61. I. M. Papisov, T. A. Pisarenko, A. A. Panasenko, V. A. Kabanov, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 156, 669 (1964).
62. S. N. Zhurkov, Dokl. Akad. Nauk SSSR, 47, 493 (1945).
63. V. A. Kargin and Yu. M. Malinskii, Dokl. Akad. Nauk SSSR, 37, 967 (1950).
64. V. A. Kargin, P. V. Kozlov, and Wang Nai-ch'ang, Dokl. Akad. Nauk SSSR, 130, 356 (1960).
65. P. V. Kozlov, V. G. Timofeeva, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 148, 886 (1963).
66. V. G. Timofeeva and P. V. Kozlov, Symposium, "Tsellyuloza i Ee Proizvodnye" (Cellulose and Its Derivatives), Izd. Akad. Nauk SSSR, 1963, p. 167.
67. V. G. Timofeeva, T. I. Borisova, G. P. Mikhailov, and M. V. Kozlov, *ibid.*, p. 174.
68. V. G. Timofeeva, V. D. Zaitseva, G. M. Bartenev, and P. V. Kulov, *ibid.*, p. 181.
69. P. V. Kozlov, A. Endrikhovskaya, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 129, 844 (1959).
70. I. N. Radinskaya, P. V. Kozlov, B. P. Shtarkman, and A. P. Ignat'eva, Vysokomol. Soed., 5, 1850 (1963).
71. P. V. Kozlov, R. M. Asimova, and A. N. Perepelkin, Vysokomol. Soed., 4, 124 (1962).
72. V. A. Kargin, T. I. Sogolova, and G. Sh. Talipov, Dokl. Akad. Nauk SSSR, 142, 844 (1962); Vysokomol. Soed., 5, 112, 1809 (1963).
73. V. A. Kargin, V. P. Shibaev, and N. A. Plate, Vysokomol. Soed., 3, 299 (1961).
74. M. V. Kazhdan, T. N. Dyumaeva, Z. Ya. Berestneva, and V. A. Kargin, Vysokomol. Soed., 8, 204 (1966).
75. V. G. Kalashnikova, M. V. Kazhdan, Z. Ya. Berestneva, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 158, 393 (1964).
76. N. A. Plate, V. P. Shibaev, and V. A. Kargin, Vysokomol. Soed., 1, 1853 (1959).

Karpov Physicochemical Institute,
Moscow

U.D.C. 541.64

CHARACTERISTIC FEATURES OF NON-EQUILIBRIUM POLYCONDENSATION†

V. V. Korshak

CONTENTS

I. Introduction 439
II. Types of polycondensation 439
1. Non-equilibrium polycondensation 440
2. Interfacial polycondensation 440
3. Polycondensation in solution 440
4. Dehydration polycondensation 440
5. Dehydropolycondensation 440
6. Polyrecombination 441
7. Polycyclisation 441
III. Exchange reactions 442
IV. The rule of the non-equivalence of functional groups 443
V. Molecular weight distribution of polymers 446

† Reported at the International Symposium on Macromolecular Chemistry in Prague, 1965.

I. INTRODUCTION

Recently there has been extensive development of new polycondensation processes leading to the preparation of a number of hetero-chain polymers which include many compounds of great practical interest since these are substances with high thermal stability, interesting electrophysical properties, biological activity, etc. Among these processes mention must be made in particular of interfacial polycondensation, dehydropolycondensation, and especially oxidative dehydropolycondensation, and also the polyrecombination reaction, the polycyclisation reaction, and certain others.

For clarity we shall adopt the conventional definition of polycondensation as a process involving the formation of high-molecular-weight compounds in which in addition to the polymer a low-molecular-weight product is formed, most often water, hydrogen chloride, and similar substances. Because of this the elementary composition of the polymer formed differs from that of the initial monomer or the initial mixture of monomers.

In the general case the polycondensation reaction of two starting materials can be represented by the following equation:

$$x\mathrm{a}-\mathrm{A}-\mathrm{a}+x\mathrm{b}-\mathrm{B}-\mathrm{b}\rightarrow\mathrm{a}-(-\mathrm{AB}-)_x-\mathrm{b}+2(x-1)\,\mathrm{ab}$$

and in the case where both functional groups enter into the composition of the same initial molecule, the reaction equation is

$$x\mathrm{a}-\mathrm{A}-\mathrm{b}\rightarrow\mathrm{a}-(-\mathrm{A}-)_x-\mathrm{b}+(x-1)\,\mathrm{ab}.$$

II. TYPES OF POLYCONDENSATION

We now know that, depending on the structure of the starting materials and the method of carrying out the reactions, polycondensation can be achieved in two different ways, namely: (1) as equilibrium polycondensation and (2) as non-equilibrium polycondensation. In addition there are probably certain reactions which exhibit the features of both types of polycondensation. Unfortunately reactions of this intermediate type have so far been little investigated.

A characteristic feature of equilibrium polycondensation is a low equilibrium constant. Very many examples of equilibrium polycondensation are known. Examples which have been particularly thoroughly investigated are the formation of polyamides or polyesters in the reactions, on heating, between dicarboxylic acids and diamines or glycols.

Equilibrium polycondensation constitutes a classical method of synthesising polymers which has been known for a long time. It has been studied thoroughly in many instances and its principal features have been established in a large number of investigations and have been described in reviews and monographs[1-9].

On the other hand, non-equilibrium polycondensation is a new process which was discovered relatively recently

and therefore it has so far been little investigated and its principal features are still the subject of study.

The present review represents a first attempt to examine the results obtained in the study of non-equilibrium processes and to elucidate the specific features of such reactions.

1. Non-Equilibrium Polycondensation

At the present time there are comparatively few cases of non-equilibrium polycondensation which have been investigated in detail. However, it is now possible to divide such reactions into two groups. The first group includes reactions which occur at a high rate under mild conditions, at low temperatures, where exchange interactions cannot occur. An example is the formation of polyamides or polyesters from the chlorides of dicarboxylic acids and diamines or dihydric phenols, which takes place very rapidly under conditions of interfacial polycondensation or in solutions.

The second group of non-equilibrium reactions includes cases of polycondensation which, although taking place fairly slowly at high temperatures, can nevertheless be classified as non-equilibrium polycondensation reactions because the polymers formed are very stable under the reaction conditions and are incapable of hydrolysis and other degradative conversions, such as, for example, interaction with the starting materials or the growing macromolecules. As a result of this stability of the macromolecules formed, degradative and other exchange processes are absent during the reaction, and this results in the irreversibility and the non-equilibrium nature of the process as a whole. Examples of such reactions are the formation of various polymers in dehydropolycondensation, polyrecombination, polycyclisation, and certain other processes, which will be examined below.

The chemical characteristics of the non-equilibrium polycondensation reactions enumerated above will be considered first.

2. Interfacial Polycondensation

Interfacial polycondensation, which was developed by Morgan[10], is carried out by mixing the reactants dissolved in two immiscible solvents, for example in water and in a hydrocarbon, hence its name: polycondensation at the interface between phases‡.

Interfacial polycondensation opens up new possibilities for the synthesis of many polymers, polyamides, polyesters, and many others and for this reason has greatly attracted the attention of investigators. In the synthesis of polyamides the reaction between the initial acid dichloride and the diamine proceeds according to the equation

$$x\mathrm{ClCOR'COCl} + x\,\mathrm{H_2NRNH_2} \rightarrow [\text{—COR'CONHRNH—}]_x + 2x\mathrm{HCl}.$$

Interfacial polycondensation is based on the acylation of diamines or bisphenols with acyl or aryl chlorides in the presence of aqueous alkali. The principal feature of this reaction is the use of reactive starting materials such as the chlorides of dicarboxylic acids, which ensures a high reaction rate.

Interfacial polycondensation was studied in detail and reviewed by Frunze et al.[11]. Polymers are synthesised in this way in practice. Polycarbonates, polyamides, polyurethanes, polyarylates, and certain other high-molecular-weight compounds are obtained in this way.

When gaseous acid chlorides are used, there arises a new modification of this process, "gaseous polycondensation", which, as shown by Sokolov et al.[12], exhibits somewhat different features.

3. Polycondensation in Solution

A second variety of polycondensation processes which take place when the chlorides of dicarboxylic acid are used is polycondensation in solution which may be carried out both at low and elevated temperatures. The polycondensation of bisphenols with the chlorides of dicarboxylic acids in solution (with heating) was used successfully by Korshak and Vinogradova[13] for the synthesis of polyarylates (polyphenylene esters of aromatic dicarboxylic acids). High-boiling solvents are used (Dinile, ditolymethane, Sovol, α-chloronaphthalene, and others), which made it possible to lower the viscosity of the reaction mass and to obtain high-molecular-weight polyesters[14]. Kwolek and Morgan[15] showed that in low-temperature polycondensation in solution in chloroform and other organic solvents it is possible to obtain polyamides, polysulphonamides, polyesters, and polyurethanes, tertiary amines being sometimes used. In solution in dimethylacetamide, hexamethylphosphoramide, hexamethylphosphoramide etc. polypyromellitimides, polyoxadiazoles, and other polymers are obtained[41,43].

4. Dehydration Polycondensation

Homofunctional dehydration polycondensation of silanediols and silanetriols, leading to the formation of organosilicon polymers[16], is also a non-equilibrium reaction, which can be represented by the equation

$$\gtrless\mathrm{Si—OH} + \mathrm{HOSi}\lessgtr \longrightarrow \gtrless\mathrm{Si—O—Si}\lessgtr + \mathrm{H_2O}.$$

It goes to completion even in the presence of an excess of water, since the reverse reaction, involving the hydrolysis of siloxane bonds, does not take place at low temperatures[17]. Since this reaction is the main stage in the synthesis of polyorganosiloxanes by hydrolytic polycondensation, the entire process may be regarded as a non-equilibrium one. This is particularly so because in most cases the first stage is the non-equilibrium hydrolysis of the chlorine atom or other groups linked with the silicon atom.

The formation of polyethers or glycols, according to the equation

$$x\mathrm{HO—R—OH} \rightarrow (\text{—OR—})_x + x\mathrm{H_2O},$$

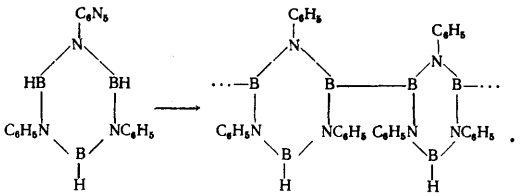
is also a case of non-equilibrium polycondensation.

5. Dehydropolycondensation

Yet another example of non-equilibrium polycondensation is dehydropolycondensation which has been used for the synthesis of high polymers only recently. Korshak

‡ The Russian author calls this type of polycondensation interphase polycondensation and refers to interfacial polycondensation as a second name for this process (Ed. of Translation).

et al.[18] showed that it may involve simple removal of hydrogen, as, for example, in the synthesis of organoboron polymers by heating *N*-triphenylborazole:



The most interesting example of reactions of this type is oxidative dehydropolycondensation which is based on the oxidation of hydrocarbons or their derivatives by oxygen or other oxidising agents and takes place with removal of hydrogen by the oxidising agent.

By oxidative dehydropolycondensation of acetylene in the presence of copper salts,

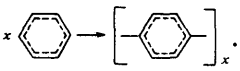
$$x\mathrm{HC{\equiv}CH} \longrightarrow [-\mathrm{C{\equiv}C}-]_x + x\mathrm{H_2O},$$

the present author obtained a new carbon polymer — "carbene".[9] The application of this reaction to diacetylene compounds of the type $\mathrm{HC{\equiv}C-R-C{\equiv}CH}$ enabled several investigators[20-23] to obtain a large number of linear polymers of a new type having the general formula

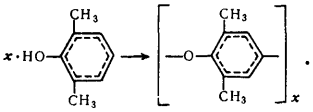
$$[-\mathrm{C{\equiv}C-R-C{\equiv}C}-]_x,$$

containing triple bonds in the chain together with phenyl and other groups.

Another example is the synthesis of polyphenylene by the oxidation of benzene in the presence of aluminium chloride and cuprous chloride, discovered by Kovacic and Kyriakis[24], which takes place as follows:



Fox and coworkers[25] showed that the oxidation of 2,6-dimethylphenol by atmospheric oxygen in the presence of a pyridine-copper complex involves a reaction leading to the formation of polyphenylene ethers:

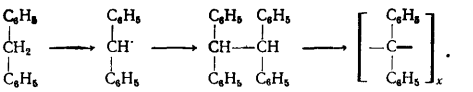


The polyethers obtained in this way are chemically stable and are of practical interest.

6. Polyrecombination

Another new example of non-equilibrium polycondensation reactions is polyrecombination. Recently increasing attention has been paid to the problem of synthesising polymers from substances which are not monomers in the strict sense of this term, i.e. they do not contain double bonds, rings, or other functional groups capable of entering into polymerisation or polycondensation reactions. One of the possible approaches to the solution of this problem involves the use of the polyrecombination reaction, discovered by Korshak et al.[26], as a result of which polymers can be obtained from a wide variety of classes of organic substances, such as saturated hydrocarbons, ethers, ketones, amines, phenols, nitriles, aldehydes, alcohols, "organoelemental" compounds, and many other substances incapable of being polymerised in the usual way[20,26-29].

Polyrecombination is a method of synthesising polymers, which in the case of diphenylmethane can be represented by the equation



The fundamental processes in polyrecombination are the formation and recombination of free radicals produced in the decomposition of t-butyl, benzoyl, and other acyl peroxides. A characteristic feature of the monomers used in polyrecombination is the presence of a labile hydrogen atom which can be readily removed by free radicals. If the monomers have two reactive hydrogen atoms, soluble products are obtained, and when there are three and more such atoms the products are insoluble three-dimensional polymers[27].

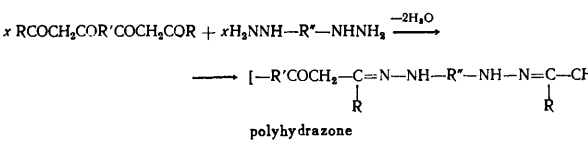
7. Polycyclisation

Polycyclisation is an extremely interesting new example of non-equilibrium polycondensation. It is a new type of reaction leading to the formation of polymers with a ring-chain structure which are interesting because they include a number of substances with exceptionally high thermal stability. Unfortunately at present there are as yet few data concerning the mechanism of the polycyclisation reaction, but those that are available suggest certain generalisations and make it possible to put forward a mechanism in a general, schematic form for these reactions, which appear to be two-stage processes.

The first stage is often an equilibrium reaction of the usual type, which takes place on heating of the reaction mixture and leads to the formation of polyamides, polyesters, polyhydrazones, and similar compounds, depending on the structure of the starting material. The features of this stage do not differ in general from those known for similar reactions. However, in many cases the first stage of this process can also be carried out in a non-equilibrium manner by interfacial polycondensation or reaction in solution.

The second stage involves the cyclisation itself, i.e. the closure of the heterocycle which is characteristic of this reaction. In most cases this stage constitutes true non-equilibrium polycondensation because it involves irreversible formation of stable aromatic rings.

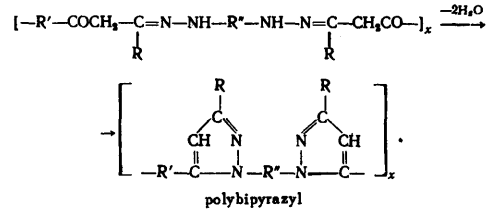
Thus in synthesis of polypyrazoles, obtained for the first time by Korshak et al.[30,31], the intermediate is a polyhydrazone formed in the reaction between bisdiketones and dihydrazines or dihydrazides which can be represented as follows:



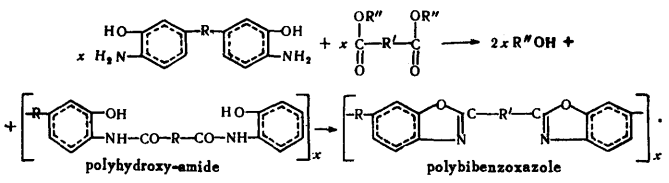
polyhydrazone

This stage is probably reversible, since condensation of dicarbonyl compounds with dihydrazines is known to be an

equilibrium process[32]. In the second stage the polyhydrazone is converted into a polypyrazole by the following reaction:

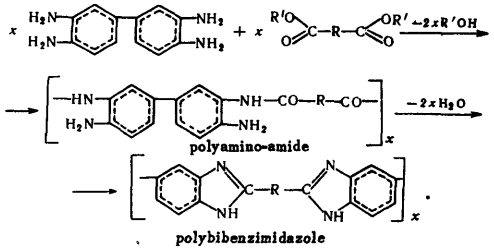


The same picture was established also in the synthesis of polybenzoxazoles obtained by a number of investigators[33-36,58]. The reaction involves the intermediate formation of polyhydroxy-amides formed from dihydroxy--diamines and dicarboxylic acid esters:

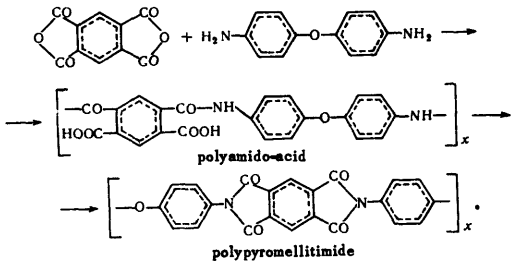


The polyhydroxy-amide formed in the first stage is unconverted by cyclisation into polybibenzoxazole. Both in this and the preceding case the reaction can be carried out with isolation of the intermediate product or can be taken at once to completion with preparation of the ring-chain polymer.

The formation of polybenzimidazoles, which has been investigated in detail by Marvel[37] and other investigators[36,38-40], probably involves the intermediate formation of a polyamino-amide:



The formation of polypyromellitimides takes place in the same way[41]:



The polycyclisation process has undergone extensive development as a result of the work of Marvel[37] and other investigators and has led to the preparation of a large number of polymers incorporating in the chain heterocycles such as triazole[42], imidazole[36,37-40], pyrazole[30,31], oxadiazole[43-45], oxazole[33-36], triazine[46], thiazole[45], pyromellitimide[41], quinoxaline[47], and others.

Having examined the most important examples of non--equilibrium polycondensation, we shall now consider certain data concerning reactions of this type. The most important characteristics of equilibrium and non-equilibrium polycondensation are the presence of exchange reactions in the first case and their absence in the second, the effect of the excess of the reactants, and finally the fractional composition of the polymers formed. The available literature data on these problems will be examined below in the sequence indicated.

III. EXCHANGE REACTIONS

The significant difference between equilibrium and non--equilibrium polycondensation consists in the fact that in the first case exchange reactions take place between the growing polymer macromolecules and also between the latter and the starting materials or low-molecular-weight reaction products (water and others). For this reason, the macromolecules formed in the equilibrium process change during its course, which is reflected in the first place in the fractional composition (polydispersity) of the polymer, while in a non-equilibrium reaction exchange processes do not occur and therefore the distribution of the polymers formed with respect to molecular weight is different.

At temperatures normally used for equilibrium polycondensation, exchange reactions between individual macromolecules play a considerable role. This has been demonstrated in a number of cases. Thus on heating of two specimens of different polyamides there is a gradual change in melting point; for example, Fig. 1 shows the change in melting point when a mixture of polyhexamethyleneadipamide and polyhexamethyleneisophthalamide is heated[48].

The melting point of the mixture falls until the melting point of the corresponding copolymer, a mixed polyamide is reached. The mixture of the two homopolymers is converted into the copolymer via a block-copolymer stage which exists for a limited period. Fig. 2 shows the variation of the content of these three products in the reaction medium in the course of the process[49].

These reactions also take place when mixtures of polymers as different as polyamides and polyesters are heated.

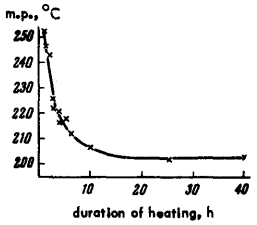


Fig. 1. Variation of the melting point of a mixture of polyhexamethyleneadipamide and polyhexamethyleneisophthalamide as a function of the duration of heating.

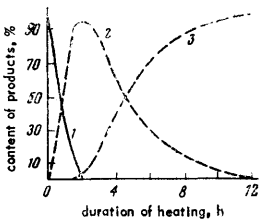


Fig. 2. Variation of the content of the homopolymer (curve 1), block-copolymer (curve 2), and mixed polyamide (curve 3) with the duration of heating of a mixture of homopolyamides.

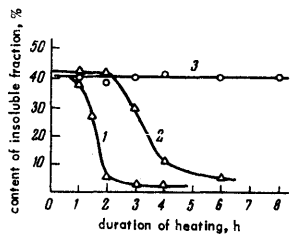


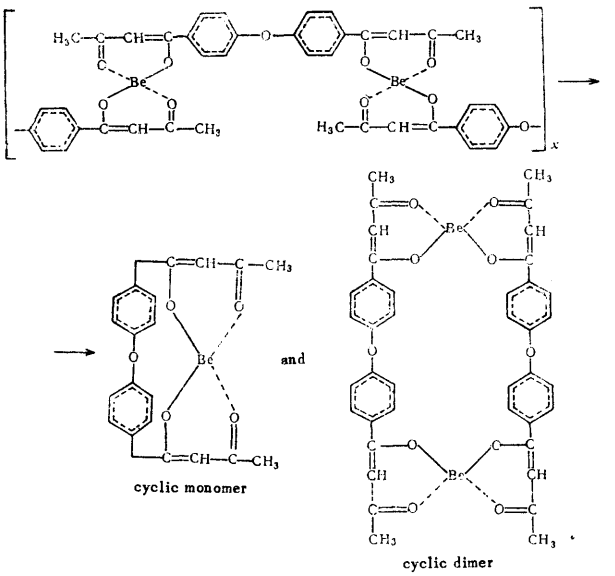
Fig. 3. Variation of the content of the benzene--insoluble fraction with the duration of heating of a mixture of polyhexamethylenesebacamide and polyhexamethylenesebacate at various temperatures: 1) 290°; 2) 280°; 3) 260°.

At a temperature in excess of 280°, and in the presence of catalysts even at 260°, a mixture of polyamide and polyester is converted into the copolymer, polyamido-ester, the process being accompanied by a change in melting point and solubility of the mixture of the starting polymers[50].

Fig. 3 shows the variation of the content of the benzene--insoluble fraction when a mixture of polyhexamethylenesebacamide and polyhexamethylenesebacate is heated at various temperatures. It is seen that at 280° and above vigorous exchange reactions take place and result in the formation of benzene-soluble polyamido-ester and the disappearance of the insoluble polyhexamethylenesebacamide.

Exchange reactions take place particularly readily in coordination polymers of the chelate type. When a mixture of two coordination polymers of different molecular weights is heated, exchange takes place and results in the molecular weight being averaged out[51]. These polymers have been found to undergo an unusual exchange reaction — exchange of one metal for another. Thus when copper acetylacetonate acts upon the chelate polymer of beryllium, the latter metal is displaced and a chelate polymer of copper is formed[49]. Exchange reactions can occur very readily in chelate polymers, particularly in dilute solutions.

Korshak et al.[51,52] found that only brief heating of a dilute solution of the polymer is sufficient for complete degradation, resulting in the conversion of the polymer into cyclo-oligomers:



When these cyclic oligomers are heated in more concentrated solutions, they are reconverted into the initial polymer. Thus here we encounter for the first time an example of a reaction involving total reversibility of the ring–polymer conversion, the equilibrium position of which depends on the concentration of the solution. The examples of exchange reactions quoted for various polymers clearly demonstrate this feature of the equilibrium polycondensation process.

On the other hand, the products formed in a non-equilibrium polycondensation reaction, under conditions ensuring their formation, are quite incapable of undergoing exchange processes. This applies both to synthesis of polymers under the mild conditions of interfacial polycondensation and to the synthesis of polymers at high temperatures under severe conditions in the case of the polycyclisation and polyrecombination reactions.

Thus on heating a mixture of products obtained by polycyclisation, exchange reactions do not occur. Korshak et al.[42] showed that, after heating for 20 h at 270° a mixture of two poly-4-amino-1,2,4-triazoles, obtained by the polycondensation of hydrazine with adipic acid in one case and with sebacic acid in the other, it is possible to isolate unchanged the initial polymers, which indicates the absence of exchange reactions between their macromolecules. Mixed poly-4-amino-1,2,4-triazoles could be obtained only by the polycondensation of the initial monomer, i.e. hydrazine, with a mixture of the two dicarboxylic acids[42].

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

The molecular weight of polymers obtained by polycondensation is determined in the first place by the relative proportions of the starting materials when the reaction takes place between two different components. In this case the *"rule of the non-equivalence of functional groups"* operates, according to which the excess of one of the starting materials, provided that it is not removed

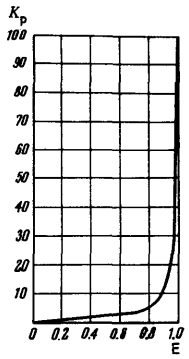


Fig. 4. Variation of the polymerisation coefficient (K_p) with the equivalence coefficient (E).

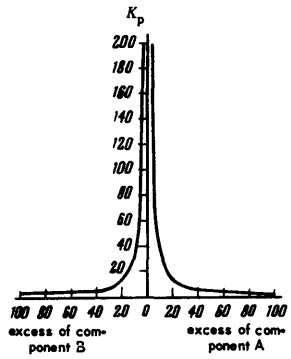


Fig. 5. Variation of the limiting value of the polymerisation coefficient (K_p) with the excess of one of the starting materials (mole %).

during the reaction, lowers the molecular weight to an extent proportional to the degree of this excess.

If the reaction is represented in the general form

$$xa - A - a + (x+1)b - B - b \rightarrow b - B - [-A - B -]_x b + 2xab$$

the equivalence coefficient, characterising this relation, can be expressed as follows[53]:

$$E = \frac{x}{x+1}$$

Fig. 4 shows graphically the relation between the equivalence coefficient and the polymerisation coefficient for the polymer being formed. It is readily seen that the closer are the relative amounts of the starting materials to equivalent proportions the higher is the polymerisation coefficient of the polymer.

The existence of a definite relation between the excess of one of the starting materials and the size of the molecule of the polymer formed leads to the following expression[54]:

$$K_p = \frac{100}{q},$$

where K_p is the polymerisation coefficient and q the excess of one of the substances expressed in mole per cent. We may note that this excess plays an additional role in equilibrium polycondensation. It causes the degradation of the growing chains and influences the polydispersity of the polymer, decreasing it.

This relation between the polymerisation coefficient and the amount of the excess component is represented graphically by two branches of a hyperbola (Fig. 5).

The validity of this relation for all the cases of equilibrium polycondensation investigated has been demonstrated for a large number of examples[55]. This relation holds also in non-equilibrium polycondensation, as can be seen from Fig. 6, where the results obtained in the synthesis of poly-2,2′-(octamethylene)-5,5′-dibenzimidazole in the presence of an excess of one of the initial substances[40], are plotted. Here the presence of an excess of each of the starting materials, i.e. both tetramine and the dicarboxylic acid ester, also results in a lowering of the molecular weight of the polymer obtained.

In practice a cessation of the growth of the molecular weight is observed at comparatively early polycondensation

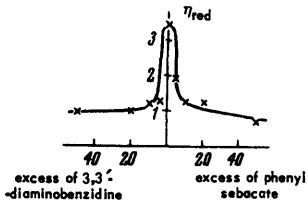


Fig. 6. Variation of the reduced viscosity of a solution of polybenzimidazole with the ratio of the starting materials (mole %).

stages, which leads to a departure of the curve from the theoretical form shown in Fig. 5. This can be explained by the presence of a number of side-reactions and also by the fact that usually all the functional groups are not completely utilised in polycondensation. For this reason, the relation between the molecular weight and the excess of the starting materials observed in practice has the form shown in Fig. 7.[55]

The presence in the reaction mass of monofunctional compounds of a similar chemical type exhibits the same effect as the excess of the starting materials. This behaviour was observed earlier for a large number of examples of equilibrium polycondensation reactions and has been found also in non-equilibrium polycondensation. Fig. 8

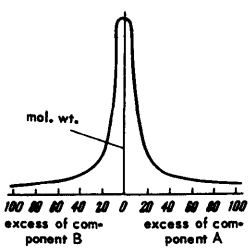


Fig. 7. A schematic representation of the experimentally observed relation between the molecular weight and the excess of the starting material (mole %).

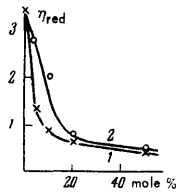


Fig. 8. Variation of the reduced viscosity of polybenzimidazole with the amount of added monofunctional reagent:
1) stearic acid; 2) α-naphthylamine.

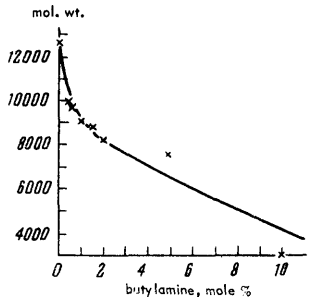


Fig. 10. Variation of the molecular weight of polyamide with the amount of added n-butylamine.

shows the effect of added monocarboxylic acid or monoamine on the molecular weight of the polybenzimidazole formed[40].

A similar relation holds also in other cases. For example, in interfacial polycondensation of hexamethylenediamine with the chloride of adipic acid the molecular weight of the polyamide formed decreases in proportion to the amount of added butyryl chloride[11] (Fig. 9).

The same effect is observed when butylamine is introduced into this reaction, as shown in Fig. 10.

In the polycondensation of dian§ with the chloride of isophthalic acid the addition of benzoyl chloride or phenol also causes a corresponding decrease of the molecular weight[11]. This is shown in Figs. 11 and 12.

The present author observed a relation between the molecular weight of the polymer formed and the amount of peroxide used in a polyrecombination reaction[27]. Fig. 13

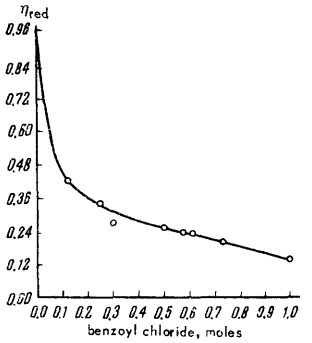


Fig. 11. Variation of the reduced viscosity of polyarylate with the amount of added benzoyl chloride.

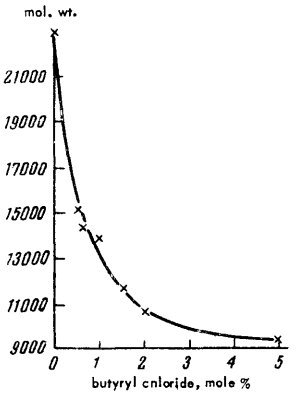


Fig. 9. Variation of the molecular weight of polyamide with the amount of added butyryl chloride.

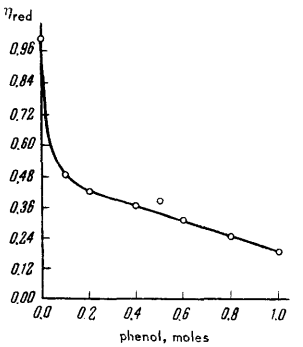


Fig. 12. Variation of the reduced viscosity of polyarylate with the amount of added phenol.

§ Bis-(*p*-hydroxyphenyl)dimethylmethane (Ed. of Translation).

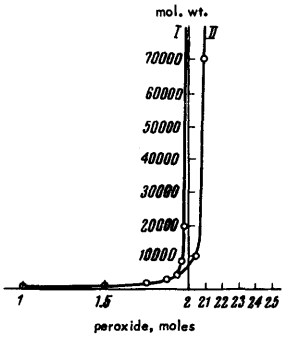


Fig. 13. Variation of the molecular weight of polydiphenylmethylene with the peroxide : : hydrocarbon ratio.

shows the calculated and observed relations between the molecular weight of polydiphenylmethylene and the amount of peroxide used for the polyrecombination. It is seen that the maximum molecular weight is attained when about two moles of peroxide are consumed per mole of the initial hydrocarbon.

V. MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS

Polymers synthesised by non-equilibrium polycondensation exhibit a wider molecular weight distribution than polymers obtained by equilibrium methods. Thus in the case of polyarylates prepared by interfacial polycondensation or reactions in solution at an elevated temperature it was found that the former show a wider distribution than the latter. To account for this difference, it may be pointed out that the polydispersity coefficient M_w/M_n for the former is about 1.5 and for the latter about 2.0. The Table presents data obtained in a study of the molecular weight distribution of polyarylate specimens prepared by the polycondensation of isophthalic acid chloride with two bisphenols under different conditions[56].

We may point out here that polycondensation at an elevated temperature is probably of an intermediate type, since in this case there is no reverse degradative reaction between the polymer and hydrogen chloride but there is a degradative reaction between the polymer formed and the initial bisphenol. Polyesters formed in equilibrium polycondensation show a smaller polydispersity.

The Table shows that the molecular weight distribution of the polyarylates prepared by interfacial polycondensation approaches that predicted by the theory put forward by Flory[1]. Polyamides were found to show a considerable difference in the polydispersity of the products obtained by interfacial condensation and at high temperatures.

Fig. 14 shows curves characterising the fractional composition of polyhexamethylenesebacamide obtained by the interfacial process and poly-ϵ-caproamide obtained in the melt[57]. The much wider molecular weight distribution of the interfacial polycondensation products is clearly evident.

Study of the polymers prepared by polyrecombination showed that they are distinguished by an even greater degree of polydispersity.

TABLE. The polydispersity coefficients of the polyarylates obtained by various methods from isophthalic acid and diols.

Polyarylate based on	Polycondensation in solution		Interfacial polycondensation	
	M_w/M_n from fractionation	degree of completion of reaction	M_w/M_n from fractionation	degree of completion of reaction
bis-(4-Hydroxyphenyl)methane	1.52	0.9795	2.03	0.9934
2,2-bis-(4-Hydroxyphenyl)-propane	1.68	0.9845	2.06	0.9810
ditto	1.60	0.9818	2.03	0.9855

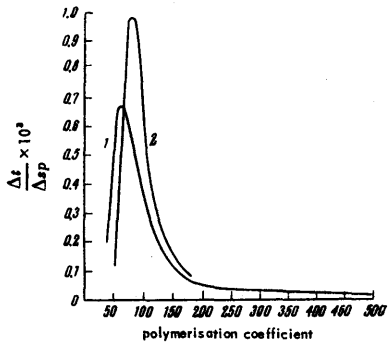


Fig. 14. Fractional composition of polyhexamethylenesebacamide (curve 1), obtained by interfacial polycondensation, and poly-ϵ-caproamide (curve 2).

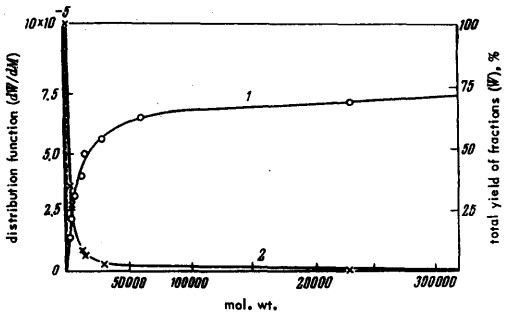


Fig. 15. Molecular weight distribution of polydiphenylmethylene: 1) integral curve; 2) differential curve.

Fig. 15 shows that the molecular weight distribution of polydiphenylmethylene is very wide[29]. The polydispersity coefficient calculated for this polymer proved to be 43. Hence it resembles in this respect high-pressure polyethylene which exhibits a very wide molecular weight distribution.

In conclusion, we may note that examination of the available data makes it possible to elucidate a number of specific features distinguishing non-equilibrium polycondensation. On the basis of the results discussed, we may

conclude that a new field of polycondensation reactions, non-equilibrium polycondensation, has arisen, whose further development and study will permit an even more extensive application of this new method of synthesis of polymers.

1. P.J. Flory, Chem.Rev., 39, 137 (1946).
2. V.V.Korshak, Uspekhi Khim., 21, 121 (1952).
3. W.H. Carothers, Chem.Rev., 8, 353 (1931).
4. G.V. Schulz, Z.phys. Chem., A 182, 127 (1938).
5. V.V.Korshak and S.V. Vinogradova, "Polyesters", Pergamon Press, Oxford, 1965, pp.72–153.
6. V.V.Korshak, Symposium, "Itogi Nauki. Khimicheskie Nauki. 7. Khimiya i Tekhnologiya Sinteticheskikh Vysokomolekulyarnykh Soedinenii. Geterotsepnye Soedineniya" (Science Compendia. Chemical Sciences. 7. Chemistry and Technology of Synthetic Macromolecular Compounds. Heterochain Compounds), Izd. Akad. Nauk SSSR, Moscow, 1961, pp. 9–47.
7. V.V. Korshak and S.V. Vinogradova, "Geterotsepnye Poliefiry" (Heterochain Polyesters), Izd. Akad. Nauk SSSR, Moscow, 1958, pp. 14–180.
8. V.V. Korshak and T.M. Frunze, "Sinteticheskie Geterotsepnye Poliamidy" (Synthetic Heterochain Polyamides), Izd. Akad. Nauk SSSR, Moscow, 1962, pp. 13–153.
9. V.V. Korshak, "Progress Polimernoi Khimii" (Progress in Polymer Chemistry), Izd. Nauka, Moscow, 1965, p. 92.
10. P.W. Morgan, SPE (Soc. Plastics Engrs.) J., 15, 485 (1959).
11. T.M. Frunze, V.V. Kurashev, and L.V. Kozlov, Uspekhi Khim., 30, 593 (1961) [Russ. Chem. Rev., 252 (1961)].
12. L.B. Sokolov, T.V. Kudim, and L.V. Turetskii, Vysokomol. Soed., 3, 1369 (1961).
13. V.V. Korshak and S.V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk., 636 (1958).
14. V.V. Korshak and S.V. Vinogradova, "Polyesters", Pergamon Press, Oxford, 1965, p. 452.
15. S.L. Kwolek and P.W. Morgan, J. Polymer Sci., A 2, 2693 (1964).
16. K.A. Andrianov, "Polimery s Neorganicheskimi Glavnymi Tsepyami Molekul" (Polymers with Inorganic Principal Molecular Chains), Izd. Akad. Nauk SSSR, Moscow, 1962, p. 18.
17. Z. Lasocki and S. Chrzczonowicz, J. Polymer Sci., 59, 259 (1962).
18. V.V. Korshak, V.A. Zamyatina, N.I. Bekasova, and L.G. Komarova, Izv. Akad. Nauk SSSR, Ser. Khim., 2223 (1964).
19. V.V. Korshak, V.I. Kasatochkin, A.M. Sladkov, Yu.P. Kudryavtsev, and K. Usenbaev, Dokl. Akad. Nauk SSSR, 136, 1342 (1961).
20. V.V. Korshak, S.L. Sosin, and A.M. Sladkov, J. Polymer Sci., 40, 1315 (1964).
21. A. Hay, J. Org. Chem., 25, 1275 (1960).
22. I.L. Kotlyarevskii, L.B. Fisher, and E.S. Domnina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1905 (1961).
23. V.V. Korshak, A.M. Sladkov, and Yu.P. Kudrjavtsev, "International Symposium on Macromolecular Chemistry", Prague, 1965, Preprints 335.
24. P. Kovacic and A. Kyriakis, J. Amer. Chem. Soc., 85, 454 (1963).
25. T.G. Fox, W.E. Godde, S. Gratch, C.M. Huggett, and J.F. Kincaid, J. Polymer Sci., 31, 173 (1958).
26. V.V. Korshak, S.L. Sosin, and M.V. Chistyakova, Dokl. Akad. Nauk SSSR, 121, 299 (1958).
27. V.V. Korshak, S.L. Sosin, and V.P. Alekseeva, J. Polymer Sci., 52, 213 (1961).
28. S.L. Sosin, V.V. Korshak, and D.G. Val'kovskii, Dokl. Akad. Nauk SSSR, 158, 915 (1964).
29. D.G. Val'kovskii, S.L. Sosin, V.V. Korshak, and S.A. Pavlova, Vysokomol. Soed., 6, 1848 (1964).
30. V.V. Korshak, E.S. Krongauz, A.M. Berlin, and P.N. Gribkova, Dokl. Akad. Nauk SSSR, 149, 602 (1963).
31. V.V. Korshak, E.S. Krongaus, and A.M. Berlin, J. Polymer Sci., A 3, 2425 (1965).
32. V.V. Korshak and E.A. Pozhil'tsova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 412 (1950).
33. V.V. Korshak, G.M. Tseitlin, A.I. Pavlova, and A.A. Izyneev, USSR P. 170 659.
34. V.V. Korshak, G.M. Tseitlin, and A.I. Pavlov, Dokl. Akad. Nauk SSSR, 163, 116 (1965).
35. V.S. Yakubovich, G.V. Myasnikov, G.I. Braz, and A. Ya. Yakubovich, Dokl. Akad. Nauk SSSR, 159, 630 (1964).
36. I. Iwakura, K. Ino, and I. Imai, J. Polymer Sci., A 2, 2605 (1964).
37. H. Vogel and C.S. Marvel, J. Polymer Sci., 50, 511 (1961).
38. T.M. Frunze, V.V. Korshak, and A.A. Izyneev, Vysokomol. Soed., 7, 280 (1965).
39. T.M. Frunze, V.V. Korshak, A.A. Izyneev, and V.V. Kurashev, Vysokomol. Soed., 7, 285 (1965).
40. A.A. Izyneev, V.V. Korshak, T.M. Frunze, and V.V. Kurashev, Izv. Akad. Nauk SSSR, Ser. Khim., 1828 (1963).
41. L. Ambroski, Ind. Eng. Chem., Prod. Res. Develop., 2, 189 (1963).
42. V.V. Korshak, G.N. Chelnokova, and M.A. Shkolina, Vysokomol. Soed., 1, 1774 (1959).
43. A.H. Frazer, W. Sweeny, and F.T. Wallenberger, J. Polymer Sci., A 2, 1157 (1964).
44. V.V. Korshak, E.S. Krongaus, and A.A. Rusanov, see Ref. 23, Preprints 316.
45. I. Mulvaney and C.S. Marvel, J. Org. Chem., 26, 95 (1961).
46. H. Brown, J. Polymer Sci., 44, 9 (1960).
47. J.K. Stille and J.R. Williamson, J. Polymer Sci., A 2, 3867 (1964).
48. T.M. Frunze, V.V. Korshak, and V.A. Makarkin, Vysokomol. Soed., 1, 500 (1959).
49. V.V. Korshak, T.M. Frunze, and Lu I-nan, Vysokomol. Soed., 2, 984 (1960).
50. V.V. Korshak, S.V. Vinogradova, M.M. Teplyakov, and Yu.A. Chernomordik, Dokl. Akad. Nauk SSSR, 147, 1365 (1962).
51. V.V. Korshak, S.V. Vinogradova, and M.G. Vinogradov, see Ref. 23, Preprints 274.
52. V.V. Korshak, S.V. Vinogradova, and M.G. Vinogradova, Vysokomol. Soed., 6, 1987 (1964).
53. V.V. Korshak, G.S. Kolesnikov, and A.V. Kharchevnikova, Dokl. Akad. Nauk SSSR, 56, 169 (1947).
54. V.V. Korshak and S.R. Rafikov, Dokl. Akad. Nauk SSSR, 48, 36 (1945).
55. V.V. Korshak, "Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry of Macromolecular Compounds), Izd. Akad. Nauk SSSR, Moscow, 1950, pp. 299–305.
56. V.V. Korshak, S.A. Pavlova, S.V. Vinogradova, and A.S. Lebedeva, Symposium, "Geterotsepnye Soedineniya" (Heterochain Compounds), Izd. Nauka, Moscow, 1964, p. 29.
57. T.I. Shein, N.D. Katorzhnov, and G.I. Kudryavtsev, Khim. Volokna, No. 1, 17 (1963).
58. B.P. 811 758 (1959); Chem. Abs., 53, 14 582 (1959).

Institute of Organo-Inorganic
("Organoelemental") Compounds,
USSR Academy of Sciences,
Moscow