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TRANSLATION

NEWS IN THE SYNTHESIS OF ORGANO-ELEMENTARY HIGH MOLECULAR COMPOUNDS

By

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FTD-TT- 63-121/1+2 Date 4 April 19 63

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News in the Synthesis of Organo-Elementary High Molecular Compounds

by

V. V. Korshak

Elemento-organic chemistry as a field of organic chemistry, not confining itself only to elemento-organogens, such as carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine and other halides, and placing in the service of organic synthesis the entire abundance of the periodic system of elements has been formed only in the past two-three decades[1]. In conformity with this the chemistry of elemento-organic high molecular compounds represents a still quite young field, and rapid development of same is explained by the fact, that many high molecular elemento-organic compounds are distinguished by high heat resistance, chemical stability and other interesting qualities, thanks to which they are finding practical application.

To satisft the needs of new technology is required a greater number of polymers with very high quality indices, namely; high heat resistance, chemical stability, greater mechanical strength, presence of electroinsulation, semiconductor and other properties.

One of the ways of solving this problem is the use of various elements for the synthesis of polymers and inclusion in this field of all elements of the periodic system[2].

At present time are manufactured in industrial scale and finding various application such elemento-organic polymers, as polymers and copolymers of fluorinated ethylene (vinylfluoride, vinylidenefluoride, tetrafluoroethylene, trifluorochloroethylene, perfluoropropylene etc.)numerous silicon-organic polymers, orthotitanic acid ester base polymers, polyphosphonitrilechlorides, phosphorylated polystyrene and others[3].

Elemento-organic compounds represent a field lying in between organic and inorganic chemistry[4], which equally pertains to elemento-organic polymers.

If in the past the basic development of polymeric chemistry followed the line of organic compounds, at present time inorganic high molecular compounds are attracting more and more attention and the field of inorganic polymers is gaining in development[5].

Elemento-organic high molecular compounds, known at present time in conformity with the classification introduced by us [6] can be divided into two groups.

The first group-homochain polymers, among which the most important are carbo-chain highmolecular compounds, macromolecules of which consist of carbon atoms, and all other elements appear to be substituents in these carbon atoms, which can be expressed by the following formula:

$$\left[\begin{matrix}-CH_2-&CH-\\ &|\\ &X\end{matrix}\right]_n$$

where X - substituent, containing various elements.

All other known at present time homochain polymers are not durable and present no practical interest. Although we known of low molecular polymers of the type $\left[\begin{matrix}-\text{Э}-\\ ||\end{matrix}\right]_n$ for the following elements[2]: silicon, germanium, tin, nitrogen, phosphorus, arsenic antimony and sulfur.

The second group of elemento-organic high molecular compounds-heterochain compounds of the type: $(-\text{Э}_1-\text{Э}_2-)_x$, where Э_1 and Э_2 - atoms or groups containing one or several different elements.

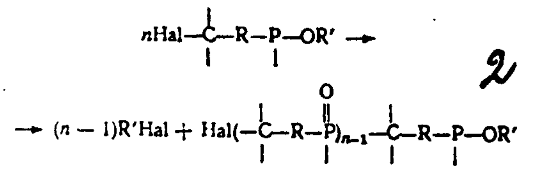
The second group is very numerous and it includes a majority of known at present time elemento-organic compounds.

Successes in the field of synthesizing and employing elemento-organic monomers and polymers are described in many reviews [3,7-9] and monographies [10-16]. Consequently this report will discuss only more important investigations in this field and briefly describe the most interesting results, obtained very recently.

Methods of Synthesizing Elemento-Organic High Polymers[3]

The basic method of synthesizing heterochain elemento-organic polymers appears to be polycondensation, with the aid of which are mainly obtained all possible silicon organic and other polymers, with inorganic chains including.

One of the new types appears to be polycondensation on the base of the A.Ye.Arbuzov reaction, investigated by M.I.Kabachnik[17] and coworkers, with the transition of tri-valent phosphorus into pentavalent in accordance with scheme:



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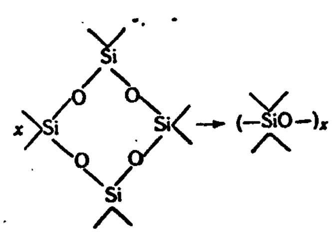
As result of this reaction is formed a group of heterochain phosphoro-organic polymers.

Polymerization does not offer the possibility of obtaining heterochain elemento-organic polymers, because there is still no knowledge about monomers, containing the carbon-metal double bond of the type >C = Э<.

But with the aid of polymerization are obtained carbochain elemento-organic high polymers, having elements in the side chains and in form of substituents.

In recent years appears a series of new methods of synthesizing elemento-organic high polymers. Great application has been acquired by the method based on polymerization of cyclic compounds. This method is widely used for the synthesis of high molecular silicon organic compounds[18]



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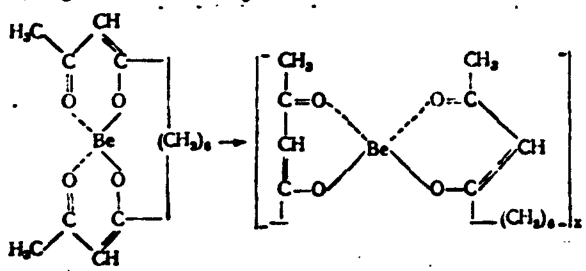
This reaction is realized in presence of acid catalysts.

Polymerization of cyclic trimers and tetramers serves as one of the methods of obtaining polyphosphoronitrilechloride and its derivatives [97].

It was shown recently[19] that the method of polymerizing cycles is also suitable for the obtainment of coordination polymers. In this case are first obtained cyclic-monomers and dimers which later polymerize easily when heated in melted state



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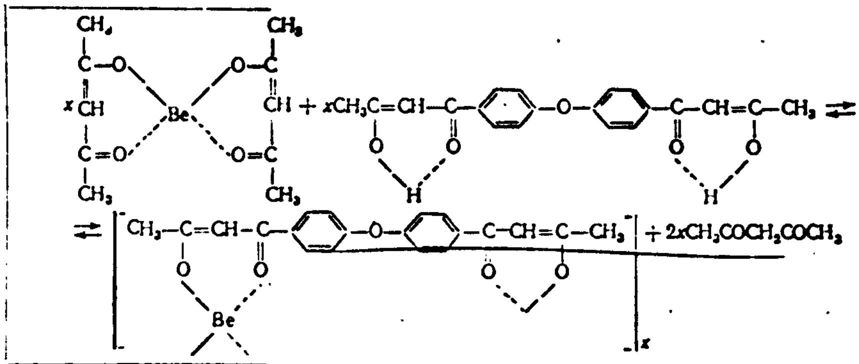
Greater development was attained by polycoordination, leading to obtainment of coordination polymers containing various metals. In role of organic ligands are used tetraketones, oxyketones, bisaminoacids etc, compounds containing complex forming groups. These polymers may also contain metals, such as copper, iron, cobalt, nickel, cadmium, zinc, beryllium etc.[20].

Polycoordination represents one of the cases of equilibrium reaction and is subject to the very same laws[21]. In particular, the molecular weight of coordination polymers depends upon the ______ completeness of removing the low-molecular product, as it was established on an example of the following reactions[21]:

See attached page (4a) for Formula 5

Polyrecombination represents a new method of obtaining high molecular compounds, which, as was shown, is suitable also for the obtainment of elemento-organic polymers [21-23]. With the aid of this method were obtained polymers, containing iron, boron, phosphorus, beryllium and others.

Reaction takes place during the heating of a proper monomer with organic peroxide



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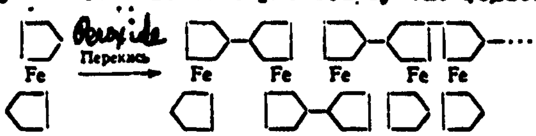
and for the case of obtaining polyferrocene it is expressed by the following equations:



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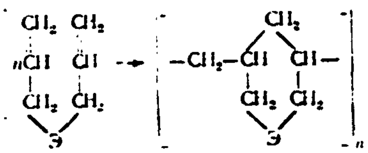
Cyclopolymerization is successfully employed for the obtainment of elemento-organic polymers containing heterocycles in the chains, and it takes place according to equation[24]:



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where Э- atom of the element. With this method were obtained[24] soluble polymers from dialylphenylphosphineoxide and dimetallylphenylphosphineoxide.

During the action of a complex catalyst $(C_2H_5)_3Al+TiCl_4$ were obtained[25] polymers from dimethyldiallylsilane.

It was shown[26], that stereoregulation of polymerization is suitable for the synthesis of elemnto-organic isotactic high molecular compounds, containing silicon and other elements in the side chain of type

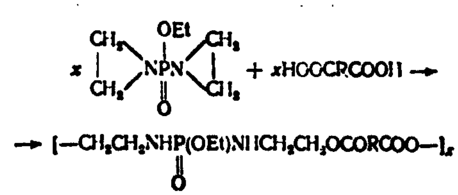
$$\left(-CH_2-\underset{\displaystyle Э}{\underset{|}{CH}}-\right)_x \qquad 8$$

The new method of obtaining elemento-organic polymers appears to be migrational copolymerization of hydrides of such elements, as silicon, phosphorus, tin, boron with unsaturated compounds [27-29]:

$$x\,CH_2{=}CH\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}H \rightarrow [-CH_2-CH_2-Si(CH_3)_2-]_x \qquad 9$$

This reaction is easily realizable also in case where instead of olefines is used acetylene and its homologues[30].

An interesting case of migrational copolymerization is the synthesis of phosphorcontaining polymers in accordance with the reaction, introduced by Grechkin[31]. The basic monomer is diethyleneamide of phosphoric acid, which easily attracts dicarboxylic acids, diamines etc. compounds



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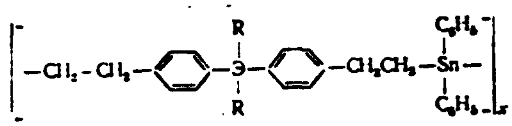
With the aid of migrational copolymerization of dihydride of diphenyltin with d-p-styrene derivatives of germanium, tin and lead were obtained[32] heterochain polymers of the type:



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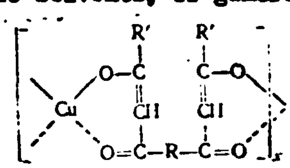
where Э- Ge, Sn or Pb.

Together with above mentioned synthesis methods of the monomers greater development is gained by the synthesis of elemento-organic polymers from ordinary organic carbochain high molecular compounds by introducing into their macromolecule different elements using this or any other method.

Polymers of Elements of the First Group of the Periodic System

In this group are known polymers, containing copper, silver, potassium and lithium. The most widely investigated heterochain polymers of copper, belong to the group of coordination polymers. They are obtained by the reaction of cupric salts or cupric acetyl acetonate with various bifunctional complexones.

Particularly thoroughly investigated were coordination polymers, obtainable with the aid of various tetraketones[33-37]. They represent green color powders, melting at 200-400° and in greater part insoluble in organic solvents, of general formula:



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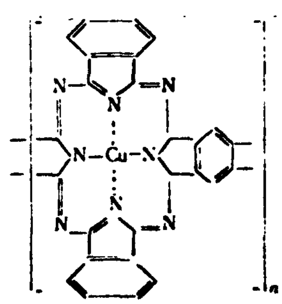
Of great interest is another group of polymers, namely polymeric phthalocyanates of copper, as for example[38]



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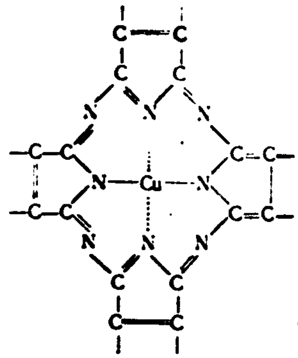
These polymers can withstand a temperature of over 500°.

The obtained [37] coordination polymers of copper and tetracyanethylene, represent a nonmelting black powder of the structure:

See attached page 6a. for Formula 14.



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Next, are known carbochain polymers, containing alkali metals. They are obtained from the reaction of polystyrene with metallic potassium in presence of potassium oxide[39,40].

Known is also polylithiumstyrene. It is obtained from polyiodine-or-bromostyrene by the action of butyllithium[39,41]. Polylithiumstyrene appears to be a highly reactive substance, capable of replacing lithium by various groups. As results of this was obtained a greater amount of products, representing polystyrene, containing in ortho-and para positions in the nucleus different groups. In this way are introduced alkyl, nitrile, carboxyl, amide, epoxy, ketone and other groups, as well as trimethylsilyl, mercapto group, trialkyltin and others[39].

Polymers of Elements of the Second Group of Periodic System

Quite a number of polymers is known, containing beryllium, zinc, cadmium and mercury. A larger group is formed by polymers, in which these metals are bound in form of a complex with tetraketones, phenols, amines, as well as other organic bifunctional complexones [20,33-37,112].

Of special interest are polymers, obtained [21] from p,p'-bis-(Acetoacetyl) of diphenyl ether and beryllium acetylacetonate. Investigation of this reaction showed that it is fully subject to the very same laws, which are charact-ristic for equilibrium polycondensation. Using equivalent amounts of initial products and assuring maximum removal of acetylacetone, it was possible to obtain the present easily soluble high polymeric compounds of beryllium with molecular weight of more than 125 thousand[21].

Synthesized were complex "cyclic" monomeric compounds. Polymerization of same during heating led to the synthesis of a number of very high molecular complex compounds of beryllium[19].

Polymeric compounds of mercury were obtained [42] by polymerization of unsaturated organo-mercury compounds of the phenyl-p-vinyl-phenylmercury, bis-(p-vinylphenyl)-mercury, acrylate and methacrylate of phenylmercury type. Introduction of mercury into high molecular compounds is known already a long time and in this a greater number of polymers was obtained. Especially, polystyrene, containing mercury in phenyl nucleus[43-45], mercury containg rubber[46], mercurated polyvinylthiophene etc.

Mercurized rubber contains mercury in double bond and in methylene groups as well. They are less heat resistant and less elastic in comparison with the basic rubber.

. It was shown, that poly-a-vinylthiophene mercurized easily under the effect of mercury isobutyrate[47].

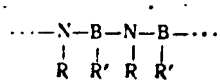
Polymers of Elements of the Third Group of Periodic System

Known are polymeric compounds of boron, aluminum, gallium and thallium.

The chemistry of polymeric boron compounds represents a new, intensively growing zone of chemistry of elemento-organic compounds, and at present time literature is bearing reviews, which summarize the achievements in this field[48].

For heterochain polymers containing boron, is characteristics easy hydrolizability, but the employment of the complexing principle allows to raise the hydrolytic stability of these compounds.

Of special interest are compounds containing boron and nitrogen simultaneously. In this case are used highly stable borazole cycles, which are bound with the aid of diisocyanates or in another way[49]. As it was possible to show recently, it is also possible to obtain a direct chain, consisting of boron and nitrogen atoms, bound with sufficiently greater radicals[50]



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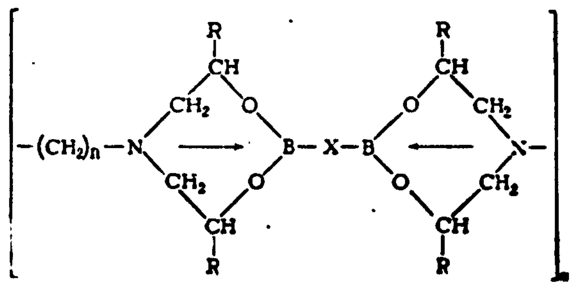
Lit.51 obtained highly stable to hydrolysis and remaining unchanged up to 300° polyesters of diboric acids with tetra-bis-oxyalkylated polymethylenediamines of structure:



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During thermal decomposition of diboranedimethylarsine adduct is obtained a quite stable[52] polymer $\left[(CH_3)_2AsBH_2\right]_x$.

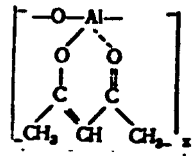
Of greater interest are also boron/aluminum combinations. In this case is obtained a chain, consisting of boron and aluminum atoms, and a cycle of the very same atoms[5].

Polymeric compounds, containing boron and phosphorus in form of cyclic and linear phosphineborine, attract greater attention[52,53]. The reaction of diborane with dimethylaminodimethylphosphine gave a highly heat resistant (up to 400°) linear phosphineborine[54].

Known is quite a large number of carbochain polymers, obtained by polymerization of unsaturated boron compounds[39].

Obtained were polymers from trivinyl-p-triallylboron[55], as well as polymers of parastyryl[56] and paravinylphenylboric acids[57]. Bis-p-vinylphenylboric acid polymerizes easily and can be used for copolymerization with styrene, as result of which is obtained a polymer, not melting even at 400°. When this trimer is heated with hydrogen peroxide it converts into a soluble product of low molecular weight, containing phenol hydroxyls [39].

An interesting type of polymers was derived from alkoxyaluminumacetylacetonate[58]. Upon cleavage of two alcohol molecules is obtained a polymeric product, having a chain of aluminum atoms and oxygen atoms, whereby the aluminum atoms are bound with acetyl acetone radicals:



17

Described was the obtainment of polymeric basic salts of organic aluminum acids by cleavage of water from basic salt by equation[59,60]

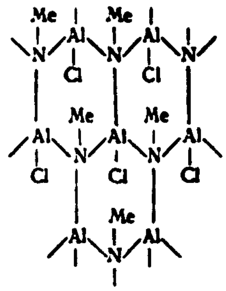
$$n\mathrm{HO{-}\underset{\substack{|\\X}}{Al}{-}OH} \rightarrow [\mathrm{{-}O{-}\underset{\substack{|\\X}}{Al}{-}}]_n + n\mathrm{H_2O} \qquad 18$$

Obtained were polyorganosiloxyanoalumoxanes[60] of the type

$$\cdots\mathrm{{-}O{-}\underset{\substack{|\\OSiR_3}}{Al}{-}O{-}\underset{\substack{|\\OSiR_3}}{Al}{-}O{-}}\cdots \qquad 19$$

Especially heat resistant were found to be polymers of this type with phenoxy-and 8-hydroxyquinoline groups in aluminum[59]. They remain unchanged when heated to 400°.

The new type of polymers represent compounds[61] of structure



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They form during the heating of the complex, obtainable from methylamine and diethylaluminumchloride:

$$nMeNH_2 \cdot Al(Et_2)Cl \rightarrow (MeNAlCl)_n + 2nC_2H_6 \quad 21$$

Known are polymers, obtained during the polymerization of vinylaluminum halides, halides of divinylaluminum and trivinylaluminum[62].

Thallium can be easily introduced into organic compounds by the reaction of thallization. And so, poly-a-vinylthiophene and polystyrene under the effect of thallium triisobutyrate convert into corresponding thalliumized organic compounds[47].

Polymers of Elements of Fourth Group of Periodic System

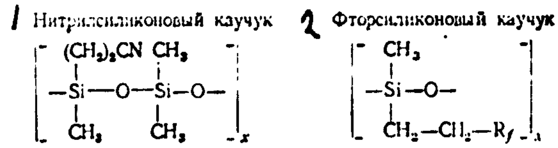
Known are polymeric compounds of carbon, silicon, titanium, germanium, zirconium, tin and lead.

The fourth group of the periodic system contains the greatest number of elements, widely used in the obtainment of various types of elemento-organic polymers. First of all we like to mention silicon, which after carbon appears to be the first element, the polymeric compounds of which have acquired greater practical application in form of various silicon polymers, representing greases, oils, liquids, as well as rubber, films and materials similar to it, distinguished by high heat resistance and widely used by industry.

Since the chemistry of silicon-organic compounds has presently attained greater development, then we will not discuss its numerous achievements, because this appears to be a theme of special review, but we will mention only the presence of numerous monographies and reviewing reports, devoted to this problem [3,8,10-12,15,16,64-66].

Of the number of silicon-organic compounds we will mention the number of polymers which gas appeared in recent years, and containing in role of substituents various polar groups[3] at the silicon atom. Among these should be mentioned cyanalkylsiloxanes, fluoralkylsiloxanes, vinylsiloxanes, as well as a number of other compounds, which found greater application, because these polymers are highly heat resistant and resistant againt oils [60,68]. Given below are formulas of certain polymers:

1. Nitrilesilicone rubber   2. Fluorsilicon rubber



22

where $R_f = CF_3$, C_2F_5, C_3F_7.

A very interesting group of new polymeric substances are polyorganometalsiloxanes. These compounds, in the composition of which is a heterochain skeleton, formed of intermittent silicon, oxygen and certain metal atoms[7,9,69]. Among the metals used for that purpose, is necessary to mention first of all aluminum, with the aid of which is obtained polyorganoalumosiloxanes [69,70]. With the aid of titanium are obtained polyorganotitanosiloxanes [69,71]. Such metals as tin, lead, antimony have also been used for the synthesis of polymers of mentioned type [59]. These compounds are distinguished by high heat resistance and are of greater interest as a new group of high-molecular elemento-organic polymers. Obtained was polyorganosiloxyphosphoralu,oxane[114], as well as polymers, containing the silicon/carbon bond in basic chain[72].

Polymerization of a number of vinylaromatic compounds[73], as well as a number of siliconoelfins[74] has been investigated.

When investigating polymerization of allyl and metallyl derivatives of a number of silanes in the presence of complex metal organic catalysts $(C_2H_5)_3Al+TiCl_4$ was obtained a number of new polymers with isotactic structure [75].

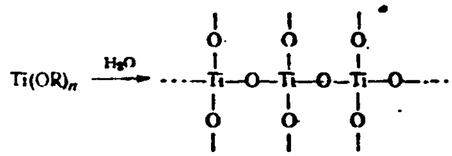
Very interesting is the polymer, containing Si-O-B bonds, stabilized with nitrogen containing compounds, playing the role of electron donors[59].

A review has been published, in which are described synthesis reactions of a number of silicon-, germanium-and stanno-organic compounds, as well as their ability to polymerize and the properties of obtained polymers [66].

Triethtlsilyl esters of polyvinyl alcohol were found to be excellent dielectrics[76].

The chemistry of polymeric titanium compounds is presently under intensive development[77,78]. Titanium does not yield true metallo-organic compounds, and all its polymeric compounds are presented by substances of the type of cyclopentadienyl titanium compounds, as well as by certain other complex compounds, listed below.

Polytitanoxanes represent titanium oxide polymers, obtainable during the hydrolysis of orthotitanic acid esters:



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They form very strong films and used in manufacturing heat resistant coatings[77-79].

A number of polymers was obtained, polymers containing titanium, e.g. tributoxytitanomonomethacrylate, which copolymerizes easily with methylmethacrylate, forming a soft substance[80], stable to moisture. Dibutoxytitanomethacrylate copolymerizes with styrene forming solid products, used as insulation materials[80]. Dipentyloxytitanodicrotonate is also polymerizable[80]. Tetrastyryltitanate polymerizes easily at 150°[81].

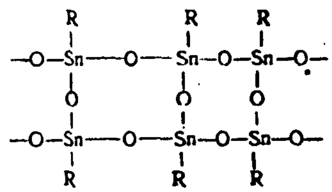
Heterochain germanium compounds represent a larger group of compounds, constructed analogously to silicon-organic compounds and resembling the latter to a certain extent[52].

Polymers, containing germnium, are also presented by a series of substances, belonging to the group of carbochain high molecular compounds and containing germanium in form of side branches. These are various derivatives of acrylicand methacrylic acids, styrene and other monomers[86].

Known is a greater number of germanium compounds, e.g. tetraallylgermanium[82], which polymerizes easily. Described are polymers of ethyltrivinyl-and diethyldivinylgermanium, obtained at high pressure[83]. Obtained were also trialkylallyl- and trialkyl-metallylgermanium, which polymerize easily under pressure in presence of tertiary butyl peroxide[84]. Dimethyldiallylgermanium yields polymers[86] in presence of $TiCl_4+Al(C_2H_5)_3$. Vinylgermanium polymerizes easily with the formation of a solid white insoluble polymer, decomposing at above 275°. Known is also methacryltriethylgermanium, which polymerizes easily[86].

In zirconium we encounter, just as was the case in titanium, lack of formability of true zirconium-organic compounds and ability of entering into bond only through complexes of various type. Known are zirconates of complex structure and polymeric nature[5].

Esters of alkylstannic acid upon heating form a heterochain polymer of following structure[52,59]:



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These polymers are infusible and insoluble. Triphenylstannan reacts with acrylic acid, forming a polymer[59]

$$(C_6H_5)_3SnH + CH_2{=}CHCOOH \rightarrow [(C_6H_5)_2SnCH_2CH_2COOH]_n \downarrow [-(C_6H_5)_2SnCH_2CH_2COOC_6H_4]_n$$

25

Polymeric compounds, containing tin, are presented at present time, like germanium, by a greater number of carbochain polymers, containing tin, bound with the side chain. They include polymers of various derivatives of acrylic and methacrylic acids[87], and styrene[42], as for example, p-triphenylstannilstyrene and p-triethylstannil-a-methylstyrene, as well as methacrylate and acrylate of triphenyl- and tri-(n-butyl)tin[42] and others[87]. At thesame time vinyl and allyl derivatives of Sn do not polymerize and only under pressure yield low molecular polymers [42,83].

Polymers of tributyltin methacrylate and its copolymers with tributyltin dimethacrylate present rubber-like substances[113].

Lead-containing polymers are represented mainly by carbochain compounds, in which lead is in the side chain. They include, just as in case of tin, various acrylic, methacrylic, styrene and vinyl polymers.

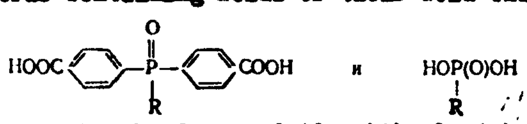
Tetravinyl-, triethylvinyl- and divinyldiethyl lead when heated with peroxides decompose with separation of metallic lead. But if polymerization is carried out under pressure, there is copolymerization with styrene or with a-methylstyrene[88]. Para-triethyl-a-methylstyrenelead polymerizes easily under pressure[89]. Acrylates and methacrylates of triphenyllead are also polymerizable[42].

Polymers of Elements of the Fifth Group of Periodic System

Polymers of nitrogen, phosphorus, arsenic, antimony and bismuth compounds are already known.

We will not touch upon polymers, containing nitrogen, because here we have no elemento-organic specificity, because nitrogen is insluded in the composition of a very large number of polymers with purely organic nature.

In recent years was obtained a greater number of phosphorus containing heterochain and carbochain polymeric products[13]. Of the number of heterochain polymers, containing phosphorus, we will mention a great number of polyamides and polyesters, containing phosphorus in basic chain[90-96]. They are obtained during polycondensation of diamines and bisphenols with phosphorus-containing acids or their acid chlorides of type



(26)

As result of reaction of phosphoric anhydride with aluminum phenolates were obtained phosphorus-containing polymers[110]. Interesting fire-resistant polyphosphone amides were obtained[111] during the heating od diamides of phenylphosphinic and other acids.

Various phosphonitrile derivatives, or as they are properly called phosphoramide derivatives, attract general attention of researchers. This, on one hand, is polyphosphonitrilechloride, then various alkyl and aryl derivatives of same, which are widely investigated in form of cyclic monomers, as well as in form of polymers of linear structure, distinguished by high heat resistance and in some instances by the presence of elasticity. Obtained recently was a polybisperfluormethylphosphonitrile $[(CF_3)_2PN]x$, highly resistant to the effect of acids[92].

Polymeric derivatives of phosphonitrile represent presently a larger group of high molecular compounds, intensively investigated by various authors. Having no possibility within the framework of this report to thoroughly discuss all these polymers, we will just refer to the reviewing report[97], in which is given a detailed description of various polymeric derivatives of phosphonitrile. Here belong also phosphineborines, which have been mentioned before. Furthermore, we know of quite many carbochain compounds containing phosphorus in the side chain. They include various vinyl polymers, containing phosphorus in form of phosphoric acid radicals, esters or some other of its derivatives. These are polymers of vinylphosphinic and aryl phosphinic acids of different type, as well as numerous copolymers of same[63,81]. Here belong polymers, containing phosphorus in the polystyrene nucleus, as well as polymers of vinylphosphinic oxides[98].

Finally, we will mention, that very great progress was made in the study of nucleinic acids, representing polyesters of phosphoric acid and playing an extremely important role in living organisms, appearing to be the agent, with the aid of which heredity symptoms are transmitted and directed synthesis of albumins from amino acids[99] is promoted. Vinylphosphinic acid ester and ester of polyvinyl alcohol have been obtained[67].

Many different polymers are known for arsenic. Among them, on one hand, are homochain polymers, containing an arsenic chain, to which salvarsan belongs[100], as well as a number of heterochain polymers, containing arsenic in basic chain, bound with carbon, oxygen and other elements.

For antimony are also known heterochain and carbochain polymers. Synthesized were easily polymerizable acrylates and methacrylates of diphenylantimony[101].

Polymers of elements of the sixth group of periodic system

Known are polymeric compounds of oxygen, sulfur and selenium. Since they all belong to carbochain organic compounds, they will not be discussed here.

Polymers of Elements of Seventh Group of Periodic Systems

The seventh group of the periodic system includes halogens, which at present time are widely represented in polymeric chemistry. We will not touch upon derivatives of chlorine, bromine and iodine, because they are known for a long time, and will discuss only derivatives of fluorine.

Among fluorine derivatives we have an enormous number of representatives of fluoroorganic polymer group, which have already acquired greater practical importance, such, as polymers of fully fluorinated ethylene, as well as not fully fluorinated ethylene and mixed fluoro-and chloro-derivatives of various form. Among these compounds should be pointed out a series of new substances, which gained importance as highly heat resistant and oil resistant rubber. The chemistry of polymers, containing fluorine, are being intensively developed and, apparently, it can be expected in the future the appearance of a number of new interesting compounds.

Among the recently appeared compounds we like to single out polymers of perfluorobutadiene[102], obtained with the aid of high pressure. Grafted copolymers of vinylidenefluoride or trifluoroethylenechloride with cyclic tetramer of dimethylsiloxane or with dimethylsiloxane rubber were found to be more stable to the effects of solvents[103].

Polymers of Elements of Eighth Group of Periodic System

Known are polymeric compounds of iron, cobalt and nickel.

The eighth group of the periodic system includes a series of metals, which are not capable of giving true metal-organic compounds, but of these are capable to form complex compounds of various form. Among these we will single out first of all compounds of the dicyclopentadienyliron type (ferrocene), which is presently used as basis for the obtainment of a number of polymers (e.g. polyferrocene, obtained by reaction of polyrecombination[22]). By the very same method were obtained also polyalkylferrocenes[104]. Polyalkylferrocenes were also obtained by alkylation of ferrocenes[105]. These polymers have interesting magnetic and electric properties, they are capable of emitting a clear paramagnetic resonance signal and, consequently, belong to the semi-conductor group[106]. Obtained was difurfuralacetylferrocene and polymers on its base[107].

Vinylferrocene polymers have a high melting point (280-295°); obtained were also its coplymers with methylmethacrylate and chloroprene[108]. Obtained was cinnamoylferrocene, which in itself does not polymerize, but yields copolymers with other monomers[109].

For many other representatives of the eighth group of elements is known a greater number of complex polymeric compounds, obtained in recent years. Such polymers were obtained for cobalt and nickel. These complex compounds are obtained during the reaction of various complexones with salts of these metals or with their acetoacetate complexes[34].

In the role of complexones for the obtainment of coordinated cobalt and nickel polymers were used various tetraketones of the type $RCOCH_2COR'COCH_2COR$[34,112].

Coordination cobal and nickel polymers represent insoluble powders, melting at 200-350°, colored in various colors depending upon the nature of the ligand and metal[34].

Concluding the discussion of known scientific material, touching upon abried characteristic of derivation methods and properties of various elemento-organic polymers, known at present time, we can say, that this field is expanding very rapidly and in the very near future we will see a greater number of new polymers, containing these metals and elements, which have so far not been used for these purposes, as well as new representatives of elements already discussed by us. These substances in a majority of instances are characterized only chemically and the fields of their application are always clear, but there is absolutely no doubt, that in the near future they will find a veriety of fields of application in polymeric chemistry and in chemical technology and will open new perspectives for their development.

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