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The Present State and Prospects for the Development of the Field of Polycondensation

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The aim of the review is to survey and examine data obtained in recent years and characterising the progress in the field of the synthesis of polymers by polycondensation methods. The rule of functionality is shown to have limited applicability and a new formulation, taking into account the structure of the monomers and the reaction conditions, is proposed.
It is also shown that the rule of the non-equivalence of the functional groups does not hold solely in equilibrium polycondensation reactions and that the polymers obtained by polycondensation methods are of the heterounit type. The ways in which anomalous units are formed and the influence of the heterounit structure on the set of properties of the polymer synthesised have been established. Data on the kinetics and mechanism of non-equilibrium polycondensation are considered.
The great importance of catalysis in polycondensation reactions as one of the most significant factors governing progress in this field is demonstrated. Methods for the synthesis of conformationally regular polymers have been discovered by studying acceptor-catalytic polycondensation.
A significant influence of solvents on polycondensation processes has been demonstrated. The characteristic features of joint polycondensation involving non-equilibrium reactions, the prospects for the further development of polycondensation processes, and the possible future of polymers obtained in this way are examined.
The bibliography includes 215 references.

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I. INTRODUCTION

The field of polycondensation has been developing at a rapid rate at the present time and the manufacture of polymers obtained by polycondensation methods has been expanding. The development of research into processes involving the synthesis of polymers by polycondensation methods has enriched polymer science in polymer formation reactions and numerous new polymers and has made it possible to understand the mechanism of polycondensation processes[1].

The aim of the present review is to indicate the advances made at the present time in the polycondensation methods for the synthesis of polymers. Clearly it is quite impossible to describe the development of this enormous field within the framework of a single article. Recognising this, the author's aim was to attempt the more modest task of demonstrating in relation to individual examples the advances made in this field and of indicating the principal trends in the development of polycondensation synthesis.

Since the time when Berzelius proposed the concept of polymers and Gay-Lussac and Pelouze obtained the first synthetic polyester by the polycondensation of a hydroxy-acid, 150 years have elapsed[2]. This was followed by the publication of communications concerning the syntheses of various polymers by polycondensation processes. Thus Liebig[3] obtained an acetaldehyde resin in 1835, Berzelius[4] synthesised the first branched polyester in 1847, and Butlerov[5] obtained polyformaldehyde in 1859 by the condensation of methylene iodide. In 1872 Bayer[6] achieved for the first time the synthesis of a phenol-formaldehyde polymer, which served as the basis for studies by many investigators. In 1909–1912 Baekeland[7] and Petrov[8] created on this basis the manufacture of phenol-formaldehyde polymers (bakelite and carbolite).

The studies by Carothers[9] on the polycondensation of dicarboxylic acids with diamines and glycols constituted an important stage in the development of polycondensation. The discovery of polysiloxanes by Andrianov in 1937 [10] led to the appearance of a new branch of polycondensation, namely the synthesis of polymers with inorganic main molecular chains[11]. In subsequent years there was a growth of the number of studies in the field of polycondensation[1,12–15].

Table 1 lists the names of individual types of polycondensation and the dates of their discovery.

Table 1. Polycondensation processes.

Name of reaction	Year of discovery	Refs.	Name of reaction	Year of discovery	Refs.
Equilibrium polyesterification	1833	[2]	Polyrecombination	1957	[22]
			Oxidative polycondensation	1960	[23]
Polyamidation	1862	[16]			
Phenol-aldehyde polycondensation	1872	[6]	Polycyclocondensation	1960	[24]
			Conformationally specific polycondensation	1960	[25]
Polyazination	1889	[17]			
Interfacial polycondensation	1898	[18]			
			Condensation polydisproportionation	1972	[26]
Polyheterocyclisation	1908	[19]			
Polycoordination	1953	[20]			
Acceptor-catalytic polycondensation	1956	[21]			

Thus one may note that polycondensation, as a fundamental synthetic process, has now provided science and technology with an enormous number of polymeric structures and has played an important role in the formulation of the fundamental ideas of polymer science[12–15]. It must be emphasised that it is also very important as a method of synthesis of natural polymers, because many of the most important biopolymers such as proteins, nucleic acids, natural rubber, cellulose, starch, glycogen, chitin, pentosans, and many others, as well as enzymes and hormones are evidently formed in living organisms via various polycondensation processes[1].

II. INDUSTRIAL PRODUCTION OF POLYCONDENSATION POLYMERS

The role of polycondensation in industry is now very considerable. It needs to be said that in general the plastics industry arose in its time as an industry based on the employment of polycondensation processes and only subsequently polymerisation processes began to develop to an increasing extent. The first synthetic industrial products were phenol-formaldehyde polymers synthesised in 1909–1912 by Baekeland and Petrov, after which glyptals and in 1920 carbamides were developed. Polymerisation polymers were produced on a large scale as early as the 1930's. At the present time polycondensation polymers also play a considerable role in the plastics and artificial fibres industry. Table 2 illustrates the world production of the most important polycondensation polymers[27–29]. It shows that the production of polycondensation polymers has doubled each 10 years. Data are listed only for the four leading polymers in this field, because the others, whose number is fairly large, make a much smaller contribution to industrial production. They include alkyd polymers, polycarbonates, polyarylates, epoxides, polyorganosiloxanes, poly(phenylene oxides), polyimides, etc. The polymers obtained by polycondensation methods occupy a fairly major place in the overall production of polymers.

Table 2. The world production of the most important polycondensation polymers (in thousands of tonnes).[27–29]

Name	Years		
	1960	1970	1980
Foam plastics	700	1600	2500*
Polycarbamides	600	2050	2560*
Polyamides	406	1897	3125
Polyesters	123	1643	5132
	1829	7190	13317
Total growth of production, %	100	393	728

*Data for 1979.

It needs to be said that, when polymers are subdivided into polymerisation and polycondensation types, one must always bear in mind the fact that such subdivision is to a large extent conventional not only as regards the meaning given to these terms but also because there exists at present an increasing group of polymers, which are obtained as a result of the simultaneous employment of polymerisation and polycondensation reactions. These include, for example, unsaturated polyesters, which are obtained in the first stage via polycondensation reactions, while in the last stage they are hardened by polymerisation processes involving their double bonds. Polyester urethanes are likewise obtained as polycondensation products in the first stage in the form of branched polyesters, which undergo joint polymerisation with di-isocyanates in the subsequent stage.

III. CERTAIN CHARACTERISTIC FEATURES OF POLYCONDENSATION

Polycondensation processes differ significantly from polymerisation processes. In the first place attention should be drawn to the greater universality of polycondensation

processes and the wide variety of the structures which can be obtained with their aid. The structures obtained by polymerisation processes are less varied. Among polycondensation polymers, there is a large group of polymers distinguished by a high thermal stability and strength, electrically conducting polymers, physiologically active polymers, etc.

It can be assumed that approximately 25000, i.e. one half, of the papers published annually and describing the synthesis of new polymers deal with polymers obtained by polycondensation[15]. Finally, yet another of the most important differences consists in the fact that these two processes differ greatly as regards the number of chemical reactions employed. In the case of polymerisation we are dealing virtually with two chemical processes: addition to a multiple bond between two atoms and addition to rings. On the other hand, several tens of chemical reactions are used in polycondensation at the present time and the number of such reactions increases each year. We have in addition a new but very promising field of polymer science involving inorganic polymers, which is almost entirely based on polycondensation, since the majority of heterochain inorganic polymers are obtained by polycondensation[30].

The same remark applies also to biopolymers, which are likewise obtained mainly by polycondensation methods[15].

After this brief description of the characteristics of polycondensation reactions, we shall deal with the present state of this field, attention being concentrated primarily on the characteristic features of polycondensation and the causes of the appearance of a heterounit structure, as well as the formation of a macromolecule, its kinetics and mechanism, and the influence of the process conditions, catalysts, and solvents on this reaction, i.e. the questions which at present determine the progress in the field of polycondensation.

Table 3. The equilibrium constants of certain equilibrium and non-equilibrium polycondensation reactions[12-14].

Reaction investigated	Starting materials	K_p
	Equilibrium polycondensation	
Polyesterification	Pentamethylene glycol + adipic acid	6.00
Polyamidation	ω-Aminoundecanoic acid	8.88
Polycoordination	Beryllium acetylacetonate + 4,4'-di-(acetoacetylphenyl) ether	4.00
	Non-equilibrium polycondensation	
Polyesterification	Dian + 2,2-di(4-hydroxyphenyl)propane diformate	$4.74 \cdot 10^3$
Esterification	Phenol + benzoyl chloride	$4.48 \cdot 10^3$
Polycyclisation	Dihydrazide of di(carboxyphenyl) ether + dichloride of di(carboxyphenyl) ether	$1 \cdot 10^{25}$
Polyamidation	Pyromellitic acid dianhydride + aminophenyl) ether	$1 \cdot 10^5$

IV. EQUILIBRIUM AND NON-EQUILIBRIUM POLYCONDENSATION

The study of the characteristic features of polycondensation processes led the present author to the conclusion that all the known polycondensation reactions can be combined into two large groups known as (1) equilibrium and (2) non-equilibrium polycondensation[12-15,31,32]. The difference between them is determined mainly by the equilibrium constant of the given process. Equilibrium polycondensation involves reactions whose equilibrium constants are below 10^3 ($K_e < 10^3$), while reactions whose equilibrium constants are above 10^3 ($K_e > 10^3$) belong to non-equilibrium polycondensation[15,33-35]. Table 3 presents examples of reactions of both types.

Equilibrium polycondensation and its features have been studied in greater detail[12,14,15,33]. These two types of polycondensation processes also differ as regards the properties of the polymers formed, the reaction mechanism, the nature and mechanism of the action of the catalysts, kinetics, molecular weight distribution, the mechanism of joint polycondensation, the structure of copolymers, and other characteristic features of these processes, which will be considered below[32-35].

Non-equilibrium polycondensation has been studied in less detail and this factor necessitates a detailed investigation of the laws controlling its course. The importance of this field is due to the fact that non-equilibrium polycondensation actually makes it possible to synthesise polymers at a higher rate and to obtain high-molecular-weight polymers with new structural units and an interesting set of physical and chemical properties[13,14,15,34,36,37].

V. THE FUNCTIONALITY OF THE STARTING MATERIALS

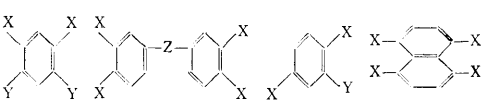
The functionality of the starting materials is one of the fundamental concepts in the field of polycondensation[38-47,143]. Kienle was the first to draw attention to this concept and emphasised its importance in processes involving the formation of three-dimensional network polymers[42].

Carothers[9] formulated the rule of the functionality of the initial monomers, pointing out that linear polymers are formed when the initial monomers are bifunctional. On the other hand, if their functionality is three and more, gel formation takes place and a three-dimensional insoluble and infusible polymer is produced. This is expressed by the relation $P = 2/f$, where P is the degree of reaction and f the functionality, i.e. the number of functional groups in the monomer molecule.

In the case of a bifunctional monomer $P = 1$, which leads to the formation of a linear polymer. For a trifunctional monomer, $P = 2/3$ and for a tetrafunctional one, $P = 1/2$, which implies the formation of three-dimensional polymers, i.e. a gel.

Subsequently many investigators turned their attention to problems of functionality and attempted to find the most effective forms of the expression for functionality and for the application of this concept to polycondensation processes[38-47].

In the course of the development of polymer science, an increasing number of instances have been observed in which the Carothers rule was not confirmed and tri- and tetrafunctional monomers proved capable of forming polymers with linear macromolecules[31,47]. The formation reactions of various polyheteroarylenes, in which tetrafunctional compounds such as tetramines, dihydroxydiamines, tetracarboxylic acids, diaminodicarboxylic acids, and similar compounds having the general formula



are used, may serve as examples. In this case the mutual arrangement of the functional groups is decisive. For an

arrangement of the functional groups which permits the formation of five- or six-membered rings, linear macromolecules of heterocyclochain polymers are obtained. This demonstrates the possibility of the formation of linear polymers made up of tri- and tetra-functional monomers, which had been previously regarded as impossible[38,47]. One must therefore conclude that not only the overall functionality of the initial monomers but also the corresponding favourable mutual arrangement of the functional groups in the unit or the initial monomers is important for the foration of linear polymers. This enabled the author to reformulate the question of the importance of the functionality of the monomers in non-equilibrium polycondensation[15,47] and to put forward a different treatment of the concept of functionality[1,15,38,47]. Functionalities of three types, designated as possible (Φ_p), practical (Φ_{pr}), and relative (Φ_r) functionalities, were proposed[47]. The possible functionality is defined as the total number of functional groups of all types contained in the monomer or oligomer molecule. The practical functionality is defined as the number of functional groups involved in the polycondensation process in the formation of bonds between the constituent units of the polymer, while the relative functionality represents the ratio of the possible and practical functionalities and is given by the equation $\Phi_r = \Phi_p/\Phi_{pr}$. The relative functionality characterises the difference between the reactivities of the reacting monomers and oligomers.

If questions of functionality are considered from the standpoint of its dependence on the structure of the monomers, then the monomers can be divided into two large groups: normal and anomalous monomers. The normal monomers obey the Carothers rule, while the anomalous monomers do not. Accordingly, the possible functionality of the normal monomers is somewhat greater than their practical functionality:

$$\Phi_p > \Phi_{pr},$$

which means that the relative functionality is greater than unity:

$$\Phi_r > 1.$$

The difference between the possible and practical functionalities

$$\Phi_p - \Phi_{pr} = \Phi_{ap}$$

represents the active possible functionality (Φ_{ap}), which determines the possibility of further growth of the molecule. Accordingly, linear polymers are formed when $\Phi_p = 2$. Three-dimensional polymers are produced when the active possible functionality is greater than two:

$$\Phi_{ap} > 2.$$

The questions involving the formation of cyclic groups are then of secondary importance, although cyclic groups of different size are formed in the synthesis of three-dimensional network polymers, which ultimately leads to a three-dimensional network construction, i.e. to a gel point[1,48–52]. It has been noted that the gel point depends on the flexibility of the polymer molecules and on the concentration of the polymer in solution[48]. One must therefore conclude that not only the overall functionality of the initial monomers but also the corresponding favourable mutual *ortho*-arrangement of the functional groups in the unit or in the initial monomers, i.e. the so-called "*ortho*-effect", is important for the formation of linear polymers.

VI. THE RULE OF THE NON-EQUIVALENCE OF FUNCTIONAL GROUPS

The rule of the non-equivalence of the functional groups is known to be valid in all instances of polycondensation where the starting materials are bifunctional[53]. The molecular weight of the polymers produced in the equilibrium polycondensation reaction is regulated on the basis of this principle by adding different amounts of monofunctional substances or an excess of one of the initial monomers. Fig. 1 illustrates this relation for equilibrium polycondensation[53]. Its investigation in non-equilibrium polycondensation for starting materials with a higher functionality showed that here too the excess of one of the starting materials has in most cases an analogous influence in the reactions of tetrafunctional monomers, which leads to a decrease of the molecular weight in proportion to the excess of one of the initial monomers. Such a relation has been observed in many instances of non-equilibrium polycondensation. Fig. 2 illustrates the dependence of the viscosity of the solution of the polyimide formed on the excess of the starting materials in the reaction of a diamine with pyromellitic acid dianhydride[54]. Fig. 3 shows that the reaction of a diamine with the dichloride of *m*-carbaboranedicarboxylic acid is also very sensitive to the excess of the starting materials[55].

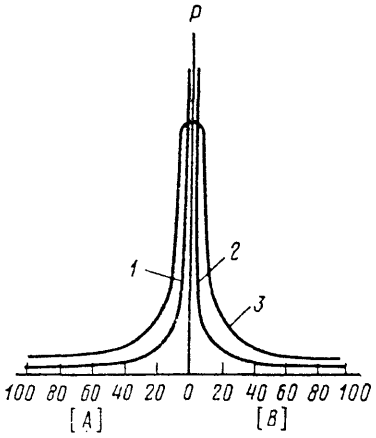


Figure 1. Dependence of the polymerisation coefficient *P* of the polymer obtained by the polycondensation reaction on the excess of the starting materials A and B: *1*) and *2*) calculated; *3*) experimental.

In general, the reactions of different tetrafunctional nucleophiles with tetracarboxylic acids or their derivatives obey the rule of the non-equivalence of the functional groups, as shown in a general form in Fig. 4.[56]

Thus the examples presented demonstrate fairly clearly a distinct dependence of the molecular weight (MW) of the polymer synthesised on the excess of one of the initial monomers also in the case of tetrafunctional monomers and hence the "rule of the non-equivalence of the functional groups" remains in force and also in relation to polyfunctional monomers in non-equilibrium polycondensation[53].

The possibility of the acceleration of the concluding stage of the non-equilibrium polycondensation reaction as a result of the introduction of monomers with more reactive functional groups than the terminal groups has been demonstrated and it has been shown that the maximum attainable molecular weight of the polymer depends on the stoichiometric composition of the reaction mass and on the relative reactivities of the functional groups of the monomer[57].

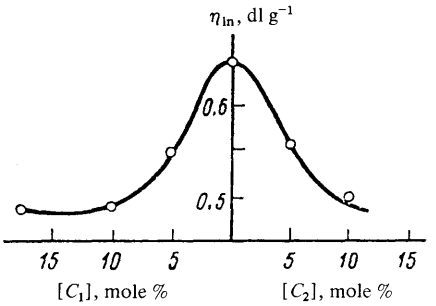


Figure 2. Dependence of η_{ln} for a solution of aniline-phthalein polypyromellitimide on the ratio of the starting materials; c_1 = dianhydride concentration; c_2 = diamine concentration.

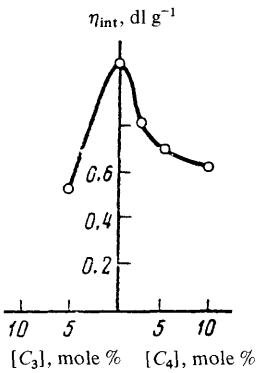


Figure 3. The influence of the ratio of the starting materials on η_{int} for 0.5% solutions of polyamido-*m*-carbaborane in DMF; c_3 = diamine concentration; c_4 = acid chloride concentration.

VII. THE HETEROUNIT STRUCTURE OF THE POLYMERS FORMED IN NON-EQUILIBRIUM POLYCONDENSATION PROCESSES

Heterounit polymers are produced in the non-equilibrium polycondensaton reaction as a result of the formation of anomalous units in the set of polycondensation reactions, illustrated in Fig.5.[58-61]

The anomalous units formed under these conditions differ in their structure from the main units of the macromolecule.

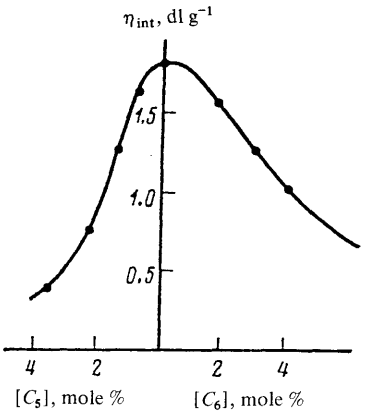
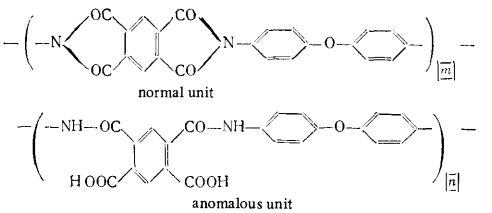


Figure 4. The influence of the excess of the starting materials on the viscosities of solutions of polymers obtained from various tetrafunctional monomers (dicarboxylic acid dihydrazides, bis-o-aminophenols, dianilinodiamines, and bisanthranilic acid diamides) by reaction with polycarboxylic acids; c_5 = nucleophile concentration; c_6 = electrophile concentration.

The formation of the anomalous units generates the so-called "heterounit" polymers[14,36,58,62-66]. The present author suggested that the structure of the heterounit polymers be expressed by the general formula

$$-[-(-M-)_{\boxed{m}}-(-A-)_{\boxed{n}}-]_x- ,$$

where M is the normal unit, A the anomalous unit, and the coefficients $\boxed{m}$ and $\boxed{n}$ denote the statistical distribution of the M and A units. The real formula of the polymers such as, for example, polyimide is therefore as follows:



In this case the anomalous units are those in which ring closure has not taken place. In other instances there is a possibility of side reactions of different character, as shown in Fig.5. The presence of the anomalous units has a significant influence on the entire set of the chemical and physical properties characteristic of the given polymer[58,63,67-69]. The study of the conditions leading to the formation of the anomalous units and hence to the appearance of heterounit polymers is one of the most important tasks in synthetic polymer chemistry, since without it it is impossible to understand and explain fully the dependence of the properties of the polymers on their structure[14,36,58,62-66]. The presence of anomalous units of different kinds has been demonstrated for many classes of polymers obtained by polycondensation methods[15,62]. These include representatives of polyamides[70], polyesters[71], polycarbonates[81], unsaturated polyesters[72], polyarylates[73,74], polybenzimidazoles[75], pyrrones[76], and polyimides[77,78]. The presence of non-cyclised and anomalous structures in polybenzoxazoles[79], polyquinoxalines[80], polytriazines[81], squaric acid polyamides[82], polysulphones[83], and other polymers[84] has been established recently. To complete

the picture, one should add that anomalous units are present also in polymers obtained by polymerisation methods from monomers and by the modification of polymers[63,64,85].

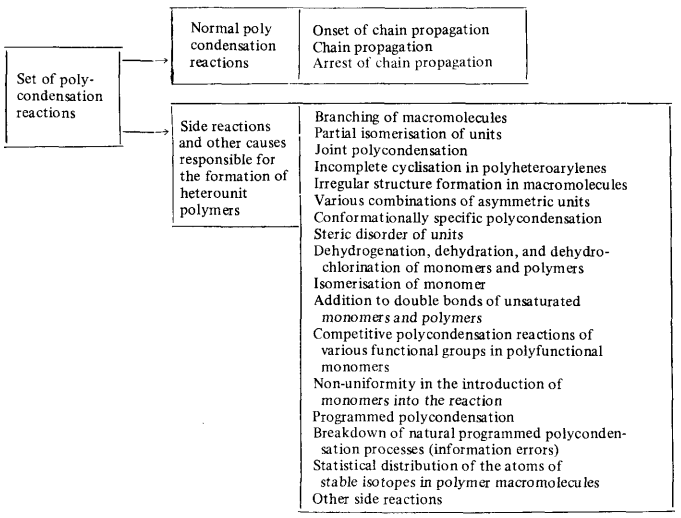
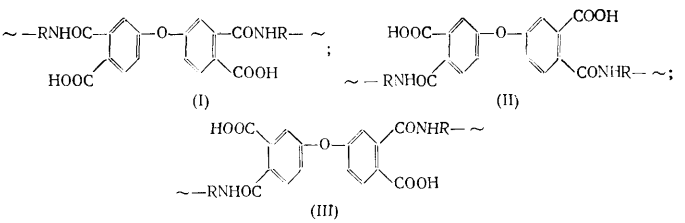


Figure 5. The set of polycondensation reactions.

Finally isotopes are a significant factor in the formation of heterounit structures. The point is that all organogenic elements from which the majority of polymers are constructed each have several stable and radioactive isotopes. Stable isotopes forming part of the composition of the polymers are distributed statistically in their macromolecules and each macromolecule therefore has a structure different from that of the others. This naturally affects the properties of the polymers, as shown in relation to deuterated polyethylene[65]. The substitution of hydrogen by deuterium in polyethylene results in an appreciable alteration of physical characteristics such as density, melting point, glass point, yield point, and chemical properties. This led to the conclusion that the presence of isotopes in macromolecules promotes the acquisition of a heterounit structure by polymers[40,41,86,87]. At the same time account must be taken of the possibility of the combination of a series of effects and the simultaneous operation, together with the isotope effect, of factors such as branching, isomerisation, etc. The influences of these effects may coincide and enhance one another.

The heterounit structure should be manifested particularly significantly in the case of biopolymers, where one may expect extremely specific and very marked manifestations of the isotope effect. In fact, we know that extremely small changes in the structures of substances such as proteins, nucleic acids, etc., have a significant influence on biological functions. At the same time it is known that different isotopes are non-equivalent as regards their physiological properties. Thus, among the causes responsible for the heterounit structure of polymers, one should include also the influence of stable isotopes in monomer and polymer molecules. Branching is a very special case in the heterounit structure of polycondensation products. It can arise as a result of various side reactions and owing to the use in the polycondensation reaction of starting materials with a functionality greater than two. For example, the addition of laproxid during the synthesis of poly(ethylene terephthalate) (lavsan) leads to the formation of a branched polyester[88].

The determination of the extent of the heterounit structure in polyamidoacids by ^{13}C NMR demonstrated the presence of three possible structures[89]:



The contents of these isomers vary within the following limits as a function of the nature of the solvent: (I) from a mole fraction of 0.33 to 0.46; (II) from 0.11 to 0.18; (III) from 0.43 to 0.49.

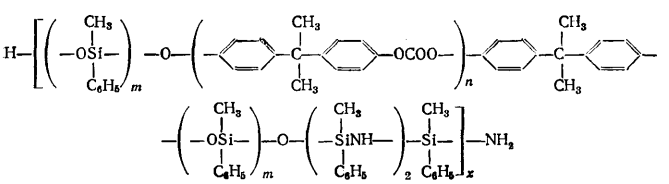
Since the presence of anomalous units in heterounit polymers influences significantly their chemical and physical properties, this factor must be taken into account in considering the relation between the structure and properties of polymers[14,44,50].

VIII. THE SYNTHESIS OF ORGANOELEMENTAL POLYMERS

An interesting feature of polycondensation processes is that this is in fact the main procedure whereby polymers containing different elements in the Periodic System are obtained. The usual organic polymers consist of elements such as carbon, hydrogen, oxygen, and nitrogen. The remaining elements are typical for organoelemental polymers. Polymers incorporating such elements, which are listed in Table 4, have now been obtained[37,40,41,86,87,90,91]. The table shows that there is a very great variety of organoelemental polymers obtained by polycondensation methods; 75 elements have already been incorporated in polymers of this kind. Evidently there is every reason to assume that further development of research into organoelemental polymers will enrich science and practical applications by a large number of new and interesting polymers.

New bonds between elements are formed in organoelemental polymers, imparting a new set of properties to the polymeric structures formed. Various heterobonds between the atoms constituting the polymer chain are presented in Table 5.

Among block copolymers, there exists an organoelemental block copolymer containing polycarbonate and polysilazasiloxane blocks having the following structure[92]:



IX. THE KINETICS AND MECHANISM OF THE POLYCONDENSATION REACTION

The kinetics of equilibrium polycondensation processes have been investigated in relation to a large number of examples[1,12,31,34,93]. However, many investigations devoted to

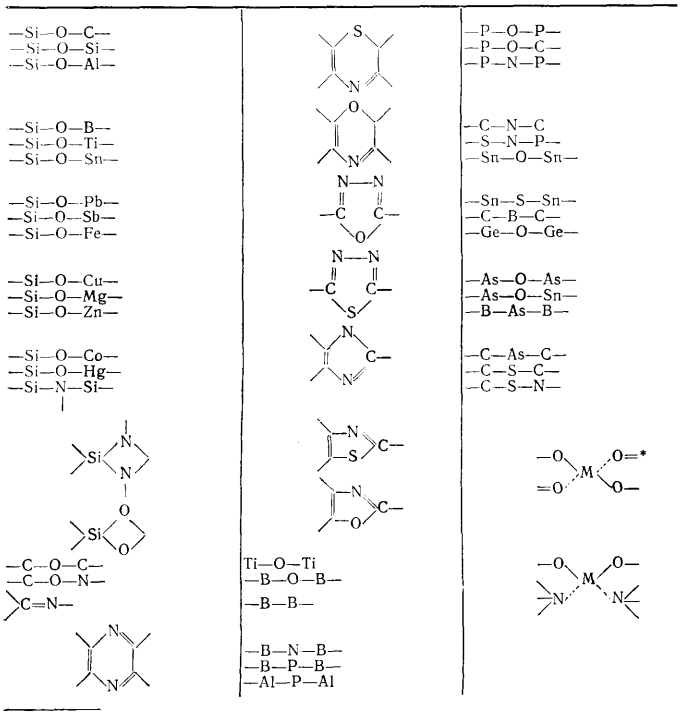
these problems are still being published. The kinetics of the non-equilibrium polycondensation reactions have been studied in less detail.

Table 4. Elements forming part of the composition of polymers obtained by polycondensation methods.

Period	Groups									
	I	II	III	IV	V	VI	VII	VIII		
1	H	—	—	—	—	—	—	—	—	—
2	Li	Be	B	C	N	O	F	—	—	—
3	Na	Mg	Al	Si	P	S	Cl	—	—	—
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
	Cu	Zn	Ga	Ge	As	Se	Br	—	—	—
5	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
	Ag	Cd	In	Sn	Sb	Te	I	—	—	—
6	—	Ba	La	Hf	Ta	W	—	Os	Ir	Pt
	Au	Hg	Tl	Pb	Bi	—	—	—	—	—
7	—	—	—	Th	—	U	—	—	—	—

Lanthanides Ce Pr Sm Eu Gd Tb Dy Ho Fr Tu Yb Lu

Table 5. Linkages introduced into organoelemental polymers via polycondensation.



*M = Ca, Sr, Ba, Hg, Be, Fe, Ni, etc.

The successful investigation of the kinetics of the formation reaction of cardo-polymers has been possible by virtue of their solubility, since the starting materials employed are diamines with bulky substituents, such as, for example, anilinephthalein[94]. The introduction of polar groups into the polyimide unit with the aid of monomers of the type of di(3-amino-4-methoxyphenyl)methane has also made it possible to obtain soluble polymers and to investigate the process kinetics[61].

The study of the kinetics of the synthesis of polymers such as polyphenylquinoxalines[95], polyimides[96–98], polybenzoxazoles[97], polyoxadiazoles[99–101], polyarylates[102] and polyphenylenes[103] has likewise been described.

The kinetic curves for the reaction of terephthalic acid chloride with phenolphthalein in the presence of triethylamine are presented in Fig.6.[104] We see that the process is extremely rapid even at low temperatures.

It is of interest that the dependence of the viscosity of the polyarylate obtained on the reaction temperature is unusual and is expressed by a curve with two maxima, as shown in Fig.7.[102,105,106] This can be explained by the complex temperature dependence of the reaction rate constant[104,105].

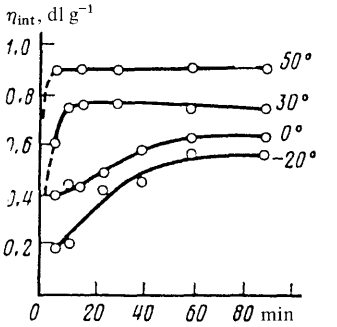


Figure 6. Variation of η_{int} of the polyarylate in the synthetic process.

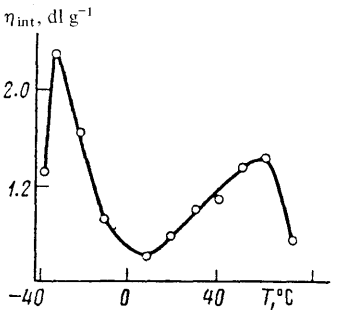


Figure 7. Temperature variation of η_{int} of the polyarylate.

Kuchanov[49] calculated the influence of the method of measuring out the monomers on the molecular weight distribution of the polymers obtained by non-equilibrium polycondensation and concluded that the number-average polycondensation coefficient is inversely proportional to the square root of the rate of introduction of the monomer.

In the single-stage synthesis of polyimide from pyromellitic anhydride and anilinephthalein in solution in nitrobenzene, the reaction should proceed as shown in Fig.8.[54] The yield of the polymer is then almost independent of the

reaction time, since the polymer is formed quantitatively after only 1 h.[107]

In the two-stage formation of polyoxadiazoles the second stage involves the closure of the heterocycle. Fig.9 presents curves describing the variation of the activation energy for the cyclisation of polyhydrazides[108]. The figure shows that an interesting feature of this process is the fact that the activation energy increases with increase of the degree of cyclisation, which is evidently associated with the increasing rigidity of the macromolecular chain and the steric hindrance to the heterocyclisation reaction.

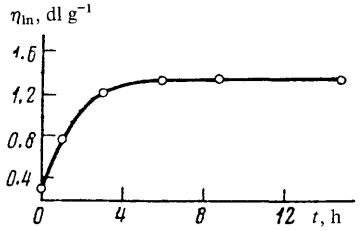


Figure 8. Dependence of η_{ln} of anilinephthalein polypyromellitimide on the reaction time.

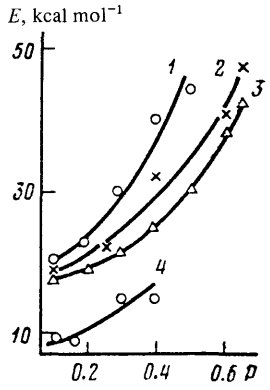
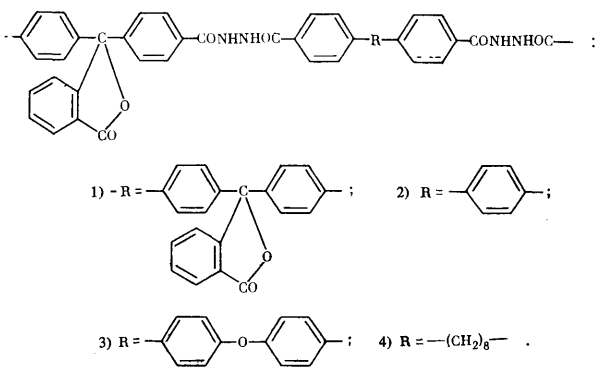


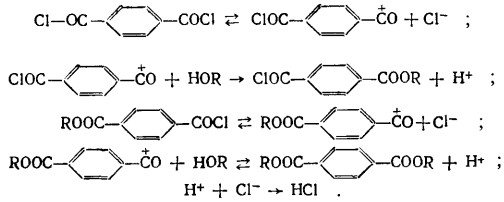
Figure 9. Dependence of the activation energy E for heterocyclisation on the degree of reaction P of the polyhydrazide having the general formula



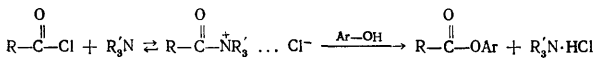
It has been found that the order in which the starting materials are mixed in the non-equilibrium polycondensation reaction has a considerable influence on the structure of the polymer formed when asymmetric monomers are used[109].

It is noteworthy that the mechanisms of various kinds of polycondensation reactions have been elucidated in detail only in a small number of instances. The mechanism of non-equilibrium polycondensation has been studied mainly in relation to polycondensation in solution[13,110].

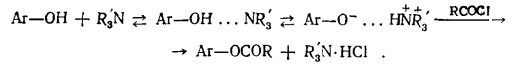
The study of the high-temperature non-equilibrium polycondensation of dicarboxylic acid chlorides with bisphenols in solution led to the conclusion that the reaction proceeds via an ionic mechanism in accordance with the equations[111,112]



The study of non-equilibrium polycondensation in solution in relation to the acceptor-catalytic polyesterification in the presence of tertiary amines led to the conclusion that the reaction can involve both the nucleophilic catalytic mechanism

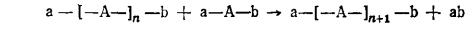


and the general base catalytic mechanism

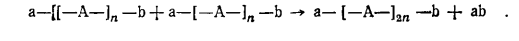


The particular pathway followed depends on the basicity of the tertiary amine and hence on its ability to form a hydrogen bond with phenol[113–116]. For a more basic amine, general base catalysis predominates[116].

An interesting feature of the polycondensation reaction is the possibility of its occurrence via two pathways, namely via the single-stage substitution



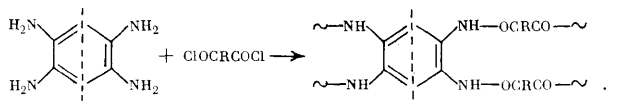
and via repeated dimerisation



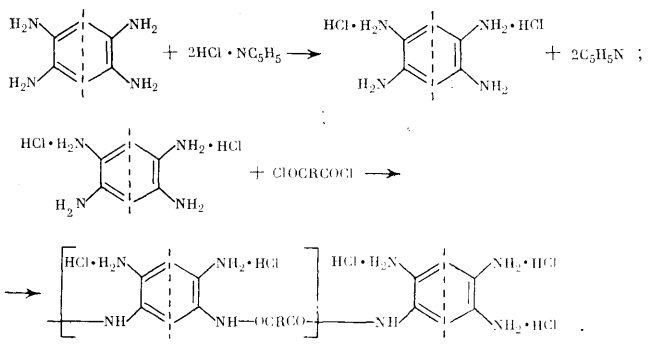
Evidently in practice both versions are realised, possibly with one of them predominating depending on the reaction conditions and the nature of the starting materials. It must be emphasised that this constitutes a significant difference between polycondensation processes and polymerisation in which there is no chain growth via repeated dimerisation.

Among the interesting results of the study of the mechanism of non-equilibrium polycondensation, mention must be made of a new procedure for the regulation of the structure of the macromolecule formed. It has been found that the addition of pyridinium chloride in the polycondensation of aromatic tetramines with carbaborane-*m*-dicarboxylic acid chloride makes it possible to obtain a linear polymer, while the reaction in the absence of this additive leads to the formation of a branched and cross-linked polyamide[117,118]. The reaction mechanism which explains the structure-regulating influence of pyridinium chloride is as follows: the reaction of the tetramine with the acid chloride gives

rise to a trimer:



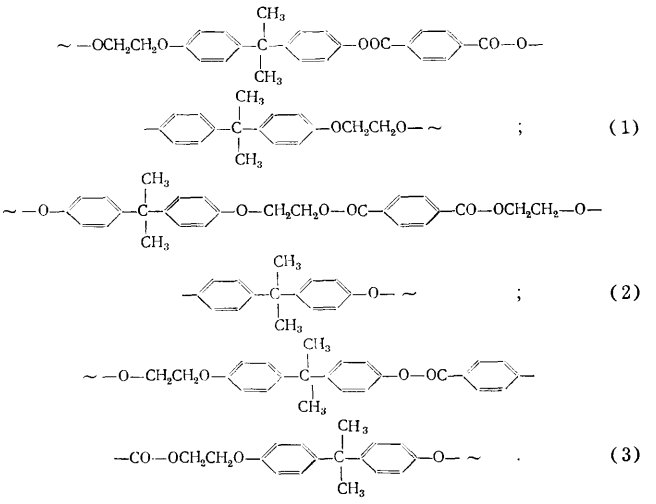
However, if pyridinium chloride is added, then the tetramine becomes bifunctional as a result of salt formation and a soluble linear polymer is therefore produced on treatment with the dicarboxylic acid dichloride:



Thus the amino-groups are neutralised, which prevents branching and terminates the growing chain at a specific reaction stage. An analogous pattern has also been observed in the reaction of bis(o-aminophenols) with acid dichlorides[66].

One of the important characteristics of polymers is the regularity of the structure of the polymer chain, which is particularly important for units with an asymmetric structure and determines the "head to tail", "head to head" and "tail to tail" dispositions.

The study of the acceptor-catalytic polycondensation of terephthalic acid chloride with the β-hydroxyethyl ether of 2,2-di(4-hydroxyphenyl)propane showed that, when the reaction is carried out under the usual conditions with the simultaneous introduction of the starting materials, a polymer with a statistical distribution of units is formed[119]. If the terephthalic acid chloride is added gradually to the reaction mixture, a difference in the reactivity of the hydroxyls is manifested and a polymer in which the "head to head" (1) and "tail to tail" (2) units predominate is obtained:



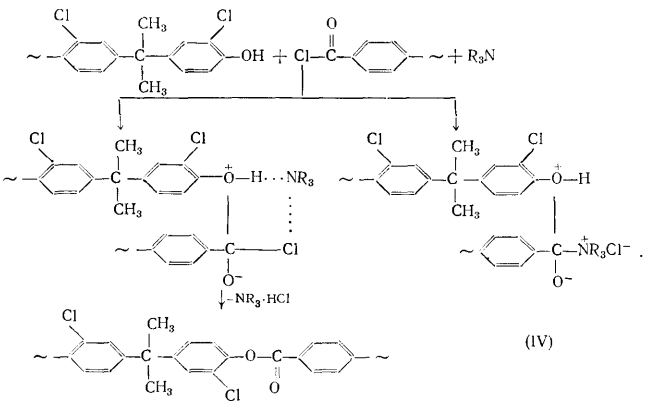
On the other hand, the "head to tail" configuration (3) is encountered more rarely. Thermodynamic methods have been recently applied on an increasing scale to the study of polycondensation processes. Thus a detailed investigation has been made of the thermodynamics of the synthesis of a series of polyheteroarylenes which led to the discovery of the temperature limits of the occurrence of the individual stages of the reaction and the thermodynamic functions of the polymers and the equilibrium constants of the process have been obtained, showing that the reactions are of the non-equilibrium polycondensation type[76,120]. Among the interesting approaches to the investigation of non-equilibrium polycondensation, mention must be made of the use of correlation analysis, whereby one can predict the reactivities of monomers with interdependent and independent reaction centres and calculate the rates of various polycondensation processes from the joint polycondensation constants[121].

A mechanism of the elementary stage in the polycondensation of diamines with pyromellitic anhydride postulating a consecutive electron and proton transfer in the electronically excited state of the complex formed by the reactant and solvent molecules has been proposed on the basis of the study of the phototransfer and thermal transfer of an electron[122].

X. CONFORMATIONALLY REGULAR POLYCONDENSATION

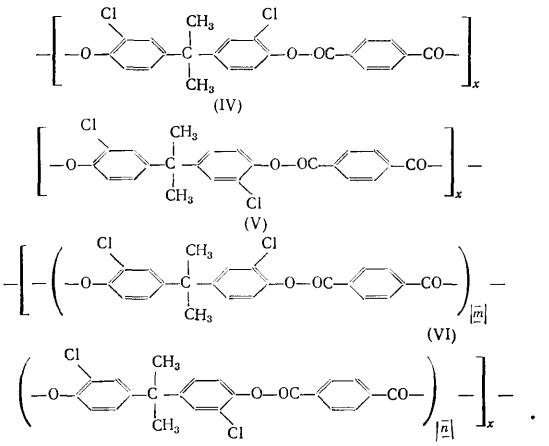
The study of the non-equilibrium polycondensation reaction in relation to the interaction of dicarboxylic acid chlorides with bisphenols in the presence of catalysts such as tertiary amines led to the formation of polyarylates whose properties differed depending on the reaction conditions and the nature of the catalysts.

The mechanism of the acceptor-catalytic polyesterification reaction occurring in this instance can be represented by the following scheme[123]:



In this case one can obtain a polyester containing two conformations of the units differing in the mutual arrangement of the halogen atoms. It has been shown for acceptor-catalytic polyesterification that the nature of the solvent and the catalyst plays a major role[25]. Thus the polycondensation of 2,2-di-(3-chloro-4-hydroxyphenyl)propane with terephthalic acid chloride leads to the formation of polyarylates with different properties, melting points, and solubilities depending on the reaction conditions[25,124]. The study of the polyarylates showed that they are conformationally regular polymers and consist of conformers with

different conformations, arising by virtue of hindered rotation[123,125]. They have the following structures:



(IV)

(V)

(VI)

Formulae (IV) and (V) represent two extreme structures: cisoid and transoid respectively. They can be regarded as analogues of the isotactic and syndiotactic structures of polyolefins. Formula (VI) corresponds to an atactic polymer containing both conformations, distributed in the polyarylate molecule either statistically or in blocks[126,127].

Similar polymers have also been obtained from other dian derivatives containing two methyl or two nitro-groups[128]. All such polymers evidently contain blocks made up of regularly distributed units. The size of the blocks depends on a number of factors and can vary within specific limits depending on the conditions of the synthesis and the nature of the solvent and the catalyst[123,125,127,129].

XI. THE MOLECULAR WEIGHT DISTRIBUTION IN THE POLYCONDENSATION PRODUCTS

The question of the molecular weight distribution in the polycondensation products has been studied in detail by a number of investigators[48,130,131]. It has now been established that, depending on the method of polycondensation, polymers with different molecular weight distribution functions are formed[131,132].

An interesting feature of the polycondensation in a solvent–precipitant system is the formation of polymers with a narrow molecular weight distribution (MWD). This is achieved by using solvents in which the polymer with chains having a length greater than the specified value P_c are insoluble[131].

The homogeneity of the reaction mass is also important for the MWD, since inhomogeneity leads to an increase of polydispersity[130]. Polycondensation yields products whose MWD can vary within wide limits. Thus, according to literature data, the polydispersity coefficient varies within wide limits ranging from 1 to 43.[32] Consequently there is no complete consistency with Flory's theory[133], according to which the polycondensation products must have the most probable distribution corresponding to a polydispersity of two. The non-equilibrium polycondensation of pyromellitic anhydride with di(4-aminophenyl) ether yielded polymers whose molecular weight distribution M_w/M_n varied from 1.53 to 3.72.[134,135] The narrower distribution can be explained by the fact that a helical conformation is products under the conditions of the synthesis, the degree of conversion into the helical form increasing when the MWD becomes wider[136,137].

The study of the MWD of the polyarylates obtained from phenolphthalein and terephthalic acid chloride by gel permeation chromatography revealed a bimodal distribution with respect to the molecular weight, as shown in Fig. 10.[138]

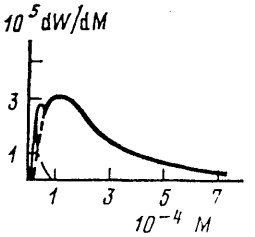


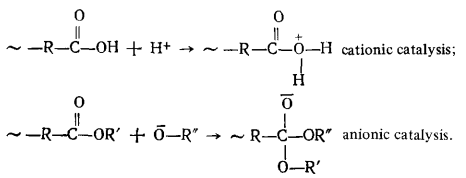
Figure 10. Molecular weight distribution curve for polyarylate.

This type of MWD can be explained by the fact that, together with the linear polyarylate, a cyclic polymer (macrorings) is formed[139]. The formation of cyclic polymers in the polycondensation reaction together with linear polymers had been observed earlier in the synthesis of polydimethylsiloxanes, poly(ethylene terephthalate), polyamides, and polyesters[140].

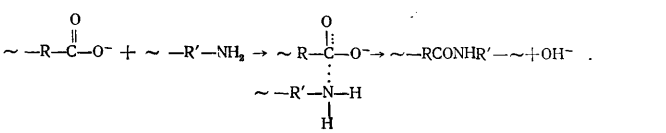
XII. CATALYSIS IN POLYCONDENSATION REACTIONS

Catalysis is known to play a major role in polycondensation processes[15,33,41,141,143]. The application of catalysts in polycondensation processes makes it possible to accelerate the reaction and to obtain polymers with a broad spectrum of properties[47,141,142,146,147].

Catalysis in non-equilibrium polycondensation reactions can proceed as cationic, anionic ionic-coordination, and free-radical process depending on the nature of the starting materials and the catalysts[15,141,142]. The intermediate complexes are illustrated schematically below:

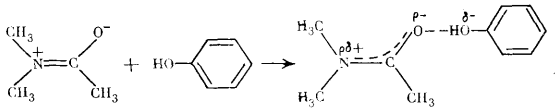


Accordingly, the mechanism of the polycondensation of a diamine with a dicarboxylic acid involving nucleophilic substitution is as follows[144]:

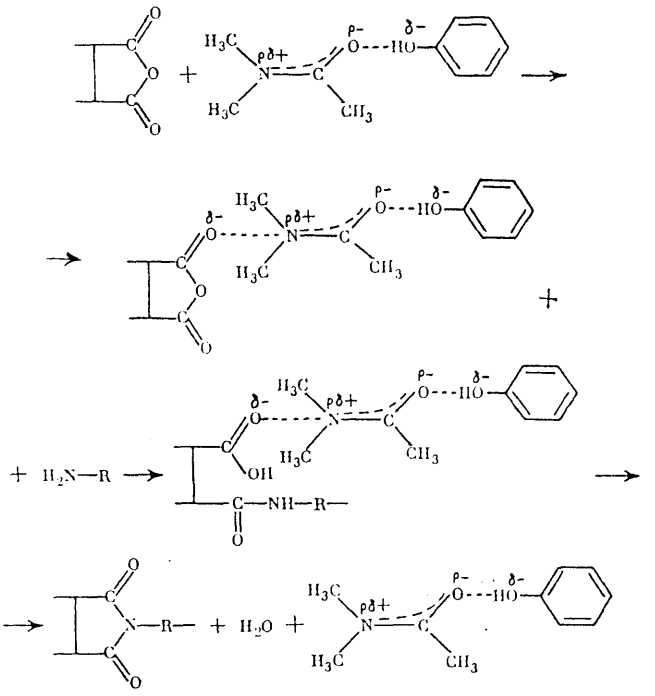


For the amide catalysis of the polyimide formation reaction, the following reaction mechanism, in which an amide–phenol

complex is formed initially, has been proposed[145]:

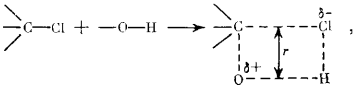


This is followed by the formation of a ternary catalytic complex:



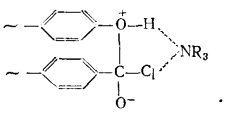
The imide ring is formed in this way and the complex is regenerated[145].

The following transition state has been proposed to account for the mechanism of the poly(ethylene terephthalate) formation reaction:



where r is the diameter of the "active component" of the activated complex[148].

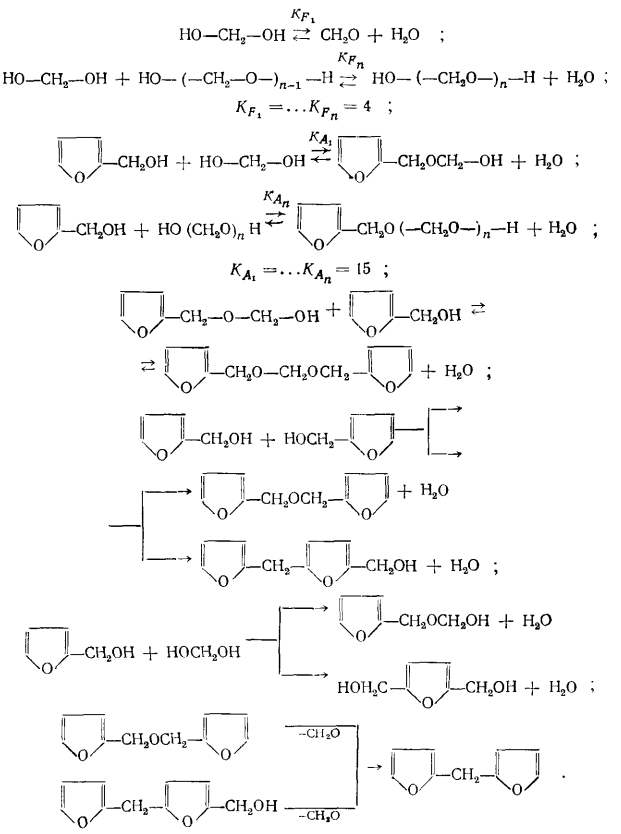
Ionic-coordination catalysis obtains, for example, in the presence of tertiary amines with formation of an intermediate complex, which probably has the following structure:



As will be shown below, the formation of such complexes facilitates the polycondensation process and makes it possible to obtain conformationally regular polymers.

Various compounds of many elements, indicated in Table 6, have now been investigated as polycondensation catalysts[15, 41, 129].

The following reaction scheme has been proposed for the condensation of furfuryl alcohol with formaldehyde in the presence of an acid catalyst (a 10% aqueous solution of 84% H_3PO_3):[149]

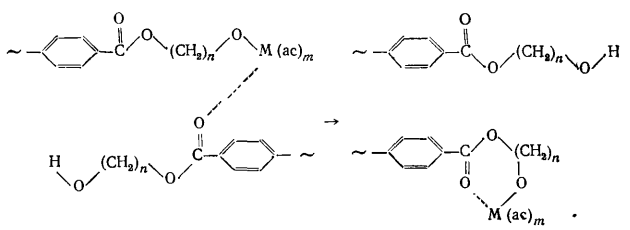


At the end of this reaction chain, difurfurylidenemethane becomes the main product.

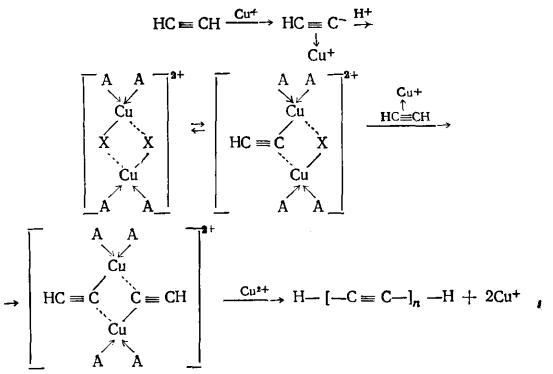
Table 6. Elements whose compounds have been used as polyesterification catalysts[15].

Period	Groups							
	I	II	III	IV	V	VI	VII	VIII
1	H							
2	Li	Be	B	C	N	O	—	— — —
3	Na	Mg	Al	Si	P	S	Cl	
	K	Ca	—	Ti	—	Cr	Mn	Fe Co Ni
4	Cu	Zn	—	Ge	As	—	—	
5	—	Sr	—	Zr	—	Mo	—	— — Pd
	Ag	Cd	—	Sn	Sb	—	—	
	—	Ba	La	—	Ta	—	—	Os Ir Pt
6	—	Hg	—	Pb	Bi	—	—	
7	—	—	—	Th	—	U	—	— — —

The effect of metal acetates as catalysts in the synthesis of poly(ethylene terephthalate) has been explained by the following scheme[147]:



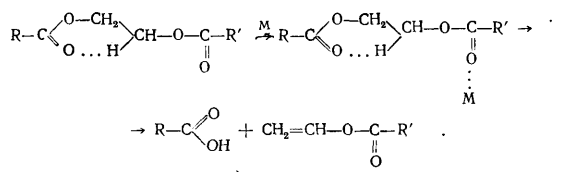
The free-radical catalysis by copper–amine complexes obtains, for example, in the oxidative polycondensation of acetylene, leading to the formation of carbyne—the third linear form of carbon[150]:



where A is the complexone residue.

The Andrianov reaction, which involves the catalytic polycondensation of organosilazanes, has been investigated on a large number of examples. Its general character has been demonstrated in relation to a series of organosilazanes and the formation of polycyclic polymers containing a trisilyl-substituted nitrogen atom in the chain has been established[151,152].

Together with the acceleration of the polycondensation, catalysts can also induce undesirable reactions involving the decomposition of the polymers, accompanied by the darkening of the products and the degradation of the macromolecules. The following mechanism of the action of metal ions as catalysts of the degradation of a polyester has been proposed[147]:



It is of interest to note that catalysts influence the reaction and the properties of polyheteroarylenes not only in the first but also in the second stage of reaction. This has been observed for polyimides obtained under the catalytic influence of phosphoric acid[153].

XIII. JOINT POLYCONDENSATION

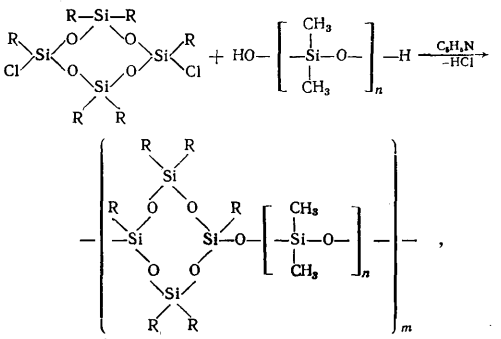
Joint polycondensation has been attracting increasing attention of investigators[103,109,154–160]. It has been established that anion-exchange resins can be used as effective catalysts in the joint polycondensation of dicarboxylic acid chlorides with bisphenols and glycols. The possibility of employing different types of anion exchangers and of obtaining copolymers with different microstructures arises under these conditions[161]. Studies of joint polycondensation have demonstrated the influence of the reactivity of the initial monomers and of the way in which the reaction is carried out on the structure of the polymer formed. Turska and co-workers derived a kinetic equation describing the joint polycondensation reaction of three bifunctional monomers A, B, and C. These monomers are selected in such a way that the monomer A reacts with the monomers B and C, but the latter do not react with one another[162]. The same workers studied the influence of the reactivity of the functional groups of the monomers on the composition of the copolymer and the structure of the macromolecular chain in the non-equilibrium polycondensation reaction[163] and determined the isokinetic temperature T_i for each pair of monomers for which the rate constants for both reactions are identical:

$$T_i = \frac{E_{AB} - E_{AC}}{R\,(B_{AB} - B_{AC})} ,$$

where E_{AB} and E_{AC} are the activation energies for the corresponding polycondensation reactions, B_{AB} and B_{AC} are the pre-exponential factors in the Arrhenius equation, and R is the gas constant.

If $K_{AB} > K_{AC}$ at a temperature below T_i, then at a temperature above T_i the relative reactivities of the monomers B and C are reversed and the latter becomes more reactive than the monomer B. Consequently the distribution of the B and C units along the macromolecular chain varies with temperature. On the other hand, at a reaction temperature equal to T_i a product of constant composition, independent of the degree of reaction and with a statistical distribution of the B and C units, is formed. Hence arises the possibility of regulating the joint polycondensation process by selecting an appropriate reaction temperature[156,163]. The joint polycondensation reaction can be directed, if so desired by the investigator, towards the formation of a statistical copolymer or a block copolymer. If, as usual, the two monomers are mixed with the intermonomer, then a statistical copolymer is always formed. On the other hand, if the intermonomer is gradually introduced into the mixture of the comonomers then a block copolymer is produced[154]. The slower the addition of the intermonomer, the more pronounced the block structure of the copolymer formed under these conditions[157].

An extremely interesting feature of polycondensation is the possibility of obtaining with its aid block copolymers having a polyblock structure, in contrast to polymerisation where block copolymers with only di- and tri-block structures are possible[110]. As an example, we quote Andrianov's synthesis[158] of block copolymers containing linear and cyclic groups, achieved by carrying out the reaction in pyridine:



where n = 2, 4, 12, 25, and 70.

The nature of the solvent in which the polyarylate is synthesised influences the structure of the copolymer obtained. The distribution of the units in the copolymer obtained by the reaction of isophthaloyl chloride with a mixture of di(4-aminophenyl) ether and di(4-aminophenyl) sulphone has been investigated as a function of the polycondensation conditions[159]. It was found that in sulpholan there is a distinct tendency towards the formation of blocks. However, in the presence of epoxypropane, which is a weaker acid acceptor, it is possible to obtain copolymers with a high content of alternating structures[159].

The order of mixing of the reactants is also extremely important. Thus, if a mixture of one diol and triethylamine is taken for the reaction after which the dicarboxylic acid chloride is added and only then the second diol is introduced, a block copolymer is obtained[109,160]. On the other hand, if triethylamine is added to a solution of the acid chloride and one diol and the second diol is only then introduced, a statistical copolymer is obtained[109].

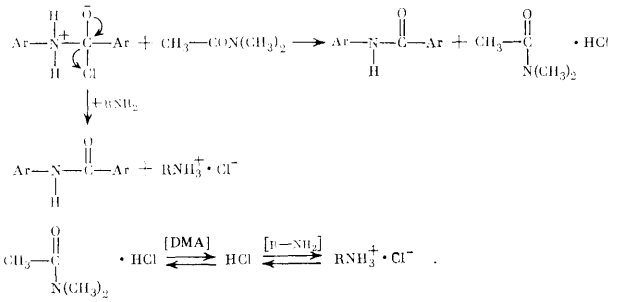
XIV. THE INFLUENCE OF SOLVENTS

The study of the mechanisms of the reactions used in non-equilibrium polycondensation has led to the discovery of the major role of solvents. This led in its turn to the discovery of conformationally specific polycondensation[25], of a method for the synthesis of block copolymers[154], etc.

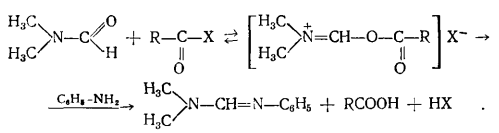
It has been shown that the nature of the solvent has a significant influence on the molecular weight and yield of the polymers formed in the non-equilibrium polycondensation of acid anhydrides and chlorides with aromatic diamines[164] and also in the reaction of phenol with formaldehyde and in other instances of polycondensation[165,166].

Sokolov found that the addition of water makes it possible to alter very appreciably the conditions in the synthesis of polyamides from dicarboxylic acid difluorides and dichlorides and diamines[156,167].

Herlinger et al.[168] showed that non-equilibrium polycondensation in solution in amide solvents proceeds via a stage involving the formation of a reaction complex of the acid chloride and the amine, which is followed by the formation of an amide linkage and the hydrochloride of dimethylacetamide:

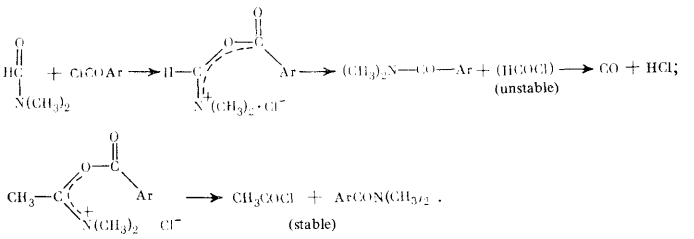


The study of the polycondensation of dicarboxylic acid halides with diamines in solution in dimethylformamide (DMF) showed that this too results in the formation of reactive adducts of the acid halides with DMF.[169] The later react with amines (for example, aniline) to form *N*,*N*-dimethyl-*N'*-phenylformamidine:

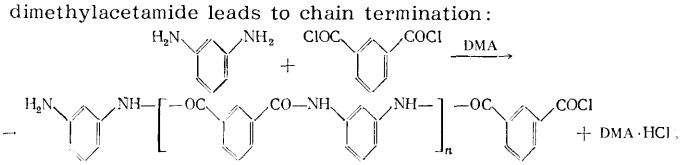


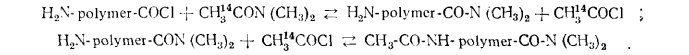
Under these conditions, the acid acceptor can also be the unreacted amine, which influences the course of the process, altering the ratio of the starting materials so that the course of the polycondensation reaction depends on the equilibrium $RNH_2.HCl \rightleftharpoons DMA.HCl$.[168]

In addition there is also the possibility of a transamidation reaction via the mechanism



This reaction, which has been studied using ^{14}C-labelled dimethylacetamide leads to chain termination:

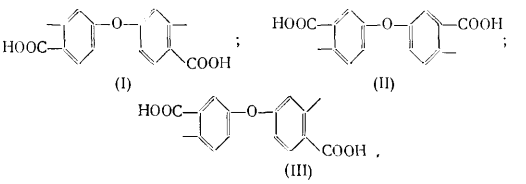




The use of the tracer atom technique (^{14}C) showed that the rates of propagation and termination of the polymer chain are in the ratio 280 : 1. Kinetic studies demonstrated that 70 to 80 °C is the upper temperature limit beyond which a polymer with a high molecular weight can not be obtained owing to the high rate of the transamidation reaction and hence of chain termination[168].

An interesting case illustrating the role of the solvent is provided by the reaction of bis-α-diketones with tetramines, which is used for the synthesis of polyphenylquinoxalines[170]. It has been found that the rate of reaction of the amino- and keto-groups in chloroform is higher by a factor of 10^5–10^6 than in tetrahydrofuran.

The nature of the solvent in which the reaction takes place has a significant influence on the process. Thus all three isomeric structures are formed in the reaction of the anhydride of bis(3,4-dicarboxyphenyl) ether with 9,9-di(4-aminophenyl)fluorene[89]:

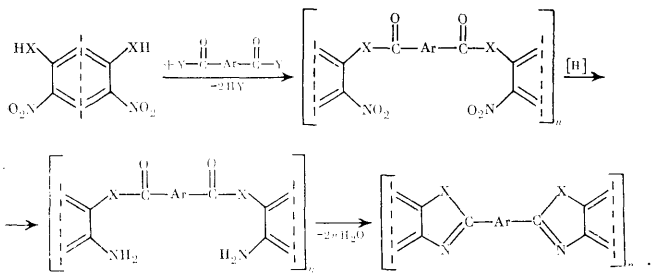


Their ratios vary somewhat depending on the nature of the solvent. Thus they are (I) : (II) : (III) = 0.33 : 0.18 : 0.49 in hexamethylphosphoramide and (I) : (II) : (III) = 0.46 : 0.11 : 0.43 in *N*-methylpyrrolidone. Steric factors and not the basicity of the amine play a significant role in this instance. It is of interest to note that the isomeric composition of the polyamidoacid in solution in *N*-methylpyrrolidone does not vary with time whereas in dimethyl sulphoxide there is a gradual enrichment in structure (I).

XV. NEW POLYMERS AND METHODS OF SYNTHESIS

We shall consider briefly certain examples characterising the advances in the creation of new polymers and the development of new methods of synthesis[171]. Great improvements

in the processes involving the synthesis of industrial polycondensation polymers (polycarbonates and carbamide and phenol-formaldehyde polymers) have been achieved recently[146,147]. Among the new synthetic processes, the reductive polyheterocyclisation reaction, constituting a new method of synthesis of polyheteroarylenes, has been described[172]. The synthetic reaction of polybenzazoles proceeds in accordance with the equation

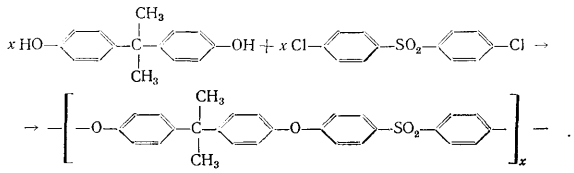


It is noteworthy that studies have been carried out recently whose aim was to seek new polycondensation methods. These include the work of Sokolov, who proposed two new methods for carrying out such reactions. These are the gas-phase polycondensation and emulsion polycondensation[173-176].

Emulsion polycondensation resembles closely interfacial polycondensation, since in both cases the reaction systems employed are heterogeneous. In emulsion polycondensation the reaction zone consists of the total volume of one of the phases and the rate-limiting stage is the chemical interaction[175,177]. The method of thin-layer interfacial polycondensation using monomeric aerosols has also been proposed[134,177].

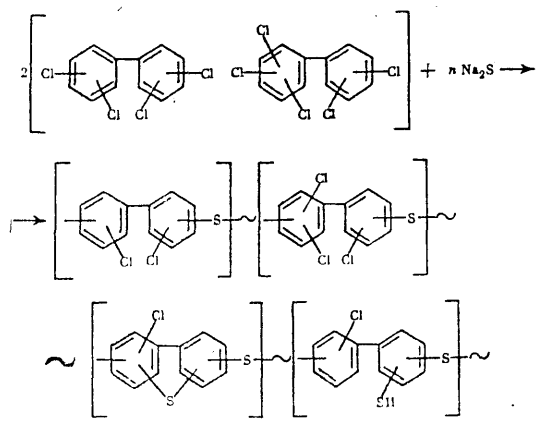
The solid-phase polycondensation used in the form of an improved modification as a method of synthesis of polyheteroarylenes should also be mentioned[178,179].

The dehydrochlorination of bisphenols and di(chlorophenyl) sulphone leads to the formation of polysulphonylethers[180,181]:



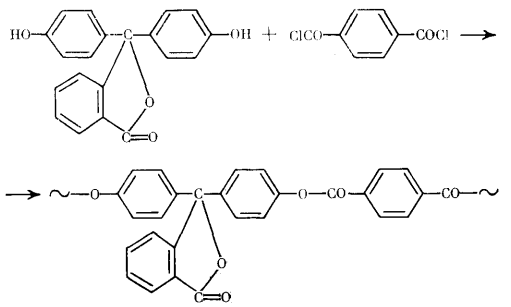
These polymers have a set of valuable properties and, in particular, they are imcombustible. The block copolymers based on oligosulphonylethers are especially interesting[182,183].

The polycondensation of polychlorobiphenyls with sodium sulphide leads to the formation of poly(biphenylene sulphides):



It is of interest that, although the functionality of the initial monomers is fairly high, soluble polymers are formed[184].

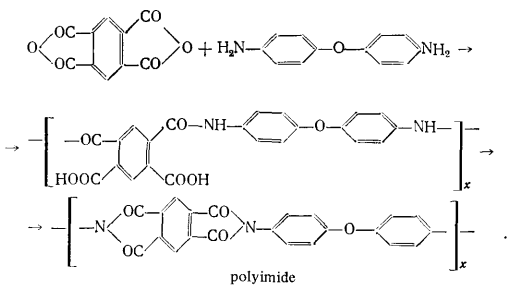
By carrying out the reaction of bisphenols with acid chlorides in the presence of tertiary amines, it is thus possible to obtain cardo-polymers[185]. The polyarylate formed in the reaction of terephthalic acid dichloride with phenolphthalein is an example of a cardo-polymer[185]:



A characteristic feature of cardo-polymers is that their chains contain carbon atoms incorporated simultaneously in cyclic groups making up the polymer chain (they are designated by circles below). Accordingly, the structure of the cardo-polymer can be represented schematically as follows:

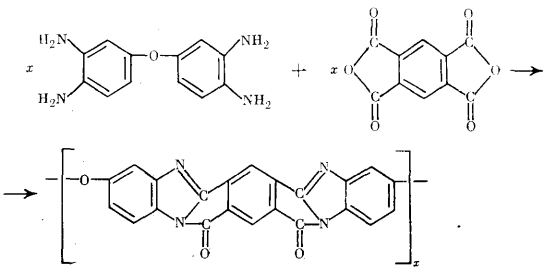


Polycyclisation comprises a large group of polycondensation reactions based on the interaction of dicarboxylic acid esters and fluorides as well as their other derivatives and tetracarboxylic acid anhydrides with diamines, hydroxyamines, mercaptoamines, and tetramines, leading to the formation of various polyheteroarylenes[37,59,63,64]. Thus polyamides, which are some of the most thermostable polymers, have been obtained by the reaction of diamines with acid dianhydrides[89,186-189]:



polyimide

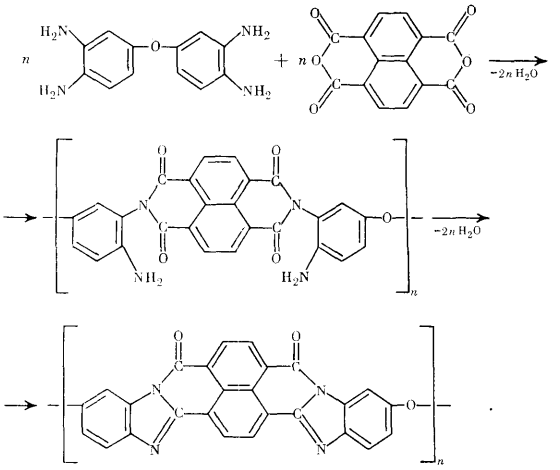
Ladder polymers, an example of which is provided by pyrrones, constitute an interesting group of thermostable polymers. The pyrrone formation reaction proceeds in accordance with the equation[37,60,190,191]



The synthesis of polyamidoacids, the corresponding polycarboximides, and pyrrones by the reaction of di(4-amino-3-carboxyphenyl)methane with the dianhydrides of pyromellitic

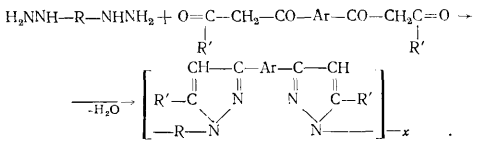
and benzophenone-3,3′,4,4′-tetracarboxylic acids has been described[192].

The study of the reaction of di(3,4-diaminophenyl) ether with the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid showed that the heterocyclisation reaction proceeds via a stage involving the formation of aminoimide rings[193]:

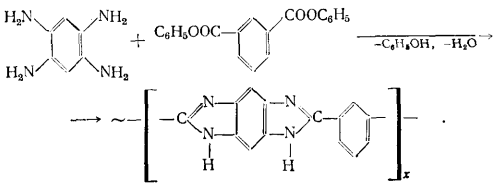


These are examples of a polycyclisation reaction which results in the formation of polymers containing various heterocycles. The great interest throughout the world in polymers of this kind can be explained by the fact that most of them are substances with high thermal stability and this feature has attracted much attention to them and has led to a very great increase in the efforts devoted to research in this field. During the last 10–15 years, when thermostable polymers have also attracted extensive interest, many hundreds if not thousands of polymers of this type have been obtained and it would be impracticable to describe the characteristics of all of them. One must quote several formation reactions of the most widely known polymers of this type in order to demonstrate their characteristic features.

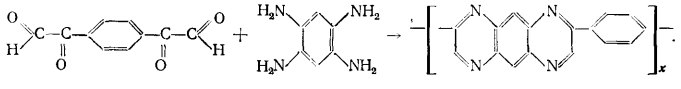
The formation reaction of polypyrazoles, where the starting materials are bis(β-diketones) and dihydrazides, proceeds in accordance with the equation[194]



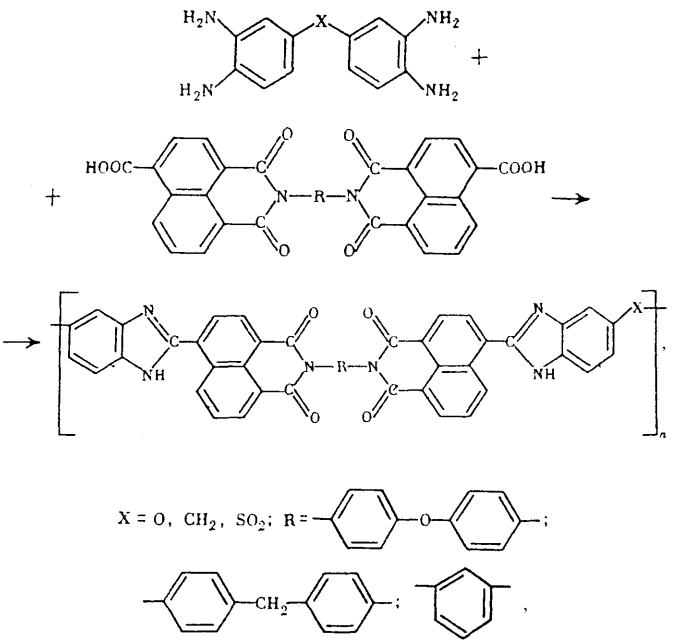
The formation reaction of polybenzimidazoles is[75,195]



Finally we may also mention the formation reaction of polyquinoxalines which involves the interaction of tetramines with dialdehydediketones or tetraketones[80,196]:



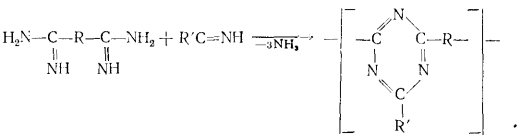
Polybenzimidazolimides, synthesised via the reaction[197]



constitute a new class of polymers. Many more reactions of this type could be quoted but those described above are sufficient to illustrate their general characteristics.

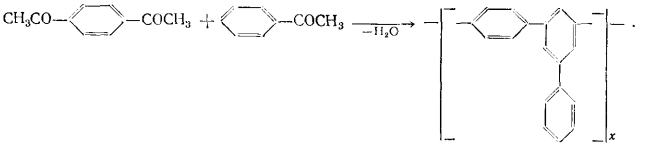
A few words should be devoted to a variety of the polycondensation reaction, namely the polycyclocondensation reaction. In contrast to the polycyclisation discussed above, where a polymer is formed initially and then a heterocycle, i.e. there is a two-stage process, the polycyclocondensation reaction proceeds in such a way that cyclisation is the first stage of the polymerisation process.

As an example, we may quote the formation reaction of triazine polymers involving the polycondensation of mono- and di-amidines[198]:



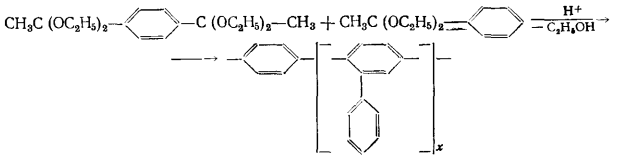
This reaction has attracted attention because the polymer obtained has rubber-like properties and a high thermal stability.

Another example is the recently discovered polycondensation reaction of ketones leading to the synthesis of polyphenylenes[199,200]:

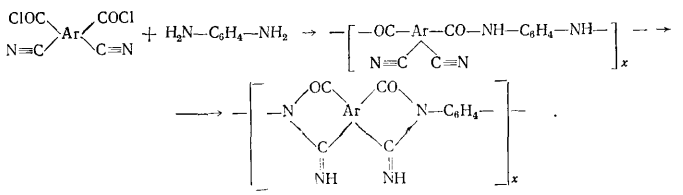


The polycondensation of acetyl groups involves the formation of a new benzene ring joined to the phenyl groups present in the initial monomer. This results in the formation of a soluble and fusible polymer. The reaction constitutes a new method of synthesis of thermostable polyphenylenes.

The reaction has been simplified by replacing the ketones by their ketals[201]. The polyphenylene formation reaction then proceeds in accordance with the equation

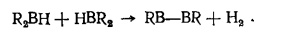


A novel instance of polycyclisation is isomerisation polycyclisation distinguished by the fact that the molecule of the initial monomer contains cyano-groups. As a result of this, low-molecular-weight products are not produced in the first stage of the reaction and instead there is addition to the triple bond with formation of a polyiminoimide[186]:



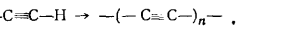
A series of polyheteroarylenes containing several heterocycles and carbocycles in the ring, for example, the imide and oxadiazole rings, the imide and benzimidazole rings, the imide and pyridine as well as pyrimidine rings in various combinations, etc. have been obtained[188,197,202].

An interesting group of dehydropolycondensation reactions is based on dehydrogenation with evolution of hydrogen[203]:

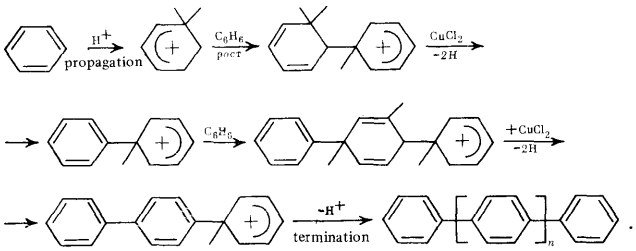


Oxidative dehydropolycondensation is a dehydrogenation reaction under the influence of oxidants and is widely used for the synthesis of various polymers.

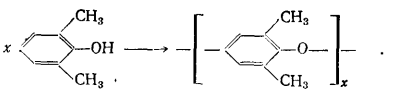
The oxidative dehydropolycondensation of acetylenic compounds is widely employed for the synthesis of polymeric structures containing triple bonds in the chain. A linear carbon polymer, namely carbyne, has been obtained by this reaction[204]:



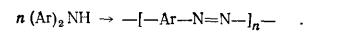
The benzene oxidation reaction, discovered by Kowacic and widely used by other investigators to synthesise polymeric structures, belongs to this class. In this case the oxidant is copper(I) chloride and the reaction thus involves the combination of residues with formation of a polyphenylene structure[205]:



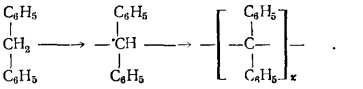
An interesting instance of the oxidative dehydropolycondensation reaction is the oxidation of 2,6-dimethylphenol, leading to the formation of poly(phenylene oxide), which is nowadays manufactured on an industrial scale[206]:



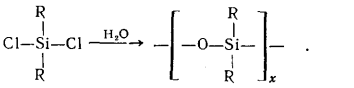
Finally we may mention the amine oxidation reaction used to obtain structures containing double bonds between nitrogen atoms as well as aromatic rings. The polymeric systems obtained in this way are of interest from various points of view[207]:



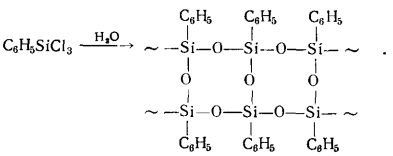
The polyrecombination reaction involves the synthesis of polymers in which the free radicals formed in the first stage from the peroxide abstract a hydrogen atom from the molecules of the initial monomer and thus give rise to free radicals which subsequently recombine to form a polymeric structure. In the case of diphenylmethane the reaction proceeds in accordance with the equation[22,208]



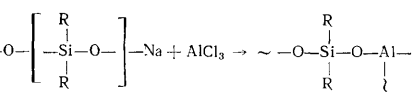
The syntheses of organoelemental polymers involving an increasing number of elements have developed very extensively. This field was initiated by the synthesis of polysiloxanes:



This reaction is used widely in industry to manufacture a wide variety of siloxane polymers and oligomers[11,209]. The use of trichlorophenylsilane as the starting material makes it possible to obtain ladder polymers of the type of polyphenylsiloxane[210,211]:



The reaction of organosiloxane blocks with metal salts leads to the formation of polyorganoaluminosiloxanes[212,213]:



The use of salts of other metals leads to the formation of polyorganometallosiloxanes[90,214].

A large number of organoelemental polymers have been obtained by the polycondensation reaction.

XVI. PROSPECTS FOR THE DEVELOPMENT OF POLYCONDENSATION

The present state of the study of polycondensation processes and their utilisation for the synthesis of polymers with a set of properties specified beforehand is characterised, as shown by the examples presented, by a series of significant achievements. There is no doubt that the further development of polycondensation synthesis will enrich polymer science in a large number of new polymers with a set of valuable properties[215]. The development of syntheses of various copolymers, among which mention may be made of

block copolymers of various types, which are of interest as starting materials for the preparation of separating membranes, is extremely promising. The synthesis of various kinds of polymers modelling natural polymers and biopolymers, particularly for use in medicine, is of great interest.

The problem of the study of the characteristic features of polycondensation is of great theoretical importance as regards control of the reactions involving the growth of the macromolecule in order to regulate the size and structure of the polymer chain. Control of the formation reaction of anomalous units, leading to the formation of heterounit polymers, is very important in this sense. This permits a more detailed regulation of the properties of the polymers obtained. The search for new reactions leading to the synthesis of polymers via polycondensation is one of the most important problems in this field. The expansion of the range of monomers and the wide variety of the structures produced are important in this instance.

It is now apparent that the development of new ways of carrying out the polycondensation reaction constitutes an important step towards advances in this field.

New possibilities for the regulation of the macromolecular structure are then created and one can synthesise the required polymers, in particular those with the required supermolecular structure, crystalline or amorphous, as well as conformationally regular polymers. Naturally problems associated with the synthesis of new polymers satisfying the needs of the modern technology and various branches of industry as regards new materials superior to those already known remain important. Among the important problems of this kind, one may point to those involving the formation of thermostable polymers, polymers with a high mechanical strength, effective adhesive properties, hardness, and elasticity, incombustible polymers, polymers with a set of specific properties of the kind possessed by semi-conductors, photosensitive polymers, etc.

In the field of polycondensation processes themselves, there is every reason to expect new advances in the immediate future involving the achievement of controlled polycondensation synthetic methods. Among problems of this kind, one may point to those involving the regulation of the molecular weight in order to obtain high-molecular-weight polymers and also the search for new polycondensation processes. A most important task is to achieve control of synthetic processes of a kind which would permit the regulation of the geometrical and heterounit structures of polymers and hence the synthesis of polymers with the required optimum set of properties. One of the most important ways of solving problems of this kind involves the wide-scale development of research into catalytic processes in polycondensation, the discovery of new ways of regulating the processes involving the synthesis of polymers in polycondensation reactions, and the expansion of the assortment of such reactions.

In conclusion one should note that, as can be seen from the examples presented, there has been considerable progress in the field of polycondensation. New synthetic reactions of polymers are being discovered and synthetic reactions already known are being investigated and improved. As a result, science is being enriched in a large number of new polymers and many of the polymers already known, now obtained by improved methods, have acquired a set of more valuable properties. Our time is characterised by a deepening of the knowledge of increasingly complex chemical reactions and the formation of new extremely complicated polymeric structures, which reflects the growing sophistication of the chemical art in the synthesis of polymers. Methods for the formation of anomalous units, leading to a heterounit structure of polymers, which is an important factor in the determination of the relation between the structure and properties of polymers, have been devised. Finally, an especially characteristic feature of the polycondensation synthesis is the synthesis of polymers not only for constructional purposes but also to an increasing extent of compounds with specific properties such as thermostable, semiconducting, electrically conducting, photoelectrically active, and biologically active polymers, biopolymers, catalysts, ion-exchange resins, and similar polymers with specific properties.

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