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Advances in the Synthetic Chemistry of Macromolecular Compounds

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The individual stages in the development of the synthetic chemistry of polymers are examined in their historical aspect. The present state of the chemistry of macromolecular compounds and the prospects for its development in the future are discussed and the types and characteristics of monomers used in polymerisation and polycondensation are considered. The entire wide variety of known polymeric macromolecules arising in various syntheses of polymers is demonstrated. Attention is drawn to the fundamentally important fact that all reactions involving the synthesis of macromolecular compounds lead to the formation of heterounit polymers, and the necessity to take into account the heterounit nature of polymers when problems of the dependence of their properties on their structure are considered is pointed out. Certain problems arising in modern technology and involving tasks soluble by synthetic methods are described and questions concerning the synthesis of polymers with specific properties are considered in relation to a number of examples. The present level of development of the syntheses of polymers by polymerisation and polycondensation methods and by the modification of existing polymers is described. The varieties of polymerisation and polycondensation processes and of the modification of existing polymers are examined (mainly in relation to new reactions, primarily those which lead to the formation of polymers of a new type). The increasing tendency towards the synthesis of polymers with specific properties, which is apparent at the present time, is emphasised.
The bibliography includes 122 references.

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I. INTRODUCTION

The chemistry of macromolecular compounds is at the present time one of the most vigorously developing branches of chemistry. The rapid rate of its development can be accounted for by the fact that the synthetic chemistry of polymers ensures the growth of important branches of polymer technology involving the manufacture of plastics, synthetic rubber, synthetic fibres, and synthetic film-forming materials. The production of these materials plays in its turn an important role in the development of many of the most important branches of new engineering and modern industry: aviation, automobile, electro- and radio-technical, machine construction, building, etc. industries.

It may be assumed that the synthetic chemistry of polymers was initiated in 1833 [1] when Berzelius [2] formulated the concept of polymerisation, which has persisted, with some modification, to the present day. Gay-Lussac [3] obtained the first synthetic polymer—a polylactide based on lactic acid, and Braconnot [4] obtained cellulose nitrate, having achieved for the first time a polymer-analogue reaction. During the 145 years since then, the field of macromolecular compounds has been enriched by a large number of new synthetic methods and polymers of different structures. At the same time, theoretical ideas concerning the mechanism of the synthesis of polymers and the characteristics of their structure and properties have been developed. Studies of Staudinger, Carothers, Flory, Natta, and others have been very important in the formation of modern concepts concerning polymers. Russian and Soviet scientists made a significant contribution to the development of polymer chemistry. The studies by Butlerov, Lebedev, Favorskii, Shorygin, Kargin, Andrianov, Medvedev, Petrov, Korotkov, Ushakov, and others laid the foundations of polymer science and technology.

The first reports of the synthesis and investigation of macromolecular compounds described the results of random successes until the investigations of Butlerov, Kekulé, and Cooper led to the creation of the structural theory of organic chemistry [5]. The elegant edifice of polymer science was subsequently created on its basis. A huge army of investigators are now concerned with the synthesis, study, and applications of new polymers: 50% of organic chemists work directly or indirectly in the field of polymers, developing new methods for the synthesis of monomers, plasticisers, initiators, inhibitors, and other substances used in the synthesis and investigation of polymers. Many investigators are occupied with the synthesis and study of polymers and an even greater number of workers deal with the application of the results of these studies in industry, where polymers are manufactured, processed, and applied. To illustrate the wide scale of studies on the synthesis of polymers, one may say that during one year about 50 000 new polymers are now synthesised, i.e. more than 160 new polymers every day or one new polymer in each 3 min. [6] This has now led to the synthesis of hundreds of thousands of various polymers, but, despite this, the rate of synthesis increases continuously each year.

The explanation is that it is precisely in the field of synthesis of polymers that the efforts of investigators have been most effective both for the developments of the theoretical foundations of polymer science and for industry, enriching it in new polymeric materials. One is therefore fully justified in claiming that the synthetic chemistry of polymers constitutes a strategic component of the development of polymer science.

The industrial production of polymers is developing just as rapidly. The world production of polymers of all types has recently exceeded 64 million tons, approaching the scale of the manufacture of steel [7].

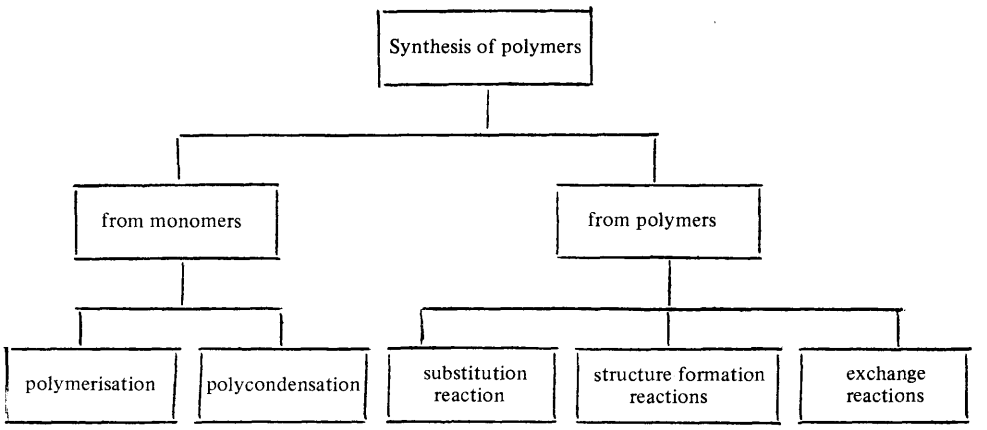


Figure 1. Scheme illustrating the fundamental ways of synthesising polymers.

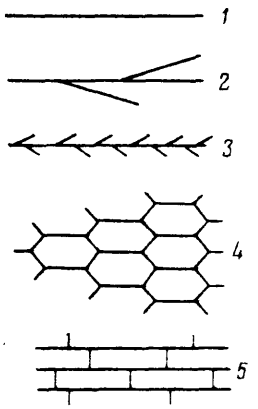


Figure 2. Shapes of macromolecules: 1) linear; 2) branched with a small number of long branches; 3) branched with a large number of short branches; 4) planar, parquet-like; 5) three-dimensional.

II. THE PRESENT STATE OF THE PROBLEM OF THE SYNTHESIS OF POLYMERS

Macromolecular compounds may be synthesised in several ways, as shown in Fig. 1. It is seen from the scheme that there are two types of synthesis of polymers: the first pathway involves the synthesis of polymers from low-molecular-weight substances by polymerisation and polycondensation and the second involves the modification of existing polymers by substitution, structure-formation, and exchange reactions.

We shall examine the present state of each of these types of synthesis in conformity with the above scheme. In the first place one should note that the advances in the synthesis of macromolecular compounds led to the formation of a wide variety of polymeric structures. As a result of the development of synthetic methods, it is now possible to obtain a wide variety of different forms of macromolecules, as shown in Fig. 2, where linear, planar, and three-dimensional forms of molecules known at the present time are illustrated. It is noteworthy that each of these forms also includes macromolecules of different types. Thus linear macromolecules may be of at least several types (Fig. 3). We see that the linear structure of the macromolecule is made up in different ways from units consisting of individual atoms or whole groups.

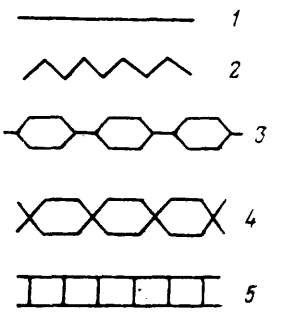
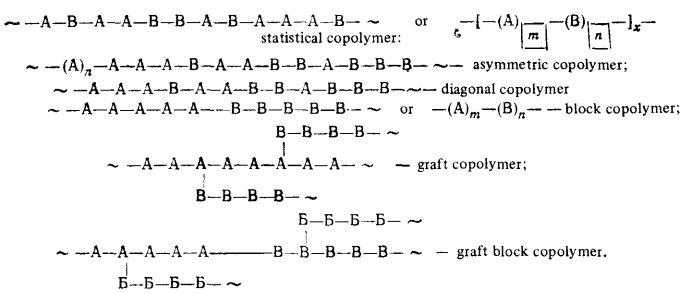


Figure 3. Forms of linear macromolecules: 1) straight ("carbene"); 2) zig-zag; 30 cyclochain; 4) cyclospiran; 5) ladder like.

There is also a wide variety of structures of macromolecular chains, particularly in different copolymers. Fig. 4 shows that the integral composition of the macromolecular chain varies along its length in various types of copolymers, starting from the usual statistical copolymers and extending via copolymers with macromolecular compositions varying along the chain (diagonal and asymmetric copolymers) to block and graft copolymers [8]. The structures of these copolymers can be represented by the

following formulae



The appearance of an increasing number of "hybrid" polymers, which are synthesised both by polymerisation and polycondensation or by the modification of existing polymers with the aid of polymerisation or polycondensation methods, should also be noted [6]. An example of "hybrid" polymers is provided by the hardening of unsaturated polyesters, which are obtained in the first stage by polycondensation, while in the second stage they copolymerise with styrene and other unsaturated monomers to form a three-dimensional copolymer [9]. Similarly, unsaturated polyamides, obtained by the polycondensation of fumaryl chloride with *N*-alkylated aromatic diamines, copolymerise with vinyl monomers to form copolymers with three-dimensional structures [10,11].

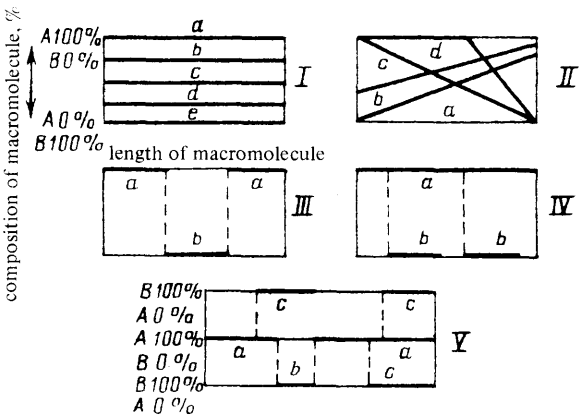


Figure 4. Variation of the integral composition along the length of the macromolecule in various copolymers: I) usual copolymers (*a*, *b*, *c*, *d*, *e*); II) variable-composition copolymers (*a*, *b*), diagonal copolymer (*c*), asymmetric copolymer (*d*); III) block copolymer [*a*) block consisting of A units; *b*) block consisting of B units]; IV) graft copolymer [*a*) main chain consisting of A units; *b*) grafted chains consisting of B units]; V) graft block copolymer [*a*) blocks consisting of A units; *b*) block consisting of B units; *c*) grafted chains consisting of B units].

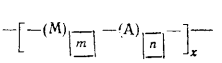
Certain polyamides are synthesised by the polycondensation of diamines with dicarboxylic acids, after which they are copolymerised with epoxy-compounds to form graft copolymers of the polyamide and epoxyalkanes [12]. Finally, block copolymers are synthesised by the reaction of poly(ethylene oxide), obtained by the polymerisation of epoxyethane, with poly(ethylene terephthalate) [13].

The wide variety of the structures of polymers, which is manifested particularly clearly in the case of copolymers, may be illustrated in relation to polypeptides. The exceptional complexity of the synthesis of polymers is associated, among other causes, also with the fact that in many instances there is a possibility of the formation of an unlimited number of isomers, since the 20 aminoacids encountered in natural proteins can form 10^{1200} macromolecules with different structures for a molecular weight of 100 000 (which corresponds to a polarisation coefficient of approximately 1000). In order to grasp the significance of this number, we may recall that the number of atoms of all the elements in the entire terrestial sphere is 10^{50}.

The enormous influence of the purity of the initial monomers on the course and result of the synthesis of polymers was established during research. The presence of impurities during polymerisation causes early chain termination, the branching of macromolecules, the formation of various unstable groups, and the formation of heterounit polymers as a result of these reactions. The presence of impurities in polycondensation also lowers the molecular weight of the polymers and leads to the formation of terminal groups of a different type, the branching of macromolecules, and other reactions leading to a heterochain polymer. Thus, since impurities as a rule are not inert in relation to the synthesis of polymers, they induce an uncontrollable modification resulting in the formation of heterounit polymers [14,15].

III. THE HETEROUNIT NATURE OF POLYMERS

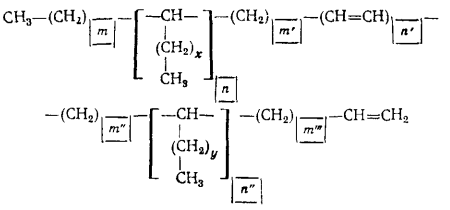
The side reactions caused by the presence of various impurities as well as side reactions of all other types (for example, isomerisation, polymerisation, branching, etc.) alter the structure of part of the polymer units and lead to the formation of anomalous units, which produces heterounit polymers [16]. Fig. 5 presents examples of various reactions leading to the formation of anomalous units in the macromolecule and of heterounit polymers. Because of these causes, heterounit polymers having the general formula



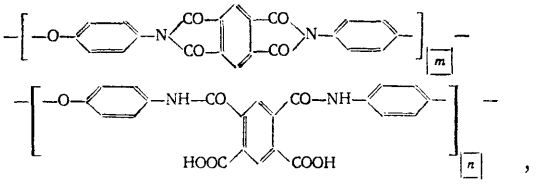
where M is a normal unit and A an anomalous unit and m and n are coefficients indicating a statistical distribution of units, are formed in all syntheses of polymers by polymerisation and polycondensation methods [14-16]. Polymer modification processes (substitution, vulcanisation, and exchange reactions) also lead to the formation of heterounit polymers [15]. For this reason, a study of the formation of a heterounit macromolecule and of its microstructure is a most important task in polymer science, since only in this way can one solve the problem of the synthesis of polymers with a set of properties specified beforehand [15]. The establishment of exact relations between the structure and properties of polymers will be possible only when all the details of the structure of macromolecules and their mutual influence become known.

The enormous importance of the heterounit nature of polymers as a factor which influences significantly the entire set of their chemical and physical properties has been demonstrated in many instances [16]. This is particularly significant in view of the fact that heterounit polymers constitute at present the dominant form of polymeric

structures. For this reason, the formula of a real polymer should take into account its heterounit nature and the presence of anomalous units. Consequently the real formula of polymers such as polyethylene, expressing its heterounit nature, is as follows[17]:



It clearly differs markedly from the idealised formula $-[CH_2-CH_2]_X-$ usually employed. The heterounit polyimide, containing non-cyclised units, whose real formula is



constitutes yet another example.

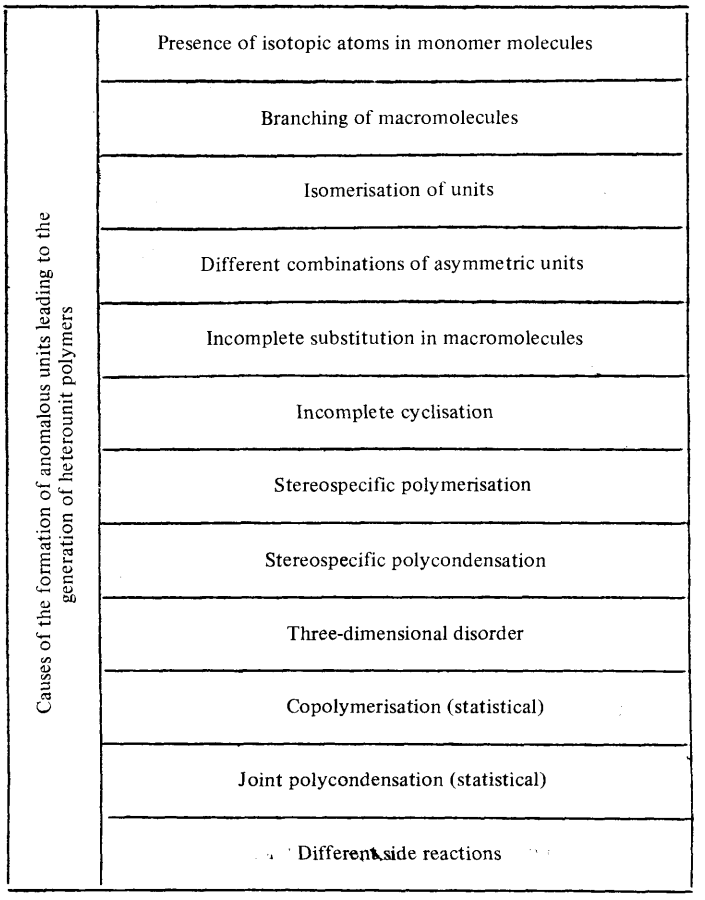


Figure 5. Causes of the formation of anomalous units leading to the generation of heterounit polymers.

In addition, the properties of polymers are influenced by the presence of the isotopes of hydrogen, carbon, and other polymer-forming elements. Thus it has been shown[18] that the replacement of hydrogen by deuterium in polyethylene alters appreciably physical characteristics such as density, melting point, glass point, yield point, and chemical properties. On this basis, it was concluded that the presence of isotopes in macromolecules leads to the formation of heterounit polymers, which affects the entire set of their physical and chemical properties. At the same time, account must be taken of the possibility of the simultaneous operation of the isotope effect and of the influence of the anomalous units arising as a result of branching, isomerisation, and other chemical reactions—these effects may coincide and enhance one another. The heterounit nature of polymers should be manifested particularly significantly in biopolymers, where one may expect very specific and very appreciable manifestations of the isotope effect. In fact, we know that, in structures such as proteins, nucleic acids, etc., very small structural changes influence significantly the biological functions. At the same time it is known that various isotopes are non-equivalent in their physiological properties. Thus, among the causes responsible for the heterounit nature of polymers, one must also point to the influence of the presence of stable isotopes in the molecules of the initial monomers and polymers.

IV. PROBLEMS OF THE SYNTHESIS OF POLYMERS WITH SPECIFIC PROPERTIES

Investigators working in the field of the synthesis of polymers are faced by complex tasks. These include tasks associated with the development of new and the improvement of existing methods for the synthesis of polymers in order to increase their yields and to improve the physicochemical characteristics of polymers and the articles made from them. At the same time problems concerning the application of methods of polymer chemistry to the synthesis of new polymers with the required set of properties, which are of practical interest and are essential for the execution of a particular task, are being solved. We shall consider certain examples of the synthesis of new polymers with specific properties.

The preparation of polymers with many practically important properties such as high heat resistance and thermal stability, non-combustibility, resistance to light, and specific electrophysical and other properties, constitutes an enormously important task[19-21]. An important branch of the synthesis of polymers involves the preparation of thermostable polymers capable of being used for a long time at high temperatures[19-22,23]. Many polymers have been synthesised for this purpose, including polyorganosiloxanes, particularly those with a ladder structure, and polyheteroarylenes, particularly polyimides, and similar structures[19,22,24,25]. Among these, polyamides based on pyromellitic anhydride and di-(4-aminophenyl) ether as well as polyoxadiazoles, polybenzimidazoles, and polybenzoxazoles proved to be particularly interesting. They are of practical interest as the starting materials for the manufacture of thermostable fibres and films. Studies on polymers for different electrotechnical purposes have been greatly developed: polymers for the manufacture of insulators, electrically conducting materials, semiconductors, polymers with photoelectric activity, etc. Many investigators have devoted much attention to the problem of the synthesis of polymeric

semiconductors and superconductors. Polymers with conjugated bonds of the polyvinylene, polyacetylene, polyphenylene, etc. type as well as polyheteroarylenes and their derivatives are obtained for this purpose [26].

The problem of the protection of the environment has faced synthetic chemists with the problem of the preparation of polymers capable of being decomposed after their utilisation, which is particularly important for packing materials. This problem is being solved in different ways, among which one of the most important is the synthesis of polymers capable of being decomposed by light. For this purpose, groups are introduced into the macromolecule increasing its sensitivity to light. On the other hand, practical problems necessitate the synthesis of noncombustible and self-extinguishing polymers, which is particularly important for the building industry and many branches of modern technology [27]. The preparation of composite and other materials with a high strength is likewise especially important [28-31]. The advantages of strengthened [reinforced?] compositions compared with traditional constructional materials are associated primarily with the possibility of a wide-scale variation of virtually all the properties of the material, which may be achieved by selecting the components and their proportions in the composition, the interaction conditions, the method of reinforcement, and other ways. Depending on the requirements which must be met by the composite materials, fibres and articles made from them, single-crystal fibres, films, hollow spheres, and other materials may be used as fillers [28].

High-strength, high-modular composite materials based on glass, boron, and carbon fibres and characterised by effective physicomechanical parameters are of special interest. The theoretical strength of steel and asbestos is 2000 and that of glass fibre is 1000 kgf mm^{-2}; on the other hand, the real strength is much lower and amounts to 250 kgf mm^{-2} for steel and 300 kgf mm^{-2} for asbestos. There is a theoretical possibility of increasing considerably the strength of articles made from polymeric materials; indeed, the strength of carbon fibres already reaches 300–400 kgf mm^{-2}. The problem of synthesising strong materials will evidently be solved also chemically, by synthesising polymers with rigid macromolecules. The ordered structure of polymers, achieved in different ways, will play a major role in this process.

Antifriction self-lubricating plastics (ASP plastics), which have found extensive applications in the construction of friction units (ball bearings, etc.) not requiring liquid lubricant, constitute a most interesting form of composite materials [31].

The problem of synthesising polymers for use in medicine with a wide variety of properties, such as thrombogenic properties, the ability to be dissipated in the organism, and conversely stability under the conditions of the living organism, pharmacological activity, etc., which are essential for the manufacture of artificial hearts, kidneys, livers, and other organs, is extremely urgent. The interesting problems of the synthesis of catalysts which are analogues of enzymes and of various biopolymer-like materials are also attracting the attention of investigators.

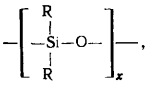
Increasing attention is being devoted to the problem of stereoregulation in the synthesis of polymers. In the field of polymerisation this involves the synthesis of stereoregular (isotactic, etc.) polymers, the synthesis of optically active polymers, the preparation of *cis*-1,4- and *trans*-1,4-polydienes, and the synthesis of stereoblock polymers. In the field of polycondensation examples of the regulation of the structure in the course of synthesis are provided by acceptor-catalytic polycondensation, the preparation of globular or fibrillar structures in polyarylates as a function of the conditions of synthesis, and the formation of right-handed or left-handed helices in polypeptides.

The study of copolymerisation and copolycondensation in order to obtain copolymers of practical value is being vigorously prosecuted [32]. Graft and block copolymerisation, which lead to new procedures for modifying polymers in a wide variety of ways, have developed greatly. Block copolymers, including polycondensation block copolymers, make it possible to obtain new types of elastomers, which do not require vulcanisation, as well as polymer systems suitable for the preparation of membranes capable of selective separation of gaseous mixtures.

Exceptionally important prospects have arisen in connection with the "chemical moulding" of polymers, which make it possible to obtain finished articles in the course of synthesis, for example, the manufacture of sheet poly(methyl methacrylate). Polyamides in the form of films or fibres can be obtained by interfacial polycondensation.

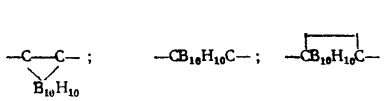
Anionic polymerisation of ϵ-caprolactam, which makes it possible to obtain poly-ϵ-caproamide in the form of finished articles of any shape which do not require mechanical working ("caprolite"), is of very great interest [33]. There is not doubt that the "chemical moulding" of polymers in the course of synthesis constitutes one of the most advanced procedures whereby one can eliminate the laborious processing steps usually employed when powdered polymers are used. In this case synthetic chemists merely copy nature, which learned a long time ago to synthesise silk, cotton, and other fibres from monomers, to form the skin of animals, blood vessels, etc.[17] There is no doubt that the polymer technology of the future will be largely based on chemical moulding processes.

The chemistry of organoelemental compounds, whose foundations were laid by A. N. Nesmeyanov, has itself become the foundation on which the edifice of the chemistry of organoelemental polymers grew [34]. K. A. Andrianov, who discovered the ability of silicon to form chains of alternating silicon and oxygen atoms, has played an outstanding role in the creation and development of the new field of the chemistry of polymers with inorganic main molecular chains. These polymers, having the structure



and known as polysiloxanes, have found an honourable place in polymer science and industry [35]. Despite the close relation between carbon and silicon, these polymers proved to constitute a completely unusual and very interesting group. Further studies showed that each element in the macromolecule makes its contribution to the set of properties of the polymer.

Polycarboranes are a very interesting group of polymers characterised by an unusual set of properties [36]. Together with various organic groups, their macromolecules contain *o*-, *m*-, or *p*-carborane rings:



Phosphorus-containing polymers, such as polyphosphazines having the structure [35]

$$-[N=P(R_2)]_x-$$

are also a promising group.

Table 1. Chemical elements in the composition of known polymers.

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

Table 2. Distribution of papers on methods of synthesis.

Method	Proportion of papers,%
Polymerisation	51.4
Polycondensation	27.1
Modification	21.5

Table 3. Distribution of papers on the synthesis of new polymers.

Method	Proportion of papers devoted to the synthesis of new polymers in terms of methods of synthesis, %	Proportion of papers devoted to the synthesis of new polymers, % of total number of papers on given method of synthesis
Polymerisation	38.9	27.7
Polycondensation	49.3	66.6
Modification	11.8	20.0

The task of finding ways of synthesising a wide range of polymers, incorporating the entire wide variety of the elements in the Periodic System, is of great importance [35]. Thus the polymeric structures known at the present time include 59 elements in Mendeleev's Table, as shown in Table 1. [37]

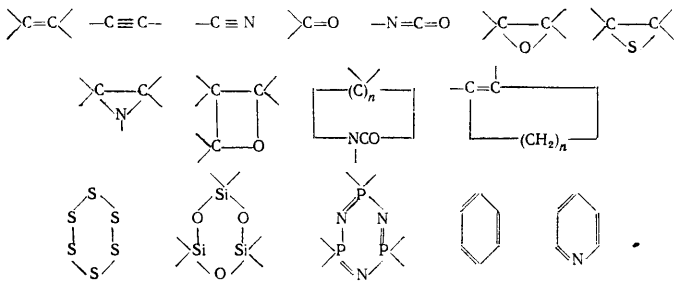
We shall consider the importance of methods of synthesis of polymers such as polymerisation, polycondensation, and modification of existing polymers. Among the chemical papers published in 1974 in the journal "Vysokomolekulyarnye Soedineniya" (Macromolecular Compounds), 89.4% were devoted to the synthesis of polymers; their distribution with respect to methods of synthesis was as shown in Table 2. The proportion of the total number of chemical papers describing the synthesis of new polymers was 32.8%. Table 3 shows how these papers are distributed with respect to methods of synthesis.

These data permit the conclusion that at the present stage studies on polymerisation are devoted mainly to the improvement of polymerisation methods, to the search for more active catalysts, and to the determination of the optimum conditions for the synthesis of polymers which are already known. Polycondensation studies involve the synthesis of new polymers to a greater extent than the improvement of synthetic reactions. The research in the field of modification, like that in the field of polymerisation, is also mainly directed to the study of chemical reactions of polymers and the improvement of modification reactions. We shall next consider the state of affairs in each of these fields of the synthesis of polymers.

V. POLYMERISATION

In considering the syntheses of polymers, one should note that a characteristic feature of polymerisation is the presence of many structures of new monomers and of many new polymerisation processes.

The range of active functional groups used to prepare polymers has been greatly extended. The most important of these, used in polymerisation, are indicated below:



Polymerisation processes, occurring as reactions involving additions to double bonds and rings, are being vigorously investigated at the present time and considerable advances may be noted in this field.

Table 4 presents the polymerisation processes known at the present time and the dates of their discovery.

A characteristic feature of the modern period is the vigorous development of research into polymerisation processes. Together with the considerable progress in the development of classical methods such as radical, cationic, and anionic polymerisation of unsaturated compounds as well as the polymerisation of heterocycles, new polymerisation processes have been discovered and investigated in detail. Among these we shall mention in the first place ionic-coordination polymerisation, migration polymerisation, polycyclotrimerisation, polydisproportionation, Diels–Alder polymerisation, 1,3-dipolar polyaddition, etc. Ziegler's discovery [50] in 1950 of catalysts for the low-pressure polymerisation of ethylene initiated the period of rapid progress in the polymerisation of olefins and other monomers. In a series of brilliant investigations by Italian scientists, Natta [46] discovered a new pathway to the development of stereospecific polymerisation processes.

Stereospecific polymerisation has become the leading field in polymer synthesis, in which many scientists of all countries are engaged. These investigations led to the

industrial manufacture of many polyolefins: polyethylene, polypropylene, ethylene–propene copolymers, many higher polyolefins, poly(*cis*-1,4-polybutadiene) and poly(*cis*-1,4-isoprene)—new types of synthetic rubbers which are complete substitutes of natural rubber, etc. As a result of studies by S.V.Lebedev, B.A.Dolgoplosk, A.A.Korotkov, and others, our country now occupies a leading place in the world as regards the technical quality and range of synthetic rubbers.

Table 4. Polymerisation processes.

Reaction	Year of discovery	References
Radical polymerisation	1839	38
Cationic polymerisation	1873	39
Anionic polymerisation	1878	40
Diels-Alder polymerisation	1926	41
Migration polymerisation	1937	42
Hydrolytic polymerisation of heterocycles	1938	43
Cyclopolymerisation	1949	44
Dehydropolymerisation	1951	45
Stereospecific polymerisation	1955	46
Onium polymerisation	1961	47
1,3-Dipolar polyaddition	1963	48
Polycyclotrimerisation of acetylenic compounds	1965	49
Polydisproportionation	1967	52

Four mechanisms of chain propagation in ionic (cationic and anionic) polymerisation are now believed to be possible:

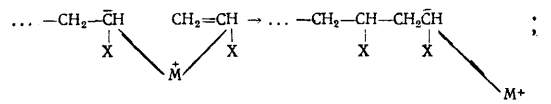
(1) polymerisation with participation of a free ion:

$$\ldots -CH_2-\overset{+}{C}HX + CH_2=CHX \rightarrow \ldots -CH_2-CHX-CH_2-\overset{+}{C}HX;$$

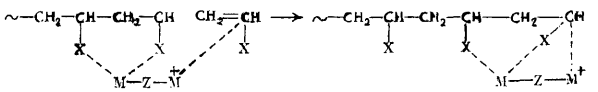
(2) polymerisation with an ion pair:

$$\ldots -CH_2-\overset{+}{C}H\ldots A^- + CH_2=CH \rightarrow \ldots -CH_2CH-CH_2\overset{+}{C}H \ldots A^-;$$

(3) two-centre coordination polymerisation:



(4) many-centre coordination polymerisation:



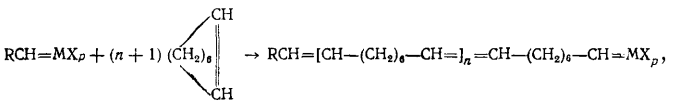
Stereoregulation is possible in each of these cases. However, in the first and second cases this possibility is realised only at low temperatures, while in the third and fourth cases the process is observed also at elevated temperatures. In the elementary chain propagation step of many-centre coordination polymerisation the polar groups of the monomer and the polar groups of the last two units of the growing chain form a complex with more than one active centre of the composite or associated catalyst, which limits the free rotation of the ends of the chains and the monomer molecules and ensures a definite disposition of the units in the elementary chain propagation step.

Isomerisation polymerisation accompanied by the isomerisation of the units has proved to be a very special case in the syntheses of polymers via both radical and particularly ionic polymerisation. This results in the formation of anomalous units and of heterochain polymers [16].

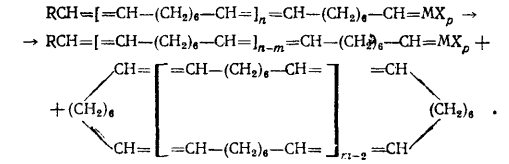
Studies on regular copolymerisation, leading to copolymers with a regular alternation of units, have been considerably developed [51]. The copolymers thus produced are frequently substances with an interesting set of properties.

A new field in polymerisation is polydisproportionation occurring in the presence of molybdenum- and tungsten-containing catalytic systems. Cyclic olefins such as cyclo-octadiene, cyclo-octene, norbornene, etc. are used as the initial monomers in this reaction [52,53].

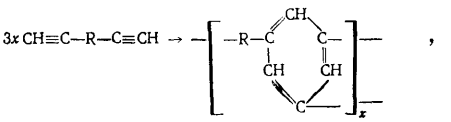
The polydisproportionation reaction proceeds in accordance with the equation

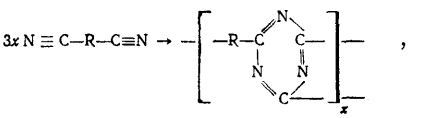


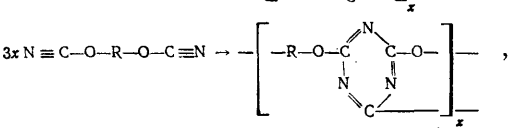
where M = Mo or W, and is accompanied by the formation of cyclic oligomers. A carbene is the intermediate active centre in this reaction, which proceeds as a chain process [54]. Cyclic oligomers are formed in this process as a result of the degradation of the active polymeric macromolecule via the reaction [55]



A new method for the synthesis of polymers with different structures, based on the cyclotrimerisation of multiple carbon–carbon and carbon–nitrogen bonds, has been developing vigorously recently. The polycyclotrimerisation of diacetylenes, dinitriles, dicyanates, and di-isocyanates, leading to the formation of benzene or triazine rings in accordance with the equations [56–58]







is particularly interesting. This reaction leads to a new way of synthesising polymers containing aromatic and heterocyclic groups in the macromolecules [59].

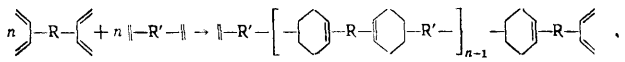
The polymerisation of aldehydes, ketones, and other carbonyl compounds has recently attracted the attention of investigators [60]. The polymerisation and copolymerisation of formaldehyde, which proceeds as a cationic process, namely

$$x\,CH_2O \rightarrow -[-CH_2-O-]_x- \quad ,$$

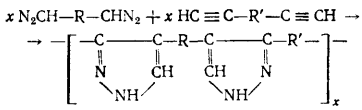
is being particularly vigorously investigated. Studies by N.S.Enikolopyan, who demonstrated the occurrence of an

unusual chain termination stage called "chain transfer with branching", have made a major contribution to the study of this process [61].

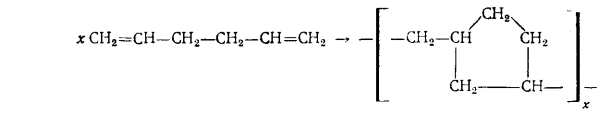
Polymers containing rings in the chain have been obtained with the aid of diene or Diels–Alder synthesis [62]. In this case it is necessary that the molecules of the initial monomer should contain a diene system and a dienophile, capable of reacting with one another under specified conditions via the mechanism



An unusual instance of polymerisation is the formation of polypyrazoles by the reaction of bisdiazo-compounds with diacetylenes via the 1,3-dipolar addition mechanism according to the equation [63]

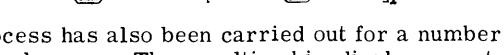


Cyclopolymerisation is a method of obtaining polymers containing cyclic groups in the macromolecular chain [44]:



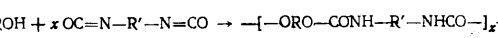
It occurs in the polymerisation of various dienes containing separated double bonds. The reaction usually yields comparatively low-molecular-weight polymers.

Dehydropolymerisation is a reaction whereby a *p*-zylylene polymer has been obtained [45]. It occurs in the formation of *p*-xylylene and is described by the following equation:

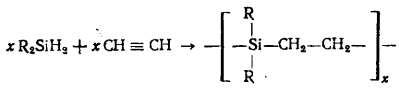


This process has also been carried out for a number of xylene analogues. The resulting biradicals are extremely reactive and readily copolymerise with other monomers.

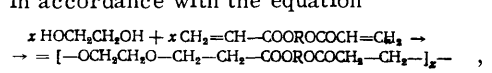
Migration polymerisation is polymerisation involving the transfer (migration) of hydrogen atoms at each stage [64]. This process is sometimes referred to as polyaddition. The polymerisation of aldehydes via the Tishchenko reaction [65], the formation of polyacetals [66], the formation of polyamides from bisoxazolones and diamines [67], and the synthesis of important polymers such as polyurethanes and polyureas by the reaction of di-isocyanates with glycols and diamines [42] are of this type. The range of these processes has been increasingly expanded recently. As examples, we may mention the formation of polyurethanes



and the synthesis of organoelemental polymers containing silicon, germanium, and tin via hydride addition [68]:

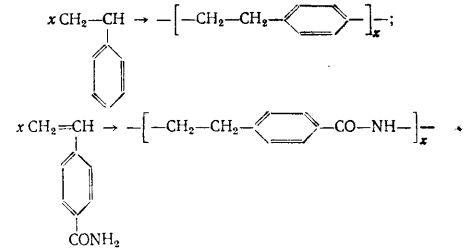


The formation of polymers via the addition of glycols or diamines to diacrylate or dimethacrylate esters, which proceeds in accordance with the equation [69]

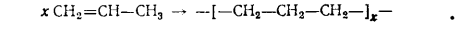


is of the same type.

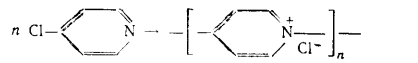
Many isomerisation polymerisation reactions also take place with migration of hydrogen [14]. Thus styrene and substituted styrenes can form polymers via the following mechanisms [70,71]:



The anionic polymerisation of propene is also accompanied by isomerisation and leads to the formation of polyethylene [72]:



Onium polymerisation has been investigated in relation to the reaction of γ-chloropyridine [47]:



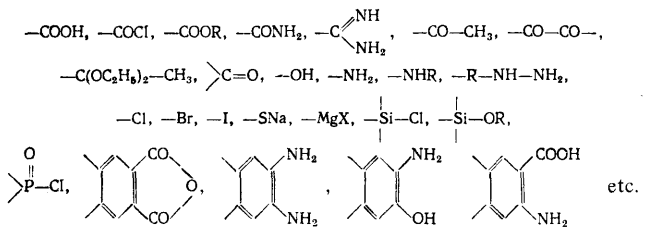
Polymerisation processes may be initiated with the aid of energetic influences such as ionising radiation, explosive impact, high pressure, mechanical action, etc. [73–75] Ionising radiation has found practical application in the initiation of polymerisation [76]. An interesting case is the initiation by this procedure of solid-state polymerisation, particularly at low temperatures [74,75].

The study of solid-state polymerisation at low temperatures enabled Semenov [77] to devise the collective interaction theory. According to Semenov, solid-state polymerisation takes place very fast when a frozen monomer is irradiated, because, as a result of a particular orientation in the crystal, the ion or radical combines not with a single monomer molecule but with a chain of molecules at once, in the region where the crystal is ideal. Thus, owing to the favourable disposition of the molecules in the crystal, there exists a kind of "seed" for the formation of macromolecules (which is not the case in liquids) and this ensures a faster polymerisation.

The polymerisation of cyclic compounds has been acquiring increasing importance as a general method for the synthesis of macromolecular compounds. Many heterochain polymers containing oxygen, nitrogen, sulphur, metals and other elements as heteroatoms have been obtained in this way. Cyclic compounds polymerise via a typical polymerisation mechanism and the process can be achieved as a stepwise (hydrolytic) polymerisation and as a chain reaction (anionic polymerisation). It is now known that all cyclic systems with sufficiently polar or polarisable bonds are capable of polymerisation regardless of their size. The polymerisation of siloxane rings, widely used as a method of synthesis of polysiloxane rubbers and other polymers, is very important [78]. Polymerisation of cyclic systems by a very rapid method, involving the use of activators, is particularly promising [79]. The use of activators in the anionic polymerisation of ϵ-caprolactam is extremely effective: it makes it possible to carry out the process over a short period at comparatively low temperatures.

VI. POLYCONDENSATION

Processes of the polycondensation type have been extensively developed in connection with the synthesis of thermostable polymer and other polymeric compounds of different types. In the first place mention should be made of the large number of monomers, containing a wide variety of functional groups, which are used in polycondensation processes, for example:



Polycondensation has been known for a long time as a general method for synthesis of polymers. It proceeds as a substitution reaction and is usually accompanied by the formation of a low-molecular-weight product [80]. Table 5 gives the dates of discovery of individual types of polycondensation.

Table 5. Polycondensation processes.

Reaction	Year of discovery	References
Equilibrium polyesterification	1833	3
Polyamidation	1862	81
Phenol-aldehyde polycondensation	1872	82
Polyazination	1889	83
Interfacial polycondensation	1898	84
Polyheterocyclisation	1908	85
Polycoordination	1953	86
Acceptor-catalytic polycondensation	1956	87
Polyrecombination	1957	88
Oxidative polycondensation	1960	89
Polycyclocondensation	1960	90
Stereospecific polycondensation	1970	91
Disproportionation polycondensation	1972	92

The study of the mechanisms of polycondensation processes made it possible to understand the laws governing their course and to devise a theory of these reactions [93,95]. The present development of polycondensation processes has led to the discovery of new polycondensation processes together with a deeper understanding of the reaction mechanism.

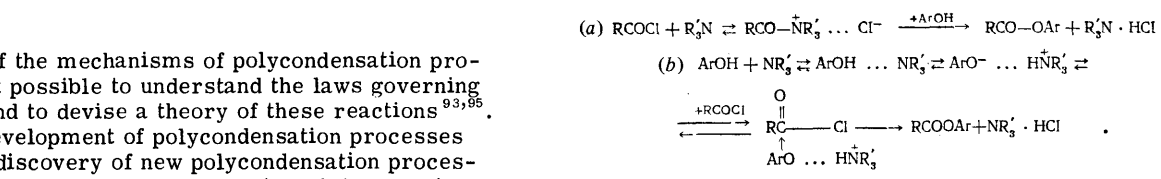
Depending on the structure of the starting materials and the way it is carried out, polycondensation can be achieved in two versions [94]: (1) equilibrium polycondensation; (2) non-equilibrium polycondensation. In equilibrium polycondensation the equilibrium constant of the reaction is in the range from 1 to 10^3, while in non-equilibrium polycondensation it exceeds 10^3 [93]. Equilibrium polycondensation proceeds as a rule at a low rate [95]. An example of this reaction is provided by the formation of polyamides from diamines and dicarboxylic acids in the melt.

Studies on equilibrium polycondensation during the period under consideration have been characterised by a deeper understanding of the fundamental characteristics of the processes and their wide-scale application in the synthesis of many new, mainly heterochain polymers (polyamides, polyesters, polyazines, coordination polymers, etc.). Equilibrium polycondensation is based on reversible elementary equilibrium reactions [95]. A new instance of equilibrium polycondensation is disproportionation polycondensation in accordance with the equation [92,96,97]

Together with equilibrium polycondensation, there are also polycondensation processes based on irreversible elementary reactions. Reactions of this type belong to the group combined under the general name "non-equilibrium polycondensation" [93]. There is a fairly large number of instances of non-equilibrium polycondensation. They include oxidative polycondensation reactions, polyrecombination, polycyclisation, as well as interfacial polycondensation, acceptor-catalytic polycondensation, and polycyclocondensation.

Non-equilibrium polycondensation is characterised by high equilibrium constants and as a rule a high rate [6,93]. An example of reactions of this type is provided by the formation of polyamides from diamines and dicarboxylic acid chlorides. There are many instances of non-equilibrium polycondensation where the reaction is comparatively slow. However, the polymers produced by the reaction are stable under its conditions and incapable of being hydrolysed or of undergoing degradative transformations, which is the reason for the irreversibility of the overall reaction. Dehydropolycondensation, polyrecombination, and polycyclisation, which were examined below, were examples of reactions of this kind.

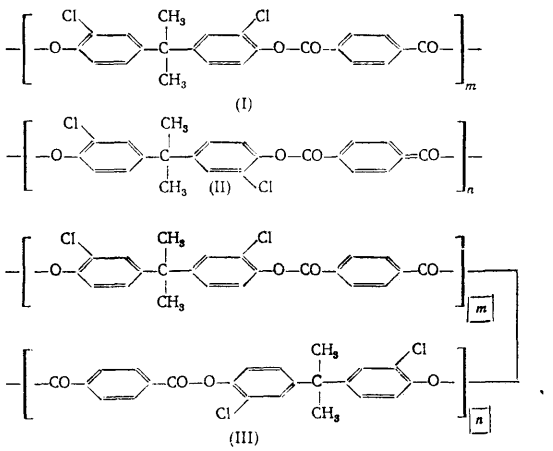
Polycondensation in solution, carried out at temperatures below 100°C, also referred to as low-temperature polycondensation, has recently attracted much attention by investigators and its various aspects are being vigorously developed. In the synthesis of polyesters from acid dihalides and diols in the presence of tertiary amines, it is referred to as acceptor-catalytic polycondensation [98]. In the synthesis of polyarylates the process proceeds via nucleophilic (a) or general base (b) catalysis in the following way:



Apart from the activities of the starting materials, the formation of macromolecules is influenced by the nature of the solvent and the tertiary amine, particularly its ability to form complexes with the starting materials. The method permits a very fine control of the structure of the polymers obtained.

Conformationally-specific polycondensation has been achieved under the conditions of acceptor-catalytic polyesterification for the reaction of 3,3'-dichlorodian with terephthalic acid chloride [91]. The reaction results in the formation of macromolecular conformers whose structure is determined by the nature of the solvent and the tertiary

amine[99,100]. The formulae of polyarylates formed by this reaction are given below:

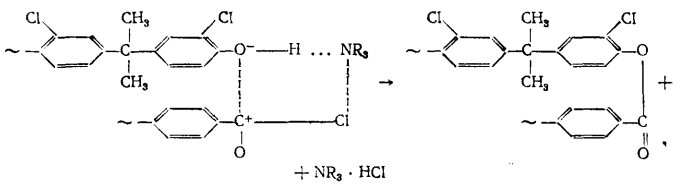


(I)

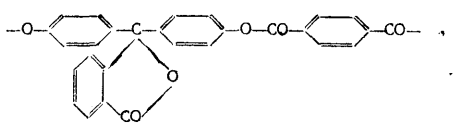
(II)

(III)

Here (I), (II), and (III) are *cis*-tactic, *trans*-tactic, and heterochain (atactic) polymers containing units of both conformations. The nature of the tertiary amine has a significant influence on the conformationally specific polycondensation, which is attributed to the formation of cyclic intermediate complexes[100]. In general base catalysis such a complex can be represented as follows:



The use of phenolphthalein and similar substances as starting materials in the reaction of an acid dichloride and a bisphenol leads to the formation of cardopolymers[101], a characteristic feature of which is that the carbon atom in the monomer residue is at the same time part of the polymer chain. The polyarylate formed from phenolphthalein and terephthalic acid is an example of such a cardo-polymer:



Oxidative polycondensation is being developed on an increasing scale as a general method for the synthesis of various polymers[102,103]. The application of this reaction to diacetylenic compounds of the type $HC\equiv C-R-C\equiv CH$ made it possible to obtain a large number of linear polymers having the general formula

$$-[-C\equiv C-R-C\equiv C-]-_x,$$

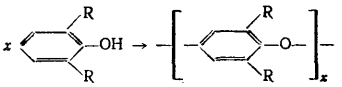
containing triple bonds in the chain together with phenyl and other groups. "Carbene", which is a linear form of carbon, has been obtained in this way from acetylene[89]. It is formed in the oxidation of acetylene in the presence of copper salts via the reaction

$$n\,HC\equiv CH \xrightarrow{Cu^{2+}} -[-C\equiv C-]_n- \quad .$$

A polyphenylene has been obtained by oxidative polycondensation from benzene[104]:



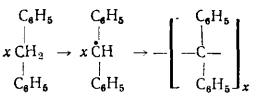
The oxidative polycondensation of 2,6-disubstituted phenols makes it possible to obtain polymeric phenyl ethers—poly(phenylene oxides):



This oxidative process takes place in the presence of catalysts (copper salts) and an oxidant[105].

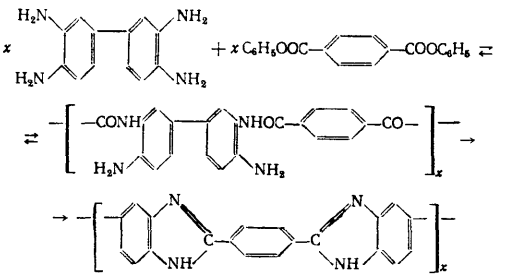
Increasing attention has been devoted recently in polymer chemistry to the problem of the synthesis of polymers with substances which are not monomers in the present sense of this term, i.e. do not contain double bonds, rings, or any other traditional functional groups. One of the ways of solving this problem is to employ a polyrecombination reaction, whereby saturated hydrocarbons and other substances incapable of polymerising in the usual way can be converted into polymers.

Polyrecombination involves the synthesis of polymers via the mechanism (when diphenylmethane is used as a starting material)[106]



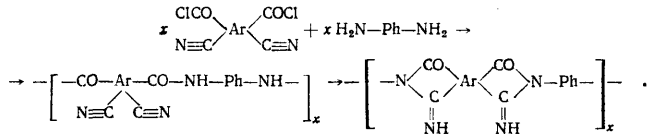
The elementary processes in polyrecombination are the formation and recombination of free radicals. A characteristic feature of the monomers used in polyrecombination is the presence of hydrogen atoms, which are easily removed by free radicals. When the monomer contains two reactive hydrogen atoms, linear polymers are obtained and in the presence of three and more atoms the products are branched and three-dimensional polymers.

Polycyclisation is a new type of reaction leading to the formation of polymers having a cyclochain structure[107]. Although in terms of its mechanism the reaction is a polycondensation process, its mechanism is in fact extremely unusual. In the first stage this involves an ordinary equilibrium reaction leading to the formation of polyamides, polyesters, polyhydrazones, and similar compounds, depending on the structure of the starting materials. The characteristics of this stage do not in general differ from those known for analogous reactions. In the second stage, cyclisation proper takes place, i.e. the closure of the heterocycle characteristic of the given reaction. This stage constitutes non-equilibrium polycondensation, since the formation of stable rings is as a rule an irreversible process, which proceeds in the case of the synthesis of polybenzimidazoles by the Marvel method in accordance with the equation[108]

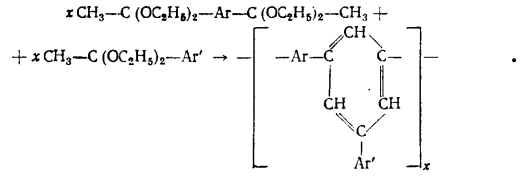


The polycyclisation reaction has been investigated nowadays in relation to the synthesis of polymers incorporating in their chains heterocycles such as thiazole, imidazole, pyrazole, triazole, oxadiazole, phthalimide, triazine, benzimidazole, benzoxazole, benzothiazole, etc.[109]

An interesting instance of polycyclisation is isomerisation polycyclisation, where the starting materials are aromatic acid dichlorides or diamines containing cyano-groups in the ring[110]. Under these conditions, the first stage involves non-equilibrium polycondensation, leading to the formation of polyamides. The latter then undergo cyclisation as a result of their addition to cyano-groups, as shown below:



Polycyclocondensation is a process involving the synthesis of polymers whose mechanism is close to that of polycyclotrimerisation[122]. Macromolecules are formed as a result of the formation of aromatic or heterocyclic units linking the molecular residues of various initial substances. As an example, one may quote the formation of polyphenylene from the diketal of *p*-diacetylbenzene and the ketal of acetophenone via the reaction



The polycondensation reactions considered above take place in the vast majority of cases as ionic processes which are extremely sensitive to the action of catalysts. The use of catalysts to accelerate the polycondensation reaction is therefore extremely effective[100].

VII. MODIFICATION OF POLYMERS

The reaction involving the modification of existing polymers has been developed on an increasing scale in the synthesis of polymers with a wide variety of structures. Whereas previously natural polymers (cellulose, starch, proteins) were subjected to modification processes, nowadays many synthetic polymers are used in this process. Table 6 presents examples and the dates of the first communications concerning the most important reactions of this type and shows that the modification reactions can be divided into three main groups: (1) chain substitution reactions; (2) structure formation reactions; (3) exchange reactions involving heterochain polymers.

Chain substitution reactions involving natural polymers (cellulose, starch, proteins, etc.) have been known for a long time and involve mainly the substitution of a hydrogen atom in a hydroxy- or amide group as well as hydrogen atoms linked to carbon in methylene or phenyl groups. These reactions have been investigated in relation to numerous examples and processes of this kind have been justified theoretically[116]. There are many side reactions as a result of which the polymers obtained are of the "heterounit" type[117]. The reactions of synthetic polymers involving the substitution of hydrogen atoms linked to carbon, halogen atoms, the sulpho-group, the phosphono-group, and alkyl-groups are of increasing importance. The introduction of polar groups such as the carboxy-, amino-, sulphonic, phosphonic, etc. substituents leads to the appearance of ion-exchange properties and is widely used in the synthesis of ion exchangers. Investigations of the grafting of carbochains and heterochain polymers on to cellulose have been greatly developed. Rogovin[118] showed that this makes it possible to modify extensively the properties of cotton and other cellulose materials. The structure of formation reactions discovered for natural polymers are being used on an increasing scale for synthetic polymers. Examples of this kind are provided by the radiation-induced vulcanisation of polyethylene and other polymers. As a result of these reactions, the structure of the macromolecules changes significantly.

Table 6. Modification processes.

Reaction	Year of discovery	Refs.
Nitration of cellulose	1833	4
Vulcanisation of rubber with sulphur	1839	111
Grafting via chain transfer	1933	112
Chlorination of poly(vinyl chloride)	1933	113
Polyester exchange reactions	1942	114
Sulphochlorination of polyethylene	1946	115

The exchange reactions of heterochain polymers constitute a specific means of synthesising copolymers by the interaction of two different polymers on heating or in the presence of catalysts. For example, a mixed polyamide is obtained from a mixture of two polyamides[119], a mixture of a polyamide and a polyester gives rise to a polyamido-ester[120], and a mixture of two polysulphides gives rise to the corresponding copolymer[121]. Polyacetals of the type of polyformaldehyde also form copolymers in the presence of catalysts[61].

In conclusion one should note that, as can be seen from the examples presented, in the field of the synthesis of polymers there has been a continuous and notable progress. New reactions leading to the synthesis of polymers are being discovered and investigated and the synthetic processes already known are being improved. Here one should note an increasing application of catalysis to polymerisation, polycondensation, and polymer modification reactions. As a result of this, science has become enriched in a large number of new polymers and many previously known polymers obtained by new improved methods have acquired a set of more valuable properties. A characteristic feature of the synthetic branch of the development of polymer chemistry is more detailed study of increasingly more complex chemical reactions, used in polymer synthesis, and the preparation of new extremely complex polymer structures, which characterises the growth of the chemical art in polymer synthesis and an extensive application of modern physical research techniques. Finally, one should note that a particularly characteristic feature of modern polymer synthesis is the endeavour to obtain polymers not only for constructional purposes, which has been characteristic of the earlier period of the development of polymer science, but to an

increasing degree to synthesise polymers with a specific set of chemical and physical properties. As an example, we may point to thermostable, non-combustible, semiconducting, electrically conducting, photoelectrically active, light sensitive, and biologically active polymers, polymers resembling biopolymers, polymeric catalysts, ion exchangers, complexones, and other polymers with a wide spectrum of specific properties.

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