Translated from *Uspekhi Khimii*, 48, 51-74 (1979) U.D.C. 541.64:547.914.3

Some Structural and Chemical Aspects of Polycondensation

E.Turska, S.Boryniec, and W.Sulkowski

Data concerning the influence of the structure of asymmetric monomers and monomers with bulky substituents on the structure and physicochemical properties of polycondensation polymers are compiled and analysed. The influence of the chemical structure of the monomers on the course of copolycondensation and the microstructure of the resulting macromolecules is explained.
The bibliography includes 79 references.

CONTENTS

I. Introduction 28
II. The steric structure of polycondensation polymers 28
III. The composition and structure of polycondensation copolymers 30

I. INTRODUCTION

The problem of the influence of the chemical structure of monomers on the course of polycondensation processes involving the synthesis of macromolecules and the structure of the resulting polymers has long been the subject of vigorous thorough research. Nevertheless, despite the advances achieved and the considerable number of published studies, there are still phenomena and relations in this field of the chemistry of macromolecular compounds whose nature is not clear. This is quite understandable bearing in mind that the problems of the structural and chemical relations embraces a wide range of processes, phenomena, and objects.

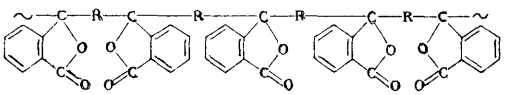
In the analysis of the structural and chemical aspects of polycondensation, it is possible to isolate two fundamental problems: (1) the influence of the chemical structure of the monomers on the reactivity of the functional groups and on the course of polycondensation; (2) the influence of the chemical structure of the monomers on the structure of the resulting macromolecules, their ability to form ordered structures, and ultimately the properties of the polymers.

Copolycondensation processes are still more complex, since, apart from the factors indicated above, the influence of the reactivity of the monomers on the microstructure of the resulting macromolecules and the influence of the microstructure of the chains of copolymers on their ability to crystallise and other properties also play a significant role.

A complete description of the structural and chemical aspects of polycondensation involves such extensive data that in the present review we shall deal only with problems of polycondensation with participation of asymmetric monomers and monomers containing bulky substituents. Polymers with interesting structures, having a set of valuable physicochemical properties, have been obtained on the basis of these monomers. Part of the review is devoted to the problem of the influence of the reactivity of the functional groups of monomers on the course of joint polycondensation processes and the microstructure of polymer chains, which makes it possible to relate the physicochemical properties of polymers to the microstructure of their macromolecules.

II. THE STERIC STRUCTURE OF POLYCONDENSATION POLYMERS

A characteristic feature of the majority of polymers obtained by polycondensation methods is the symmetrical structure of the monomers employed; the stereoregularity of the structure has therefore not been investigated for a long time. However, as in the synthesis of polymers by polymerisation methods, one can foresee the possibility of the synthesis of stereoregular polymers by polycondensation methods. The principal essential condition for this purpose is known to be the use of monomers capable of forming asymmetric units. Thus the employment of optically active monomers makes it possible to synthesise polymers with a sterically regular alternation of fragments. The use of monomers containing carbon atoms with two different and two identical substituents yields atactic polymers. The polyarylates obtained from phenolphthalein and different dicarboxylic acids are an example of polymers of this type[1-7]. The following schematic formula illustrates the structure of an atactic polyarylate of this kind:



According to Korshak and coworkers[8-16], when ring-substituted bisphenols are used, polymers having various crystallographic forms are produced under the conditions of acceptor-catalytic polyesterification, depending on the nature of the solvent and the tertiary amine. The polyarylate obtained from 2,2-di-(3-chloro-4-hydroxyphenyl)-propane and terephthalic acid in the presence of pyridine is crystalline and gives rise to narrow NQR signals. This was the first stereoregular polymer of this type obtained by polycondensation. The use of the dichlorides of isophthalic and 1,1'-oxybisbenzene-4,4'-dicarboxylic acid instead of the dichloride of terephthalic acid leads to a decreased degree of crystallinity of the polymers and a consequent improvement of their solubility. A general feature has been observed for all the acid dichlorides employed—the precipitation of the polymer from the reaction mixture (dioxan, dichloroethane, acetone, and nitrobenzene) during synthesis promotes the formation of

polyarylates with a high degree of crystallinity (stereoregularity) compared with the polymers which remain in solution. Korshak and coworkers established that a decrease of the distance between the carbonyl groups in the acid fragment has a favourable influence on the crystallisability of the polymers, which is apparently associated with the increased regularity of the macromolecular structure.

Korshak[1-4] postulates that polymers with a regular structure and without defects (anomalous fragments) in their macromolecules should have more close-packed chains, should crystallise more readily, and should possess more effective mechanical and physical properties than polymers with a non-regular structure. This is to some extent confirmed by data concerning the dependence of the melting points of the copolymers on the amount of the second monomer introduced into the copolymer. If the treatment is confined to a consideration of those copolymers which contain only small amounts of the second monomer, then the melting point is found to decrease with increasing content of the second monomer, i.e. the monomer which increases the number of anomalous fragments in the polymer chain.

Chemical defects in macromolecules are also an important factor determining the ability of polymers to crystallise. The greater the number of defects, the greater the irregularity of the macromolecules, and the smaller the capacity of the polymer for crystallisation, other conditions being equal.

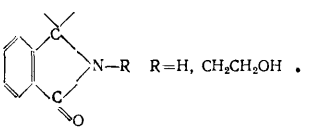
The influence of the chemical structure of the initial monomers on the ability of polycondensation polymers to crystallise is manifested in many instances. This phenomenon can be illustrated in a particularly interesting manner in relation to cardo-polyarylates. A large number of cardo-polyarylates, containing cardo-groups such as the phthalide, phthalimidine, fluorene, anthrone, cyclohexane, norbornane, and other groups, have been synthesised by polycondensation[1-37]. Cardo-polyarylates are obtained by non-equilibrium polycondensation: low-temperature (acceptor-catalytic) polycondensation[1-19,23-30], high-temperature polycondensation in solution[6,7,19,31,32], and interfacial polycondensation[1-6,17-23]. In interfacial polycondensation account must be taken of the specific behaviour of cardo-monomers of the phenolphthalein type in aqueous alkaline media. However, Morgan[18] and Korshak and coworkers[20-23] established that conversion of phthalide derivatives into phthalimidine derivatives makes it possible to synthesise macromolecular polyarylates by interfacial polycondensation. The use by the authors of phthalimidine derivatives such as phenolphthalein imide and 2-β-hydroxyethyl-3,3-di-(4-hydroxyphenyl)phthalimidine, containing functional groups with appreciably different reactivities, leads to the formation by interfacial polycondensation of cardo-polymers with free >NH and NCH_2CH_2OH groups respectively, which permits their chemical modification. The joint polycondensation of the above bisphenols and the dichloride of isophthalic or terephthalic acid results in the formation of a cross-linked copolymer under certain conditions.

Acceptor-catalytic polycondensation has come to be widely used in recent years as a method for the synthesis of cardo-polyarylates[1-19,24-30]. Korshak and coworkers[10,11,25,30] obtained by this method phenolphthalein polyterephthalates. The synthesis was carried out in a medium (dichloroethane) in which the polymer is soluble and in a medium (acetone) from which the polymer is precipitated during synthesis. It was established that the nature of the solvent employed affects the molecular weight of the polymer, as low-temperature polyesterification in a metastable solution (a mixture of the solvent and precipitant) leads to the formation of polyarylates with a narrow molecular-weight distribution[12]. The yield and molecular weight of the polyarylate depend appreciably on the sequence in which the monomers are introduced[14,26].

Many cardo-polyarylates have been synthesised by the high-temperature polycondensation of dicarboxylic acid dichlorides and bisphenols in organic solvents. The study of the kinetics of the reaction of terephthalic acid dichloride with 9,9-di-(4-hydroxyphenyl)fluorene and certain bisphenols of the type of norbornane enabled Korshak and coworkers[31,32] to suggest an ionisation mechanism for this reaction. It was established that the polycondensation of phenolphthalein and dicarboxylic acid dichlorides in ditolylmethane leads to the formation of polymers which are precipitated from solution. The synthesis of such polyarylates in more polar chlorinated solvents or nitrobenzene takes place in solution, according to Korshak and coworkers[6,7], with formation of polymers having better physicomechanical properties. This phenomenon was explained by the fact that, in a medium dissolving the polymer, macromolecules having uncoiled rigid conformations and giving rise to a fibrillar structure are formed, whereas the polymer obtained in ditolylmethane gives rise to irregular globular structures. Thus in the synthesis of polymers with rigid macromolecular chains it is necessary to take into account the influence of the reaction medium on the formation of the corresponding conformations.

All the cardo-phenolphthalein polyarylates are amorphous non-crystallising polymers. Korshak and coworkers[2-5] suggest that their structure is analogous to that of atactic polymers. However, one must assume that under certain conditions it is possible to obtain a crystalline stereoregular phenolphthalein polyarylate. The possibility is indicated by the finding that the cardo-polyarylates formed by di-(4-hydroxyphenyl)fluorene and 9,9-di-(4-hydroxyphenyl)-10-anthrone with terephthalic acid crystallise and the conditions of their synthesis influence, according to Vinogradova et al.[33], not only the molecular weight of the polyarylates but also their structure.

Studies by Korshak and coworkers[22,23] showed that, by using an appropriate solvent, it is possible to synthesise a stereoregular crystalline cardo-polyarylate containing asymmetric groups. Thus, crystalline phthalimidine polyarylates containing NH groups have been synthesised. The formation of the crystalline structure of the polymer is probably associated with decreased solubility of the given polyarylate and increased rigidity of its macromolecules by hydrogen bonding between the phthalimidine groups and the electron-accepting groups of the macromolecules. This effect is manifested even more clearly in *N*-β-hydroxyethylphthalimidine:



During recent years much attention has been devoted to cardo-polyarylates containing carborane rings[34-37]. The carborane-containing polyarylates obtained by Korshak and coworkers are characterised by an increased thermal stability, a high degree of order in their structure, and other properties of practical interest.

Investigations have established that a mixed crystalline polyarylate may be obtained when even one of the monomers is capable of forming a crystalline homopolyarylate and this monomer is taken in a large excess [38].

The data presented show that the chemical structure of the monomers and particularly the presence of asymmetric bulky substituents influence significantly not only the course of the process but also the structure and properties of the polymers obtained.

III. THE COMPOSITION AND STRUCTURE OF POLYCONDENSATION COPOLYMERS

1. General Postulates

A significant change in the properties of polymeric materials obtained by polycondensation can be achieved by synthesising copolymers, i.e. by carrying out the joint polycondensation of a large number of monomers.

The physicochemical characteristics of copolymers are in many respects determined by their chemical composition by the inhomogeneity of their composition, and by the different chemical structures of the macromolecular chains. Without considering here the important factor of the average chemical composition, on which the properties of the copolymer depend significantly, one should note that the chemical inhomogeneity and the inhomogeneity of the structures of macromolecules are very important, although it is very difficult to control them in the course of the synthesis.

The inhomogeneity of chemical composition is associated with the presence in the copolymer macromolecules of different elementary units in different proportions. In polycondensation copolymers, which are the subject of the present review, an inhomogeneity of the composition is observed, but it is not as important as for polymerisation copolymers. The stepwise nature of the copolycondensation process and the occurrence of reactions between macromolecules promote an equalisation of the compositions of the individual macromolecules formed in the early stages of the process. Nevertheless the results of fractionation studies have shown that the chemical composition of polycondensation copolymers is inhomogeneous [39,40].

Another problem concerning the microstructure (microheterogeneity) of copolymer chains is associated with the different ways in which the corresponding units alternate along the macromolecular chain. Even copolymers with identical molecular weights and identical chemical compositions may differ appreciably in the distribution of units and their sequence. A quantitative estimate of the microheterogeneity of copolymers involves the measurement of the relative contents of the corresponding chain units having a definite chemical structure. Modern research methods make it possible to determine the sequence of only small fragments of the chain—with a length not exceeding 3–4 units. Analysis of the sequence of units throughout the macromolecule is based on the hypothesis that the processes responsible for the chain microstructure are entirely random. The experimental determination of the alternation (sequence) of units in copolymer chains is based on the measurement of a property of the polymer which depends on the number of units of definite types and on the order in which they are joined together. Depending on the nature of the copolymer investigated, such a property may be, for example, the absorption intensity at certain frequencies in the ultraviolet or infrared regions, the melting point, the glass point, and the presence of chemical functional groups characteristic of a given structure [41,42]. High-resolution NMR has acquired the greatest importance in recent years in the study of the microstructures of copolymers. The relative intensities of the signals of the corresponding nuclei make it possible in many instances to determine accurately the fraction of chemical groups characteristic of a particular type of alternation.

The properties of the copolymer depend strongly on the sequence of units in its macromolecules; this applies particularly to the extreme cases of the distribution of elementary units. If it is assumed that the copolymer is made up to two types of main units c_1 and c_2, their distribution may be as follows:

(a) a distribution characterised by the maximum number of linkages between the units c_1 and c_2. This sequence corresponds to a regularly alternating structure of the copolymer chain:

$$\sim -c_1-c_2-c_1-c_2-c_1-c_2-\sim;$$

(b) a distribution distinguished by the maximum number of linkages between units of one type. Such a sequence corresponds to a block structure of the copolymer chain:

$$\sim -c_1-c_1-c_1-c_1-c_2-c_2-c_2-c_2-\sim;$$

(c) chains with an intermediate distribution of units may manifest a tendency towards irregular alternation or to a block structure, or their structure may be completely disordered:

$$\sim c_1-c_1-c_2-c_1-c_2-c_2-c_2-c_1-c_1-c_2-\sim .$$

A copolymer with a completely disordered distribution of units is called a statistical copolymer.

The problem of the sequence of units in polycondensation copolymers has been the subject to theoretical considerations long before the development of experimental methods permitting the study of the microstructure of copolymers. A mathematical treatment of the problem was published as early as the 1950s by Case [43] and Beste [44]. In subsequent years the studies by Yamadera and Murano [45] and Kuchanov and coworkers [46,47] assumed a considerable importance.

A quantitative description of the microheterogeneity of polycondensation copolymers may be achieved in two ways. Like polymolecularity or the inhomogeneity of composition, microheterogeneity is described with the aid of the corresponding distribution function. The distribution functions for both types of units make it possible to describe exactly the nature and degree of order in the chemical structure of chains. A theoretical treatment of this problem has been described by Beste [44] and Kuchanov [48].

Another widely used method for the description of the microheterogeneity of copolycondensation products is based on a numerical characteristic of the degree of order in the structure of copolymer chains. The method of numerical estimation of the chemical structures of polycondensation copolymers from high-resolution NMR data, used by the majority of workers, was first introduced in the classical study of Yamadera and Murano [45]. They investigated the microheterogeneity of copolyesters obtained by the high-temperature copolycondensation of glycols with dimethyl dicarboxylates and also the nature of the changes in microheterogeneity owing to exchange reactions between poly(ethylene terephthalate) and poly(ethylene sebacate). Yamadera and Murano [45] developed a method for the estimation of the degree of

order in the chemical structure of copolymer chains in relation to the copolyester obtained by the latter reaction. For example, the chains of the copolymer obtained from ethylene glycol (G), dimethyl terephthalate (T), and dimethyl sebacate (S) may contain three types of diads — two homodiads T–G–T and S–G–S and one heterodiad T–G–S. The intermonomer G, which joins together the T and S comonomers in the chains, has different environments in the above diads, which induces the appearance of three different signals in the NMR spectra. The intensity of these signals enabled the authors to determine the mole fractions of the terephthalate x_T and the sebacate x_S:

$$x_T = \frac{S_{TGS}}{2} + S_{TGT}, \quad (1)$$

$$x_S = \frac{S_{TGS}}{2} + S_{SGS}, \quad (2)$$

where S_{TGT}, S_{SGS}, and S_{TGS} are the fractions of the above diads respectively.

The probability of the appearance in the copolymer chain of the T unit after the S unit is defined by the relation

$$P_{TS} = \frac{S_{TGS}}{2x_S}; \quad (3)$$

and the probability of the appearance of the S unit after the T unit is correspondingly

$$P_{TS} = \frac{S_{TGS}}{2x_T}. \quad (4)$$

According to Yamadera and Murano[45], the quantity characterising the microheterogeneity of the copolymer is the sum of the above probabilities. These workers denoted the above quantity by B and called it the degree of randomness. Kuchanov[46] called the same quantity the coefficient of microheterogeneity (K_M) and Slonim and coworkers[49] used the term "coefficient of non-regularity". For the example under discussion,

$$K_M = B = P_{ST} + P_{TS} = \frac{S_{TGS}}{S_{TGS} + 2S_{TGT}} + \frac{S_{TGS}}{S_{TGS} + 2S_{SGS}}. \quad (5)$$

When $K_M = 1$, the arrangement of the T and S units in the chains is disordered. If $K_M < 1$, there is tendency towards the formation of blocks. The quantity $K_M = 0$ corresponds to a mixture of homopolymers. When $K_M > 1$, the number of consecutively connected diads of the same type diminishes and the limiting case $K_M = 2$ corresponds to a regularly alternating copolymer. The number-average lengths of the sequences of T and S units are respectively

$$\bar{L}_{nT} = \frac{2x_T}{S_{TGS}} = \frac{1}{P_{TS}}. \quad (6)$$

$$\bar{L}_{nS} = \frac{2x_S}{S_{TGS}} = \frac{1}{P_{ST}}. \quad (7)$$

Consequently

$$K_M = \frac{1}{\bar{L}_{nT}} + \frac{1}{\bar{L}_{nS}}. \quad (8)$$

However, these equations are valid only when any macromolecule contains a fairly large number of units.

Experimental conclusions reached from the study of Yamadera and Murano[45] under consideration concern the microheterogeneity of the copolymers obtained by copolycondensation and exchange reactions. Since the values of K_M calculated from NMR data for the above copolymers are close to unity, the authors speak of a random distribution of units in the macromolecules obeying the Bernoulli statistics.

When the method proposed by Yamadera and Murano[45] is used, one must not forget that the coefficient of microheterogeneity K_M can serve only as a very approximate characteristic of the alternation of units in the copolymer chains and that its value does not in many instances yield an exact idea about the real macromolecular structure. An example illustrating the ambiguity of the description of the chain structure with the aid of the K_M coefficient has been given by Turska and Matlangiewicz[50]. According to the postulates of Yamadera and Murano, K_M close to unity indicates a random distribution of units in the copolymer chain. However, a value of K_M close to unity characterises, for example, a copolymer made up of units of two types, linked into dimeric sequences, i.e. the copolymer

$$\sim\!-c_1c_1c_2c_2c_1c_1c_2c_2c_1c_1c_2c_2-\!\sim$$

whose chain structure is entirely ordered. One can quote many similar examples. The use of a method which would permit the estimation of the distribution of units in longer chain fragments would make it possible to obtain more accurate data about the real structure of macromolecules.

Despite the ambiguity indicated above, the method of Yamadera and Murano is widely used by many workers investigating the microstructure of copolymers.

As already noted, Eqn. (8) is valid only for fairly long macromolecular chains. Since polycondensation products contain not unduly long chains, there is a risk that such simplification of the description can lead to appreciable inaccuracies. This problem has been considered by Slonim and coworkers[49], who proposed a modified method for the estimation of the microheterogeneity of chains of finite length. These workers consider a copolymer formed in the reaction between an intermonomer and two comonomers c_1 and c_2 which do not react with one another. The copolymer macromolecule can be represented schematically as follows:

$$R-(c_i)_p-(a-c_i)_n-a_q-R',$$

where R and R′ are the end groups, $i = 1$ or 2, p and $q = 0$ or 1 depending on the molar ratio of the monomers and the intermonomer, and n is the degree of polymerisation. Taking into account the above assumptions, the authors[49] derived a relation defining the coefficients K_M for the copolymer macromolecule:

$$K_M = \frac{1}{N-1}\left(\frac{N-\bar{L}_1}{\bar{L}_1} + \frac{N-\bar{L}_2}{\bar{L}_2}\right), \quad (9)$$

where $\bar{L}_1$ and $\bar{L}_2$ denote the average lengths of the block ac_1 and ac_2. For very long chains ($N \gg \bar{L}_n$), Eqn. (9) is converted into Eqn. (8).

The authors[49] used Eqn. (9) to estimate the microheterogeneity of the chains of the copolymer obtained from ethylene glycol (the intermonomer) and dicarboxylic acids — malonic and sebacic (the comonomers). According to the authors, a tendency is observed in the product towards the formation of block structures, as shown by the values of K_M, which lie in the range 0.78–0.89 for a series of experiments. It is of interest that both the

physicochemical parameters of the copolymers investigated required for the calculation of K_M (the composition and degree of polymerisation) have been determined by NMR.

Another method of characterising the microstructure of polycondensation of copolymers has been described in a theoretical study by Gritsenko[51]. The author analyses the nature of the distribution of units in copolymer chains for the simultaneous and consecutive introduction of the reactants into the reaction zone.

An important aspect of the problem of the microstructure of copolymer chains has been examined by Sawada[52,53], who defines the conditions which must be fulfilled in order that the synthesis of a polycondensation copolymer should lead to a product with a definite type of structure of macromolecular chains. Sawada characterises the degree of order in the structure of the copolymer with the aid of a parameter γ, which he introduced: $\gamma = -1$ corresponds to a block structure, $\gamma = 1$ corresponds to a regularly alternating structure, and $\gamma = 0$ corresponds to a copolymer with a statistical distribution of units in the macromolecular chains. Sawada's theory explains the statistical structure of the chains of copolymers obtained in the melt by the influence of the high process temperature. According to the author, under the conditions of low-temperature processes, there is a possibility of the formation of macromolecules with a more ordered structure.

However, the thermodynamic approach to the solution of the problem of the structure of copolymers developed by Sawada gives rise to certain objections. The author does not take into account in his treatment the dependence of the enthalpy ΔH on temperature. One can also assume that an experimental test of Sawada's theory will encounter major difficulties due to the complexity of the selection of the corresponding systems and the similarity of the temperature of low- and high-temperature copolycondensations.

The most extensive studies on the synthesis and chemical structure of polycondensation copolymers have been made in the course of many years by members of the Institute of Organoelemental Compounds of the USSR Academy of Sciences under the direction of Academician V.V. Korshak. He has made a major contribution both to the theory and practice of copolycondensation processes. Many conclusions which follow from the work of Korshak and coworkers concerning acceptor-catalytic copolycondensation can be extended also to other copolycondensation methods. Many of these studies embrace the problems of the synthesis of new polycondensation copolymers from various monomers. Another field of study is associated with the determination of the chemical structure of copolycondensation products. The influence of various factors, particularly factors such as the reactivity of the functional groups, the mode of introduction of the monomers into the reaction medium, etc., on the nature of distribution of units in the copolymers obtained by acceptor-catalytic copolycondensation has been investigated[54-56]. Together with theoretical studies, experimental investigations are being carried out at the Institute of Organoelemental Compounds on the microstructure of polycondensation copolymers by NMR.[54,57,58] The results of the theoretical and experimental research by Korshak and coworkers have been surveyed in recent years in a number of reviews[47,59,60].

In Poland studies on the synthesis and properties of polycondensation copolymers have been made by Jedlinski and coworkers[30,61,62]. The aromatic copolyesters containing bisnaphthol rings, which they obtained, are characterised, in particular, by a high thermal stability and are effective electrical insulators.

2. Kinetic Description of the Copolycondensation Process

In order to characterise the processes involving the synthesis of polycondensation copolymers, account must be taken of the fact that the copolycondensation process in all its varieties is a result of a superposition of two or more simultaneous or consecutive reactions between the functional groups. Consequently the difference between polycondensation and copolycondensation is entirely quantitative and the methods used to carry out the two processes are in principle identical. We shall therefore not consider the elements of theory and practice common to all polycondensation processes. Only certain characteristics of the kinetics of copolycondensation, associated with the simultaneous occurrence of reactions between functional groups having different reactivities, require separate consideration.

A homopolycondensation reaction can be described, after introducing certain simplifying assumptions, with the aid of simple formal kinetic equations. Taking into account these assumptions, the copolycondensation process can be regarded as a series of parallel (synchronous reactions) with participation of two or more functional groups and it can also be described by formal kinetic equations assuming that the rate of the process as a whole is determined by the rates of these reactions.

A simple example of copolycondensation is the reaction between the functional groups of three bifunctional monomers. The independent functional groups of one of the monomers are capable of reacting with the independent functional groups of the other two monomers, which are incapable of reacting under these conditions with one another. The first monomer is called the intermonomer; it binds identical or different copolymers into diads in the chains of the resulting copolymer. Having denoted the intermonomer by A and the comonomers by B and C, the structure of such a copolymer can be represented schematically as follows:

$$\cdots\text{—A—B—A—B—A—C—A—B—A—C—A—C—}\cdots$$

The copolymer is formed as a result of consecutive reactions of functional groups of type A with groups B and C, the reactions being governed by kinetic constants k_{AB} and k_{AC} respectively. If the irreversibility and second order of both reactions are assumed, the standard kinetic equations for the concentrations of the functional groups can yield relations between the compositions of the copolymer and the monomer mixture on the one hand, and the kinetic constants for the process and the initial concentrations of the monomers for different degrees of reaction, on the other[63,64]. In particular, the equation for the composition of a polycondensation copolymer becomes

$$\frac{dc_B}{dc_C} = \alpha\frac{c_B}{c_C}, \quad \alpha = \frac{k_{AB}}{k_{AC}}, \tag{10}$$

where c_B and c_C are the concentrations of the functional groups of the comonomers B and C.

The limitations of Eqn. (10) refer mainly to the limits of its applicability. Sokolov and Kurglova[65] believe that the composition equation is inapplicable to copolycondensation under homogeneous conditions in solution or in the melt. In order to attain fairly high molecular weights

of the copolymer under such conditions, not only an equimolar ratio of the reacting functional groups but also a high degree of reaction are necessary. However, when the degree of reaction is high, the composition of the copolymer becomes the same as that of the initial mixture of monomers regardless of the difference between the reactivities of their functional groups. The excess of functional groups of one type precludes, in its turn, a high molecular weight of the copolymer. According to the authors [65], Eqn. (10) can be used for copolycondensation processes at the boundary of two immiscible liquid phases, although it is known that classical kinetic equations cannot be used to describe processes occurring in heterogeneous systems.

Another limitation is associated with the identification of the monomer concentration in Eqn. (10) with the concentration of its functional groups. Evidently the concentrations of the functional groups do not change solely as a result of reactions between the monomer molecules. One should add that the equation has been obtained without taking into account the reversibility of the polycondensation reactions. The introduction of the rate constants for the reverse reactions into the kinetic equations would create significant difficulties in the calculations.

The copolycondensation process is known to be accompanied by side reactions, which can have a very significant influence on its course. The side reactions affect also the composition of the copolymer formed. In certain cases this influence may be determined exactly by an appropriate modification of the composition equation. An example of reactions in which the monomers B and C react with a compound D present in the system, apart from their reaction with the intermonomer A, is given in Sokolov's monograph [66].

One of the assumptions in the derivation of the composition equation is that the reactivities of all the functional groups are the same and do not change during the copolycondensation. However, systems in which the reactivity of a functional group depends on whether it is the first (monomer) or second (oligomer or polymer) to react are encountered much more frequently. Allowance for the different reactivities of the first and second functional groups requires, even in the simplest case, the use of a computer for the calculations.

Such calculations have been made by Sokolov and coworkers [67] for the copolycondensation of an intermonomer A with two comonomers B and C. In this process two reactions take place between the comonomers and the intermonomer and two reactions between the oligomers or polymers. The monomers and oligomers or polymers participate in the four reactions. Six kinetic equations for a process of this kind characterise the decrease in the concentrations of the individual functional groups during the reaction. The results show that the composition of the copolymer formed depends on the ratio of the reactivities of the functional groups of the monomers B and C and on the ratio of the reactivities of the first and second groups in each comonomer. The composition of the copolycondensation products is influenced significantly also by the degree of reaction. The difference between the reactivities of the first and second functional groups of the intermonomer does not affect the composition of the copolymer.

Kuchanov [46], who examined only low-temperature copolycondensation, reached similar conclusions. He believes that the rapid interchain reactions in high-temperature copolycondensation lead to a random, statistical distribution of units in the copolymer chains.

The term "copolycondensation" embraces all the processes involving the synthesis of polycondensation copolymers in which the reaction mechanism corresponds to one of the known polycondensation mechanisms and the chains of the macromolecules formed made up of two or more types of units. Even if one omits processes involving synthesis using trifunctional monomers (because they differ significantly) and the treatment is confined to the copolycondensation of bifunctional monomers, the range of the possible different versions is very wide.

The kinetic equations used to describe copolycondensation processes must contain formal expressions corresponding to a particular type of process. This requirement is valid even when different types of processes can be described by the same general kinetic relations.

The simplest copolycondensation which is most often encountered in laboratory practice is the copolycondensation of three monomers: the intermonomer A and the comonomers B and C. A correct kinetic analysis of even this not unduly complex system requires that one takes into account the mechanism of the reaction and the way it is carried out. The high-temperature copolycondensation of the above three monomers under homogeneous conditions is a kinetically simple case. However, even in this simple instance the use of formal kinetic equations requires many assumptions, the most important of which are as follows: 1) Flory's postulate that the reactivities of the terminal groups are the same and independent of the size of the macromolecule; 2) the postulate that the reacting system is homogeneous; 3) the postulate that the volume and mass of the system remain constant during the process; 4) the postulate that the reaction is irreversible under the given conditions; 5) the postulate that side reactions, primarily chain transfer reactions, do not occur under the conditions considered.

A critical consideration of each of the above postulates permits the following conclusions.

1. The hypothesis that the reactivities of the functional groups are the same is used very frequently and in principle yields a satisfactory approximation to real systems. However, it is valid also if there are no significant differences between the reactivities of the functional groups of the monomer molecules and the molecules of oligomers and polymers. The appearance of such a difference is largely caused by the structure of the monomer molecules. For example, it is known that the first OH group in ethylene glycol is more reactive than the second. After the substitution of the first group, the reactivity of ethylene glycol falls appreciably, which gives rise to significant differences in the employment of this monomer. On the other hand, bisphenols, for example, bisphenol A (dian) do not exhibit an appreciable difference between the reactivities of the first and second functional groups. The above hypothesis cannot therefore lead in all cases to a satisfactory approximation by the kinetic description to the real situation.

2. The postulate that the system is homogeneous is extremely indefinite, although it is used by all investigators of the kinetics of polycondensation in solution. In general this hypothesis is fulfilled only for a solution which constitutes a homogeneous system and must not contain a deposit (an insoluble monomer or the precipitated polymer). The evolution of a gaseous side product is as a rule neglected. However, bearing in mind that this not unduly accurate hypothesis is generally accepted for the description of homopolycondensation processes in solution

and yields a satisfactory agreement between theory and experiment, one can also adopt it for copolycondensation processes.

3. The postulate that the volume and mass remain constant throughout the process when a gaseous product is removed from the reaction system is likewise inaccurate. Despite this, many investigators employ this assumption, since the error caused by its inaccuracy is frequently small and may be disregarded. This hypothesis leads, however, to appreciable errors when a side product with a high molecular weight is removed from the process in the melt. For example, in the synthesis of the polyester from terephthalic acid dichloride and dian the relative error associated with the removal of hydrogen chloride is about 8% for the reaction in the melt. For the reaction in solution, the error diminishes by more than an order of magnitude. It can then be legitimately disregarded and one can assume with an adequate degree of approximation that the volume of the reaction mixture is constant for polycondensation in solution.

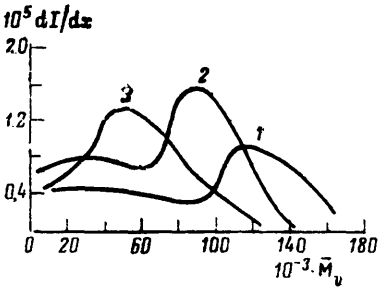


Figure 1. Differential MWD curves for a polycarbonate containing dian and inorganic compounds as admixtures: 1) specimen before heat treatment; 2) specimen heat-treated for 4 h at 260°C; 3) specimen heat-treated for 9 h at 260°C.

4. The postulate that the formation of the copolymer is a reversible reaction is in principle inapplicable to a process carried out under conditions where the equilibrium is not displaced by the constant removal of the side product from the reaction medium. However, if the equilibrium is effectively shifted towards the formation of the polymer, the above hypothesis can be adopted. One must take into account the fact that the efficiency of the displacement of the equilibrium in general diminishes with increasing degree of reaction. The hypothesis that the reaction is irreversible therefore yields an accurate description of the process for low degrees of the latter and is much less accurate for high degrees of reaction.

5. The hypothesis that there are no side reactions can also lead to major errors depending on the process conditions. Side reactions as a rule accompany polycondensation processes. However, according to literature data[60], one can select conditions such that side reactions virtually do not take place and may be disregarded. Nevertheless, this hypothesis cannot be adopted without an experimental test under the selected conditions. Presumably, under the conditions of high-temperature polycondensation in solution, the contribution of side reactions involving interchain exchange is small. Kinetics studies on the high-temperature polycondensation of dian chloroformate with dian in solution[68] showed that, under certain process conditions, chain transfer reactions may be disregarded, because their rate is too small to be measured under such conditions. These observations were confirmed subsequently in other systems. Studies on the dependence of the molecular weight distribution (MWD) of polycarbonates on the duration of their heat treatment showed in their turn that admixtures greatly influence the course of the process and the extent of side reactions[69]. In particular, it has been observed that chain transfer reactions occur in the presence of a very low content of impurities in the reaction mixture. In the absence of impurities, chain transfer reactions hardly take place. Figs. 1 and 2 show how the molecular weight distribution functions for polycarbonates, both contaminated and without impurities, vary after heat treatment. Evidently heat treatment influences appreciably only the MWD of the polycarbonate with impurities.

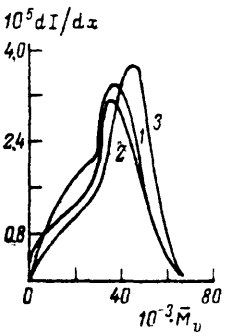


Figure 2. Differential MWD curves for a polycarbonate without admixtures: 1) specimen before heat treatment; 2) specimen heat-treated for 4 h at 260°C; 3) specimen heat-treated for 9 h at 260°C.

The above considerations suggest that, although the assumptions can lead in many cases to discrepancies between theoretical and experimental data, nevertheless there exist systems and polycondensation conditions for which they can be used without much error. Polycondensation and copolycondensation in solution under appropriate conditions may be classified as processes of this kind. This fact makes it possible to employ the fundamental equations of formal kinetics for the kinetic analysis of such processes.

We shall now consider the homogeneous high-temperature copolycondensation in solution of the intermonomer A with the comonomers B and C. Suppose that the composition of the initial monomeric mixture corresponds to equimolar proportions of the functional groups and that all the simplifying assumptions formulated above for the derivation of Eqn. (10) are valid. Using the normal kinetic equations, it is possible to derive expressions describing the time dependence of the concentrations of the individual types of functional groups[69]:

$$-\frac{dc_B}{dt} = \frac{k_{AB}c_C^0}{(c_B^0)^{1/\alpha}} c_B^{1/\alpha+1} + k_{AB}c_B^2, \qquad (11)$$

$$-\frac{dc_C}{dt} = \frac{k_{AC}c_B^0}{(c_C^0)^\alpha} c_C^{\alpha+1} + k_{AC}c_C^2, \quad (12)$$

where c_B^0 and c_C^0 are the initial concentrations of the functional groups B and C respectively. These equations can be numerically integrated on a computer for arbitrary values of the parameters. Knowing the values of c_B and c_C, it is easy to determine the degree of reaction p and the mole fractions of the bonds formed in the copolymer between the monomers A and B (x_{A-B}) and A and C (x_{A-C}):

$$p = \frac{c_B^0 + c_C^0 - c_B - c_C}{c_B^0 + c_C^0}, \quad x_{A-B} = 1 - x_{A-C} = \frac{c_B^0 - c_B}{c_B^0 + c_C^0 - c_B - c_C}, \quad (13)$$

and to obtain an equation for the kinetic curve for the process:

$$\frac{dp}{dt} = (1-p)(k_{AB}c_B + k_{AC}c_C). \quad (14)$$

3. Experimental Study of High-Temperature Polycondensation

Eqns. (11) and (12) show that the complex relation between the concentrations of the functional groups and the reaction time is evidence for the complexity of the copolycondensation processes. The concentrations of the functional groups c_B and c_C are influenced during copolycondensation by the relative reactivities of both groups in their reactions with the groups of the intermonomer and also by the initial composition of the reaction mixture. The determination of c_B and c_C as well as k_{AB} and k_{AC} (Table 1) by kinetic investigation of the corresponding polycondensation processes permits the calculation by Eqn. (14) of the theoretical $dp/dt = f(p)$ curve. Comparison of the theoretical curve and the experimental curves for the monomer A–terephthalic acid dichloride, monomer B–dian, and monomer C–tetrachlorodian [70] systems established that Eqn. (14) constitutes a satisfactory approximation for the description of the kinetics of the copolycondensation process (Fig. 3).

Table 1. The rate constants k and activation energies E for the polycondensation of terephthaloyl chloride with bisphenols in solution in α-chloronaphthalene.

Biphenol	10^3k, litre mole^{-1} s^{-1}				E, kcal mole^{-1}
	180° C	190° C	200° C	220° C	
Dian	1.19	1.78	2.78	4.40	15.3
Dimethyldian	0.49	0.85	1.29	4.10	23.6
Tetramethyldian	0.14	0.17	0.35	1.09	19.2
Tetrachlorodian	0.10	0.15	0.34	0.86	23.9
Dinitrodian	0.08	0.15	0.25	0.68	23.7

The applicability of Eqn. (14) to other systems has been demonstrated in a study of the kinetics of the copolycondensation of terephthalic acid dichloride (A) with dian (B) and phenolphthalein (C) in solution [71]. The polycondensation rate constants k_{AB} and k_{AC} were determined at 220°C in α-chloronaphthalene as 52.4×10^{-4} and 27.0×10^{-4} litre mole^{-1} s^{-1} and graphical relations between the degree of reaction and reaction time were constructed. As an example, Fig. 4 presents one of such graphs. Evidently the experimental points fit satisfactorily on the theoretical curve. Analogous relations, plotted for the copolycondensation of terephthalic acid dichloride with dian and tetrachlorodian also revealed a satisfactory agreement between the experimental and theoretical data.

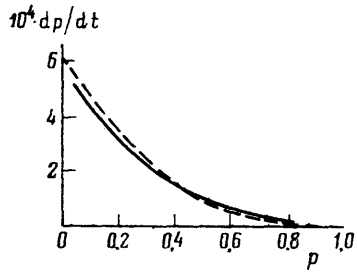


Figure 3. Dependence of dp/dt on the degree (p) of copolycondensation; continuous line—experimental curve; dashed line—theoretical curve.

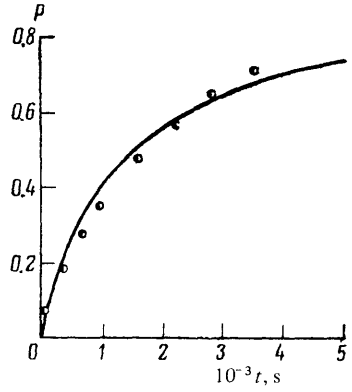


Figure 4. Dependence of the degree of reaction in α-chloronaphthalene at 220°C on the duration (t) of the copolycondensation of terephthalic acid dichloride (c_A^0 = 0.2 M) with dian (c_B^0 = 0.08 M) and phenolphthalein (c_C^0 = 0.12 M). Continuous line—theoretical curve; circles—experimental data.

The undoubted applicability of Eqn. (4) to the description of the degrees of certain high-temperature copolycondensation reactions in solution permitted its extension to an arbitrary number of comonomers (B, C, D,..., N) [73]:

$$\frac{dp}{dt} = (1-p)(k_{AB}c_B + k_{AC}c_C + k_{AD}c_D + \cdots + k_{AN}c_N). \quad (15)$$

The concentrations of the functional groups of the reacting comonomers are linked by the relation

$$\frac{c_B^0}{c_B} = \left(\frac{c_C^0}{c_C}\right)^{k_{AB}/k_{AC}}, \quad \frac{c_C^0}{c_C} = \left(\frac{c_D^0}{c_D}\right)^{k_{AC}/k_{AD}}, \ldots \quad (16)$$

Eqns. (15) and (16) were solved numerically for the copolycondensation of terephthalic acid dichloride (A) with dian (B), tetrachlorodian (C), and phenolphthalein (D) in α-chloronaphthalene at 220°C. Fig. 5 presents the dependence of the degree of copolycondensation and the concentration of the functional groups B, C, and D which failed to react on the reaction time. The most active groups are exhausted at the beginning of the processes and those with a lower reactivity at later stages. The variation of the fractions of functional groups which have not reacted with copolycondensation time can be conveniently represented graphically for the given system of monomers in an equilateral triangle. The vertices of the triangle correspond to 100% contents of the functional groups. As the copolycondensation proceeds, the fraction of less reactive groups in the reaction mixture increases (Fig. 6).

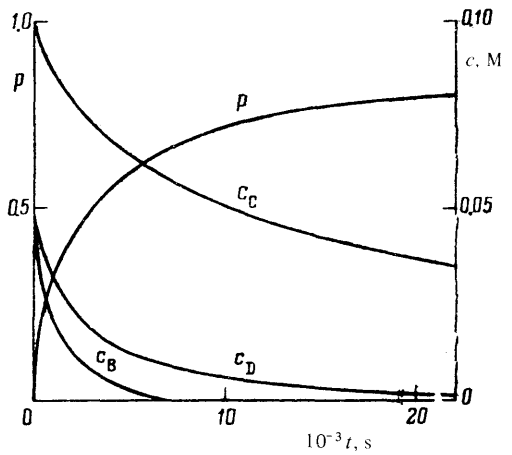


Figure 5. Dependence of the concentrations of the functional groups which have failed to react and the degree of reaction on the duration of the copolycondensation of terephthalic acid dichloride (A) with dian (B), tetrachlorodian (C), and phenolphthalein (D) at 220°C in α-naphthalene [calculated from Eqn. (16)].

It is seen from the above considerations that the nature of the variation of the chemical composition of the copolymer formed may be foreseen and its composition calculated with the aid of Eqn. (16). The composition of the copolymer obtained from terephthalic acid dichloride, dian, and tetrachlorodian has been determined experimentally and it has been established that, under the conditions of high-temperature copolycondensation in solution in α-chloronaphthalene at 220°C, the ratio of the monomers in the reaction mixture varies with reaction time [74]. Thus the study of samples of the reaction mixture by thin-layer chromatography showed that the more reactive dian virtually disappears after only 20 min of copolycondensation, while the less reactive tetrachlorodian can still be detected 80 min after the start of the reaction.

The compositions of the copolymers obtained from terephthalic acid dichloride, phenolphthalein, and dichlorodian were determined by elemental analysis.

Fig. 7 illustrates the dependence of the content of dichlorodian in the copolymers on the duration of copolycondensation. It is readily seen that, in conformity with theoretical considerations, the composition of the copolymer varies as the reaction proceeds. This phenomenon is undoubtedly associated with the different reactivities of the functional groups of the comonomers.

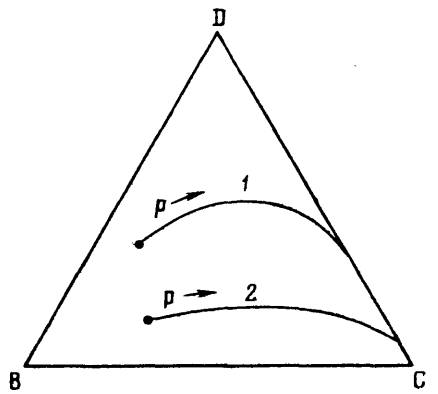


Figure 6. The mole fractions of the functional groups which failed to react in the copolycondensation of terephthalic acid dichloride (A) with dian (B), tetrachlorodian (C), and phenolphthalein (D) at 220°C in solution in α-chloronaphthalene. Curves *1* and *2* correspond to different initial conditions.

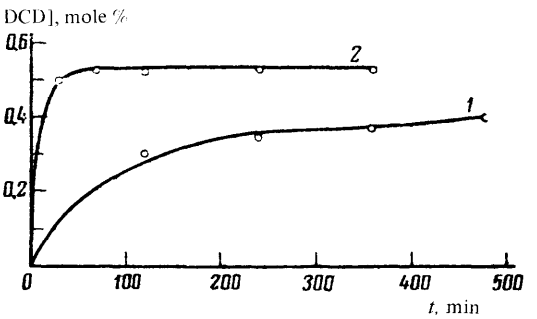


Figure 7. Dependence of the content of dichlorodian (DCD) in the 0.5 : 0.5 : 1 copolymer of dichlorodian, phenolphthalein, and terephthalic acid dichloride on the reaction time; reaction temperature (°C): 1) 180; 2) 242 (isokinetic temperature).

Data indicating the inhomogeneity of the compositions of the copolyesters synthesised from terephthalic acid dichloride, bisnaphthol, and dian were obtained by fractionation and by plotting integral and differential MWD curves for the copolymers. According to theoretical studies [75,76], fractionation of copolymers does not yield an exact characteristic of either the inhomogeneity of the

macromolecules with respect to size or of the inhomogeneity of their chemical composition. However, it follows from these studies that it is possible to select a system in which fractionation is based solely on the molecular weight of the macromolecules. Fractionation in the system where the result obtained is influenced by another parameter (chemical composition) nevertheless does not permit the elimination of the influence of the first parameter. Thus, although it is impossible to determine the distribution function with respect to composition by fractional precipitation, one can observe the chemical inhomogeneity of copolymers if different results are obtained in different systems. It has been found that the solvent (chloroform + ethanol)–precipitant (ethylene glycol) system is relatively insensitive to the chemical composition of the copolymer investigated. This factor enables us to obtain fractions with virtually identical compositions and to plot MWD curves having the shape typical of polycondensation polymers. The same samples, fractionated in a solvent (tetrachloroethane + phenol)–precipitant (n-heptane) system, give rise to fractions differing in chemical composition, and the MWD curves differ appreciably from those obtained previously.

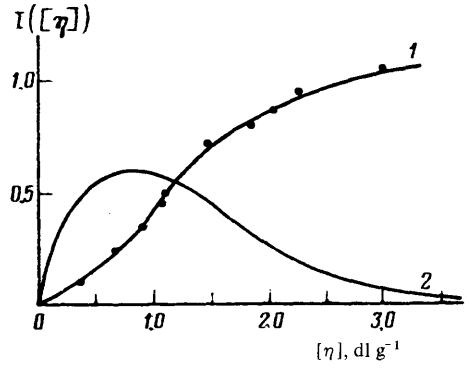


Figure 8. Isokinetic (curve *1*) and differential (curve *2*) MWD curves for the copolyarylate of terephthalic acid dichloride, dian, and bisnaphthol obtained by fractionation in the chloroform + ethanol (5 : 1 by weight)–ethylene glycol system at 25 °C.

Figs. 8 and 9 also illustrate MWD curves for both systems, whose comparison leads to the conclusion that the polycondensation copolymers are chemically inhomogeneous.

Thus the experimental data suggest that, when there are differences between the reactivities of the comonomers, the more reactive comonomer is comparatively rapidly exhausted, while the gradual disappearance of the less reactive monomer continues up to high degrees of reaction.

We believe that the consecutive introduction of comonomers into the reaction should be reflected in the microstructure of the macromolecules of the copolycondensate. Similarly, if the reactivities of the two comonomers are the same or almost the same and the composition of the copolymer remains constant regardless of the degree of reaction, the microstructure of the macromolecules must be affected.

Consequently a new problem arises—that of the selection of a system in which both comonomers would have the same activity. It can be solved theoretically fairly readily. It is known[77,78] that the temperature dependence of the reactivity of the terminal groups during high-temperature condensation obeys the Arrhenius equation. If a polycondensation reaction between functional groups A and B take place in the system, then the temperature dependence of the reaction rate constant is

$$\ln k_{AB} = D_{AB} - \frac{E_{AB}}{RT}, \qquad (17)$$

or, for a reaction between functional groups A and C:

$$\ln k_{AC} = D_{AC} - \frac{E_{AC}}{RT}, \qquad (18)$$

where D_{AB}, D_{AC}, E_{AB}, and E_{AC} are constants characteristic of the corresponding polycondensation reactions, T is the temperature (K), and R the gas constant.

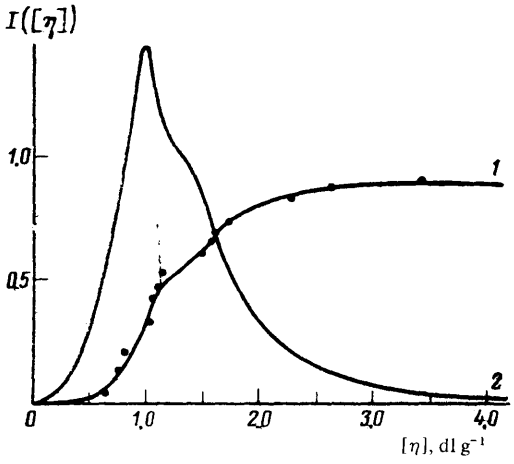


Figure 9. Integral (curve *1*) and differential (curve *2*) MWD curves for the copolyarylate of terephthalic acid dichloride, dian, and bisnaphthol obtained by fractionation in the phenol + tetrachloroethane (1 : 3 by weight)–*n*-heptane system at 25 °C.

The reactivities of the comonomers B and C in their reaction with the intermonomer A are equal, whereupon $k_{AB} = k_{AC}$. This happens at a temperature which is called the isokinetic temperature (T_{is}):

$$T_{is} = \frac{E_{AC} - E_{AB}}{R(D_{AC} - D_{AB})}. \qquad (19)$$

At any instant during the copolycondensation process, carried out at the isokinetic temperature, the concentrations of the functional groups of the two comonomers B and C which have not reacted are proportional to the initial concentrations c^0_B and c^0_C. The probabilities of the reaction of both functional groups at any instant are therefore identical and equal to the mole fractions of the given comonomers in the mixture of monomers; consequently, the structures of macromolecular chains formed at the isokinetic temperature should be statistical.

However, the existence of the isokinetic temperature does not alone imply that reaction can be carried out at this temperature. For high-temperature copolycondensation in solution, the range of temperatures suitable for reaction is only a few tens of degrees. On the one hand, this range is restricted by the low rates of both reactions at low temperatures and, on the other, by the thermal instability of the monomers in the solvent above 200°C. However, Turska et al.[79] found that there exist monomer systems whose isokinetic temperature is in the range accessible to study. They determined T_{is} graphically using the Arrhenius coordinates $\lg k = f(1/T)$. The point of intersection of the experimental straight lines corresponds on the abscissa axis to a quantity which is the reciprocal of the isokinetic temperature (Fig. 10). Table 2 lists the isokinetic temperatures found by Turska and coworkers.

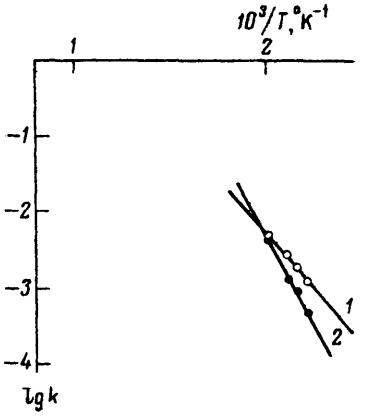
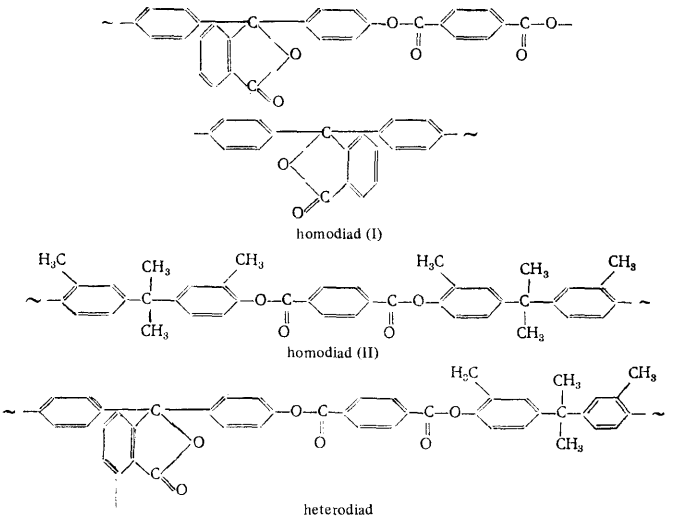


Figure 10. Graphical determination of the isokinetic temperatures for dian (line *1*) and dimethyldian (line *2*) in the reaction with terephthalic acid dichloride in α-chloronaphthalene.

Table 2. The isokinetic temperatures for the copolycondensation of the comonomer systems investigated (the intermonomer is terephthalic acid dichloride).

Comonomers		T_{is}, °C
B	C	
Dian	Phenolphthalein	155
Dian	Dimethyldian	229
Dian	Tetramethyldian	341
Dian	Dinitrodian	366
Dian	Dichlorodian	355
Dian	Tetrachlorodian	340
Phenolphthalein	Dimethyldian	200
Phenolphthalein	Dinitrodian	307
Phenolphthalein	Dichlorodian	242
Phenolphthalein	Tetramethyldian	280
Phenolphthalein	Tetrachlorodian	287

As an example, we shall consider one such system, consisting of terephthalic acid dichloride (the intermonomer A), dimethyldian, and phenolphthalein (the comonomers B and C). It was established by thin-layer chromatography, infrared spectroscopy, and elemental analysis of the reaction products that, when the process is carried out at $T_{is} = 200$°C, the composition of the copolymer hardly changes with the degree of reaction. The microstructure of the copolymer was studied by high-resolution ^{1}H NMR, whereby the contents of the homo- and hetero-diads in the macromolecules were determined:



Preliminary studies showed that the signal of the phenylene protons of the terephthalic acid residue in the ^{1}H NMR spectra of the polyesters investigated is a singlet ($\delta = 8.4$ p.p.m.). In order to resolve this signal into individual components due to homo- and hetero-diads, tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-3,5-dioneeuropium [Eu(fod)$_3$] was used as an additive. Fig. 11 shows that, in the presence of Eu(fod)$_3$, it is possible to distinguish clearly signals in the ^{1}H NMR spectrum corresponding to the chemical shifts of the phenylene protons of the intermonomer in the homo- and hetero-diads.

The constancy of the composition of the copolycondensate synthesised at the isokinetic temperature, observed by other methods, was confirmed by ^{1}H NMR. Use was made for this purpose of Eqn. (5) quoted above. The values of K_M determined by ^{1}H NMR for copolymers synthesised at the isokinetic temperature (with a high accuracy) proved to be unity, which corresponds to a statistical distribution of units in their macromolecules. This result confirms the validity of our theoretical considerations.

The problem of the nature of the copolycondensation process at temperatures fairly different from the isokinetic temperature is no less interesting. For the above system of monomers, a study was made of the composition and structure of the copolymers obtained at 180° and 220°C, i.e. at temperatures above and below T_{is}. At a temperature different from T_{is} the reactivities of the comonomers are different and, when, for example, $k_{AB} > k_{AC}$, the monomer B reacts faster and the macromolecules of the oligomers and polymers in which it predominates are formed faster and in greater amounts. The concentration of the functional groups of the comonomer B decreases very rapidly almost up to complete exhaustion, after which new molecules are formed in which the comonomer C predominates or molecules where chains containing mainly the less active comonomer C join onto the chains

already formed and begin to grow. Depending on the degree of reaction for which the process is terminated, copolymers are obtained with different degrees of structural inhomogeneity, but there is always a tendency towards a block structure. One may expect the formation in the macromolecule of internal blocks of the more reactive comonomer, while the ends of the chains should contain primarily the less reactive comonomer. For very high degrees of reaction, the interactions between the macromolecules should lead to the formation of multiblock copolymers with different internal blocks, but always with the less reactive comonomers at the ends of the chain.

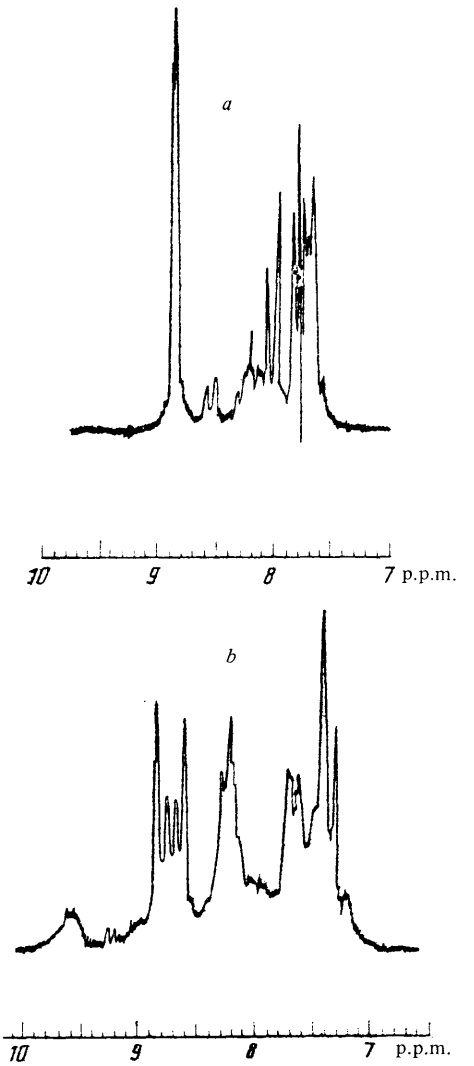


Figure 11. ^{1}H NMR spectrum of the copolyester of terephthalic acid dichloride, dian, and phenolphthalein: *a*) without $Eu(fod)_3$; *b*) with added $Eu(fod)_3$.

In order to confirm the validity of this reasoning, the composition of the copolymer was determined in the course of the reaction. In conformity with earlier considerations, above the isokinetic temperature (220°C) the more reactive comonomer proved to be dimethyldian, which disappeared faster from the reaction mixture, while phenolphthalein, the less reactive comonomer failed to react for a long time. Below the isokinetic temperature (180°C), phenolphthalein proved to be more reactive and dimethyldian failed to react for a long time. The study of the microstructure of the copolymers by ^{1}H NMR using $Eu(fod)_3$ showed that the coefficient of microheterogeneity of the copolymers is $K_M = 0.87$ in both cases.

The difference between the numerical values of K_M for the copolymers obtained at the isokinetic or another temperature indicates a difference between the microstructures of their molecules. The values of the parameter K_M show that copolymers with a completely random statistical chain structure are formed at the isokinetic temperature, while at a non-isokinetic temperature there is a tendency towards the formation of block structures. One should take into account the fact that, for high degrees of reaction, the synthesis of copolymers at isokinetic and non-isokinetic temperatures should lead to the formation of products of the same compositions but with a different structure of macromolecular chains.

oOo

The present review of studies in the field of copolycondensation permits the conclusion that there is as yet no generally recognised equation giving a complete description of the observed phenomena. One should also note that no attempts have been made at an experimental confirmation of the results of the majority of very interesting theoretical studies. Although one should bear in mind that a satisfactory agreement between experiment and theory does not alone demonstrate the validity of the theory, nevertheless the assumptions made in the development of the theory can then be regarded as admissable.

The reason for the discrepancies between different workers' views is apparently the lack of justification of the attempts to describe extremely varied copolycondensation processes in terms of a single theory. It may be that hypotheses which are correct for one group of processes are inadmissible for another. The introduction of limitations as regards the applicability of the theoretical ideas which have been developed should reduce to a large extent the discrepancies in this field. Studies dealing with definite groups of processes hardly involve contradictions under these conditions and in addition permit more general conclusions in many instances. These may include the demonstration of a significant influence of temperature on high-temperature copolycondensation in solution, where even a slight change of temperature in the region of T_{is} may alter the macromolecular structure. Consequently, instead of being a purely kinetic parameter, temperature becomes a parameter which influences the composition and structure of copolymers. Presumably this conclusion is valid also for other groups of copolycondensation processes.

REFERENCES

1. V.V.Korshak and S.V.Vinogradova, "Neravnovesnaya Polikondensatsiya" (Non-Equilibrium Polycondensation), Izd.Nauka, Moscow, 1972.
2. V.V.Korshak, Uspekhi Khim., 42, 695 (1973) [Russ.Chem.Rev., No.4 (1973)].
3. V.V.Korshak, Vysokomol.Soed., A15, 298 (1973).
4. V.V.Korshak, Vysokomol.Soed., A19, 1179 (1977).

5. V.V.Korshak, S.V.Vinogradova, and S.N.Salazkin, Vysokomol.Soed., 4, 339 (1962).
6. S.V.Vinogradova and Ya.S.Vygodskii, Uspekhi Khim., 42, 1225 (1973) [Russ. Chem.Rev., No.7 (1973)].
7. V.V.Korshak, S.V.Vinogradova, and U.S.Vygodskii, J.Macromol.Sci., C11, 45 (1974).
8. V.V.Korshak, T.A.Babushkina, V.A.Vasnev, S.V.Vinogradova, A.V.Vasil'ev, and G.K.Semin, Izv.Akad.Nauk SSSR, Ser.Khim., 1921 (1970).
9. V.V.Korshak, G.L.Slonimskii, S.V.Vinogradova, A.A.Askadskii, A.V.Vasil'ev, V.A.Vasnev, and K.A.Bychko, Dokl.Akad.Nauk SSSR, 199, 607 (1971).
10. S.B.Dolgoplosk, V.P.Mileshkevich, P.M.Valetskii, V.V.Korshak, S.V.Vinogradova, E.Yu.Pogodina, N.G.Sviridova, G.V.Gryaznova, E.N.Nevin, L.V.Shirokova, and L.K.Eremina, Vysokomol. Soed., B19, 748 (1977).
11. S.V.Vinogradova, V.A.Vasnev, V.V.Korshak, A.V.Vasil'ev, and L.V.Dubrovina, Vysokomol. Soed., A13, 770 (1971).
12. S.V.Vinogradova, V.V.Korshak, A.V.Vasil'ev, and V.A.Vasnev, Vysokomol.Soed., A15, 2015 (1973).
13. V.V.Korshak, S.V.Vinogradova, V.A.Vasnev, A.V.Vasil'ev, A.A.Askadskii, T.A.Babushkina, G.L.Slonimskii, G.K.Semin, Yu.K.Godovskii, and E.S.Obolonkova, Vysokomol.Soed., A16, 291 (1974).
14. V.V.Korshak, S.V.Vinogradova, V.A.Vasnev, E.B.Musaeva, A.P.Gorshkov, G.K.Semin, and L.N.Gvozdeva, Dokl.Akad.Nauk SSSR, 226, 350 (1976).
15. V.V.Korshak, S.V.Vinogradova, T.M.Babchinitser, M.G.Keshelava, V.A.Vasnev, Ts.A.Gogudze, and D.Ya.Tsvankin, Vysokomol.Soed., A18, 2103 (1976).
16. V.V.Korshak, S.V.Vinogradova, V.A.Vasnev, E.B.Musaeva, L.N.Gvozdeva, and M.M.Dezhanashvili, Vysokomol.Soed., A20, 888 (1978).
17. P.W.Morgan, "Condensation Polymers: By Interfacial and Solution Method" (Translated into Russian), Izd.Khimiya, Leningrad, 1970.
18. P.W.Morgan, J.Polymer Sci., A2, 437 (1964).
19. P.W.Morgan, Macromolecules, 3, 536 (1970).
20. S.V.Vinogradova, V.V.Korshak, S.N.Salazkin, and S.V.Bereza, Vysokomol.Soed., 6, 1555 (1964).
21. V.V.Korshak, S.V.Vinogradova, S.N.Salazkin, and S.V.Bereza, USSR P.241 013 (1963); Byul. Izobret., No.13 (1969).
22. V.V.Korshak, S.V.Vinogradova, S.N.Salazkin, and L.J.Komarova, Europ.Polym.J., 10, 967 (1974).
23. V.V.Korshak, S.N.Salazkin, L.A.Beridze, and S.V.Vinogradova, Vysokomol.Soed., A15, 841 (1973).
24. S.V.Vinogradova, V.A.Vasnev, V.A.Mitaishvili, and A.V.Vasilyev, J.Polymer Sci., A-1, 9, 3321 (1971).
25. V.V.Korshak, S.V.Vinogradova, and V.A.Vasnev, Vysokomol.Soed., A10, 1329 (1968).
26. S.V.Vinogradova, V.A.Vasnev, and V.V.Korshak, Vysokomol.Soed., B9, 522 (1967).
27. V.V.Korshak, S.V.Vinogradova, V.A.Vasnev, T.M.Mitaishvili, and A.V.Vasil'ev, Dokl.Akad.Nauk SSSR, 187, 1297 (1969) [cf ref.27! (Ed.of Translation)].
28. S.V.Vinogradova, V.A.Vasnev, V.V.Korshak, T.I.Mitaishvili, and A.V.Vasil'ev, Dokl.Akad. Nauk SSSR, 187, 1297 (1969).
29. V.V.Korshak, S.V.Vinogradova, and V.A.Vasnev, Dokl.Akad.Nauk SSSR, 191, 614 (1970).
30. Z.Jedliński and D.Sek, Europ.Polym.J., 7, 827 (1971).
31. R.S.Velichkova, V.V.Korshak, S.V.Vinogradova, V.V.Ivanov, A.T.Ponomarenko, and N.S.Enikolopov, Izv.Akad.Nauk SSSR, Ser.Khim., 859 (1969).
32. S.V.Vinogradova, V.V.Korshak, G.Sh.Papava, and N.A.Maisuradze, Izv.Akad.Nauk SSSR, Ser. Khim., 820 (1970).
33. S.V.Vinogradova, S.N.Salazkin, L.A.Beridze, A.N.Mzhel'skii, A.A.Askadskii, G.L.Slonimskii, and V.V.Korshak, Izv.Akad.Nauk SSSR, Ser.Khim., 931 (1969).
34. V.V.Korshak, N.I.Bekasova, and L.G.Komarova, J.Polymer Sci., A-1, 8, 2351 (1970).
35. V.V.Korshak, N.I.Bekasova, and L.G.Komarova, Vysokomol.Soed., A12, 1866 (1970).
36. V.V.Korshak, S.V.Vinogradova, A.I.Kalachev, P.M.Valetskii, A.S.Titova, and V.I.Stanko, Vysokomol.Soed., A14, 1306 (1972).
37. S.R.Rafikov, I.V.Zhuravleva, R.S.Ayupova, A.I.Kalachev, P.M.Valetskii, S.V.Vinogradova, and V.V.Korshak, Vysokomol.Soed., A15, 1706 (1973).
38. H.Baber, Makromol.Chem., 10, 13 (1953).
39. E.Turska, Vysokomol.Soed., A15, 393 (1973).
40. L.Pietrzak, Doctoral Thesis, Łodź Polytechnic, Łodź, 1972.
41. H.J.Harwood, Angew.Chem., 77, 405 (1965).
42. H.J.Harwood, Angew.Chem., 77, 1124 (1965).
43. L.C.Case, J.Polymer Sci., 26, 333 (1957).
44. L.Beste, J.Polymer Sci., 36, 313 (1959).
45. R.Yamadera and M.Murano, J.Polymer Sci., A-1, 5, 2259 (1967).
46. S.I.Kuchanov, Vysokomol.Soed., A15, 2140 (1973).
47. V.A.Vasnev and S.I.Kuchanov, Uspekhi.Khim., 42, 2194 (1973).
48. S.I.Kuchanov, Vysokomol.Soed., A16, 1125 (1974).
49. Ya.G.Urman, N.Ya.Slonim, S.G.Alekseeva, R.S.Barshtein, and V.S.Kalinina, Vysokomol. Soed., A17, 1539 (1975).
50. E.Turska and L.Matlangiewicz, J.Appl.Polymer Sci. (in the Press).
51. T.M.Gricenko, J.Macromol.Sci.-Chem., A9, 357 (1975).
52. H.Sawada, J.Polymer Sci., B-1, 659 (1963).
53. H.Sawada, J.Polymer Sci., B-2, 507 (1964).
54. S.V.Vinogradova, V.V.Korshak, P.O.Okulevich, Yu.I.Perfilov, and V.A.Vasnev, Vysokomol.Soed., B15, 470 (1973).
55. V.V.Korshak, S.V.Vinogradova, P.O.Okulevich, Yu.I.Perfilov, and V.A.Vasnev, Dokl.Akad.Nauk SSSR, 204, 1129 (1972).
56. S.I.Kuchanov, Vysokomol.Soed., A18, 1878 (1976).
57. V.V.Korshak, S.V.Vinogradova, P.O.Okulevich, Yu.I.Perfilov, V.A.Vasnev, and E.I.Fedin, Izv. Akad.Nauk SSSR, Ser.Khim., 1629 (1972).
58. V.V.Korshak, S.V.Vinogradova, S.I.Kuchanov, V.A.Vasnev, G.D.Markova, and A.I.Tarasov, Vysokomol.Soed., A16, 1992 (1974).
59. V.V.Korshak, S.V.Vinogradova, S.I.Kuchanov, and V.A.Vasnev, J.Macromol.Sci.Rev.Macromol. Chem., C14, 27 (1976).
60. S.V.Vinogradova, Vysokomol.Soed., A19, 667 (1977).
61. Z.Jedliński, D.Sek, and B.Dziewiecka, Europ. Polym.J., 13, 871 (1977).
62. D.Sek, Europ.Polym.J., 13, 967 (1977).

63. G. A. Shtraikhman, Zhur. Prikl. Khim., **32**, 673 (1959).
64. K. Tyuzyo, J. Polymer Sci., **A-1**, 3, 3654 (1965).
65. L. B. Sokolov and T. O. Kruglova, Vysokomol. Soed., **2**, 704 (1960).
66. L. B. Sokolov, "Polikondensatsionnyi Metod Sinteza Polimerov" (The Polycondensation Method for the Synthesis of Polymers), Izd. Khimiya, Moscow, 1966.
67. V. Z. Nikonov, L. B. Sokolov, G. V. Babur, Yu. V. Sharikov, and E. A. Emelin, Vysokomol. Soed., **A11**, 739 (1969).
68. A. Dems, J. Pieniążek, and E. Turska, Bull. Acad. Polon. Sci., Ser. Sci. Chim., **13**, 177 (1965).
69. E. Turska and M. Siniarska-Kapuścińska, Europ. Polym. J. Supplement, 431 (1969).
70. E. Turska, S. Boryniec, and L. Pietrzak, J. Appl. Polymer Sci., **18**, 667 (1974).
71. S. Boryniec, K. Krakowiak, and E. Turska, Polimery, **20**, 179 (1975).
72. E. Turska, S. Boryniec, and R. Jantas, J. Appl. Polymer Sci., **20**, 1849 (1976).
73. S. Boryniec, Faserforsch. u. Textiltechn., (in the Press).
74. E. Turska and L. Pietrzak, Polimery (in the Press).
75. A. B. Litmanovich and A. V. Tonchev, Neftekhimiya, **3**, 336 (1963).
76. L. G. Kudryavtseva, A. D. Litmanovich, A. V. Tonchev, and V. Yu. Shtern, Neftekhimiya, **3**, 343 (1963).
77. S. R. Rafikov and V. V. Korshak, Dokl. Akad. Nauk SSSR, **64**, 211 (1949).
78. E. Turska and A. Dems, Polimery, **15**, 425 (1970).
79. E. Turska, S. Boryniec, and A. Dems, J. Appl. Polymer Sci., **18**, 671 (1974).

The Polymer Institute,
Polish Academy of Sciences,
Zabrze, Poland

Łodź Polytechnic Institute,
Poland