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Advances in the Field of Organoelemental Polymers

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This review deals with organoelemental polymers containing the elements of various Groups in the Periodic System. The major role of these polymers in many fields of modern technology and national economy is demonstrated. The methods of synthesis of organoelemental polymers used at present and the prospects for the development of this field in the future are considered. It is shown that the heterounit structure of the polymer is a common phenomenon in the chemistry of macromolecular compounds, characteristic also of organoelemental polymers. It has been established that the presence of stable isotopes in polymer macromolecules is one of the causes of the appearance of the heterounit structure.
The bibliography includes 113 references.

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INTRODUCTION

The chemistry of organoelemental polymers as an independent branch of polymer science has been formulated only in the last forty years. It is characterised by rapid development, which can be accounted for by the possession by organoelemental polymers of valuable qualities such as, for example, high thermal stability, chemical stability, incombustibility and many other specific properties, which make them irreplaceable in practical applications; they have therefore found extensive applications in a number of fields of modern technology.

A.N.Nesmeyanov has pointed out that one of the most important ways of creating new polymers is to employ for their synthesis different elements of Mendeleev's Periodic System.[1] The chemistry of organoelemental compounds is a science of the boundary between inorganic and organic chemistry, which is undoubtedly its positive aspect, since it makes it possible to obtain polymeric compounds combining useful qualities characteristic of compounds of most branches of chemistry.[2] Because of this, many elements of the Periodic System, capable of forming various polymeric compounds, have been the object of chemical research and some of the polymers obtained have already found practical applications in a number of branches of modern technology.[3]

Thus organoelemental macromolecular compounds such as numerous organosilicon polymers, polymers based on various metals and their derivatives, poly(phosphonitrilic chloride) and its various modifications, phosphorylated polystyrene, a series of organoboron compounds, particularly those containing carbaborane groups, and many polymers, and copolymers of fluorinated ethylenes are being manufactured at present on an industrial scale and have found a wide variety of applications.

The concept of organoelemental compounds has been put forward by Nesmeyanov and has been accepted by many investigators.[4]

The history of the chemistry of organoelemental compounds began with the investigations of Andrianov,[5] who obtained in 1937 for the first time organosilicon polymers, and demonstrated their practical value; since that discovery, the field of organoelemental macromolecular compounds has begun to develop.

Undoubtedly one of the most important trends in the future progress of polymer science will be a wide-scale employment of elements of the Periodic System for the synthesis of various polymers;[6] the number of elements used for this purpose increases every year. At the present time 75 elements have already been employed in the synthesis of various macromolecular compounds.[6-8] Among the 106 elements known at present, only the noble gases (6 elements) and the 12 elements belonging to Groups I and VII of the Periodic System, which are univalent and can only play the role of terminating groups, are incapable of producing polymers. Thus, the remaining 88 elements are capable of functioning as chain-forming elements, giving rise to polymeric macromolecules.

Table 1. Elements entering into the composition of the organoelemental polymers synthesised.

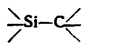
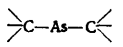
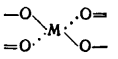
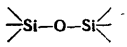
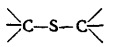
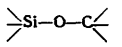
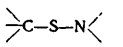
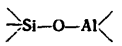
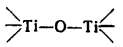
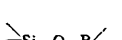
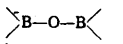
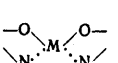
Period	Groups									
	I	II	III	IV	V	VI	VII	VIII		
1	H	—	—	—	—	—	—	—	—	—
2	Li	Be	B	C	N	O	F	—	—	—
3	Na	Mg	Al	Si	P	S	Cl	—	—	—
4	K	Ca	—	Ti	V	Cr	Mn	Fe	Co	Ni
	Cu	Zn	Ca	Ge	As	Se	Br	—	—	—
5	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
	Ag	Cd	In	Sn	Sb	Te	I	—	—	—
6	—	Ba	La	Hf	Ta	W	—	Os	Ir	Pt
	Au	Hg	Tl	Pb	Bi	Po	—	—	—	—
7	—	—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

Lanthanides: Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.
Actinides: Th and U.

These elements give rise to bifunctional and polyfunctional atoms and groups. The formation of polymeric macromolecules with a homochain structure is fairly common with elements such as boron, carbon, silicon, phosphorus, sulphur, germanium, arsenic, selenium, tin, antimony, tellurium, bismuth, and polonium (in all, 13 elements). Among these elements of the Periodic System, carbon is distinguished by an exceptional ability to form unusually long chains in carbochain polymers, while the remaining elements enumerated above can produce homochain polymers

to a much lesser extent. However, in contrast to this, the number of elements able to participate in the formation of heterochain polymers is very considerable and such compounds include more examples than homochain polymers.

Table 2. The bonds introduced into the composition of organoelemental polymers.

Bond	Bond	Bond
		
		
		
		
		

heating to a temperature exceeding 350 °C, polysiloxanes readily depolymerise, forming cyclic siloxanes. The Si–C bonds then remain unchanged, while the Si–O bonds are ruptured. This difference in behaviour can be explained by the mechanism of the accompanying reaction in which the bonds are rearranged via the formation of an intermediate compound.[13] This reduces the energy barrier to the rupture of the Si–O bond and a cyclic siloxane is formed in accordance with the equation

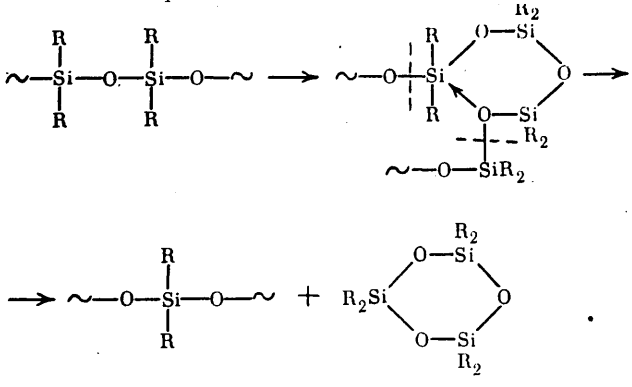
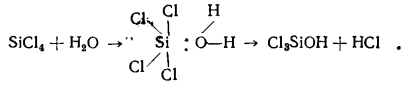


Table 4. The bond energies in heterochain organoelemental polymers.[11,12]

Bond	E_b, kcal mol^{-1}	Bond	E_b, kcal mol^{-1}
B—O	119,3	As—O	64.5
B—N	104,3	Al—C	61.6
B—C	100,0	C—S	61.5
P—O	81,7	Si—S	60.9
C—O	79,0	Si—C	57.6
Si—O	89,3	As—C	54.6
Sb—O	71,0	N—O	37.0
C—N	66,0		

Many other reactions of silicon compounds can be explained in the same way, i.e. by the transition of silicon to a quinquevalent state, as happens, for example, in the hydrolysis of silicon tetrachloride:[15]



However, there are also other ideas concerning the mechanism of these reactions.[16] The bond energies listed in Tables 3 and 4 refer to the homolytic type of bond dissociation reactions. However, bond dissociation reactions of the heterolytic type are encountered among organoelemental compounds much more frequently than those of the homolytic type and it is therefore necessary to take into account the "ionic bond energy", which is characteristic of the reactions which proceed as follows:

$$AB \rightarrow A^- + B^+.$$

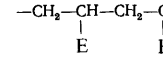
Thus, one can understand why the Si–H bond, for which the homolytic bond dissociation energy is 76.0 kcal mol^{-1}, while the ionic bond dissociation energy is 222.9 kcal mol^{-1}, is more stable in heterolytic reactions than the Si–Cl bond, for which the above energies are respectively 91 and 190 kcal mol^{-1} and the overall energy, amounting to 281 kcal mol^{-1}, is lower than the overall energy in the former case, where it is 298.9 kcal mol^{-1}.[15]

The bonds between the elements in organoelemental polymers are of a different character for different elements. It is possible to arrange the elements in three groups depending on the type of bond characteristic of them,[17] as can be seen in Fig. 1.

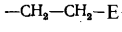
III. METHODS OF SYNTHESIS OF ORGANOELEMENTAL POLYMERS

Organoelemental polymers can be synthesised by means of reactions involving both the polycondensation and polymerisation of the corresponding monomers and via a series of direct modification reactions of various polymers. This results in the formation of polymers of the following three types:

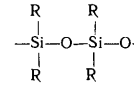
(1) carbochain polymers with an organic main chain of the macromolecule and organoelemental side groups (E):



(2) heterochain polymers containing carbon atoms in the main chain together with those of other elements:



(3) heterochain polymers with an inorganic main chain and organic side groups, such as, for example, polysiloxanes, etc.:



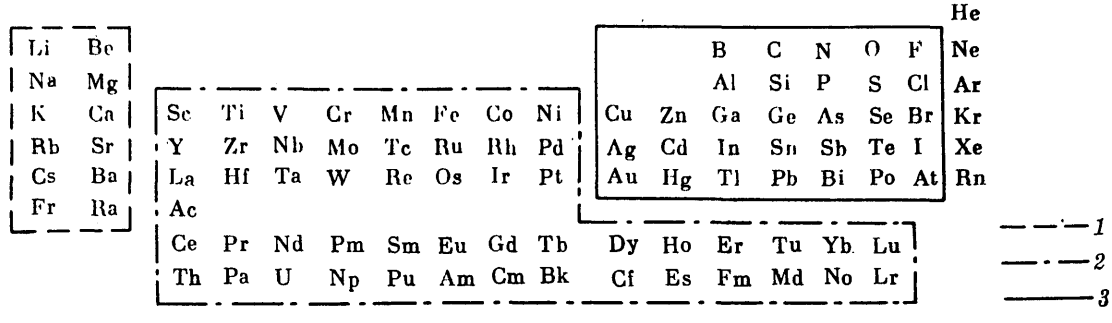


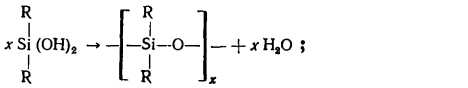
Figure 1. Distribution of the elements in groups as a function of the character of the bond between the atoms: 1) ionic bond type; 2) *d* orbital bond type; 3) covalent bond type.

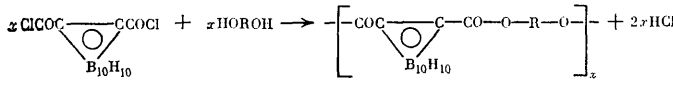
A characteristic feature of organolemeental polymers is the fact that whereas bonds of the $s-p-\sigma$ and $\sigma-\pi$ types are most characteristic of organic compounds, in organoelemental compounds there are also d orbital π-bonds: $d_\pi-p_\pi$ and $p_\pi-p_\pi$, where one or several free electron pairs of the atoms are bound directly to the atom of the element having unoccupied p_π or d_π low-energy orbitals and a suitable symmetry. There are also other types of interaction, which has been demonstrated in relation to numerous new types of compounds belonging to the groups of metallocenes, hydrides, carbaboranes, coordination polymers, etc.

Apart from the elements of the Second Period in the Periodic System, i.e. carbon, nitrogen, and oxygen, bonds of the p_π type are rarely encountered for other elements. Bonds involving $d_\pi-p_\pi$ orbitals are more common in organoelemental compounds, but such bonds are incapable of polymerisation. As a result of this, linear organoelemental polymers are usually synthesised by the polycondensation of bifunctional monomers or by the polymerisation of heterocycles. The advances in the synthesis of organoelemental polymers have been described in a series of reviews and monographs.[4,9-11,14-24]

Several different types of reactions have been used to synthesise organolemental polymers.

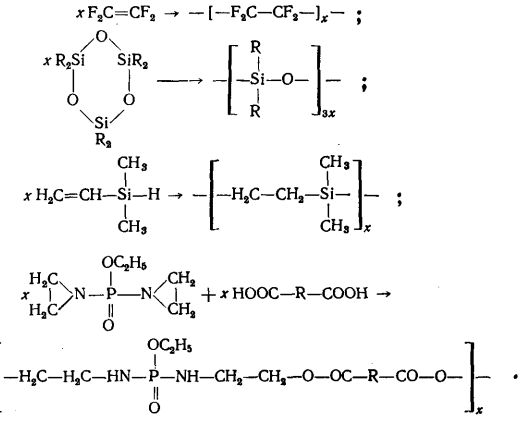
1. Polycondensation of monomers having two and more identical or different functional groups, for example:[25,26]



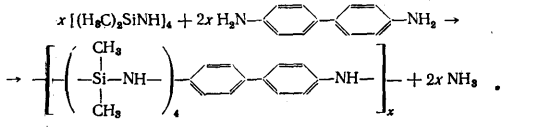


In this case heterochain organoelemental polymers are produced. Two versions of the reaction are then possible, namely "equilibrium" and "non-equilibrium" polycondensations differing in the magnitude of the equilibrium constant,[20,21] which is less than 10^3 for equilibrium polycondensation and more than 10^3 for non-equilibrium polycondensation.

2. Polymerisation of monomers having double bonds or heterocycles and also the migration copolymerisation of the hydrides of silicon and other elements, for example:



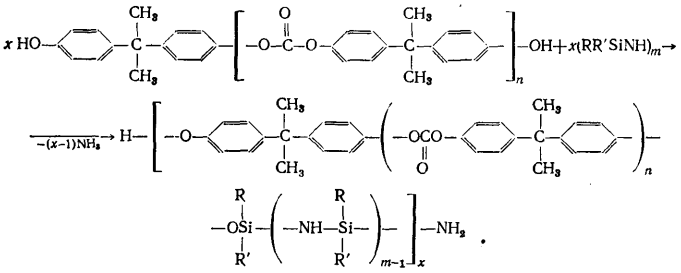
3. Combined polymerisation-condensation processes:



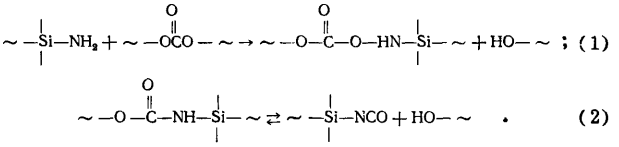
The reaction proceeds not only with the opening of the silazane ring (polymerisation) but also with evolution of ammonia (polycondensation).[27]

The studies[28-35] in which polymers with inorganic and organic molecular chains were obtained by combined polymerisation-condensation processes are of interest. Such polymers can be synthesised from organocyclosilazanes having the general formula $[RR'SiNH]_3$ and diamines or diols. The reaction proceeds both in the presence and absence of catalysts with evolution of ammonia and formation of Si–N bonds in the macromolecular chain. The products exhibit a high thermo-oxidative stability and, depending on the structure of the cyclosilazanes and diols are either solid rubber-like substances with high elasticity or viscous liquids.

The products of the interaction of organocyclosilazanes with oligocarbonate-diols have been described:[28]



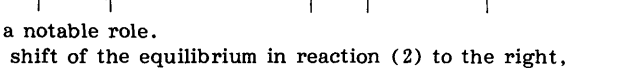
The polymers were obtained by reactions in solvents and in bulk. The reaction in bulk proceeds at a much higher rate but side reactions reduce the molecular weight of the polymer and lead to a less ordered structure of the latter owing to the degradation of the polycarbonate and silazane blocks and the appearance of urethane and isocyanate groups in the macrochain via the following mechanisms:



(1)

(2)

At higher temperatures the side reaction

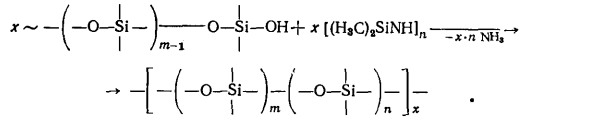


(3)

plays a notable role.

The shift of the equilibrium in reaction (2) to the right, which entails an increase in the concentration of OH groups capable of reacting with the less reactive NH groups in the linear sections of the chain, gives rise to the possibility of condensation reactions leading to the additional evolution of ammonia.

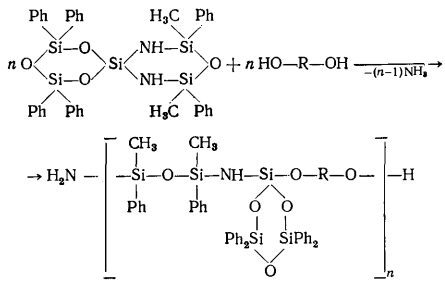
Not only organic diamines and diols but also organosilicon diols can be used in the reactions with diorganocyclosilazanes. Results of practical interest have been obtained by the reaction of $\alpha\omega$-dihydroxypolydimethyl(methylvinyl)siloxanes and dimethylcyclosilazanes:



The rubbers based on such polymers are superior as regards their physicomechanical parameters after thermal ageing to the rubbers based on industrial raw rubber.[29]

Polycarbonate-silazasiloxane block copolymers have been described.[30] They contain not only polycarbonate and silazasiloxane blocks but also urethane groups and have a branched structure.

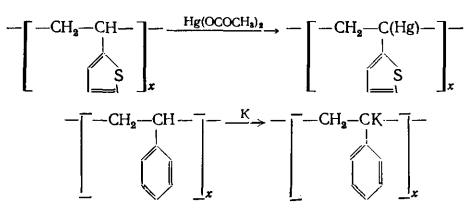
In connection with the different reactivities of the Si–N and Si–O bonds in relation to hydroxy-compounds,[31,32] studies of the polycondensation of organo-spiro-bicyclosilazasiloxanes with organic and organosilicon diols of different structure are of interest. In the ideal case the reaction proceeds via the scheme



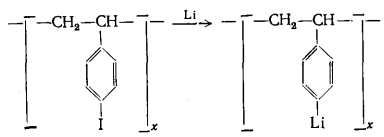
Polymers soluble in organic solvents and cross-linked polymers have been obtained. The block copolymers of organocyclosiloxanes with diols are of great practical interest for the development on their basis of thermostable greases, thermoplastic materials for the storage of information,[33] compositions for coatings,[34,35] etc.

4. The modification of polymers by treatment with metals and their compounds leads to the formation of various organoelemental polymers:

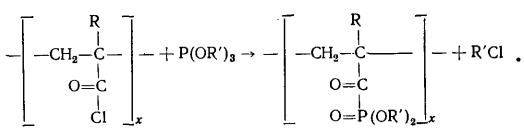
(a) By substituting hydrogen atoms in the polymer chain,[36,37] for example:



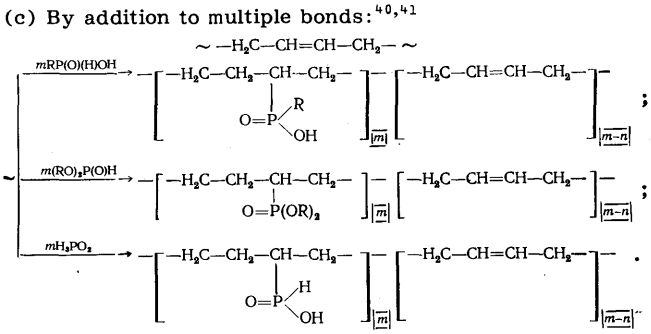
(b) By substituting iodine atoms in poly-p-iodostyrene:[38]



or by substituting chlorine atoms in the polymer:[39]

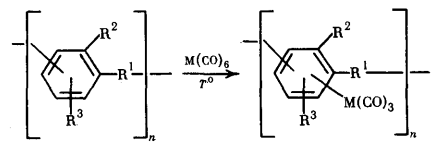


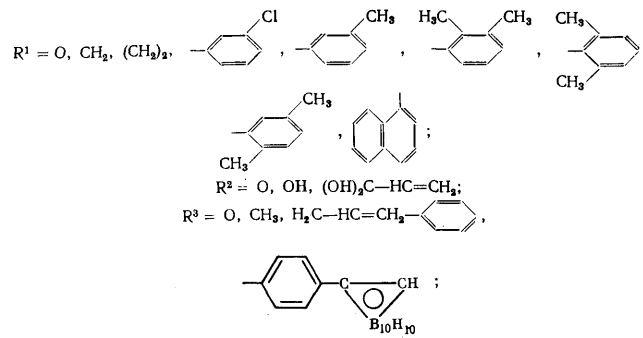
(c) By addition to multiple bonds:[40,41]



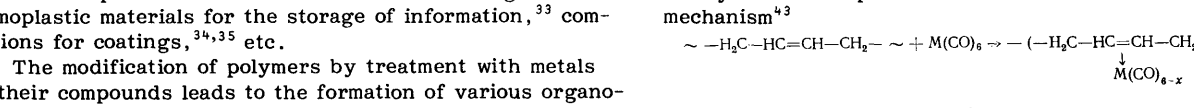
(d) By the π-complex formation reaction involving polymers.

π-Arenemetal tricarbonyl polymeric or oligomeric complexes have been obtained via the following mechanism:[42]





Polymeric π-complexes of metals are obtained via the mechanism[43]



The reactions of the chlorides of *o*-, *m*-, and *p*-carbaboranedicarboxylic acids with cellulose lead to the formation of the corresponding cellulose esters which are able to produce a residue on heating with a high "coke content".[44]

There exist also a wide variety of other modification reactions leading to the formation of organoelemental polymers. They all result in the formation of heterounit polymers.

IV. THE HETEROUNIT STRUCTURE OF ORGANOELEMENTAL POLYMERS

The concept of the heterounit structure of polymers is equally applicable to organoelemental polymers, as it is in fact to all other macromolecular compounds, being a general phenomenon in this field of chemistry.[45,46] The syntheses of polymers involve various side reactions leading to the formation of anomalous units and hence to the appearance of heterounit polymers. Various reactions and other causes responsible for the formation of anomalous units in the polymerisation and polycondensation of monomers and also in the modification of polymers are presented below. The statistical distribution of isotope atoms, which occurs in all polymers, should be added to this factor. As a result, a more correct formula for real polymers is as follows:

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

where M is the normal unit, A the anomalous unit and *m* and *n* are coefficients indicating the statistical distribution of anomalous units of different kinds. On the other hand, the formula usually employed, i.e.

$$-[-M-]_x-$$

is idealised and is never really valid.

The formation of heterounit polymers as a result of various side reactions proceeds differently depending on the character of the latter. This is clearly seen when the

characteristics of the polycondensation, polymerisation, and modification reactions are compared (Figs.2, 3, and 4). Each of these reactions involves numerous chemical transformations of different kinds which results in many different anomalous units and heterounit structures of different types. Fig.2 presents the set of polycondensation reactions, including numerous reactions leading to a heterounit structure.[45] Fig.3 presents the set of all the possible polymerisation reactions, including normal reactions and those resulting in a heterounit structure.[45] Finally, Fig.4 presents the set of modification reactions, including those resulting in a heterounit structure,[45] which happens mainly in incomplete substitution processes.

Set of polycondensation reactions	Normal polycondensation reactions	Onset of chain growth
		Chain growth
		Arrest of chain growth
	Polycondensation reactions and other causes of the formation of heterounit polymers	Branching of macromolecules
		Partial isomerisation of units
		Joint polycondensation
		Incomplete cyclisation in polyheteroarylenes
		Irregular structure formation in macromolecules
		Different combinations of asymmetric units
		Conformationally-specific polycondensation
		Steric disorder of units
		Dehydrogenation, dehydration, and dehydrochlorination of monomers and polymers
		Isomerisation of monomer
		Addition to the double bonds of unsaturated monomers and polymers
		Competing polycondensation reactions of various functional groups of polyfunctional monomers
		Non-uniformity in the involvement of the monomers in the reaction
		Programmed polycondensation
		Disturbance of natural programmed polycondensation processes (information errors)
		Statistical distribution of atoms of stable isotopes in polymer macromolecules
		Other side reactions

Figure 2. The set of polycondensation reactions.

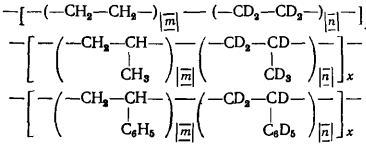
An important feature of organoelemental polymers, which is frequently encountered in practice, is the possibility of the formation of both linear and branched or three-dimensional polymers. This difference is determined by the functionality of the initial monomer or oligomer.[50] It is therefore necessary to distinguish the following types of functionality, namely the possible functionality Φ_p, the practical functionality Φ_{pr}, and the relative functionality Φ_r. When the possible functionality $\Phi_p = 2$, a linear polymer is produced whereas in the case where the values of the possible functionality are greater than 2 the product is a branched or a three-dimensional polymer.[51]

Set of polymerisation reactions	Normal polymerisation reactions	Onset of chain growth
		Chain growth
		Chain termination
	Polymerisation reactions and other causes of the formation of heterounit polymers	Branching of macromolecules
		Partial isomerisation of units
		Joint polymerisation
		Different combinations of units
		Stereospecific polymerisation
		Recombination of macroradicals
		Disproportionation of macroradicals
		Partial dehydrogenation of polymers
		Partial dehydrochlorination of polymers
		Partial dehydration of polymers
		Irregular structure formation in macromolecules
		Steric disorder of units
		Statistical distribution of atoms of stable isotopes in polymer macromolecules
		Other side reactions

Figure 3. The set of polymerisation reactions.

V. STABLE ISOTOPES AS A CAUSE OF THE HETEROUNIT STRUCTURE OF ORGANOELEMENTAL POLYMERS

Among the causes giving rise to a heterounit structure of polymers, mention should be made of the presence of stable isotopes of polymer-forming elements, which are distributed statistically in the macromolecular chain. The influence of isotopes has been demonstrated particularly strikingly in relation to the copolymers of ethylene, propene, and styrene by comparing them with their deuteriated analogues.[46-48] The copolymers have the following structures:



In all the cases investigated, a distinctive effect of the content of hydrogen isotopes on the properties of the polymers was observed.

Table 5 lists the stable isotopes of the elements used to synthesise polymeric structures.

Table 5. The stable isotopes of polymer forming elements.[49]

Element	Stable isotopes	Relative distribution, %
Hydrogen	H, D	H (99.984), D (0.016)
Boron	^{10}B, ^{11}B	^{10}B (18.8), ^{11}B (81.2)
Carbon	^{12}C, ^{13}C	^{12}C (98.9), ^{13}C (1.1)
Nitrogen	^{14}N, ^{15}N	^{14}N (99.6), ^{15}N (0.4)
Oxygen	^{16}O, ^{17}O, ^{18}O	^{16}O (99.76), ^{17}O (0.04), ^{18}O (0.20)
Silicon	^{28}Si, ^{29}Si, ^{30}Si	^{28}Si (92.6), ^{29}Si (4.3), ^{30}Si (3.1)
Chlorine	^{35}Cl, ^{37}Cl	^{35}Cl (75.4), ^{37}Cl (24.6)

Set of modification reactions	Normal modification reactions	Substitution of a hydrogen atom, a halogen atom, and a hydroxy-group
		Structure formation in polymers
		Exchange reactions of heterochain polymers
		Degradation of macromolecules
		Elimination of water, hydrogen halide, etc.
		Isomerisation of macromolecules
	Modification reactions and other causes of the formation of heterounit polymers	Incomplete substitution of a hydroxy-group, a hydrogen atom, a halogen atom, etc. in the polymer macromolecule
		Grafting to macromolecules
		Partial oxidation of macromolecules
		Irregular structure formation in macromolecules
		Partial degradation of macromolecules
		Incomplete exchange in heterochain polymers
		Partial structure formation in polymer
		Partial addition to multiple bonds
		Partial elimination of water, hydrogen halide, etc.
		Incomplete isomerisation of macromolecules
		Statistical distribution of atoms of stable isotopes in polymer macromolecules
		Other side reactions

Figure 4. The set of modification reactions.

VI. SURVEY OF POLYMERS IN TERMS OF GROUPS IN THE PERIODIC SYSTEM

The organoelemental polymers known at the present time are divided into two large groups depending on the structure of the main chain—homochain and heterochain polymers.[9,11] Among homochain polymers, the group with the largest number of representatives is that of carbochain polymers. Homochain polymers based on other elements are extremely few in number and are not quite so important. However, we may mention that homochain polymers of the following eight elements are known at the present time: C, B, Si, Ge, P, S, Sb, and Se.

Heterochain polymers based on a large number of elements in the periodic system are a much more important class of organoelemental polymers. Almost all the elements are capable of forming heterochain polymers. Various polymers of the elements in the Periodic System, starting from Group I and extending to Group VIII, are now known. Heterochain polymers containing the following Group I elements have been described: H, D, Li, Na, K, Cu, and Ag. Among them, the copper and hydrogen compounds are of practical importance. Polymers containing isotopes of various elements are of considerable interest for the understanding of the characteristic features of the reactions and properties of polymers.[46-49] Thus polymers containing a heavy hydrogen isotope (deuterium) are important for the explanation of the heterounit structures of a series of polymers. "Heavy" polymers in which the hydrogen has been fully or partly substituted by deuterium have been obtained with the aid of this procedure. The properties of such "heavy" polymers differ significantly from those of their hydrogen analogues.[46-49] "Heavy polyethylene", "heavy polypropylene", and "heavy polystyrene" have been obtained in this way:[46-49]

$$-\left[-CD_2-CD_2-\right]_x- \quad -\left[-CD_2-\underset{CD_3}{CD}-\right]_x- \quad -\left[-CD_2-\underset{C_6D_5}{CD}-\right]_x- .$$

Heterochain organoelemental polymers containing the following Group II elements are known: Be, Mg, Zn, Ca, Ba, Cd, and Hg. Homopolymers and copolymers of metal-containing alkali and alkaline earth metal (Ca, Sr, and Ba) monomers have been described.[52-54] Magnesium compounds have found particularly extensive applications in organic synthesis.

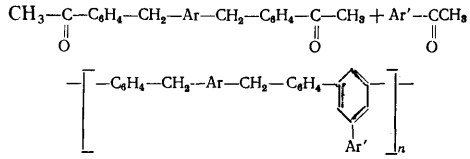
Polymers containing B, Al, Ga, Ce, and Tl are known for Group III elements. Polymers containing boron and aluminium have attracted particular attention among them. The formation of coordination polymers as well as a wide variety of condensation reactions leading to the formation of macromolecular compounds are characteristic of Group III elements.

The homochain polymers of boron, whose main chian consists only of B–B bonds, constitute a group of polymers with a small number of representatives, which can apparently be accounted for by their tendency to oxidise and hydrolyse.[55,56] Depending on the molecular weight, the polymers are colourless or yellow or brown powders. Some polymers are soluble in organic solvents, but no solvents have been found for the majority of them. The thermal stability of the polymers with B–B bonds does not exceed 200 °C. Heterochain boron compounds with B–C bonds have not found practical application because of the considerable tendency of the B–C bond to hydrolyse and, in aliphatic compounds, to oxidise.

Polymers containing polyhedral borane groups have appeared only in the last 15–20 years. The information available in the patent literature indicates their possible use as protective coatings on glass, wood, metals, and other surfaces.[57] In compositions with other polymers, they can be used as thermostable rubbers[57] or as highly effective rocket fuel.[58]

The discovery of carbaborane was the first step towards the creation of a new field of the chemistry of organoboron polymers containing carbaborane fragments. Carbaborane-containing polymers are obtained by both polymerisation and polycondensation methods. However, the polycondensation method of synthesis has come to be most widely used. Among the carbaborane-containing polymers of the polycondensation type, polyphenylenes,[59-63] phenol-formaldehyde polymers,[64-67] polyesters, polyamides,[68-76] and polysiloxanes[77-87] have been most thoroughly investigated at the present time.

Polyphenylenes, the first stage in the synthesis of which can be represented schematically in the following manner have been described:[59,60]



where Ar = *o*-, *m*-, or *p*-carbaboranylene and Ar′ = phenyl, benzyl, or *o*-, *m*-, and *p*-carbaboranyl.

It has been noted[59,60] that the polycondensation reactions of the above compounds proceed unambiguously and are accompanied by the formation of dyphone and also linear and cyclic polyvinylene fragments. The oligophenylenes synthesised contain *o*-, *m*-, or *p*-carbaborane groups in the main macromolecular chain and in some cases also in the side chain and are highly soluble in many organic solvents. All the carbaborane-containing oligophenylenes have low molecular weights (MW = 1100–4600) and their softening temperatures are in the range 150–220 °C; at 400–500 °C in an inert atmosphere in the course of 4 h or in a pressing process involving heating to 400–450 °C (and a pressure of 1000 kg cm^{-2}), they are converted into infusible and insoluble three-dimensional polymers as a result of their interaction via terminal acetyl and ketyl groups. Polyphenylenes with *o*-, *m*-, and *p*-carbaborane fragments in the main chain exhibit an enhanced adhesion to glass fibre, which amounts to 250–350 kg cm^{-2}, and have been recommended as thermostable binders for glass plastics.[60]

Oligophenylenes containing carbaborane fragments in the side chain have been obtained.[59,62] The authors noted that the introduction of carbaborane fragments into the side chain of polyphenylene increases the thermal stability of the latter, but this effect is smaller than for the polyphenylenes containing carbaborane groups in the main macromolecular chain.

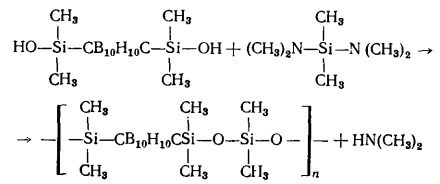
In order to simplify the synthesis of polyphenylene with *o*-carbaborane frgaments, the more readily available ethyl ketal or acetylbiphenylyl-*o*-carbaborane has been used instead of 4-acetylbenzyl-*o*-carbaborane, the synthesis of which is technologically complex.[61,63] The oligophenylenes obtained were less soluble in organic solvents but their thermal stability proved to be greater.

Studies on the synthesis and properties of carbaborane-containing phenol-formaldehyde oligomers of the resol type have continued in recent years.[64,65] The chemical reactions occurring in resols and resites based on 1,2-bis(4-hydroxyphenyl)-*o*-carbaborane on heating under various conditions have been studied. It has been established that in the temperature range 50–200 °C the formation of resol structures proceeds via the usual mechanism not involving the *o*-carbaborane groups. Above 200 °C, significant chemical transformations of the *o*-carbaborane fragments of resites take place and the degree of conversion depends on the heating conditions (in air or *in vacuo*). The high-coke residue from *o*-carbaborane-containing resites its due to the oxidation of the B–H bond in the *o*-carbaborane nuclei, which has been confirmed by X-ray diffraction and EPR data.[64–66] Adhesives with a high strength and thermal stability have been obtained from *o*-carbaborane-containing resol oligomers.[67]

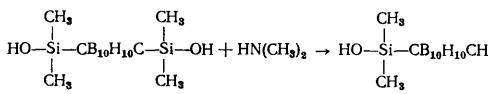
There has been an increase of interest recently in the study of the properties of the polyesters and polyamides with carbaborane fragments obtained previously.[68–76] The structural-chemical transformations of *o*- and *m*-carbaborane-containing polyarylates on isothermal heating in the temperature range 225–235 °C have been investigated by infrared spectroscopy. It has been established that processes involving the rupture of the ester linkage, changes in the carbaborane fragments (a change in the B–H bond and the appearance of the B–O–B bond), and the formation of cross-linked structures take place at a temperature as low at 225 °C. A comparative study of the thermal stabilities of polyarylates with various structures has been carried out.[70] Problems concerning the chemical stability of polyamides with carbaborane-containing fragments and their anti-friction properties have been examined.[71–76]

The most numerous and best investigated class of carbaborane-containing polymers is that of carbaboranesiloxane polymers. Investigations of the synthesis of *m*-carbaborane-containing polysiloxanes of the "Dexsil" type and of their properties are being continued vigorously. The difficulty of the synthesis and vulcanisation of these polymers, in which a high thermal stability is combined with elasticity, prevents their practical application.

A new method of synthesis of linear "Dexsils" is based on the condensation of an *m*-carbaborane-containing disilanol with a reactive silane, for example, bis(*NN*′-dimethylamino)-dimethylsilane or bis(*NN*′-dimethylcarbamato)dimethylsilane, under mild conditions:

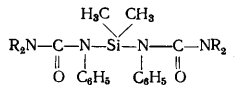


The side reaction

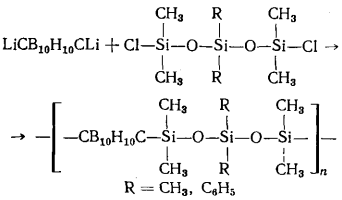


prevents the formation of "Dexsils" with higher molecular weights.

"Dexsils" with molecular weights in excess of 25000 have been synthesised using stable bis(ureido)silanes as reactive silanes:[77,78]



Another, very convenient method of synthesis of "Dexsils" directly from *m*-carbaborane via the following mechanism has been proposed:[79]



However, the molecular weights of the polymers thus obtained are low.

Studies have been made of the thermal, thermo-oxidative, and hydrolytic stabilities of poly-*m*-carbaboranylene-siloxanes.[80,81] The practical value of poly-*m*-carbaboranylenesiloxanes, in which a high thermal stability (up to 500 °C) is combined with excellent fire resistance (oxygen index 62), has been noted in Peters' review.[82] These polymers have found extensive applications as liquid phases in gas chromatography for the separation of organosilicon and

organic substances[83] and for the analysis of polycyclic aromatic hydrocarbons.[84]

Adhesive compositions, capable of being used for a long time at 600 °C and of withstanding a temperature of 1200 °C for brief periods, have been produced on the basis of *m*-carbaborane-containing polysiloxanes.[85] Poly-*m*-carbaboranylenesiloxanes are used for the coating of conductors and other articles which have to withstand a temperature of ~300 °C[82,86] and also as lubricating materials for high-temperature nuclear equipment.[87]

Thus the literature data published in recent years permit the conclusion that boron-containing polymers and particularly carbaborane-containing polymers have attracted the attention of investigators. The study of the properties of these polymers and their modifications and the search for new simpler ways of synthesising them are of particular interest.

Polymers containing the following Group IV elements have now been synthesised: C, Si, Ti, Ge, Zr, Sn, and Pb. This group of polymers has the greatest number of representatives: polymers containing carbon and silicon are of particular importance in practice.

The continued interest in the creation of new materials with a set of valuable properties, some of which are characteristic of organosilicon polymers (frost resistance, thermal stability, permeability, etc.) has stimulated further development of studies on the synthesis and properties of polyorganosiloxanes and copolymers based on them.[88]

The polydiethylsiloxane rubber, which has been studied in detail recently,[89,90] has extremely interesting properties. The properties of various block copolymers containing fragments of the polydiethylsiloxane chain as a flexible block have attracted attention. Polycarbonate-siloxanes, polycarbonate-urethane-siloxanes, polysulphone-siloxanes, and polyarylate-siloxanes have been most thoroughly investigated and have been adequately described.[91,92]

Polyorganosiloxanes containing metal atoms in the polymer chain have found extremely varied practical applications.[93] Polyaluminoorgano-siloxanes are used as catalysts of the hardening of various organosilicon oligomers.[93] Polystannoorganosiloxanes are employed as hydraulic liquids, thermostable coatings, inhibitors of the oxidation of siloxane liquids, and modifying agents for rubber mixtures based on siloxane raw rubbers.[93] Polytitano-organosiloxanes, polyvanadium-phenylsiloxanes, and polyzirconium-aluminophenylsiloxanes are effective catalysts of various processes.[93] A technology for the industrial manufacture of many polymers has been developed.[94]

Among polymers containing Group V elements, extremely numerous and practically important products with elements such as N, P, As, Sb, and Bi are encountered. Among them the nitrogen and phosphorus compounds are especially important. The introduction of a phosphorus atom into the macromolecules of various polymers makes it possible not only to imporve their important properties such as thermal stability and colour fastness,[95] fire resistance,[96] hydrophilicity,[97] and physicomechanical indices but also to synthesise polymeric materials capable of ion exchange as well as polymers possessing oxidation-reduction properties and biological activity.[98]

Phosphorus-containing polymers can be synthesised by polymerisation, polycondensation, and chemical modification methods. The copolymerisation of unsaturated organic monomers with an organophosphorus monomer is one of the promising ways of obtaining organophosphorus polymers, which permits an extensive modification of the properties of various polymeric materials.

Organophosphorus monomers enter into the free-radical copolymerisation reaction with virtually all the usual vinyl monomers and the introduction of small amounts of phosphorus frequently imparts new and valuable qualities to the polymers. The diene, methacrylate, and styrene derivatives of phosphorus are of greatest interest for copolymerisation.[99]

Depending on the chemical nature of the fragments incorporated in the copolymer chain, the copolymers of phosphonodienes are plastics or rubber-like materials and, by virtue of the presence of polar phosphoryl groups, they exhibit an improved adhesion to glass, metals, and other surfaces. When phosphonodienes are introduced into a copolymer, the most significant effect is manifested in the improvement of the fire resistance of the material. Methods for the preparation of transparent colourless, incombustible organic glasses have been developed on the basis of copolymers of methyl methacrylate and phosphono-2,3-dienes.[99]

The introduction of phosphorus-containing groups into the polymer chain leads to the self-stabilisation of polymers.[100] The introduction of such groups via the copolymerisation of the monomers has not so far become of great practical importance. However, this procedure has significant advantages in special methods for the processing of polymers, in particular for the formation of poly(vinyl chloride) materials from solution.[101]

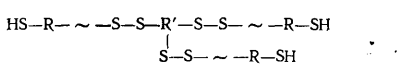
The most important feature in the chemical modification of polymers involves the introduction of phosphorus-containing groups via polymer-analogue reactions.[41,102] Phosphorylation of synthetic rubbers increases their thermal stability and lowers their combustibility.[100] Phosphorylation of chlorosulphonated polyethylene greatly improves its technological properties and strength parameters.[100] The study of the phosphorylation reactions of chloromethylated polystyrene and the copolymers of styrene with aromatic vinyl compounds has shown that the polymers obtained possess ion-exchange properties, effective mechanical properties, and improved porosity and thermal stability.[100] The phosphorylation of polymers at the stage in which degradation processes develop gives rise to a secondary stabilisation of the polymeric products and improves their operating characteristics.[100]

There has been an appreciable growth of interest in the last decade in polyphosphazenes—polymers with inorganic main molecular chains consisting of alternating phosphorus and nitrogen atoms in organic or organoelemental frameworks surrounding the phosphorus atom. The interest in these polymers is due to their high thermal stability and fire resistance,[104] their effective elastic properties,[105] and their improved resistance to degradation by oxidants and reductants.[95]

The use of polyphosphazenes for medical purposes, which has been developing in two directions, is of great interest. The first application involves the study of their biological compatibility and thrombogenic properties in order to elucidate the possibility of using such polymers in surgery. Thus the high stability of polyfluoroalkoxyphosphazene as regards clotting, compared with ftoroplast-4 [a type of PTFE] and polyethylene for medical purposes has been demonstrated.[106] In combination with the constancy of its physicomechanical and mechanical properties after prolonged contact with a medium close in composition to that of blood, this renders this polymer extremely promising for the manufacture of articles used in vascular surgery. The other type of research on polyorganophosphazenes for medical purposes involves the synthesis of polyphosphazenes as carriers of medicinal drug molecules and as absorbable surgical materials.[107]

For Group VI elements, polymers containing O, S, Cr, Se, Mo, W, and U are known; the most important of these are oxygen- and sulphur-containing polymers. The great interest of investigators in sulphur-containing polymers and their increasing practical use are associated with their valuable properties and the ready availability of the raw materials combined with the simple methods of their synthesis.

Interesting representatives of sulphur-containing polymers are polysulphide oligomers containing sulphur in the main chain. The majority of industrial polysulphide oligomers have a weakly branched structure with terminal SH groups:



The presence of such end groups, which are readily oxidised under mild conditions makes it possible to employ these oligomers as a basis for the preparation of composite materials (materials for hermetic seals, mastics, and casting compositions).[108]

The different operating conditions for hermetic materials of different brands are striking. Thus the minimum operating temperature varies from −30° to −60 °C, while the maximum operating temperature varies from +80° to +140 °C. The difference between the minimum operating temperatures of hermetic materials can be accounted for by the recipe specifying their composition. The maximum operating temperature usually depends on the presence, type, and amount of the modifying additive, the type of vulcanising agent, and the filler. Polysulphide oligomers are non-toxic, burn with difficulty, and are non-explosive. Hermetic materials based on them do not have a harmful effect on man.[109]

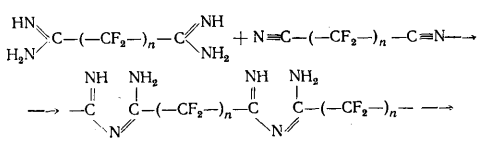
Among the polymers containing Group VII elements, compounds with F, Cl, Br, I, and Mn are known, those containing fluorine and chlorine being most widely used. Many fluorinated plastics play an important role in the development of modern technology.

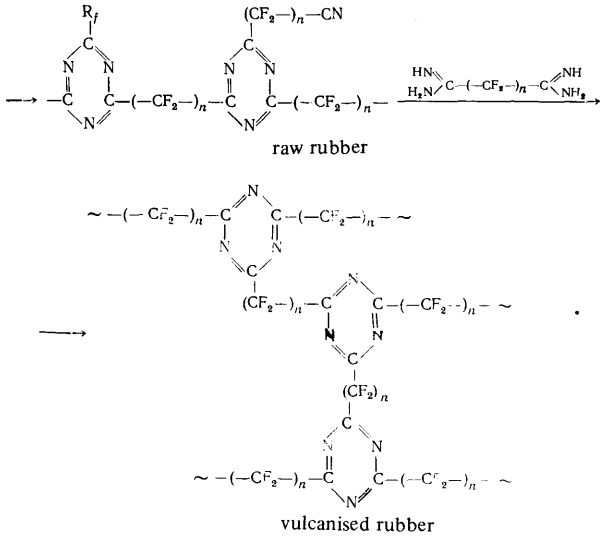
Carbochain fluorine-containing polymers are most widely used at the present time. Among them, polytetrafluoroethylene (PTFE) is the most thermostable polymer. It is resistant to the action of oxygen up to comparatively high temperatures, but it is a high-melting crystalline material and becomes ealstic only at temperatures close to the decomposition temperature. Despite its unique properties, the making of articles from PTFE is fairly difficult. Methods based on sintering an mechanical treatment are largely employed.

In order to obtain elastomers from fluorinated hydrocarbons, it is necessary to disturb the regularity of the structure of the polymer chain in order to rule out or diminish crystallisation. For this purpose, various "hinged" groups are introduced by copolymerising PTFE with fluorinated or non-fluorinated monomers. Tetrafluoroethylene copolymerises effectively with both fluorinated and non-fluorinated monomers, forming numerous copolymers with a wide range of valuable properties. In recent years it has been possible to create a series of tetrafluorethylene copolymers which, whilst retaining many of the valuable properties of PTFE, can be worked with the aid of the usual equipment.[110]

The introduction of the triazine ring into chains of perfluorinated polymers makes it possible to increase the thermal stability of the raw rubber and gives rise to the possibility of obtaining rubbers whose vulcanisation network has a thermal stability not inferior to that of the main chain. Methods are known for the introduction into some of the triazine rings of perfluorinated groups with functional substituents, which can be employed for vulcanisation.[110]

The starting material for the preparation of perfluoroalkylenetriazine rubbers consists of the dinitriles of perfluorinated dicarboxylic acids:





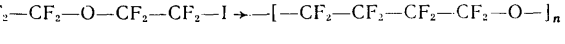
raw rubber

vulcanised rubber

According to literature data the rubbers produced from triazine raw rubbers retain a fairly tensile strength after heating for a long time. Perfluoroalkylenetriazine raw rubbers are resistant to the action of strong acids, but are decomposed by bases, including ammonia.

Apart from the triazine ring, other heterocyclic systems can be introduced into the polymer chain; oxadiazoles, benzimidazoles, thiadiazoles, pyromellitimides, etc.

Perfluorinated rubber-like polymers based on olefin oxides can be synthesised from diiodo-derivatives in the presence of mercury on irradiation with ultraviolet light. The resulting elastomer has excellent low-temperature properties and a high thermal stability:[110]



Despite the interesting properties of this elastomer, it is only a model compound, because of the difficulty of obtaining the initial diiodo-derivatives. A method of synthesis suitable for practical application has not yet been found.

Fluorinated olefins are usually copolymerised with tetrafluoroethylene or vinylidene fluoride in an aqueous emulsion and it is also possible to carry out the process in a solvent.

At temperatures up to 200–250 °C, the structure of the raw fluororubbers does not undergo appreciable changes for a long time. In terms of their resistance to organic liquids, particularly at high temperatures, the rubbers prepared from the raw fluoro-rubbers are appreciably superior to the rubbers obtained from all other sources. In view of the extremely wide range of applications of raw fluoro-rubbers (materials for hermetic seals), their most important parameter is the residual compressive deformation. Because of this, investigators have concentrated their efforts on improving this characteristic.

Group VIII elements of the Periodic System which have entered into the compositions of polymers synthesised are iron, cobalt, and nickel. The three elements form part of various thermostable coordination polymers whose properties are determined by the chemical nature of the ligand and the metal forming the coordination centre.

The infusibility and insolubility of the majority of the coordination polymers restrict their wide-sclae application. Studies designed to obtain metal complex iron, cobalt, and nickel polymers without their conversion into a three-dimensional structure, which ensures the retention of solubility by the polymers, are therefore of great interest.[111,112] The polymeric complexes synthesised contain metal carbonyl

fragments in the polymer chain, are soluble in organic solvents, and are capable of forming strong films and coatings with a high degree of adhesion to glass and metals. After the films have been subjected to a heat treatment, they undergo structure formation and an increase in strength and the polymer acquires at the same time new properties. Thus the decomposition of the iron tricarbonyl complex in the polymer matrix involves the formation of a metallic phase and the film acquires ferromagnetic properties.[113]

Metal-containing polymers have found applications in a wide variety of fields: an application associated with the improvement of various properties of polymers and compositions based on them and an application based on the appearance of new properties due to the presence of the metal in the main chain or a side chain.[21]

It is thus clear that the development of the fields of organoelemental polymers has now placed at the disposal of polymer science a considerable number of organoelemental polymers, many new examples of which are being added each year.

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In conclusion of the discussion of the advances in the synthesis and investigation of organoelemental polymers, we may conclude that a new major field of polymer science has now arisen and is developing vigorously.

At the present time this field embraces a large number of organoelemental polymers, for the synthesis of which 75 elements of Mendeleev's Periodic System have been used and the number of polymers of this type increases rapidly. Organoelemental polymers are substances with a wide range of specific properties which depend both on their composition and on their chemical structure.

As a result of the wide-scale application of the elements of the Periodic System in the synthesis of polymers, not only a quantitative growth and the appearance of many new qualitative changes in the structure of the groups forming the polymer macromolecules but also the appearance of a new set of properties have been observed.

The considerable advances in the synthesis and study of groups of organoelemental polymers such as polysiloxanes, polymetallosiloxanes, phosphorus-containing polymers (including polyphosphazenes), organoboron (including various polycarbaboranes), organosulphur, and coordination polymers of the chelate type (including polyferrocenes), as well as polymers incorporating various fluorocarbons and their copolymers must be specially emphasised.

Organoelemental polymers include a large group of thermostable polymers, a series of substances with valuable biological properties, and also substances with a high electrical conductivity and semiconducting properties, a high elasticity, and an oustanding strength and hardness.

The main task of the investigators concerned with polymers is the expansion of the range of organoelemental macromolecular compounds, the development of new and improvement of existing methods of synthesis of such substances, and the study of their properties with the aim of their practical application.

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