked structures (skeletons), which prevent the formation of the conformers necessary for the occurrence of the intramolecular reactions. In addition, it is necessary to take into account the possibility of the appearance of loops, nodes, etc.

We shall consider the approaches, described in the literature, to a quantitative description of the products of branched polycondensation accompanied by cyclisation. Here we shall state the conditions which must be imposed on the possible values of c_{ij}^{σ} in a particular model and hence shall define the initial postulates underlying each of them. In the first place we may note that, if we put $c_{ij}^{\sigma} = 0$ for all the functional groups, we arrive at the ideal polycondensation model, naturally subject to the condition that Flory's principle holds for intermolecular interactions, which henceforth will be always understood. In order to carry out calculations on the irreversible polycondensation of a monomer RA^f with allowance for intramolecular reactions, Hoeve[252] extended the statistical Stockmayer method[180]. It was assumed that in the macromolecules formed each monomeric unit may form part of not more than one ring, so that the homopolymer molecules differ not only by the degree of polymerisation, as in Stockmayer's treatment[180], but also by the numbers of monomeric units in rings of different sizes present in them. Hoeve[252] was able to solve the corresponding combinatorial enumeration problem and hence could determine the MWD of the polymer up to the gel point and the critical conversion p^*. His assumption that each monomeric unit belongs to not more than one ring is equivalent to the condition $c_{ij}^{\sigma} = 0$ for all the functional groups connected by two and more chains. It should not influence the result significantly when the number of such groups is comparatively small, i.e. for a small fraction of cyclic bonds. However, the statistical method used in the calculation can be justified only for equilibrium process conditions. On the other hand, the statistical characteristics of the configurational structure of the polymers obtained under the conditions of equilibrium and in its absence should differ in this model (this can be readily shown, for example, for the specific case where $f = 2$). The results obtained[252] for an irreversible process are therefore erroneous. On the other hand, at equilibrium it is possible to deduce from them that the critical conversion p^* is smaller than its value for the corresponding ideal system and to a greater extent the lower of the concentration of monomeric units, i.e. the higher the dilution of the reaction mixture.

In order to deduce the initial postulates underlying other models, we shall consider the effective concentration $c_i^{\sigma} = \sum_j c_{ij}^{\sigma}$ set up in the vicinity of a definite functional group i of a macromolecule by all other groups in this molecule. The quantity c_i^{σ} defines the probability that the ith group is involved in any intramolecular cyclisation reaction and in the general case depends not only on the rigidity and configuration σ of the macromolecule but also on the site occupied by the ith group in the latter.

The same system was considered by Pis'men and Kuchanov[206] as in Hoeve's study[252], but only the kinetic method was used and there were different model assumptions. In the derivation of the corresponding kinetic equations for the concentrations of the macromolecules the authors assumed that the probability of the involvement of a functional group of the molecule in a cyclisation reaction is proportional to the total number of groups in this molecule. Examination of the solution of the equations derived showed[206] that, within the framework of the model considered, the gel point is absent in its classical definition. For a fairly low value of the parameter ϵ (equal to the ratio of the probabilities that the functional groups is involved in intramolecular and intermolecular reactions respectively), the instant of gel formation is defined mathematically not as a point but as a narrow (narrower the lower the value of ϵ) range of conversions, during which there is a sharp change in the weight-average degree of polymerisation, although the latter never becomes infinite[206]. This model corresponds to the assumption that the effective concentration c_{ij}^{σ} for any pair of functional groups in the reaction mixture is the same regardless of, for example, the number and length of the chains

connecting them. Consequently this assumption completely ignores the conformational structure of the molecules. The value of c_i^σ for all the functional groups in each macromolecule is then independent of i and is proportional to their total number in the molecule.

On the analogous model assumption, the same system, but under equilibrium conditions, was considered by Harris[251] and Whittle[243] (Harris[251] proposed yet another model, which will be analysed below). In the first of these studies Stockmayer's statistical approach was used[180], but the molecules differed not only by the number l of monomeric units but also by the number s of their intramolecular bonds, so that the probability of any molecule was determined by the values of l and s. It was assumed that any group can form an intramolecular bond without any restrictions, including a cyclic bond, with any group in the system, i.e. no restrictions were imposed on the set of configurations considered. In the second study[243] the calculation was performed with the aid of the principle of detailed balancing together with elements of graph theory. It was found[243] that the weight-average degree of polymerisation of products becomes infinite at an infinitesimal conversion, which is qualitatively inconsistent with the corresponding result[206] for an irreversible process. The absurdity of the value $p^* = 0$ obtained, which the authors themselves noted[243,251], is associated with the complete neglect of the conformational and configurational structure of the molecules in the model. The probability of any molecule with definite values of l and s is in this case proportional to the number of all possible steric configurations with the given values of these quantities. This number increases with increasing l and s (much faster than in the case of trees) and, for macromolecules with a high degree of polymerisation, becomes so large that the probability of a macroscopic gel molecule becomes non-zero however low the conversion.

Another model for calculations on the products of the polycondensation of a monomer RA^f has been proposed by Irzhak et al.[259]. In this case the intramolecular reaction is regarded as one of the variants of chain termination where any functional group can be involved in the cyclisation reaction regardless of the others and can thereby lose the capacity for further participation in the process. In conformity with this hypothesis, it is suggested that the calculation be carried out with the aid of a special branching process. In order to take into account the intramolecular reactions, particles of another type, incapable of multiplication and corresponding to the groups which have reacted with formation of cyclic bonds, were introduced into the model. The model corresponds to the ideal polycondensation of the initial monomer in the presence of a monofunctional impurity giving rise to chain termination, and the model therefore permits a simple calculation of any statistical characteristics of the polymer. Apart from the conversion, a parameter of this model is the probability of cyclisation, i.e. the probability that a group which has reacted is involved in a cyclic bond. The critical conversion p^*, calculated in this way, increases for larger values of this parameter. An attempt has been made[260,261] to calculate it and to justify the proposed model in the case where only groups joined by a single chain can take part in an intramolecular reaction. For this purpose, the probability of the cyclisation of any group is represented by the sum of the probabilities of their reaction with formation of rings of all possible sizes. In the calculation of these probabilities use is made of the conformational statistics of a freely jointed chain and also of the hypothesis that the size of any ring formed when two groups interact is equal to the difference between the numbers of generations of the genealogical tree (Fig. 2) in which they are located. However, such an attempt to calculate the probability parameters within the framework of the same statistical method is incorrect, because two functional groups, even those in the same generation, may be joined by a chain of arbitrary length and therefore the ring formed when they react can also be of any size. In fact the model proposed by the authors[259-261] is based on the hypothesis that the effective concentration c_i^σ for any functional group in the reaction system is independent at each instant of the molecule to which the given group belongs and of the site where it is located within the molecule. This is equivalent to the employment of the Flory principle for intramolecular reactions. Hence it follows, in particular, that the statistical characteristics of products, including the critical conversion, are independent, as for ideal polycondensation, of whether or not the process is carried out under equilibrium conditions.

In fact this hypothesis also constituted the basis of an earlier study by Kilb[253], who calculated the critical conversions in the $RA^2 + SB^f$ and $RA^2 + S_1B^2 + S_2B^f$ systems, in which the condensation reaction takes place only between groups of different types. Kilb was able to complete the calculation only for the first of these systems. In contrast to previous workers, he used for this purpose Flory's statistical method, which is fairly cumbersome and is not one most convenient for calculation, having extended it to the case where each functional group can be involved in the cyclisation reaction with a certain probability. Although this computational scheme is technically more complex than that employed in other studies[259-261] (particularly because the assumptions underlying it are less evident), the two schemes are fully equivalent from the standpoint of the final results. All the conclusions and remarks which we have made concerning the initial postulates of the model devised by Irzhak and coworkers[259-261], including the cyclisation probabilities associated with the calculation, are fully applicable also to Kilb's results[253].

Yet another model for calculations on the equilibrium polycondensation of the monomer RA^f accompanied by cyclisation, which resembles, from the standpoint of the initial assumptions, the models just described, was proposed by Harris[251] in order to obtain more likely results than those which follow from his first model. He again used Stockmayer's method, distinguishing molecules in terms of the degree of polymerisation and the number of bonds, but he significantly decreased the number of allowed steric configurations. Harris suggested for this purpose that each functional group of the molecule, having the configurational structure of a tree, can form a cyclic bond with a definite number of other groups of the same molecule, which is independent of the degree of its polymerisation (but not with all the groups, as in the first model). With increase of the number of cyclic bonds in the molecule, the number of groups remaining in it diminishes and there is a proportional decrease of the number of groups capable of forming a bond with the given group. On these assumptions, Harris was able to complete the calculation of only the gel point for the system. It was found that the critical conversion increases with dilution of the reaction mixture and there exists a dilution above which there is no gel formation whatever the conversion. The initial assumptions of Harris's model are as follows. Flory's principle holds for the

intramolecular reactions of the functional groups of tree-like molecules, i.e. the concentration c_i^{σ} for such molecules is independent of both i and σ. For the groups of other molecules, the values of c_i^{σ} depend only on σ and decrease with increase of the number of cyclic bonds in proportion to the number of terminal groups remaining in the molecules.

Finally, we shall consider the computational scheme proposed by Gordon and coworkers [254-258]. It makes it possible to calculate the statistical characteristics of the polycondensation and cyclisation products derived from one and several monomers, both before and after the gel point, including the critical conversion, even in the presence of the substitution effect. For this purpose, the authors [254-258] suggest that a branching process be used with an additional type of particles, corresponding to the functional groups which have reacted with formation of cyclic bonds. However, in contrast to Irzhak and coworkers [259-261], Gordon and coworkers suggest [254] that the probability that an arbitrary particle reproduces a particular number of other particles in the next generation depends, as for the first order substitution effect, on the number of functional groups which have reacted in the monomeric unit corresponding to the given particle. The authors [254-258] believe that the computational scheme which they proposed can describe fairly satisfactorily any branched polycondensation process involving intramolecular reactions regardless of whether or not it is carried out under equilibrium conditions, provided that the probability parameters of the corresponding branching process are specified in the appropriate manner. They also attempted to justify their model for the case where only functional groups linked by a single chain can participate in the cyclisation reaction, so that each edge of the molecular graph can form part of not more than one ring. By cutting any one edge in such a ring in an arbitrary fashion, it is possible to convert the set of such cyclic graphs into the corresponding set of trees. (In the theory of graphs the trees thus obtained are called chord trees, hence the name "the model of chord trees" [257].) Pendant vertices of yet another type, called cyclic, which appear in pairs as a result of each cut, are added in this procedure. It is suggested that [257,258] these trees, represented as rooted trees, are manifestations of the branching process.

However, this interpretation, which does not go beyond the framework of the statistical method itself, is incorrect. Indeed, suppose that two cyclic vertices, separated by a trail of length n, appear on cutting an edge. If one of the vertices is located in a certain generation of the genealogical tree, the other must be present in one of the nearest n generations. However, such obligatory appearance of particles of a specified type cannot be described, in principle, by any branching process whose particles reproduce others independently in each generation. The chord tree model is actually based on the assumption that the value of c_i^{σ} for an arbitrary functional group is determined solely by the number of groups which have already reacted in the monomeric unit containing it and is proportional to this number, i.e. the method is based on one of the variants of the generalised Flory principle for cyclisation reactions.

Thus, despite the fairly large number of models proposed, the problem of the theoretical description of branched polycondensation processes accompanied by intramolecular reactions is virtually in the very initial stage of its solution. In fact all the models now available are based on various arbitrary assumptions in no way related to specific physicochemical features of the systems considered. In particular, Flory's principle for intramolecular reactions, in contrast to intermolecular reactions, still has no physicochemical justification. Because of this, one cannot at present specify even approximately the class of suggested systems described by a particular model among those described above. The only way of testing their adequacy therefore involves a comparison of calculated results with experimental data for specific processes. However, the available experimental data [262-268] do not permit a sufficiently correct solution of the problem for systems investigated in the studies quoted above, since it is not known what contribution arises from intramolecular reactions proper relative to ideal systems. Furthermore, when attempts were made to compare the theory with experiment [263-268], the authors used adjustable parameters whose values were not determined from independent experimental data.

In conclusion we may note that, as shown by recent studies [269-274], the diagram technique of the theory of quantum fields [269] and the simulation of the process on a computer by the Monte Carlo method [270-274] may prove promising in the development of new computational methods for the solution of the problem of taking into account intramolecular reactions in branched polycondensation.

4. Related Systems

The methods for the quantitative description of branched polycondensation analysed above can be applied in the calculation on many other systems. They include the cross-linking of reactive oligomers by the polycondensation method, cyclotrimerisation, certain processes involving the synthesis of inorganic polymers, and others.

The synthesis of a three-dimensional polymer frequently takes place in two stages: oligomeric chains with terminal functional groups are obtained initially and are then structured in the presence of a bifunctional cross-linking agent. If the intermediate oligomers are linear, a polyfunctional branching agent is also added. A quantitative description of the products of such processes requires the solution of two different problems. The first consists in finding the distribution with respect to the lengths of internodal chains and the free ends of the macromolecules, while the second consists in determining the probabilities of various steric configurations of branched polymers.

Virtually all the published theoretical studies [275-278] were devoted to the first, simpler of the two problems. As stated in an early investigation by Case [275], the approach to its solution is analogous to that used in the calculation of the MWD of cross-linked linear polymers. However, in terms of the general formulation, where the initial compounds have arbitrary MWD and functionalities, this type of problem has not been solved. Calculations have only been made on certain specific systems by statistical [275,278] and kinetic [276,277] methods.

The same methods as in calculations on the products of branched polycondensation can be used in the solution of the second problem. In particular, when ideality of the system is assumed, the dependence of the gel point on the functionalities and proportions of the initial compounds may be found from the formulae for the corresponding ideal polycondensation. The justification of this calculation was demonstrated experimentally in relation to structure formation in oligobutadiene di-isocyanates with the

aid of an aromatic triamine.[279] A method has been proposed[280] for the determination of the weight-average functionality of polymers undergoing cross-linking, from the measurement of the gel point during their hardening. It employs computational formulae[181] for the dependence of the critical conversion p^* on the functionality of the initial monomers in ideal polycondensation. This method has been used to determine the functionality of oligobutadienes with terminal carboxy-[281,282] and hydroxy-groups[282] with glycerol[281] and hexamethylene di-isocyanate[282] as the cross-linking agents.

A study by Zabrodin et al.[283] was devoted to the calculation of the statistical characteristics of the branched polymers obtained when oligomers with reactive terminal groups are cross-linked by the polycondensation method. The proportions by weight of the free ends and of the gel fraction as well as the concentrations of its elastically active chains were calculated by the statistical method assuming that the system is ideal.

From the standpoint of the theory, polycyclotrimerisation processes, which constitute a promising method for the synthesis of three-dimensional polymers, are very close to polycondensation[284,285]. Six-membered elementary carbocycles and heterocycles, each of which is formed in the reaction of three functional groups of the monomers, serve as intramolecular linkages in this instance. Since the branching capacity m of an intramolecular linkage in such polymers is three (whereas in polycondensation products it is $m = 2$) gel formation is possible even in the polycyclotrimerisation of bifunctional monomers ($f = 2$). A rigorous quantitative theory of polycyclotrimerisation and of the analogous more general processes with an arbitrary value of m has been developed by Yamabe and Fukui[258-288] on the assumption that the system is ideal. Using Stockmayer's statistical method[180], they calculated the MWD and the gel point of the products of the polycyclotrimerisation of a monomer having an arbitrary functionality f and then extended these results to any value of m and an arbitrary distribution of the initial compounds with respect to the number of their functional groups. The authors[288] then set up a general quantitative theory of reactions involving the simultaneous formation of intramolecular linkages of different functionalities m. In the same study[288] the MWD and the proportion by weight of the sol fraction were calculated. In an attempt to take into account the formation of non-elementary rings in the polymer the authors[286] used in the calculation of the MWD of the cyclotrimerisation product the statistical approach devised by Harris[251], which he used to describe polycondensation processes. Naturally all the critical remarks made above concerning the justification and the limits of applicability of this approach remain in force also for cyclotrimerisation. A calculation on this process without taking into account macrorings can be carried out also with the aid of the methods of the theory of branching processes[289].

The quantitative theory of polycondensation can be applied also to the description of the equilibrium products of processes involving the formation of inorganic polymers. Here it is necessary to establish which structural units in such polymers correspond to the monomeric units, intramolecular linkages, and terminal functional groups in polycondensation macromolecules. Certain ligands usually correspond to monomeric units, while bridging atoms (for example, oxygen or sulphur) or groups of atoms correspond to intramolecular bonds. Thus the theory of ideal branched polycondensation has been applied[290] to silicate melts. The experimental gel point, the weight fraction of the gel beyond the gel point, and the concentrations of mono-, tri-, and tetra-mers were compared with the values calculated from the formulae of this theory. The experimental and theoretical gel points virtually agreed, but no such agreement was obtained for the weight fractions of the gel at some distance from the gel point. According to the author[290], this is associated with the intense cyclisation beyond the gel point.

Numerous experimental studies by Van Wazer and coworkers[291] were devoted to the investigation of various phosphorus-containing polymers, for example, poly-(phosphoryl chloride), polyphosphoryldimethylamide, polyphosphate esters, polyphosphorothioate esters, and others. An appropriate theory, using the methods for the enumeration of graphs, was devised for their quantitative description[292,293]. The results obtained in these studies[292,293] actually correspond to those which arise from the theory of branched equilibrium polycondensation taking into account the substitution effect[238]. This theory makes it possible to calculate the critical conversion at the gel point from the known equilibrium concentrations of the monomeric units with a definite number of linkages. These concentrations for a number of phosphorus-containing polymers have been found experimentally from NMR spectra[294-297]. The conversions at the gel point, evaluated from these experimental data, are in satisfactory agreement with the values determined in the same studies[294-297] by the viscometric method. The results confirm the validity of the "substitution effect" model for the description of the inorganic systems investigated.

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The general quantitative theory of ideal systems, permitting the calculation of the most important physicochemical parameters of the products of many specific polycondensation processes, which may be regarded as ideal with adequate accuracy for practical purposes, can now be regarded as complete. At the same time there are just as many systems which, for different reasons, are not described by this theory. Calculations on such systems require the allowance for various factors in the kinetic model leading to the deviation of the system from ideality. The greatest advances have been achieved in this field in the quantitative description of polycondensation with the substitution effect owing to the possibility of employing the generalised Flory principle. Much more modest results have been obtained in attempts to take into account in the theory the long-range order effects, which are decisive when molecular cyclisation is considered, and also the possible influence of the conformational and configurational structure of the molecules on the reactivity of their functional groups. The number of unsolved problems in this field greatly exceeds the number of those which have been solved, which is due to the necessity to take into account the conformational statistics of macromolecules in kinetic calculations. Progress in the development of the theory of such non-ideal systems is possible only when joint efforts are made by chemists and physicists, since the given problem lies at the boundary between chemical kinetics and the statistical physics of polymers.

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