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Non-equilibrium Copolycondensation in Homogeneous Systems

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Theoretical and experimental data for the composition and structure (microheterogeneity) of copolymers obtained by non-equilibrium copolycondensation in homogeneous systems are considered. The effect of the relative reactivities of the comonomers, the reactivities of the first and second groups of the intermonomer, the order and duration of addition of the initial compounds to the reaction zone, and other factors on the composition and microheterogeneity of the copolymers has been demonstrated in relation to interbipolycondensation. The available experimental literature data have been compared with the results of calculations based on a quantitative theory of homogeneous copolycondensation.
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I. INTRODUCTION

Copolycondensation embraces the polycondensation of three and more monomers when none can condense independently under the conditions of the given process. When such condensation is possible, for example, when hydroxy- or amino-acids are employed as the monomers, copolycondensation includes also processes involving two monomers. Since the chains of polycondensation copolymers contain two or more types of units, they will differ from one another by their composition and structure (microheterogeneity) as well as the degree of polymerisation. An important task in the study of copolycondensation (and incidentally in copolymerisation in general) is the determination of quantitative relations between the reactivities of the monomers and the process conditions on the one hand and the characteristics of the polymer obtained as the product on the other. However, whereas for radical polymerisation this has been largely achieved as early as 20 years ago[1,2], systematic studies on copolycondensation on these lines were begun only in the very recent years.

Possibly this is because in the early stages of the investigation of polycondensation mainly equilibrium processes were studied. The synthesis of high-molecular-weight products by this method is known[3,4] to require, firstly, an equimolar mixture of monomers and, secondly, the reaction must be continued up to conversions close to 100%. In this method of copolycondensation the entire initial monomer is present in the polymer chains at the end of the reaction and hence the problem of composition does not arise. The inhomogeneity of the composition of the copolymer should not be unduly great, because the distribution of the equilibrium copolycondensation products with respect to composition should be very narrow. This factor, which makes it possible to assume with a high degree of accuracy that all the macromolecules have the same chemical composition, is specific to equilibrium copolycondensation and generally speaking does not apply to copolymerisation. In the latter process the possibility of appreciable inhomogeneity in composition arises because a copolymer appreciably enriched in one of the monomers can be formed in the early stages, while in subsequent stages it may be enriched in the other monomer. In equilibrium copolycondensation the vigorous occurrence of exchange reactions "mixes" the compositions of the individual macromolecules, eliminating thereby the above cause of inhomogeneity of the composition and leading to a random (statistical) distribution of units in the copolymer chains. Consequently, equilibrium copolycondensation results in the formation of macromolecules with a statistical distribution of units which have virtually identical compositions corresponding to that of the initial monomeric mixture. Hence it is clear that in equilibrium copolycondensation there is no need to determine the dependence of the statistical characteristics of the copolymer on the process conditions. This problem does however become very urgent for non-equilibrium copolycondensation, which is characterised by the absence of exchange and degradative reactions[5]. In this case the difference between the homophase and heterophase methods of carrying out the process, the chemical reactions of which may be complicated by the effects of diffusion and adsorption of the reactants on the interface, is shown particularly clearly. In conformity with the title of the review, we shall consider only processes involved in homogeneous copolycondensation; these are the simplest and most systematically investigated both theoretically and experimentally. Naturally any quantitative description of the macrokinetics of heterophase copolycondensation is impossible without a preliminary determination of the general characteristics of homogeneous processes.

The review does not deal with processes associated with the molecular weight distribution and with the molecular weights of polycondensation copolymers. This is because, on the one hand, there are at present no reliable experimental data whereby an unambiguous quantitative relation can be established between the above parameters and the reactivities of the initial compounds and conditions under

which they are injected. On the other hand, since the chain termination rate constants are unknown, it is impossible to compare the theoretical molecular-weight distributions and molecular weights with the observed values. The range of problems considered in the present review (chemical composition and structure of the chains in the copolymer macromolecules) is independent of side reaction leading to chain termination and the above characteristics of copolymers are determined only by the relations between the chain propagation rate constants.

In connection with the development of new methods for the investigation of high-molecular-weight compounds and in particular the considerable progress achieved in the application of high-resolution nuclear magnetic resonance (NMR), it has become possible to obtain reliable quantitative data for the compositions and structures of copolycondensation products.

The high accuracy of this method makes it possible, when the appropriate theory is available, to discover detailed features of the kinetics of the formation of copolymer chains. The fruitful application of high-resolution NMR to the study of products of homogeneous copolycondensation made it possible, despite the relatively small number of studies in this field, to establish the general characteristics of the process and has greatly stimulated the development of its quantitative theory.

II. CLASSIFICATION OF PROCESSES IN HOMOGENEOUS NON-EQUILIBRIUM COPOLYCONDENSATION AND METHODS OF QUANTITATIVE DESCRIPTION OF THE COPOLYMERS

Linear copolycondensation of compounds containing not more than two functional groups has been investigated theoretically and experimentally to the greatest extent. The simplest instances of linear copolycondensation, which at the same time exhibit all the characteristic features, are bipolycondensation and interbipolycondensation. The first case, where at least one of the two initial compounds employed in the reaction is capable of self-condensation under the conditions of the given processes, can be achieved, for example, with monomers of the amino- or hydroxy-acid type. The second case, where three monomers A–R–A, B–S–B, and C–I–C are involved in the reaction, is more common. The first two, called the comonomers, do not react directly with one another, but each condenses with the third component (the intermonomer).

The interbipolycondensation products can be divided into copolymers belonging to one or different classes. The former are formed from comonomers with identical functional groups. An example of such copolymers is provided by mixed polyamides synthesised from two diamines and one dicarboxylic acid chloride or from one diamine and two dicarboxylic acid chlorides. In order to synthesise copolymers of the second group, it is necessary to employ comonomers with different functional groups. Polyamidoesters obtained by the copolycondensation of a diamine and a glycol with a dicarboxylic acid, may serve as an example of such copolymers.

The chains formed in the course of interbipolycondensation have the structure...–IRIRISIRI–..., in which the comonomer units alternate with the intermonomer units. In order to characterise the composition of the copolymer, it is sufficient to indicate the fraction of units of one of the comonomers, P_R or P_S, while the fraction of the second is determined from the self-evident equality $P_R + P_S = 1$.

In order to describe the inhomogeneity of the composition of the copolycondensation products, one can introduce a distribution function for the macromolecules with respect to size (the number of polymer units) and composition. By analogy with the molecular weight distributions (MWD), this function is known as the size–composition distribution (SCD).

The simplest unit suitable for the description of the chain structure (microheterogeneity) of copolymers is a triad. Homotriads (RIR and SIS) and heterotriads (RIS) are distinguished. In the simplest description of the nature of the distribution of the units R and S in the copolymer chain, one can specify the fractions of the P_{RR}, P_{SS}, and P_{RS} triads of various types. The inhomogeneity of the interbipolycondensation products is estimated quantitatively in terms of the microheterogeneity coefficient K_M, which is expressed in terms of the fractions of various triads by means of the relation

$$K_M = \frac{P_{RS}}{P_{RS} + 2P_{RR}} + \frac{P_{RS}}{P_{RS} + 2P_{SS}} . \quad (1)$$

For a mixture of two homopolymers, $P_{RS} = 0$ and correspondingly $K_M = 0$, while for a copolymer with a regular alternation $P_{RR} = P_{RS} = 0$, which corresponds to $K_M = 2$. Between these two extreme cases, corresponding to fully ordered arrangement of units in macromolecules, there are all possible values of the microheterogeneity coefficient, $K_M = 1$ corresponding to a statistical (i.e. the most disordered) distribution. Consequently the absolute deviations of K_M from unity can be used for a quantitative assessment of the degree of order in the distribution of units in the copolymer and from the latter one can infer the direction of the deviation—the tendency of the monomer residues towards a regular alternation in the chains ($K_M > 1$) or (when $K_M < 1$) towards the formation of long blocks of both comonomers. It has been shown [6] that the composition and the average block lengths L_R and L_S of a copolymer with a fairly high molecular weight most molecules of which consist of numerous blocks, can be determined with the aid of the relations

$$P_R = P_{RR} + \frac{P_{RS}}{2}, \; P_S = P_{SS} + \frac{P_{RS}}{2}, \; L_R = \frac{2P_R}{P_{RS}}, \; L_S = \frac{2P_S}{P_{RS}} \quad (2)$$

in terms of the fractions of various triads. In this case Eqn. (1) assumes a particularly clear form:

$$K_M = \frac{1}{L_R} + \frac{1}{L_S} . \quad (3)$$

Another more detailed method of describing the microheterogeneity of copolycondensation products, which however is more difficult to test experimentally, consists in finding the distribution functions for blocks of various comonomer units with respect to their lengths.

III. INITIAL COMPOUNDS

1. Reactivity of Bifunctional Monomers

The view according to which one of the main factors influencing the composition and structure of copolymers obtained by non-equilibrium polycondensation is the relative reactivity of the comonomers is widely held at present [7,8]. Evidently, this question is closely related to the problem of the constancy of the reactivity of the functional groups of polyfunctional monomers. This type of constancy is as a rule postulated in a theoretical examination of various aspects of polycondensation processes [9].

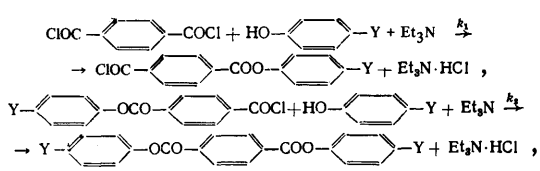
However, there is at present no doubt that the reactivity of the functional groups of many monomers changes in the course of the process[4,5].

Comparatively recently a number of studies were published in which the reactivity of certain initial aromatic compounds widely used in non-equilibrium polycondensation was estimated from the p-electron density at the corresponding atom of the functional group: the nitrogen atom of the NH_2 group in diamines and tetramines[10,11], at the oxygen atom of the OH group in bisphenols[12], and at the carbon atom of the COCl group in dicarboxylic acid chlorides[13].

A preliminary conclusion concerning the reactivity of dicarboxylic acid chlorides was reached with the aid of nuclear quadrupole resonance (NQR) spectra. It has been established that the frequency of the chlorine atom in COCl depends on the electron density in the carbonyl group[14]. A convenient criterion of the capacity of the bisphenol and diamines components for involvement in the polycondensation process is provided by the acid–base properties of their functional groups: phenolic[15,16] or amino-groups[17,18]. Sokolova and Sokolov[19] suggest that the thermochemical method be employed for rapid estimation of the reactivity of the dicarboxylic acid chloride, the principle of which consists in the determination of the heats of reaction of the given monomer with solvents.

Special evidence is not required to show that the methods discussed above can yield only a preliminary fairly qualitative idea about the reactivity of the monomer. Thus, on the one hand, the change in any one characteristic, for example the pK for the acid dissociation of bisphenols, can in some cases entail an increase of the reactivity of the monomers and a decrease in others[15]. On the other hand, it is known that the variable influence of polar effects on the reactivity of a particular functional group depends significantly on various factors: the type of reaction, its mechanism, the nature of the solvent, temperature, etc.[20]

A more effective method for the solution of the above problems is based on kinetic studies of the reactions of bifunctional monomers with monofunctional compounds, which are carried out under conditions close to those in polycondensation. An example of such a reaction is provided by the acylation of phenols by terephthaloyl chloride in the presence of triethylamine (Table 1):



which simulates acceptor–catalytic polyesterification:

$$ClOC-Y'-COCl+HO-Y''-OH+2Et_3N \rightarrow \cdots-CO-Y'-COO-Y''-O-\cdots+2Et_3N\cdot HCl.$$

The data presented in Table 1 show that the rate constant ratio for the first and second COCl groups is not constant and depends on the structure of the phenol. As shown recently,[21] it is important to note that the reactivity of the second group of the bifunctional monomer relative to the first may not only decrease (Table 1, Nos. 1–3) but also increase (Table 1, No. 4).

Kuritsyn and Kuritsyna[22], Sokolov and Kuritsyn[23], and Vorob'ev et al.[24] reported the results of kinetic studies on the reaction of carboxylic acid chlorides with aniline and its derivatives (Table 2). They observed that the ratio of the reactivities of the first and second acid chloride groups depends significantly on the nature of the aromatic amine.

The reactivity of the first COCl group of terephthaloyl chloride (Table 2) in the reaction with aniline (in benzene at 25°C) is higher than that of the first COCl group in isophthalic and carborane-m-dicarboxylic acid chlorides by factors of 1.6 and 2.7 respectively.

Table 1. The results of a kinetic study of the reaction of terephthaloyl chloride with phenols in the presence of triethylamine in dioxan at 30°C[21].

No.	Y in 	$2k^1$	k^2	$\varkappa=\frac{k^1}{k^2}$	No.	Y in 	$2k^1$	k^2	$\varkappa=\frac{k^1}{k^2}$
		litre^2 m^{-2} s^{-1}					litre^2 m^{-2} s^{-1}		
1	CH_3	23±2	4.7±0.3	2.46	3	Cl	34±2	15±1	1.12
2	H	20±1	6.8±0.8	1.49	4	NO_2	96±5	62±3	0.78

A kinetic study of the reaction of bisphenols with substituted benzoic acid chlorides in the presence of triethylamine established that the reactivities of the first and second phenolic groups of 2,2-di-(4-hydroxyphenyl)propane and di-(4-hydroxyphenyl) ether are the same (Table 3).[25]

Table 2. The rate constants for the reactions of dicarboxylic acid chlorides with aromatic amines in benzene at 25°C.

Aromatic amine	$k^1\cdot10^2$	$k^2\cdot10^2$	k^1/k^2
	litre mole^{-1} s^{-1}		
Isophthaloyl chloride (Refs.22 and 23)			
m-Chloroaniline	3.9	2.5	1.5
p-Chloroaniline	14.6	9.4	1.5
Aniline	49.6	2.9	1.7
m-Toluidine	98.0	4.9	2.0
Terephthaloyl chloride (Refs.22 and 23)			
m-Chloroaniline	4.51	1.6	2.7
p-Chloroaniline	18.6	5.0	3.7
Aniline	80.9	19	4.2
m-Toluidine	138	30	4.6
p-Toluidine	220	45	4.9
Carborane-*m*-dicarboxylic acid chloride (Ref.24)			
Aniline	29.9	16.2	1.8
Benzophenone-4,4′-dicarboxylic acid chloride (Refs.22 and 23)			
m-Chloroaniline	8.56*	51*	1.7
Naphthalene-2,6-dicarboxylic acid chloride (Refs.22 and 23)			
m-Chloroaniline	2.45	1.5	1.6

*At 45°C.

The problem of the effect of the length of the macromolecule on the reactivity of its terminal groups is undoubtedly of independent interest. Until recently, studies on these lines have hardly been made. Recently, Turska and coworkers[26] established that the rate constant for non-equilibrium polyesterification in solution is influenced by the solvent power of the organic medium. The explanation is that the reactivity of the terminal groups of the macromolecule depends on chain length.

A number of studies have been published lately in which the relative reactivities of the comonomers (diols) in the interaction with the intermonomer (terephthaloyl chloride) were estimated from the contents of the comonomer residues in the polymeric product (Table 4).[27-29]

Table 3. The results of kinetic studies of the reaction of bisphenols with substituted benzoyl chlorides in the presence of triethylamine in dioxan at 30°C.[25]

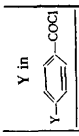
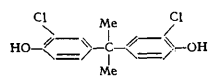
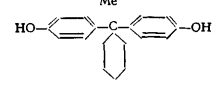
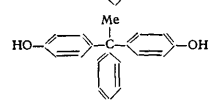
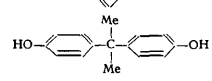
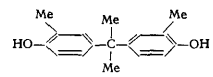
Y in 	$2k^1$	k^2	k^1/k^2
	litre^2 mole^{-2} s^{-1}		
Hydroquinone			
H	0.80±0.08	0.34±0.04	1.18
NO_2	48±5	21±1	1.13
2,2-Di-(4-hydroxyphenyl)propane			
H	0.52±0.06	0.26±0.04	1.00
NO_2	38±2	18±1	1.04
Di-(4-hydroxyphenyl)ether			
Me	0.44±0.04	0.21±0.02	1.03
H	0.86±0.09	0.40±0.03	1.07
Cl	3.1±0.3	1.5±0.1	1.01
NO_2	73±5	37±2	0.99

Table 4. The results of the determination of the relative reactivities of diols in polycondensation with terephthaloyl chloride in the presence of a tertiary amine in dichloroethane at 40°C.[27,28]*

Reference diol formula	pK_{A_1} in dimethyl sulphoxide at 25°C (Ref.15)	Copolycondensation constants r' pyridine	triethylamine
	12.5	(1.00)	(1.00)
	13.0	0.64	0.40
	13.0	0.50	0.40
	13.1	0.59	0.30
	13.1	0.19	0.16
$HO(CH_2)_6OH$	15.1**	1.20	0.03
H_2O	15.7**	—	0.02

*The molar ratios of the diols, terephthaloyl chloride, and triethylamine were 1 : 1 : 1 : 2 and those of the diols, terephthaloyl chloride, and pyridine were 1 : 1 : 1 : 6.
**pK_{A_1} in water.

2. The Order of Introduction of the Initial Compounds into the Reaction Zone

In the synthesis of copolymers by non-equilibrium copolycondensation several methods for the introduction of the initial compounds into the reaction zone are employed. Single-stage copolycondensation is frequently carried out in such a way that all the initial compounds are present in the reaction zone from the very beginning of the process. This order of introduction of the monomers is most frequently employed in the synthesis of copolymers by both non-equilibrium and equilibrium copolycondensation[3-5]. In two-stage copolycondensation the initial compounds (these are usually the comonomers) are introduced into the reaction zone in succession at specified time intervals.

One of the ways of carrying out the process involves three-stage copolycondensation which some investigators employ for the synthesis of block copolymers[30,31]. In this procedure each comonomer is subjected initially to polycondensation with the intermonomer in different reaction vessels. In one system the intermonomer is present in an excess and in the other in a deficiency, but the overall molar amounts of the interacting functional groups are as a rule equal in both vessels. At the end of the polycondensation the systems are combined, which results in copolycondensation between the intermediates formed.

In the synthesis of copolymers by non-equilibrium polycondensation a gradual introduction of one of the initial compounds, usually the intermonomer, into the reaction zone has begun to be used recently[29,32]. This order of addition of the initial compounds frequently leads to the formation of block copolymers.

IV. THEORY OF NON-EQUILIBRIUM COPOLYCONDENSATION IN HOMOGENEOUS SYSTEMS

1. Composition of the Copolymers and Its Inhomogeneity

The task of the theory of copolycondensation is to establish quantitative relations between the average composition of the copolymer, the inhomogeneity of its composition, and the structure of its chains on the one hand and the proportions and reactivities of the initial compounds and the method of their introduction into the reaction zone on the other. As stated above, for equilibrium copolycondensation this task is trivial but for the non-equilibrium processes discussed in this review it becomes important.

It is noteworthy that a similar problem arises also in radical copolymerisation and considerable advances have been made in its solution[1,2]. However, the processes discussed in this review have many important characteristics which distinguish them from copolymerisation and therefore require separate analysis. The first of these differences is a qualitatively different mechanism of polymer chain propagation, which generally speaking makes it impossible to regard chain propagation in copolycondensation as the usual Markov process[1,2]. Another important difference is in the time scales of the formation of polymer chains in the two processes. In radical copolymerisation the chain-formation time, which is comparable to the lifetime of the radical, usually constitutes a negligible proportion of the duration of the process itself. The latter factor, which makes it possible to regard the conditions governing the formation of each individual chain as unaltered, does not hold in copolycondensation where the time required for the formation of high-molecular-weight products is comparable to the duration of the process. The third characteristic feature of copolycondensation kinetics is the possibility of the interdependence of the reactivities of the functional groups of the initial monomers. As will be shown below, this phenomenon plays the leading role in the formation of the copolymer chain microstructure.

At present the number of computational theoretical studies described in the literature and dealing with homogeneous copolycondensation is extremely small. The first classification of these processes was made by Shtraikhman[33], who also derived an equation for the composition of the interbipolycondensation products when all the initial compounds are introduced simultaneously into the reaction zone. The composition of the copolymer is then defined thus:

$$P_R = \frac{[A]_0 - [A]}{[A]_0 - [A] + [B]_0 - [B]}; \quad P_S = \frac{[B]_0 - [B]}{[A]_0 - [A] + [B]_0 - [B]}, \quad (4)$$

where the variation of the concentrations of the functional groups of the comonomers [A] and [B] with their initial values $[A]_0$ and $[B]_0$, the reactivities, and the degree of reaction is found by solving differential equations describing the process kinetics. From these equations for the case of the unaltered reactivities of all the functional groups A, B and C, Shtraikhman[33] and, independently, Beste[34] obtained the relations

$$\frac{[A]}{[A]_0} = \left(\frac{[B]}{[B]_0}\right)^r, \quad [A] + [B] = [A]_0 + [B]_0 - [C]_0 p, \quad (5)$$

where $p = \{[C]_0[C]\}/[C]_0$ is the conversion, [C] and $[C]_0$ are the current and initial concentrations of the functional groups of the intermonomer C–I–C, and r is its relative reactivity in condensation reactions with the comonomers A–R–A and B–S–B. The variation of the composition of the products with conversion has been investigated[35] on the basis of Eqns. (4) and (5) for different values of the parameter r and different proportions of the monomers. For initial compounds with interdependent functional groups, it is impossible to obtain mathematical formulae analogous to Eqn. (5) and the composition of the copolymer was calculated for individual specific instances on a computer[36]. However, it is noteworthy that the problem of the determination of the composition of the non-equilibrium homogeneous interbipolycondensation products with simultaneous introduction of all the initial compounds arises only when they are present in non-equimolar proportions whereupon the final reaction products are oligomers with a small number of units. In order to obtain high-molecular-weight products in this process, it is necessary (as in equilibrium copolycondensation) to carry out the reaction between rigorously equimolar amounts of the monomers until a high conversion approaching 100% is reached. With this method of simultaneous introduction of the starting materials, the composition of the copolymer is always the same as that of the initial monomer mixture and the problem of its calculation does not arise.

Another situation obtains when any one of the initial compounds is gradually introduced into the reaction zone, which may lead to the formation of high-molecular-weight products even when the initial molar ratios of the monomers deviate appreciably from unity[37,38]. For this purpose, it has been necessary to introduce the monomer in excess into the reaction zone at a rate many times less than the rate of its chemical interaction. A typical example of a process of this kind is provided by interbipolycondensation with gradual introduction of the intermonomer into the reaction zone. When all the functional groups of the monomers are independent, the Shtraikhman–Beste equation [Eqn. (5)] is again valid for this process. However, when the intermonomer is introduced fairly slowly, high-molecular-weight products can be formed long before the reaction of the two monomers. This happens when the reactivity of one of the comonomers greatly exceeds that of the other. The process can then be arbitrarily divided into two stages. At the end of the first stage, which is analogous to the polycondensation of the more reactive comonomer with an excess of the intermonomer, high-molecular-weight products are already formed, although the second comonomer has still hardly reacted. Consequently, in this method of carrying out the process it is possible to obtain a high-molecular-weight polymer the composition of which differs from those of the initial compounds. At the beginning the polymer is enriched in the more reactive comonomer and then, as conversion increases and this monomer is exhausted, the copolymer composition begins to approach that of the monomer mixture. The smaller the difference between the reactivities of the comonomers the less distinct are the two stages of the process and the smaller the molecular weight of the products at intermediate conversions. In the limiting case of equal reactivities of the comonomers high-molecular-weight products are formed only after the complete conversion of both comonomers.

It is noteworthy that theoretically only one case is possible in the synthesis of high-molecular-weight products in homogeneous irreversible polycondensation with simultaneous introduction of a non-stoichiometric mixture of the initial compounds[39]. For this, it is necessary that, following the reaction of the first functional group of the monomer taken in excess, the reactivity of the second group should increase sharply. If it were possible to select such an intermonomer, then, in the course of its homogeneous irreversible interbipolycondensation with a mixture of two comonomers having markedly different reactivities, the composition of the resulting copolymer would differ from those of the initial compounds even when the latter are introduced simultaneously. However, the above case is hypothetical, since so far monomers in which the reactivity of the second group greatly exceed that of the first have not been found.

For the same average composition of the polymerisation copolymers, their properties may[40] differ considerably depending on the type of distribution of the compositions of the individual macromolecules, i.e. on the inhomogeneity of the composition of the products. Despite its great practical importance, until recently the problem of this type of inhomogeneity of polycondensation copolymers was not investigated. The method of calculations on the kinetics of homogeneous irreversible polycondensation developed by Kuchanov and Pis'men[41,42] makes it possible to calculate the distribution of the macromolecules with respect to size and composition (DSC) in copolycondensation[6]. It is noteworthy that this method is very general, since the calculation based on it does not impose any limitations either on the number of the initial compounds, or on the relative reactivities of their functional groups (they can be interdependent), or on the number of these groups in the monomer molecules. The latter factor permits the calculation of DSC not only of linear but also of branched products. Another general approach to the calculation of DSC, based on methods of the theory of random processes, has been proposed[43]. However, the relations obtained by the authors cannot be used to describe the copolycondensation of monomers with interdependent functional groups. Their results[43] include as a special case the formulae derived by Cito[44] for the products of the interbipolycondensation of a stoichiometric mixture of monomers with the same reactivities.

On the basis of Kuchanov's results[6], it is possible to show that the kinetic calculation of the distribution of the homogeneous irreversible copolycondensation products

with respect to size and composition leads to the important conclusion that there is a virtual absence of inhomogeneity in the composition of polycondensation copolymers. This is valid provided that their average degree of polymerisation is fairly high. This conclusion does not apply to oligomeric products, the length of which is comparable to that of an individual block. On the other hand, if most of the macromolecules consist of many blocks, then calculation shows that all these molecules may be regarded as having identical compositions to a high degree of accuracy. The latter conclusion is diametrically opposed to Turska's view[7], according to which the composition of the above copolymers should not be inhomogeneous. A conclusion of this kind can be reached when the relations governing the formation of chains in radical copolymerisation are extended to copolycondensation processes. However, one then fails to take into account the fact that the time required for the formation of each individual chain constitutes in the first instance a negligible proportion of the duration of the process itself, while in the second instance, is comparable to this duration.

2. Calculation of the Chain Structure of the Copolymers

In devising a quantitative theory of homogeneous copolycondensation, the most complex problem is that of the calculation of quantities characterising the microheterogeneity of the products. An attempt at a quantitative description of the chain structure of polycondensation copolymers was made by Sawada[45,46], who related by a statistical method the microheterogeneity of the copolymer to the changes in the thermodynamic potentials in the course of the chemical reaction. Since his relations[45,46] do not contain kinetic constants explicitly, they do not make it possible to discover the effect of the reactivities of the monomers on the chain structure.

The coefficient of microheterogeneity K_M defined by Eqn. (1) is a simple characteristic of the copolymer chain structure which can be conveniently determined both theoretically and experimentally. Kuchanov's calculation[6] of K_M for interbipolycondensation products with simultaneous introduction of all the monomers shows that the nature of the distribution of units in the chains is determined mainly by the interdependence of the reactivities of the functional groups in the intermonomer. If these groups are independent, then according to theory $K_M = 1$ and the distribution of units is always statistical for any conversion, proportions of the monomers, and their reactivities. This conclusion disproves the view put forward by some investigators[7,35] that the products of non-equilibrium homogeneous copolycondensation have a block structure. In contrast to copolymerisation, a statistical distribution of the chain units of polycondensation copolymers can occur however large the difference between the reactivities of the comonomers. A general correspondence has been established between the functional group reactivity difference in the intermonomer and the distribution of chain units in the copolymer[6]. If following the reaction of the first group of the intermonomer the reactivity of the second group increases, a tendency of the monomer units towards alternation should be observed ($K_M > 1$); in the opposite case an increase of the reactivity of the second group should entail the appearance of a tendency towards the formation of blocks ($K_M < 1$). For the same intermonomer with interdependent reaction centres, the order in the distribution of chain units in the copolymer increases with the difference between the reactivities of the comonomers.

Theoretical study of the dependence of K_M on the method of introduction of the monomer[47] has shown that there is a possibility of obtaining block copolymers in homogeneous non-equilibrium copolycondensation even when an intermonomer with independent functional groups is involved. This case occurs when the intermonomer is introduced fairly slowly into the reaction zone. When the intermonomer is introduced at a rate much lower than that of the condensation reaction, the following expressions are obtained for the average block lengths and K_M:

$$\frac{1}{L_R} = \alpha_S \mathcal{J}, \quad \frac{1}{L_S} = \alpha_R \mathcal{J}, \quad K_M = (\alpha_R + \alpha_S)\mathcal{J}, \tag{6}$$

$$\mathcal{J} = \int_0^1 \frac{r x^{r-1}\, dx}{\alpha_S + \alpha_R x^{r-1}}, \tag{7}$$

which depend only on the mole fractions α_R and α_S of the comonomers and their relative reactivity parameter r, but are independent of the rate of supply of the intermonomer to the reaction zone. The variation of K_M with r for $\alpha_R = \alpha_S$ (Fig. 1) shows that an increase of the difference between the reactivities of the comonomers leads in the present instance to the formation of longer blocks.

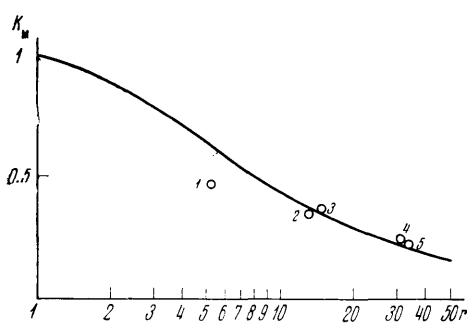


Figure 1. Theoretical variation of the microheterogeneity coefficient with the relative reactivity parameter of the comonomers on slow introduction of the intercomponent (see Table 9 for the significance of the experimental points).

The results obtained by Kuchanov[47] can be used to calculate the K_M for the products of two-stage interbipolycondensation. In this case, apart from its variation with α_R and α_S, K_M depends only on the parameter κ which is equal to the ratio of the reactivities of the first and second groups of the intermonomer in its reaction with the monomer which is introduced first. A plot of K_M against κ for an equimolar ratio of comonomers with independent functional groups is presented in Fig. 2. The same plot evidently describes single-stage copolycondensation with simultaneous introduction of all the initial compounds in the limiting case where the reactivities of the comonomers differ markedly. κ then refers to the reaction of the intermonomer with the more reactive comonomer.

The second method of describing the microheterogeneity of copolymers consists in specifying a distribution function with respect to the block lengths of different monomeric units. A distribution function of this kind was calculated

for the first time by Beste[34] for the products of the interbipolycondensation of a stoichiometric mixture of monomers with independent functional groups. Using a statistical method, he obtained the following expression for the fractions of the comonomer units entering into a block with a length n:

$$W_R(n) = (1 - \nu_{RR})^2 n \nu_{RR}^{n-1}, \; W_S(n) = (1 - \nu_{SS})^2 n \nu_{SS}^{n-1} . \quad (8)$$

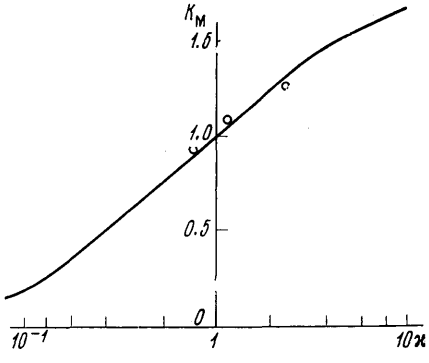


Figure 2. Theoretical variation of the microheterogeneity coefficient with the reactivity ratio of the functional groups of the intermonomer in stage-by-stage interbipolycondensation (see Table 6 for the significance of the experimental points).

The parameters of the distributions defined by Eqn. (8) are expressed in terms of the initial mole fraction α_R and α_S of the comonomers and their conversions p_A and p_B:

$$\nu_{RR} = \alpha_R p_A^2, \; \nu_{SS} = \alpha_S p_B^2 . \quad (9)$$

As stated above, only the statistical copolymer is formed in the case considered by Beste. Calculation of the distribution of blocks with respect to length in the chains of arbitrary copolymers based directly on kinetic process equations leads to Eqns. (8) precisely[47]. However, it is significant that the parameters of distributions (8) are not determined in the general case by relations (9) but are expressed in terms of the concentrations of the triads T_{RR} and T_{SS} and the initial concentrations of the comonomers:

$$\nu_{RR} = \frac{2T_{RR}}{[A]_0}, \; \nu_{SS} = \frac{2T_{SS}}{[B]_0} . \quad (10)$$

When the functional groups of the initial compounds are independent, Eqns. (10) become identical with Eqns. (9).

For long macrochains, the microheterogeneity coefficient may be related to the parameters of distributions (8):

$$K_M = 2 - \nu_{RR} - \nu_{SS} . \quad (11)$$

Since for a statistical copolymer $K_M = 1$, according to Eqn. (11) the relation $\nu_{RR} + \nu_{SS} = 1$ should hold. In the general case of chains of arbitrary length, K_M cannot be expressed in terms of the parameters ν_{RR} and ν_{SS}.

In order to describe the structure of the copolymers obtained as a result of interbipolycondensation, it is necessary to specify with the aid of functions (8) two parameters ν_{RR} and ν_{SS}. By virtue of the condition $\nu_{RR} + \nu_{SS} = 1$, it is sufficient to specify only one independent parameter for a statistical copolymer. Eqns. (1), (2), (8), (11), and (10) show that, in order they characterise quantitatively the microheterogeneity of polycondensation copolymers, it is sufficient to determine the proportions of triads of various types. Calculation of the triad concentrations directly on the basis of the kinetic process mechanism[6,47] makes it possible to relate the nature of the distribution of units in the chains to the process conditions and the reactivities of the monomers. On the other hand, the proportions of triads of various types in the copolymer can be determined experimentally with a high degree of accuracy by ^{1}H NMR.

Copolycondensation processes involving initial compounds of the ARC type capable of self-condensation have characteristics qualitatively different from those discussed above. It has been noted[6] that, in the bipolycondensation of monomers the functional groups of which are independent, a statistical copolymer is not formed. This last factor constitutes a significant difference between the above process and interbipolycondensation where the condition of the independence of the functional groups of the intermonomer was itself sufficient for the formation of products with a statistical distribution of units. Only a simplified case of comonomers of the A–R–C and B–S–C types, when both contain the same functional group C and all the groups are independent, has been considered in quantitative terms. For this special case, Lavalou[48] derived equations describing the composition and subsequently the microheterogeneity coefficient of the copolymer was calculated[6]:

$$K_M = \frac{2(\alpha_R p_B + \alpha_S p_A)(p_A + p_B)}{[p_A + \alpha_R (p_A + p_B)][p_B + \alpha_S (p_A + p_B)]} . \quad (12)$$

The value of K_M defined by Eqn. (8) is always greater than unity and tends to it with increase of the degree of reaction. Consequently, despite the fact that intermediates in the above bipolycondensation process exhibit a tendency towards an alternation of units, the distribution of the latter in the high-molecular-weight copolymer is statistical. When the reactivities of all four functional groups of the comonomers are different, statistical copolymers are not formed at all.

V. APPLICATION OF HIGH-RESOLUTION NMR SPECTROSCOPY IN THE ANALYSIS OF POLYCONDENSATION COPOLYMERS

NMR spectroscopy is at present the principal physical research technique whereby it is possible to characterise quantitatively the distribution of the units in the macromolecules of copolymers. The essential feature of this method, which allows the determination of the contents of homo- and hetero-triads in copolymers, is that the chemical shifts of the protons of the intermonomer residue depend in some cases on which comonomer residues adjoin the given compound in the polymer chain. Fig. 3 shows that the chemical shifts of the signals corresponding to the phenylene proton of the terephthalic acid residue in the NMR spectra of polyesters vary with its environment. The integrated signal intensities are proportional to the relative contents of triads in the copolymer.

Only a few studies in which high-resolution NMR was used to determine the structures of polycondensation copolymers have now been published and these refer exclusively to polyesters.

The first time when high-resolution NMR was used to investigate the structures of polycondensation copolymers was published in 1965 when Harada and Veda[49] investigated the compositions and structures of ethylene glycol,

diethylene glycol, and terephthalic acid copolyesters (Table 5, No. 4).

NMR spectroscopy was also used by Yamadero and Murano[50] and Slonim and coworkers[51] to determine the structures of a number of polyesters synthesised by equilibrium polycondensation in the melt (Table 5). Hamb[52] used this method to investigate the structures of polyesters synthesised by the reaction of poly(ethylene terephthalate) with terephthalic acid and the diacetate of di-2,2-(4-hydroxyphenyl)propane (Table 5, No. 3). In 1972 it proved possible to employ NMR for the elucidation of the structures of copolyesters based on ethylene glycol and terephthalic and isophthalic acids[53]. The introduction of chelate complexes of europium into the test solution enabled the author to increase the difference between the chemical shifts of the signals due to the ethylene glycol residues entering into different triads.

In 1972 Korshak et al.[54] published for the first time data on the structures of copolymers obtained by non-equilibrium polycondensation. They employed terephthalic acid chloride as the intermonomer and various bisphenols and hexamethylene glycol as the comonomers. This choice of initial compounds enabled the authors to determine quantitatively by NMR spectroscopy to within 5% the contents of homo- and hetero-triads in copolyesters (Table 5, No. 1).

Table 5 shows that copolyesters based on intermonomers such as ethylene glycol or terephthalic acid are suitable for the quantitative determination of triads by high-resolution NMR.

Despite certain limitations of the applicability of the NMR method in the study of polycondensation copolymers, its importance in such applications is very great. The method opens up wide prospects for the elucidation of the overall dependence of the compositions and structures of polycondensation copolymers on the reactivities of the initial compounds and reaction conditions.

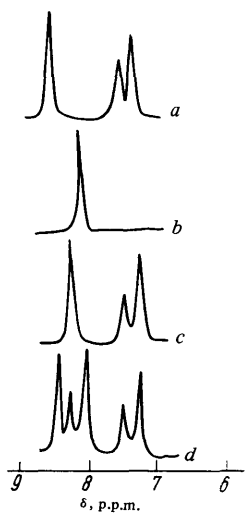


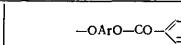
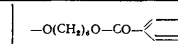
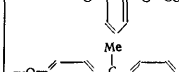
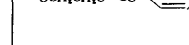
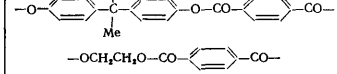
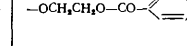
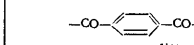
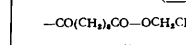
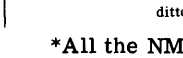
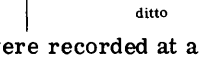
Figure 3. The NMR spectra of tetrachloroethane solutions of polyterephthalates (Table 5, No. 1): *a*) 2,2-bis-(3-chloro-4-hydroxyphenyl)propane (dichlorodian); *b*) hexamethylene glycol; *c*) regular alternation of dichlorodian and hexamethylene glycol residues; *d*) statistical distribution of dichlorodian and hexamethylene glycol residues.

VI. EXPERIMENTAL DATA FOR THE COMPOSITIONS AND STRUCTURES OF COPOLYMERS OBTAINED BY NON-EQUILIBRIUM COPOLYCONDENSATION IN HOMOGENEOUS SYSTEMS

The experimental data for the effect of various factors, including reaction time, for the compositions and structures of copolymers obtained by non-equilibrium copolycondensation in homogeneous systems were not available in 1972. However, it was postulated that under the conditions of non-equilibrium condensation it is difficult to obtain copolymers with a statistical distribution of fundamental units[7,8,30,35].

In her report at the Third Microsymposium on Polycondensation Processes, Turska[7] emphasised that "when there is a difference between the reactivities of the initial comonomers, there are altogether no grounds for the expectation of a statistical distribution of monomer residues" in copolycondensation products obtained under non-equilibrium conditions.

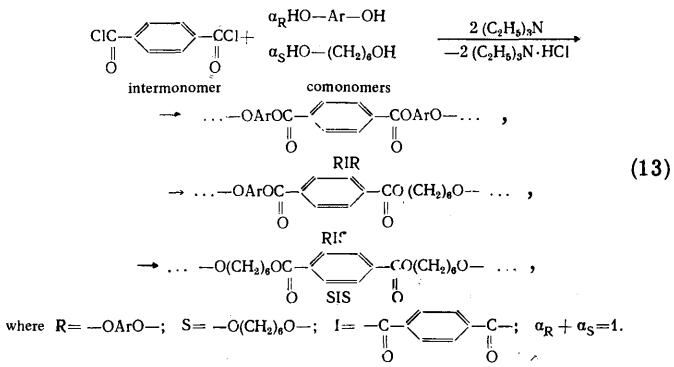
Table 5. Polycondensation copolymers investigated by high-resolution NMR spectroscopy.

No.	Fundamental unit of copolymer		Chemical shifts of group "I" protons in triads (δ scale), p.p.m.			Conditions of recording of NMR spectra*			References
	R—I	S—I	R—I—R	R—I—S	S—I—S	temp., °C	solvent for copolymers	concn. of soln.	
1			8.4	8.3	8.1	130	*sym*-Tetrachloroethane	16%	54
						34	ditto	10%	32
2			7.95	(7.85)**	7.77	70	Trifluoroacetic acid	0,05 g ml^{-1}	50
3			8.35	8.25	8.15	—	ditto	—	52
4			(8.06)**	(8.03)**	8.0	80	*o*-Chlorophenol	0.1 g ml^{-1}	49
5			4.47	4.27	4.07	70	Trifluoroacetic acid	0.05g ml^{-1}	50
6	ditto	ditto	4.70	4.47	4.27	125	*sym*-Tetrachloroethane	15—20%	51

*All the NMR spectra were recorded at a frequency of 60 MHz.

**Found from the NMR spectra quoted by the authors for the copolymers with a 1 : 1 molar ratio of the comonomer residues.

In 1972 Korshak and coworkers[29,54] were the first to report experimental data for the compositions and structures of copolymers obtained by non-equilibrium polycondensation in solution. They chose for investigation polyesters obtained by acceptor-catalytic copolycondensation in the presence of tertiary amines:



(13)

Acceptor-catalytic polyesterification is known to be a typical non-equilibrium process in which exchange reactions hardly occur[55].

The relative contents of the RIR, SIS, and RIS triads in the copolyesters obtained were determined by NMR spectroscopy (Table 6, No. 1 and Fig. 3). The degree of disorder in the copolymer (B) calculated in accordance with Yamadero and Murano's scheme[50] is identical in its significance to the microheterogeneity coefficient K_M.

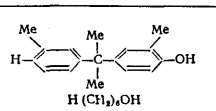
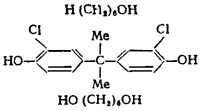
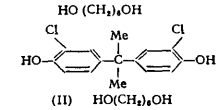
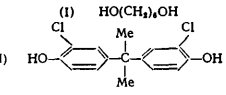
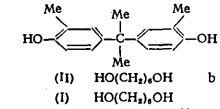
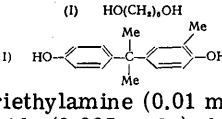
1. Single-stage Copolycondensation

The study of the dependence of the composition of the copolymers obtained by single-stage non-equilibrium polycondensation in homogeneous systems yielded results, which agreed fully with the earlier hypotheses (see, for example, Turska[7]). It was found that the composition of the linear copolymers formed by non-equilibrium copolycondensation in solution for low degrees of reaction with respect to the intermonomer is enriched in the more reactive comonomer[32]. Subsequently the fraction of the less reactive comonomer in the copolymer increases and, when the reaction reaches completion, the composition of the resulting high-molecular-weight compound is the same as that of the mixture of initial compounds. An example of such a process is provided by the acceptor-catalytic copolycondensation of terephthaloyl chloride with 2,2-bis-(3-chloro-4-hydroxyphenyl)propane and hexamethylene glycol in the presence of triethylamine (under these conditions, the reactivity of the bisphenol is more than 30 times greater than that of the glycol[27]). Fig. 4 shows that, as the reaction proceeds, the contents of the comonomers (bisphenol and glycol) in the copolyester become equal to their initial values, i.e. $P_R = P_S = 0.5$.

Turska[7] reported the results of the fractionation of two copolymers synthesised by single-stage non-equilibrium copolycondensation, which indicate the inhomogeneity of the compositions of the products.

Interesting experimental data were obtained in a study of the structures of the copolymers formed by non-equilibrium copolycondensation in solution using the single-

Table 6. The structures of the copolyesters obtained by non-equilibrium acceptor-catalytic polycondensation in solution in one (Nos. 1 and 2) and two (Nos. 3–6) stages[29,32].

No.	Initial diol formula		r	Content of triads, m.f.[c] R–I–R	R–I–S	S–I–S	Content of units, m.f.[c] P_R	P_S	Mean block length L_R	L_S	Microheterogeneity coefficient K_M
1		a	5.3	0.19	0.62	0.19	0.50	0.50	1.6	1.6	1.24
2		a	33	0.22	0.56	0.22	0.50	0.50	1.8	1.8	1.12
3		b	∞	0.25	0.54	0.21	0.53	0.47	1.9	1.8	1.09
4			∞	0.16	0.64	0.20	0.48	0.52	1.5	1.6	1.28
5		b	∞	0.19	0.64	0.17	0.51	0.49	1.6	1.5	1.28
6			∞	0.16	0.66	0.18	0.49	0.51	1.5	1.5	1.32

a. triethylamine (0.01 mole) added to dichloroethane solution (25 ml) of terephthaloyl chloride (0.005 mole), bisphenol (0.0025 mole), and hexamethylene glycol (0.0025 mole) at 40°C and polyesterification continued for 1 h.
b. Triethylamine (0.01 mole) added to dichloroethane solution (25 ml) of terephthaloyl chloride (0.005 mole) and bisphenol (0.0025 mole) at 40°C. Hexamethylene glycol (0.0025 mole) introduced after 30 min and the reaction continued for a further 1 h.
c. m.f. = mole fraction.

stage method[29,32]. Thus it was established that the structure of the macromolecules formed in single-stage non-equilibrium copolycondensation (see Scheme 13) in homogeneous systems depends little on the differences between the reactivities of the comonomers (Table 6, Nos. 1 and 2). Moreover, it was shown that the distribution of units in the polymer chains of the copolyesters obtained under the above conditions is close to the statistical distribution. The microheterogeneity coefficient is approximately unity and is independent of the molar ratio of the comonomers in the initial mixture.

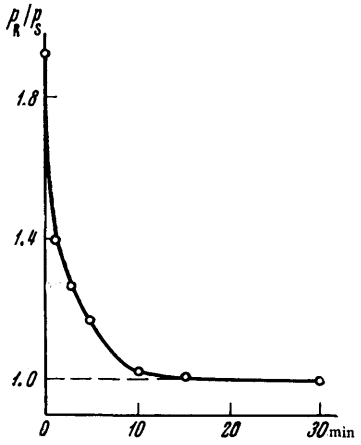


Figure 4. Variation of the composition of the copoly-terephthalate of 2,2-bis-(3-chloro-4-hydroxyphenyl)propane dichlorodian and hexamethylene glycol with reaction time (see footnotes in Table 6).

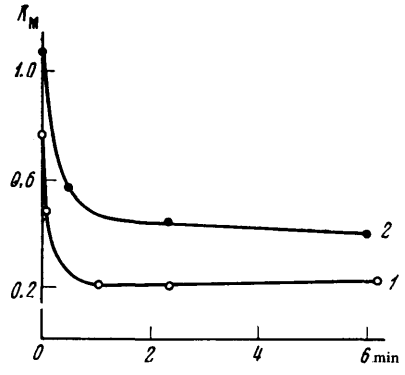


Figure 5. Variation of the microheterogeneity coefficient of the copolyester with the time taken to introduce the solution of terephthalic acid chloride into the solutions of the other components: 1) 2,2-bis-(3-chloro-4-hydroxyphenyl)propane dichlorodian, hexamethylene glycol, and triethylamine; 2) 2,2-bis-(3-methyl-4-hydroxyphenyl)propane dimethyldian, hexamethylene glycol, and triethylamine (dichloroethane, 30°C).

The study of the influence of the duration of the copolycondensation on the structure of the copolymers obtained by the reaction of terephthaloyl chloride with certain pairs of comonomers having different copolycondensation constants showed[32] that at the beginning of the reaction the copolymer is enriched in the RI units containing the more reactive comonomer, but subsequently the relative contents of the units formed by different comonomers become equalised (Table 7). It is important to emphasise that the coefficient of microheterogeneity of copolyesters remains constant throughout the reaction, the value of K_M showing that the distribution of fundamental units in the macromolecules is nearly statistical.

Table 7. Dependence of the composition and structure of the copolyesters of 2,2-bis-(3-chloro-4-hydroxyphenyl)propane, hexamethylene glycol and terephthalic acid on the duration of copolyesterification*.

Reaction time, min	Yield of copolyester, %	η_{int} (0.5% soln. in *sym*-tetrachloroethane at 25°C), dl g^{-1}	Content of fundamental units, m.f.**		Microheterogeneity coefficient K_M
			P_R	P_S	
0.5	59	0.08	0.66	0.34	1.09
1	60	0.09	0.58	0.42	1.19
3	76	0.11	0.56	0.44	1.10
5	81	0.14	0.54	0.46	1.17
10	89	0.19	0.51	0.49	1.12
15	91	0.25	0.51	0.49	1.12
60	93	0.52	0.50	0.50	1.12

*See footnote a to Table 6.
**m.f. = mole fraction.

Thus, as a result of the difference (r = 5.3–33) between the reactivities of the comonomers, the composition of the copolymer changes as non-equilibrium polycondensation proceeds, while the distribution of fundamental units remains constant and nearly statistical.

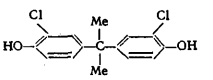
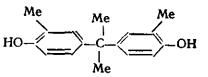
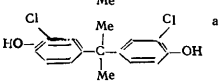
2. Two-stage Copolycondensation

One of the methods of synthesising block-copolymers proposed previously by a number of workers involves the introduction of the comonomers into the reaction sphere stage by stage[8,30]. However, until recently there were no experimental data confirming the block structure of the copolymers prepared by this procedure.

It is interesting to note that the stage-by-stage method of introduction of the initial comonomers into the reaction zone as it were simulates the case of simultaneous copolycondensation when the copolycondensation constant for the comonomers is high ($r \to \infty$). Initially fragments comprising the intermonomer and the more reactive comonomer are formed and the less reactive comonomer only then begins to react with these fragments, which leads to the formation of the copolymer.

The first study of the copolyester obtained by two-stage non-equilibrium copolycondensation in solution was published in 1972.[29] Certain results of these investigations are presented in Table 6 (Nos. 3–6). It was found that the distribution of units in the chains of the copolyesters obtained by stage-by-stage polycondensation is nearly statistical. Thus, even the simulation of an infinite difference between the reactivities of the comonomers did not lead to the formation of block-copolymers. When the stage-by-stage polycondensation of terephthaloyl dichloride with 2,2-bis-(3-chloro-4-hydroxyphenyl)propane and hexamethylene glycol was carried out for different molar ratios of the latter, block-copolymers were not obtained either.

Table 8. The structures of the copolyesters obtained by two-stage non-equilibrium acceptor-catalytic polyesterification in the presence of triethylamine with gradual introduction of the intermonomer in stage I (dichloroethane, 40°C)[29,32,56].

No.	Order of addition of initial compounds		Content of units, m.f.[c]		Block length		Microheterogeneity coefficient K_M
	stage I	stage II	P_R	P_S	L_R	L_S	
1	$HO(CH_2)_6OH$[a]		0.48	0.52	1.6	1.7	1.23
2	ditto [b]	ditto [a]	0.47	0.53	5.6	6.0	0.34
3		$HO(CH_2)_6OH$	0.54	0.46	3.6	3.0	0.61
4	 [a]	ditto	0.53	0.47	9.1	7.7	0.24
5	ditto [b]	»	0.58	0.42	12.5	10.0	0.18

a. In the first stage terephthaloyl chloride was added in the solid state over a period of 1 s.
b. Terephthaloyl chloride added in dichloroethane solution over a period of 15 min.
c. m.f. = mole fraction.

3. Gradual Introduction of the Intermonomer into the Reaction Zone

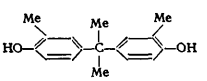
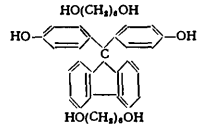
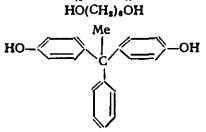
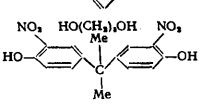
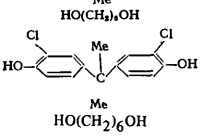
Block-copolyesters were synthesised with a gradual introduction of the intermonomer (terephthaloyl chloride) into the reaction zone[29,32,56], both in the solid state and as a solution. In the first case the rate of introduction of the intermonomer into the reaction zone was determined by the rate of its dissolution and in the second case by the rate of injection.

In the stage-by-stage synthesis of comonomers in the presence of triethylamine when terephthaloyl chloride was introduced in the first stage in the solid state, a statistical or a block sequence of fundamental units in the macromolecules was obtained depending on the reactivity of the diol (Table 8, Nos. 1, 3, and 4). The use of the relatively unreactive hexamethylene glycol in the first stage leads to a statistical distribution of the fundamental units in the copolyester. An increase of the reactivity of the comonomer used in the first stage causes a decrease of the microheterogeneity coefficient of the copolyester and a corresponding increase in block length. Thus the smallest microheterogeneity coefficient of the copolymers was obtained when dichlorodian ($r \simeq 33$), i.e. the most reactive of the comonomers investigated, was employed in the first stage.

The addition of solid terephthaloyl chloride to a solution of diols with $r \neq 1$ in the presence of triethylamine also leads to the formation of block-copolymers (Table 9). It was established that the size of the blocks in the copolyesters[54] depends significantly on the particular difference between the reactivities of the comonomers or, what amounts to the same thing, on their copolycondensation constant. An increase of the copolycondensation constant promotes an increase in block size and a decrease in the coefficient of microheterogeneity of the copolymers (Table 9).

The formation of block-copolymers with $K_M = 0.2-0.4$ when the intermonomer is introduced in the solid state into a solution of the comonomers with $r \gg 1$ was noted for different molar ratios of the initial diols[32]. However, the formation of block-copolymers on introduction of solid terephthalic acid did not occur when the acceptor-catalyst employed was pyridine[32], which is much less effective than

Table 9. The structures of the copolyesters obtained by single-stage non-equilibrium acceptor-catalytic polyesterification in the presence of triethylamine with the introduction of solid terephthaloyl chloride into the reaction zone (dichloroethane, 40°C).[54]

No.	Initial diols (1 : 1 molar ratio)		Content of units, m.f.*		Block length		Microheterogeneity coefficient K_M
	formula	r	P_R	P_S	L_R	L_S	
1		5.3	0.50	0.50	4.4	4.4	0.46
2		12.6	0.50	0.50	5.6	5.6	0.36
3		13.3	0.51	0.49	5.4	5.1	0.38
4		31	0.49	0.51	8.2	8.5	0.24
5		33	0.50	0.50	9.2	9.2	0.22

*m.f. = mole fraction.

triethylamine. Indeed, it has been shown for the benzoylation of *p*-nitrophenol in dioxan at 30°C that the reaction rate constant decreases from 6.48×10^{-2} to 5.92×10^{-2} litre^2 mole^{-2} s^{-1} on passing from triethylamine to pyridine[57]. Since acylation in the presence of pyridine is much slower, there is sufficient time for the complete dissolution of the solid intermonomer introduced into the reaction space, which leads to its greater involvement in the reaction and hence to the conditions of single-stage non-equilibrium copolycondensation in solution. Consequently, regardless

of the difference between the reactivities of the comonomers, in the presence of pyridine copolymers with a statistical distribution of units were obtained under these conditions[32]. In the presence of pyridine block-copolymers were obtained only after a slow introduction of the intermonomer solution into a solution of the comonomers and the acceptor-catalyst. This method of introduction of the intermonomer was investigated in detail in relation to the reaction of terephthaloyl chloride with two pairs of comonomers in the presence of triethylamine in dichloroethane solution at 40°C (Table 8, Nos. 2 and 5 and Fig. 5)[29,32,56]. It was observed that, when the entire solution of terephthalic acid chloride is added at once to the solution of the bisphenol, hexamethylene glycol, and triethylamine, the microheterogeneity coefficient of the resulting copolymers approaches the value corresponding to a statistical distribution of units. When the intermonomer is introduced into the reaction zone over a fairly long period, the microheterogeneity coefficient of the copolyester decreases, tending to a limiting value, which depends on the copolycondensation constant of the comonomers (Fig. 5).

4. Three-stage Copolycondensation

As already mentioned above, in three-stage copolycondensation each comonomer undergoes polycondensation with the intermonomer in different reaction zones. In one case the intermonomer is introduced in excess relative to the comonomer and in the other in a deficient amount such that the overall molar amounts of the functional groups of the intermonomer and the comonomers are the same in both reaction spaces. At the end of the polycondensation in the two systems, the latter are combined, and the reaction begins to proceed between the intermediates formed in the first stages.

Table 10. The structures of the copolyesters obtained by three-stage non-equilibrium acceptor-catalytic polycondensation in the presence of triethylamine (dichloroethane, 40°C).

No.	Molar ratios		Content of units, m.f.*		Block length		Microheterogeneity coefficient K_M
	terephthaloyl chloride: dichlorodian	terephthaloyl chloride: hexamethylene glycol	P_R	P_S	L_R	L_S	
1	0.5:1	1.5:1	0.48	0.52	2.4	2.6	0.81
2	0.7:1	1.3:1	0.45	0.55	3.2	3.8	0.57
3	0.9:1	1.1:1	0.44	0.56	5.9	7.7	0.30

*m.f. = mole fraction.

Many workers[30,31] use three-stage copolycondensation as a method of synthesising block-copolymers, although until recently there was no experimental evidence for the structures of the resulting copolymers. One could only presume that the block length in such copolymers depends on the molecular weight of the products obtained in the first stages. Thus, it was reasonable to conclude that, with increase or decrease of the excess of the intermonomer, relative to the comonomers, the block length in the copolymers will change.

It was established quite recently that the degree of disorder and length of the blocks in the copolymer are determined to a considerable extent by the deviation from equivalent amounts of the functional groups (Table 10).[32] Thus the smallest microheterogeneity coefficient of the copolymer was obtained for the closest approach to the equivalent amounts of the groups of the intermonomer and comonomer at each of the first stages (Table 10, No. 3).

Thus, experimental study of the structures of the copolymers obtained by non-equilibrium copolycondensation in a homogeneous system yielded the following relations. 1. The introduction of the entire intermonomer into the reaction zone at the beginning of non-equilibrium copolycondensation leads to the formation of copolymers with a nearly statistical distribution of polymer chain units regardless of the differences between the reactivities of the comonomers employed. 2. The stage-by-stage introduction of the comonomers into the reaction zone is not a sufficient condition for the formation of block-copolymers. 3. For the synthesis of copolymers with a block structure by single-stage non-equilibrium polycondensation in solution, it is necessary that the reactivities of the initial comonomers should be different and that the rate of introduction of the intermonomer is lower than the rate of its reaction with the more reactive monomer. By varying the above factors, it is possible to obtain block-copolymers with different lengths of the block fragments.

VII. COMPARISON OF THEORY WITH EXPERIMENT

The above experimental data are not only in qualitative agreement with the theory of homogeneous non-equilibrium copolycondensation developed by Kuchanov[6,47] but also provide a quantitative confirmation of the calculated relations. The microheterogeneity coefficients of copolyesters determined by ^{1}H NMR can be conveniently compared with the theoretical K_M, which are determined, in particular, by the relative reactivities of the functional groups of the initial compounds. Since the comonomers employed in the investigations[29,32,54,56] contained independent functional groups, and those in the intermonomer were interdependent, the interbipolycondensation processes involving them are generally characterised by four kinetic chain propagation constants. The microheterogeneity coefficients of the copolymers obtained in such processes are determined by three independent parameters κ_A, κ_B, and r_1. The first two of these are equal to the ratio of the reactivities of the first and second groups of the intermonomer in its reactions with each of the comonomers and the parameter r_1 characterises the relative reactivities of the comonomers in their reactions with the first groups of the intercomponent. The reactivities of the comonomers in relation to the second groups of the intercomponents (parameter r_2) can be simply expressed in terms of the above parameters: $r_2 = 2_1\kappa_A/\kappa_B$. When the condition $\kappa_A = \kappa_B = \kappa_1$ holds, it is evident that $r_1 = r_2 = r$ and therefore K_M is determined by the two parameters x and r. When $\kappa_A \neq \kappa_B$, the concept of the relative reactivity parameter of the comonomers r becomes purely qualitative, since only r_1 and r_2 have a definite quantitative significance.

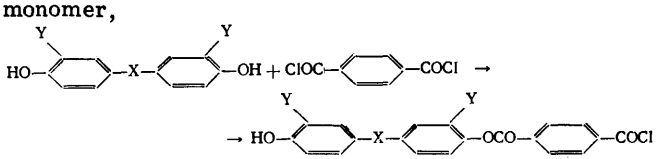
It is simplest to compare theory with experiment in two-stage interbipolycondensation where the second comonomer is introduced into the reaction zone after the first has already reacted. For a specified ratio of the comonomers, K_M is determined according to theory only by the value of κ for the comonomer introduced first and is independent of the parameters r_1 and r_2. The theoretical curve relating K_M to κ for different amounts of the

comonomers is presented in Fig. 2. The Figure also compares the experimental K_M taken from Table 6 taking into account the κ from Table 1. Clearly there is a good quantitative agreement between the theoretical and experimental data, the difference between them being within the limits of experimental error. It follows from Fig. 2, that the parameters κ found, on the one hand, by analysing the structures of the copolymers and, on the other, from kinetic measurements virtually agree. In the first case the synthesis of copolyesters is carried out in dichloroethane solution and in the second the acylation rate constants are determined in dioxan. The small differences between the values of κ obtained by the two independent methods permit the conclusion that the solvent has only a weak influence on the ratio of the rate constants for the first and second groups of the intermonomer. One must emphasise that the solvent does have a very marked influence on the absolute values of the acylation rate constants. For example, the rate constant for the reaction of *p*-nitrophenol with benzoyl chloride in the presence of triethylamine increases almost by four powers of ten on passing from dioxan to dichloroethane [28].

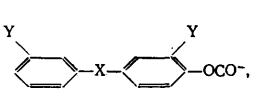
Fig. 1 illustrates the influence of the relative reactivity parameter of the comonomers r on the structure of the copolymers obtained on slow introduction of the intermonomer. It shows that all the experimental points taken from Table 9, with the exception of one, fit satisfactorily on the theoretical $K_M - r$ curve defined by Eqns. (6)–(7) for $\alpha_R = \alpha_S = 0.5$. This agreement should be regarded as satisfactory bearing in mind that, both in the derivation of Eqns. (6) and (7) and in the experimental determination of r in accordance with Eqn. (5), no account was taken of the difference between κ_A and κ_B. The latter factor implies that the values of r quoted in Table 4 yield in general only a preliminary estimate of the relative reactivities of the comonomers. Since r is intermediate between r_1 and $r_2 = r_1\kappa_A/\kappa_B$, the estimate will be more accurate the smaller the difference between κ_A and κ_B and hence between r_1 and r_2. It is therefore clear that the r quoted in Table 4 for 2,2-bis-(3-methyl-4-hydroxyphenyl)propane and 2,2-bis-(3-chloro-4-hydroxyphenyl)propane, which differ appreciably in the values of the parameter κ, constitute only a conventional quantitative characteristic of the relative reactivities of the above comonomers. This explains why the experimental K_M for 2,2-bis-(3-methyl-4-hydroxyphenyl)propane does not fit on the theoretical curve in Fig. 1.

Comparison of r for the bisphenol–glycol comonomer pair and the values of κ for terephthaloyl chloride (in relation to the phenolic component) found by any procedure shows a definite relation between these parameters. By comparing the results presented in Tables 1 and 4, it is seen that κ diminishes with increase of r. The reactivity of the bisphenol increases, i.e. r increases, in the case of non-equilibrium polycondensation under consideration when substituents Y with more pronounced electron-accepting properties are introduced into its molecule [15].

When a bisphenol of this kind interacts with the intermonomer,



a new group



the electron-accepting properties of which are to a large extent determined by the nature of Y, is formed in place of the COCl group. As the electron-accepting properties of Y become more marked, the reactivity of the second acid chloride group of the intermonomer may become not only comparable to that of the first group but may actually exceed it, which is in fact observed in the reaction of many substituted phenols with terephthaloyl chloride. The experimental microheterogeneity coefficients of the products obtained when all the initial compounds are introduced at once, are presented in Table 6. It is noteworthy that these values are close to the K_M for the copolymers formed in two-stage interbipolycondensation (Table 6). This result, which also follows from theory, is quite reasonable for comonomer pairs with a large value of the parameter r. As a result of the appreciable difference between reactivities, mainly the more reactive comonomer (bisphenol) reacts at the beginning of the process and hexamethylene glycol reacts only after some time when the bisphenol has been exhausted. Thus the distribution of units in the copolymer is close to that obtained in the two-stage process, when the bisphenol is added first. Since the above rule holds better the greater the difference between the reactivities of the comonomers, the maximum departure from it is to be expected for the bisphenol with the smallest value of r in relation to hexamethylene glycol. This conclusion is confirmed by the experimental data in Table 6.

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Thus, the results presented in the review show that a quantitative theory of non-equilibrium copolycondensation in homogeneous systems has now been established. The conclusions of this theory have been quite convincingly confirmed by experimental results. Further study on copolycondensation should probably have the following two aims. Firstly, a similar theoretical and experimental treatment of non-equilibrium copolycondensation processes in heterophase systems is needed. Secondly, systematic studies are required on the influence of the compositions and structures of the polycondensation copolymers on their properties. The solution of this problem will make it possible to employ successfully the data quoted in this review for the synthesis of copolymers with specified properties.

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