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Synthesis and Chemical Reactions of Metal-containing Macromolecules

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The synthesis of polymers containing "non-organic" elements has been discussed in the literature, the most exhaustive monographs being those of Andrianov[1], Nametkin and coworkers[2], Gefter[3], and others. There have also been a large number of publications concerning the problem of the synthesis of polymers containing alkali metals, alkaline earth metals, heavy metals, and transition metals.

The present review deals with the most important studies on the synthesis and chemical reactions of metal-containing polymers of various types. Metal-containing polymeric compounds are understood as organometallic polymers with organic principal chains containing a direct carbon-metal bond (regardless of the type of metal), saltlike compounds, in particular those with macromolecule-oxygen-metal bonds, and also complex polymeric compounds containing, for example, coordinated atoms of 3*d* transition metals.

Wherever possible the reactivities of metal-containing molecules and their low-molecular-weight analogues have been compared. The review mentions unsuccessful attempts to prepare metal-containing macromolecules and their reaction products[4]; the studies where the formation of these compounds was inferred only from the change in the colour of the reaction mixture[5] and also those where the possibility of metallation was admitted merely in principle[6] are not included. In the preceding review on the synthesis of metal-containing polymers[7], the problems of their reactivity were hardly dealt with owing to the lack of sufficient factual data at the time.

The bibliography includes 111 references.

CONTENTS

I. Introduction 1082
II. Organometallic polymers derived from Group I, II, and III metals. The use of lithium-containing polymers for the initiation of polymerisation and the preparation of polyfunctional polymers 1083
III. Organometallic polymers derived from heavy metals. Metallated polymers and stabilisation 1086
IV. Transition metal complexes with macromolecular ligands 1088
1. Reactions with participation of the metal-ligand bond 1088
2. Reactions of a coordinated macromolecule 1090
V. Factors determining the properties of various types of polymer-metal bonds 1092
VI. Characteristics of the chemical reactions of metal-containing macromolecules due to their polymeric nature 1092

I. INTRODUCTION

Metal-containing polymers as well as low-molecular-weight organometallic and complex compounds are interesting primarily from the standpoint of the reactivity of the bond formed by the metal. The bonds between the metal and the polymer chain may be of fundamentally different types. Covalent polymer–metal bonds are extremely reactive and this has been used in many chemical reactions involving macromolecules.

Coordinate bonds of the type C–O–M←O, C–O–M←N, etc. are particularly interesting, since they are formed in many of the most important biochemical systems. The nature of bonds of this kind changes significantly as a function of the metal and the ligand coordinated to it; the coordination centres are as a rule quasiaromatic systems.

The saltlike metal–polymer bond, for example C–O–M or CO–O–M, is widely used in ion exchange; many publications have dealt with metal-containing polymers of this type[8] and therefore we shall not consider them in detail.

Dative polymer–metal π interaction is assumed, for example, for copper(I), silver(I), and gold(I) acetylides in which electrons are transferred from the bonding π_n acetylene orbitals to the *d* orbitals of the metal and from the latter to the unoccupied antibonding π_g orbitals of acetylene; a recent review by Sladkov and Ukhin[9] dealt with this problem.

Depending on the nature of the polymer–metal bond, various applications of metal-containing compounds are possible.

When a fairly stable bond (for example a saltlike bond) is formed by the metal with polymers, the latter may be used and have been used to detect and separate traces of metal ions and to separate ions quantitatively to achieve a high degree of purification of water and organic solvents. Here we have the entirely realistic problem of the application of salt forming polymers for medical and agricultural purposes associated with the introduction and elimination of metals from organisms.

When a reactive metal–polymer bond is formed, as happens in true organometallic compounds, the polymers may be used as catalytic systems for chemical reactions of different kinds. One of the most important fields in the modern physical chemistry of polymers is concerned with the search for macromolecular catalysts and the study of the mechanism of their action. The long-chain structure of the molecule containing in the chain active centres capable of interacting with one another, with the additional possibility of altering the shape of the molecule sorbing selectively particular reactants, makes polymer catalysis noteworthy not only from the theoretical (simulation of biocatalysis) but also from the practical standpoint of the achievement of particular oxidation–reduction, polymerisation, hydrolytic, etc. reactions. Effective catalysts of this type may be both organometallic polymers and complex polymeric compounds obtained by the coordination of variable-valence metal ions to polymeric ligands of a wide variety of types.

Recently polymeric substances have been employed with increasing frequency in medical practice and therefore increasing attention has been devoted to the problems of

the synthesis and investigation of new polymeric systems with physiological activity and a set of properties necessary for their employment in medical practice (blood substitutes, oxygen-transferring agents, medicinal preparations, materials for artificial internal organs). In their theoretical aspect, the studies on macromolecular compounds are coming into increasingly close association with the investigation of biopolymers and the simulation of biological systems, where complex-forming polymers as model systems are already of particular interest.

II. ORGANOMETALLIC POLYMERS DERIVED FROM GROUP I, II, AND III METALS. THE USE OF LITHIUM-CONTAINING POLYMERS FOR THE INITIATION OF POLYMERISATION AND THE PREPARATION OF POLYFUNCTIONAL POLYMERS

Recently most attention has been devoted to the study of the chemical reactions of macromolecules of two types: containing alkali metals (mainly lithium) and heavy metals (mainly tin). This can be understood if one remembers the wide range of reactions of which low-molecular-weight organolithium compounds are capable, on the one hand, and also the great interest in low-molecular-weight organotin compounds as stabilisers for a wide range of polymers, antiseptics, etc., on the other.

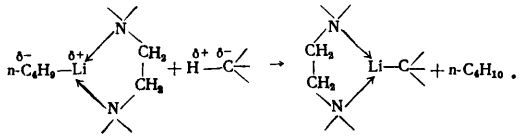
Among all the possible syntheses of organometallic polymers derived from Group I, II, and III metals, the following may be employed: (1) direct replacement of a hydrogen atom for a metal atom, for example by metallic lithium [10] (RH + Li → RLi + H); (2) metallation consisting in the reaction of a metal, for example lithium, with a halogeno-derivative of the polymer [11] (RX + 2Li → RLi, LiX); (3) metallation of polymeric hydrocarbons by lithium alkyls [12] (RH + R'Li → RLi + R'H); (4) exchange reaction between a low-molecular-weight organolithium compound, for example N-C_4H_9Li, or C_6H_5Li, and a halogeno-derivative of the polymer [13] (RX + R'Li → RLi + R'X); (5) addition of the metal hydride to a double bond of the polymeric hydrocarbon [5].

The first reaction has not been achieved for polyolefins owing to the lack of sufficiently reactive C–H bonds (the energies of the $-\overset{|}{\underset{|}{C}}-H$ bonds in polyethylene and in polypropylene are 128 and 80 kcal mole^{-1} respectively).

The use of the second reaction for the introduction of lithium into polyolefins is also difficult for the following reasons: judging from the literature data [14], an increase of the yield of the organolithium compound containing the metal at a saturated secondary carbon atom may be expected only when the reaction temperature is reduced and this involves the necessity to carry out the reaction under heterogeneous conditions, since both components (the polymer and metallic lithium) are insoluble in the reaction medium at low temperatures.

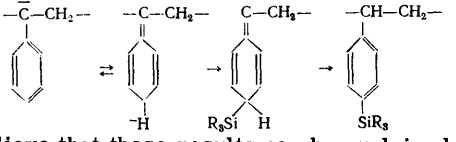
In order to introduce the metal into aryl-containing polymers by the third method, the authors of the review, Yampol'skaya, and Okhlobystin employed the reaction of the complex of butyl-lithium with *NNN'N'*-tetramethylethylenediamine, which is familiar in the chemistry of low-molecular-weight compounds; the starting materials employed in this reaction were acetic polystyrene and aryl-containing polyolefins–copolymers of α-methylstyrene and α-methyl-*p*(*m*)-methylstyrene and propene [15].

The high reactivity of the complex of n-butyl-lithium with *NNN'N'*-tetramethylethylenediamine can be accounted for by the increase in the ionic character of the C–M bond owing to the vigorous solvation of the lithium atom. The metallation of aryl-containing polymers by hydrogen–metal exchange takes place as a result of nucleophilic attack by the anion of the complex on the benzene hydrogen (in styrene polymers and copolymers of α-methylstyrene and propene) or on the methyl group attached to the arene ring [for poly-*p*-methylstyrene and copolymers of α-methyl-*p*(*m*)-methylstyrene and propene]:



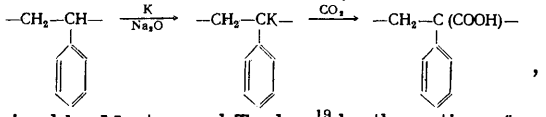
Although the formation of metal derivatives is in fact complicated by competing reactions, nevertheless the degree of metallation is quite sufficient for further reactions of such polymers with compounds containing the appropriate functional groups [16].

Chalk subsequently investigated the metallation of polystyrene by the butyl-lithium–*NNN'N'*-tetramethylethylenediamine complex [17] and compared it with the metallation of a low-molecular-weight model (toluene) [13] under the same conditions. With the aid of successive trimethylsilylation and treatment with dimethyl sulphate or D_2O, it was shown that, whereas toluene is substituted by lithium mainly in the side chain (up to 90.8%) and only slightly in the ring (the yields of derivatives substituted in the *meta*-, *para*-, and *ortho*-positions were 5.3, 1.8, and 2.0% respectively), polystyrene is substituted by lithium almost exclusively in the ring (20–25%) and only slightly in the chain (1–2%), regardless of the duration of the reaction; the substitution takes place to the extent of 80% in the *para*-position and to the extent of 20% in the ortho-position. The author proposes the following mechanism of such "anomalous" course of the reaction:



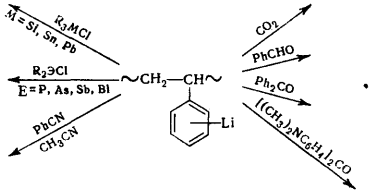
We believe that these results can be explained by the steric hindrance to the reaction in the benzyl-position of the polystyrene chain (see p. 1093).

Poly-α-potassiostyrene, which is subsequently converted into poly-α-phenylacrylic acid,



was obtained by Morton and Taylor [19] by the action of metallic potassium on polystyrene, but these data were not confirmed subsequently.

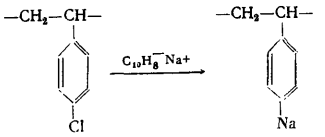
The fourth method has been most widely used for the metallation of polyhydrocarbons; here the principal investigations have been carried out by Braun and coworkers [7]. They discussed comprehensively the metallation of halogen-containing polymers in a number of publications [20–23]; they investigated a large number of reactions of polylithiostyrene:



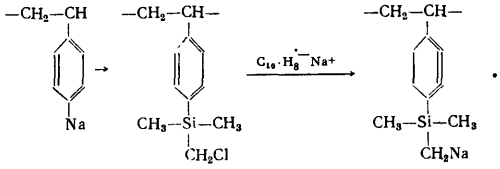
Apart from the reactions indicated in the above scheme, the reactions of poly-*p*-lithiostyrene with O_2, SO_2, nitroso- and nitro-compounds, phenyl isocyanate and thiocyanate, orthoformic ester, pyridine, dimethylformamide, etc. have been described. Braun also obtained an insoluble lithium-substituted polystyrene starting with a cross-linked (degree of cross-linking 2%) polymer of iodostyrene and styrene with a high content of the latter. Then he replaced lithium by residues of nicotine, comphor, camphorsulphonic acid, and other organic groups [21], as well as groups containing "non-organic" elements [22]; by allowing the copolymer to react with sulphur powder, he obtained mercaptopolystyrene [23]. Thus the chemical reactions of lithium-substituted polystyrene made it possible to introduce virtually any functional group into polystyrene. It has been noted that in the reaction of butyl-lithium with iodinated polystyrene, the order of addition of the reactants is very important (polymer to a solution of the organometallic compound and not vice versa) in order to prevent the cross-linking of the chains [21].

Lithium derivatives of polystyrene have also been obtained by Leavitt and Matternas [24] by the metallation of poly-*o*- or poly-*p*-bromostyrene; to suppress the Wurtz–Fittig reactions, the metallation was carried out at a high concentration of butyl-lithium and a low temperature (−35°); subsequently the lithium-substituted polystyrene was substituted by tin with the aid of R_3SnCl.

Greber and coworkers [5] carried out a series of studies on the metallation of halogen-containing polymers (for poly-*p*-chlorostyrene and its copolymer with styrene) by sodionaphthalene in tetrahydrofuran or dimethoxyethane:

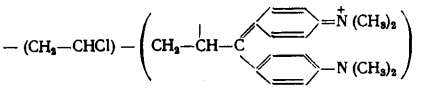


The authors employed the metallated polymers obtained as polymeric initiators of polymerisation or for the introduction of functional groups (for example the dimethylchloromethylsilyl group), which are in turn capable of undergoing further metallation:



By this type of metallation of poly(vinyl chloride), Greber prepared a polyhydrocarbon of unknown structure with a high content of cyclopropane groups. Fig. 1 shows that, in the metallation of poly-*p*-chlorostyrene, 2 g-atoms of sodium are consumed for each g-atom of chlorine; this implies that the Wurtz side reaction (interchain cross-linking) hardly occurs under these conditions [5].

Several attempts have been made to achieve the reaction of poly(vinyl chloride) or poly(vinyl bromide) with organometallic compounds such as diethylzinc [25], trityllithium and its analogues [26], and sodionaphthalene [26]. The reaction of poly(vinyl chloride) with butyl-lithium was investigated in greatest detail by Shiina and Minoura [6]. It leads to only partial metallation of the polymer, since in this case the competing reactions are as for halogenopolystyrenes, butylation and dehydrochlorination. The lithium-substituted fraction of poly(vinyl chloride) was employed in polymerisation initiated by CO_2, Michler's ketone, etc. For example the polymeric analogue of Malachite Green was obtained:



The authors note that the attempts to carry out the reaction of poly(vinyl chloride) with phenyl-lithium and sodionaphthalene were unsuccessful [6].

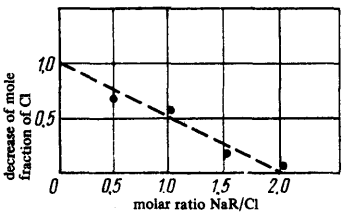
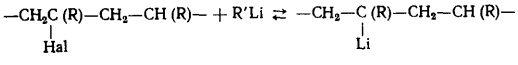


Figure 1. Metallation of poly-*p*-chlorostyrene (M = 78 000) with $NaC_{10}H_8$.

It has been found that the metallation of halogen-containing polymers, for example polychlorotrifluoroethylene, may be achieved by treatment with a solution of the given metal in liquid ammonia; lithium, sodium, calcium, barium, and magnesium have been used [27]. The introduction of sodium may be achieved also with the aid of a solution of sodionaphthalene in dimethoxyethane [28]. Examination under the electron microscope of a polymer film after its immersion for 2–3 s in the metallating solution shows that the metallating component penetrates to a depth of 10^{-4} cm. Metallation of this kind increases the adhesion of adhesives to films of the above type.

The exchange reaction between a low-molecular-weight compounds RLi, for example n-butyl lithium or phenyllithium, and polymers were carried out by the authors of the review and Yampol'skaya [29] for halogeno-derivatives of polyolefins:



where R = H or CH_3 and R′ = n-C_4H_9 or C_6H_5.

Chlorinated and brominated polyethylene and chlorinated polypropylene were employed as halogen-containing polyolefins. The reaction involving the substitution of a halogen by lithium is reversible; its equilibrium position is determined by the relative stabilities of the corresponding carbanions. Therefore in the reaction of halogenopolyolefins with n-butyl- and phenyl-lithium one cannot expect a high yield of the metallated products: the stabilities of the butyl and polymeric anions are comparable and the phenyl anion is actually more stable than the polymeric anion. Indeed the amount of lithium in the polymeric molecule, determined by direct titration, proved to be low (lithium-substituted polyethylene containing 0.85% of lithium was obtained from chlorinated polyethylene containing 24.5% of chlorine, i.e. only 22% of the chlorine present was replaced by lithium). To increase the degree of metallation, it is necessary to employ an excess of the organolithium compound; moreover, the

rate of reaction increases in the presence of highly solvating solvents, for example tetrahydrofuran (THF).

Being reversible, the reaction is complicated by the competing process involving the nucleophillic substitution of the halogen by the group R′ of the organolithium compound:

$$-CH_2-\underset{\underset{Hal}{|}}{CR}- + R'Li \rightarrow -CH_2-\underset{\underset{R'}{|}}{CR}- + LiHal\ .$$

The side condensation reaction can also lead to the formation of cross-linked products of the following type:

$$\begin{array}{l} -CH_2-\underset{\underset{Hal}{|}}{CR}- \\ \qquad + \\ -CH_2-\underset{\underset{Li}{|}}{CR}- \end{array} \rightarrow \begin{array}{l} -CH_2-CR- \\ \qquad\quad | \\ \qquad -CR-CH_2- \end{array}\ .$$

As a result of second side reaction, dehydrochlorination under the influence of the nucleophillic organometallic compound:

$$-CH_2-\underset{\underset{Hal}{|}}{CR}-CH_2-CHR- + RLi \rightarrow -CH=CR-CH_2-CHR-\ ,$$

double bonds appear in the chlorinated polyethylene. The degree of metallation of brominated polyethylene by n-butyl-lithium is very insignificant; dehydrobromination is the dominant reaction in this case.

The reaction of chlorinated polypropylene is more unambiguous—when treated with phenyl- and n-butyl-lithium, it undergoes only condensation and dehydrochlorination reactions. This is in fact understandable, since an increase in the mobility of the chlorine atom at the tertiary carbon atom in the chlorinated polypropylene molecule leads to an increase of the proportion of dehydrohalogenation at the expense of metallation.

As mentioned previously (see, p. 1084), lithium-containing polymers react with various organic compounds such as dialkyl(aryl)chlorophosphines, trialkyl(aryl)chlorosilanes, trialkyl(aryl)chlorostannanes, carbonyl compounds, etc., with formation of the corresponding derivatives[30].

The high reactivity of metallated polyethylene and the copolymers of polyethylene and polypropylene with styrene permitted their application as polymeric initiators in the ananionic polymerisation of many monomers; methyl methacrylate, acrylonitrile, isoprene, and styrene. As a result of this reaction, copolymers with polyolefinic main chains and side chains comprising units of the grafted comonomers were obtained; the reaction is complicated by the homopolymerisation of the monomers by the excess n-butyl-lithium[31].

The hydrometallation of polyhydrocarbons and their derivatives was in fact achieved in the 1950's when Morton and coworkers[32] showed that alfin catalysts can cause, apart from the polymerisation of dienes, a side reaction involving the metallation of the macromolecule formed.

This method of metallation of polymers has been achieved by the addition of, for example, organoaluminium hydrides to unsaturated polymers, in particular a copolymer of styrene and butadiene[33]:

$$-CH_2-CH-CH_2-CH- + HAlR_2 \rightarrow -CH_2-CH-CH_2-CH$$

(the phenyl ring is retained; $CH=CH_2$ and $CH_2-CH_2-AlR_2$ substituents)

and enabled Greber and coworkers[33] to prepare a series of aluminium-containing polymers; the metallation kinetics (bromometry) are presented in Fig. 2.[33]

The same workers[34] demonstrated the intermediate formation also of another kind of metallated polymer—with a C=N–M bond, for example:

$$-CH_2-\underset{\underset{C\equiv N}{|}}{CH}- \xrightarrow{+RMgCl} -CH_2-\underset{\underset{RC=N-MgCl}{|}}{CH}-\ ,$$

by the reaction of lithium alkyls or alkyl(aryl)magnesium halides with copolymers containing nitrile groups (acrylonitrile–styrene).

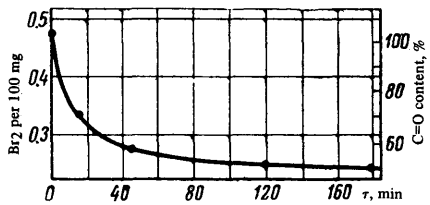
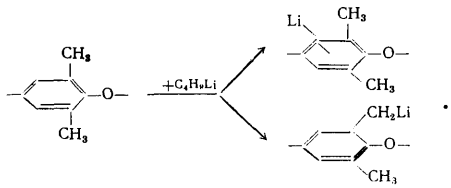


Figure 2. Decrease with time of the degree of unsaturation of the butadiene–styrene copolymer during metallation.

Greber employed metallated aluminium-containing polymers as macromolecular Ziegler catalysts (in a mixture with transition metal chlorides: $TiCl_4$, $TiCl_3$, $VOCl_2$, etc.).[35]

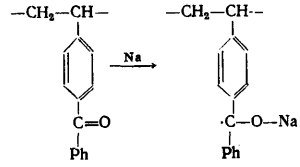
Hulot et al.[36], who repeated and revised Greber's data, investigated the interaction of unsaturated polymers (a styrene–butadiene copolymer and polyisopropene) with dibutylaluminium hydride and titanium tetrachloride as a function of the reaction conditions (effect of the order of addition and the relative amounts of the reactants and also temperature). They showed that a soluble and homogeneous polymeric catalyst of the Ziegler type is obtained only following the exhaustive metallation of the polyhydrocarbon by dialkylaluminium hydride at 130°C and subsequent reaction with titanium tetrachloride. The polymeric initiator thus obtained was used in the polymerisation of ethylene; graft copolymers containing 80% of the styrene–butadiene copolymer and 20% of the grafted monomer were also synthesised.

Chalk and Hay[37] achieved the metallation of polymers containing oxygen, namely substituted polyphenylene oxide; they employed poly-2,6-dimethyl-1,4-phenyl ether:



With the aid of butyl-lithium, both the ring (about 20%) and the alkyl group (about 80%) are metallated. The mode of metallation depends on the duration and temperature of the reaction. The authors believe that the use of potassio- and sodio-derivatives for this purpose leads to the preferential metallation of the alkyl substituents (demonstrated by trimethylsilylation). The authors believe that the initial stage of the process is ring-metallation, assuming that this stage is accompanied by the migration of the substituent to the benzyl position.

Other oxygen-containing metallated polymers (polymeric metal ketyls) were described by Braun and Löflund[38]. They were prepared by treating poly-*p*-vinylbenzophenone with sodium powder; the solutions of sodiopoly-*p*-vinylbenzophenone were employed as polymeric initiators of the radical polymerisation of vinyl monomers, for example acrylonitrile[38]:



The type of reaction between inorganic salts and polymeric epoxyethane is not entirely clear, although it can be classified as an interaction between a metal and an oxygen-containing polymer[39]. The proof of the occurrence of such interaction is the appreciable lowering of the degree of crystallinity of the polymer in the presence of 10–30% KI (the two substances being completely compatible) (Fig. 3) quoted by the authors.

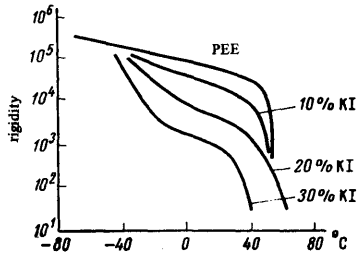
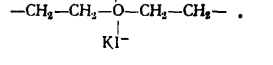


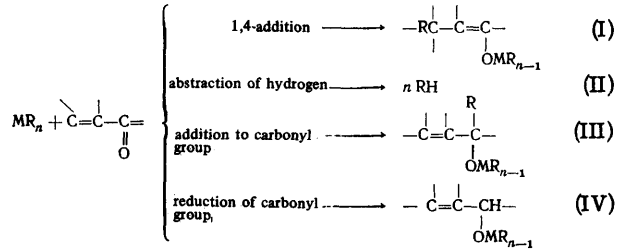
Figure 3. Dependence of the modulus of rigidity on KI content in polyepoxyethane (PEE).

The finding that in the adduct investigated there is one salt molecule for nine polymer units suggests that ion–dipole interaction takes place but it is not clear which ion is directly linked to the chain:



A similar capacity is shown also by potassium fluoride, potassium chloride, potassium bromide, rubidium fluoride, and rubidium iodide, but not lithium chloride and lithium bromide; probably other polyethers, for example polyoxypropylene, are also capable of undergoing reactions of this kind[39].

An interesting mechanism for the reaction between organometallic compounds and ketones (at a low-molecular-weight level) has been put forward by Tsuruta and coworkers[40]. The reactions of a large number of organometallic compounds (RLi, RMgX, AlR_3, ZnR_2, $CaZnR_4$) with $\alpha\beta$-conjugated ketones such as phenyl vinyl (and also isopropenyl, β-styryl, isopropylidene, and benzylidene) ketone and methyl phenyl ketone have been investigated. It was found that, when $(C_4H_9)_2Zn$ and $(n\text{-}C_4H_9)_3Al$ are used, the principal stages are 1,4-addition and abstraction of hydrogen; other possible reactions (reduction of the carbonyl group, addition to the carbonyl group) take place to a lesser extent:



The contributions of the reactions (calculated from the amount of hydrocarbon produced by a particular mechanism) depend markedly on the nature of the organometallic compound:

Organometallic compound	Reaction (I)	Reaction (II)	Reaction (III)	Organometallic compound	Reaction (I)	Reaction (II)	Reaction (III)
RLi	1	1	1	ZnR_2	1	2	—
RMgX	1	1	1	$CaZnR_4$	1	2	—
AlR_3	1	3	—				

Metallation reactions of a similar type can undoubtedly be carried out also at a macromolecular level.

In conclusion of the section, we may point to another class of polymetallated oxygen-containing polymers, namely metal-containing derivatives of cellulose. Its alkoxides, not containing an excess of the alkali metal, are obtained by treatment with sodium in ammonia[41] or by an exchange reaction with sodium alkoxide[42]; however, the mechanism of the reaction of cellulose with metals leading to the formation of metal-containing derivatives in solutions of the complexes of these metals has not as yet been adequately elucidated. Cellulose metallated in this way is highly reactive in alkylation, etherification, and other reactions[42].

One may conclude that the reactivity of polymeric organometallic compounds is on the whole lower than that of their low-molecular-weight analogues. This is probably due to the great scope for the delocalisation of the charge in the polymeric cryptocarbanion (see p. 1092) and also the factors complicating the reactions and specific to polymers, which have been discussed on p. 1092.

III. ORGANOMETALLIC POLYMERS DERIVED FROM HEAVY METALS. METALLATED POLYMERS AND STABILISATION

The introduction of heavy metals such as mercury, thallium, tin, or lead into polymers has been mentioned in the literature from 1957†. The introduction of mercury into polymers was investigated in fair detail by Smirnov[43] and later by Traylor[44], who mercuated polystyrene with mercury(II) acetate; mercury-containing polymers have been obtained by the action of mercury(II) butyrate on polystyrene and poly-α-vinylthiophen[45]. The substitution of polystyrene and poly-α-vinylthiophen by thallium(III) isobutyrate takes place similarly to mercuration[46]. The substitution of cellulose derivatives by mercury and thallium has been investigated by Rogovin and coworkers[47];

†We shall not consider the phenomenon of association, which is well known in the chemistry of organometallic compounds of the type $[R_XM]_n$.

recently they obtained the corresponding tin and lead derivatives [48].

The sulphonated copolymers of styrene and divinylbenzene have been mercurated with mercury(II) perchlorate [49]. Polymers and copolymers of butadiene are oxymercurated by mercury(II) acetate at the double bond and also in the allyl position [50]. The reactivity of the mercurated specimens was investigated in acylation by acetyl chloride and benzenesulphonyl chloride.

In order to modify chlorinated polyethylene and poly(vinyl chloride), the authors of the review and Purinson [51] introduced organotin groups, having developed special methods for the synthesis of such tin-substituted polymers. Dimetallic mixed organic derivatives of lithium and tin, capable of reacting with chlorine atoms, for example triphenylstannyllithium or tributyl stannyllithium, were chosen for the introduction of R_3Sn groups into polymeric molecules:

$$-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2X- + R_3SnLi \rightarrow -CH_2-\underset{\underset{SnR_3}{|}}{CH}-CH_2-CH_2- + LiCl, \quad (I)$$

where X = H or Cl and R = C_6H_5 or n-C_4H_9.

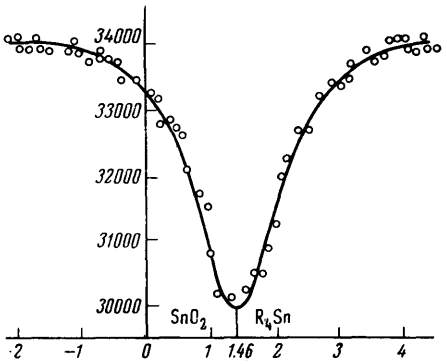


Figure 4. Mössbauer spectrum of triphenylstannated chloropolyethylene.

The structure of triphenylstannylated chloropolyethylene was confirmed by Mössbauer (gamma-resonance) absorption spectroscopy without recoil [52]. The isomeric shifts relative to SnO_4 in the Mössbauer spectra of the stannated polymers correspond to compounds of the type R_4Sn (Fig. 4). The stannation reaction via mechanism (I) is accompanied by a reaction in which lithium is introduced into chloropolyethylene by triphenylstannyllithium:

$$-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2- + LiSnPh_3 \rightarrow -CH_2-\underset{\underset{Li}{|}}{CH}-CH_2-CH_2- + Ph_3SnCl, \quad (II)$$

which results in the formation of an insoluble fraction via the interaction of the lithium-substituted chloropolyethylene with the initial chloropolyethylene:

$$\begin{array}{l} -CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2- \\ -CH_2-\underset{\underset{Li}{|}}{\overset{+}{C}H}-CH_2-CH_2- \end{array} \rightarrow \begin{array}{l} -CH_2-\underset{|}{CH}-CH_2-CH_2- \\ -CH_2-\underset{|}{CH}-CH_2-CH_2- \end{array} + LiCl. \quad (III)$$

We may note that cross-linking can also occur via the formation of macroradicals without the intermediate formation of the lithium-containing polymer:

$$-CH_2-\underset{\underset{Cl}{|}}{CH}- + Ph_3SnLi \rightarrow -CH_2-CH- + (Ph_3Sn)_2 + LiCl. \quad (IV)$$

Reactions (II), (III), and (IV), which compete with the triphenylstannation reaction (I), take place to a considerable degree in heptane (for chloropolyethylene) or in tetrahydrofuran [for poly(vinyl chloride)]; in such cases fully soluble stannated polymers are formed [52].

Among all the possible chemical reactions of stannated poly(vinyl chloride), its interaction with hydrogen chloride, simulating the mechanism of the stabilisation of poly(vinyl chloride) by organotin compounds, is of greatest interest. The reaction of triphenylstannylated poly(vinyl chloride) in tetrahydrofuran with dry hydrogen chloride supplied at a constant rate was investigated. The kinetics of the dehydrochlorination of various specimens of triphenylstannylpoly(vinyl chloride) are presented in Fig. 5. The rate of dehydrochlorination was determined from the change in the amount of chloride ions bound by the polymer (curve *1*) and from the content of chloride ions in the gaseous reaction products absorbed by water (curve *2*). The dearylation of polymeric organotin compounds has also been investigated by the nuclear gamma-resonance method [30].

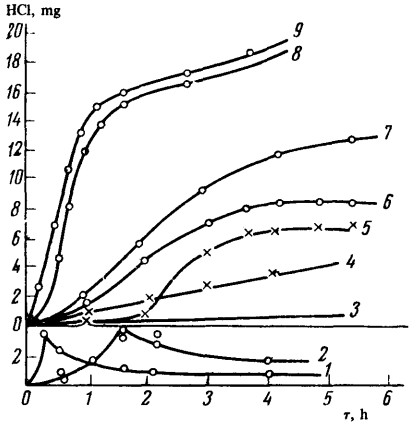
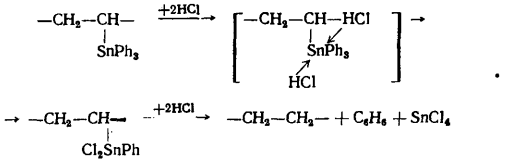


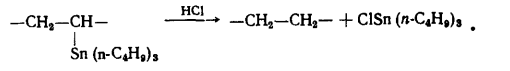
Figure 5. Kinetics of the dehydrochlorination of triphenylstannylpoly(vinyl chloride) (SPVC): 1) 0.05 g of SPVC, bound HCl; 2) 0.05 g of SPVC, free HCl; 3) mixture of 0.05 g of SPVC and 1 g of PVC, bound HCl; 4) mixture of 0.05 g SPVC and 1 g of PVC, free HCl; 5) 0.05 g of SPVC, total HCl; 6) 0.05 g of PVC, free HCl; 7) mixture of 0.05 g of SPVC and 1 g of PVC, total HCl (experimental); 8) 1 g of PVC, free HCl; 9) mixture of 0.05 g of SPVC and 1 g of PVC, total HCl (calculated).

According to the mechanism adopted by the authors, substituents at the tin atom are not split off one by one but in pairs: initially the two phenyl groups and then the third phenyl group and the polymer chain together; the

intermediate formation of a hexacoordinate complex with tin is postulated:



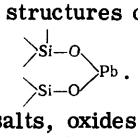
However, the analogous reaction of tri-n-butylstannated poly(vinyl chloride) with dry hydrogen chloride takes place in virtually only one stage with formation of tri-n-butyltin chloride and polyethylene [52]:



Since it is known that alkyl substituents are split off from the tin atom with greater difficulty than aryl substituents and the difficulty increases with increase in their chain length, it is understandable why phenyl groups are split off before the polymer chain, whereas in the case of butyl substituents such a sequence no longer holds. The overall study of the reactions of triphenyl and tri-n-butyltin derivatives of poly(vinyl chloride) with hydrogen chloride enabled the authors to make certain conclusions concerning the mechanism of the stabilisation of poly(vinyl chloride) by low-molecular-weight organotin compounds [30].

In conclusion of the section dealing with polymers metallated by heavy metals, the following point may be noted. There is no doubt that in the step involving the stabilisation of any polymer by compounds of heavy metals the latter are incorporated in the chain. Thus it was shown recently [53] that the basic lead sulphates PbO.$PbSO_4$, 3PbO.$PbSO_4.H_2O$, and 4PbO.$PbSO_4$ enter into complex formation reactions with the double bonds of poly(vinyl chloride), which appear in the latter on heating, and this leads to a weakening of the colour of the polymer owing to the breakdown of the double bond conjugation chain. It was noted that the introduction of various metal compounds into polymers, for example polyorganosiloxanes, significantly lowers the rate of their depolymerisation and decomposition. Therefore it was suggested that various metal compounds be introduced into polymer compositions; studies of this kind are listed in detail in a review by Balykova and Rode [54].

Thus Rafikov and coworkers [55] showed that the stabilising effects of titanium and iron acetylacetonates, alkoxyacetylacetonates, and also oxides on the thermal degradation of polydimethylsiloxane is due to their reaction with macromolecular chains, which leads to the formation of new high-molecular-weight compounds with metal atoms in the siloxane chain. Basic cerium acetylacetonate probably reacts with the terminal groups of the siloxane chains, forming new -Ce-O-Si- bonds [56]. The effect of many metals (metal oxides) on the thermal stability of polyalkylarylsiloxanes and their resistance to thermal oxidation has been demonstrated by Atkins et al. [57], who suggested that the treatment of the polymer with PbO leads to the formation of structures of the type



The interaction with salts, oxides, or alkoxides of metals of different Groups in the processing of polymers may be regarded as similar examples of the metallation of polymer chains: thus crystals, mainly of basic salts, insoluble in the rubber are formed in carboxylate rubbers obtained by the copolymerisation of butadiene with acrylic acids and in vulcanisation by divalent metal oxides or hydroxides [58]; the list of examples of this kind may be extended.

Whereas the polymeric derivatives of light metals can find application in the introduction into the chain of a wide variety of functional groups for the purpose of extensive chemical modification of polymers, polymeric derivatives of heavy metals are of course much less suitable for this. Therefore the number of studies on chemical reactions with participation of heavy metals is also significantly smaller. Almost all the investigations of polymer derivatives of heavy metals described in the literature deal mainly with problems of polymer stabilisation in one form or another.

IV. TRANSITION METAL COMPLEXES WITH MACROMOLECULAR LIGANDS

Two fundamentally different classes of macromolecular complexes are known [59]. Macromolecules the main chain of which contains the metal and fragments when the latter is eliminated may be obtained by the polycoordination of polyvalent ions to polydentate low-molecular-weight ligands. Regardless of the type of ligand, polymeric complexes of this kind are called polycoordination polymers; they have been extensively described by Marvell, Korshak, Vinogradova and coworkers, Baylar, Berlin, and others [60].

Macromolecules containing the metal in side chains can be prepared by the coordination of transition metal ions to macromolecular ligands already synthesised; in this case the metal can be readily removed or replaced by another without the breakdown of the main chain of the macromolecule. Polymeric complexes of this type, which will henceforth be referred to as complexes with macromolecular ligands, include in fact also the ion-exchange resins capable of the formation of chelates; the latter were investigated by Sansoni, Hering, and others [61].

In principle, all the complexes with macromolecular ligands discussed in the literature were obtained by the reaction of the complex-forming groups of the macromolecule with metal ions [59]. The few investigations in which a complex in the finished form, for example an acid metal-complex dye, are introduced into a poly(vinyl alcohol) [62] or Wofatit matrix [63], are an exception.

The reactivity of complexes with macromolecular ligands of various types is determined by the fact that both the metal–ligand bonds and the polymeric ligands can take part in chemical reactions.

1. Reactions with Participation of the Metal–Ligand Bond

The reactivity of the metal–macromolecular ligand coordinate bond is shown in the catalysis of a number of organic and inorganic reactions, in its participation in the so called ligand exchange reactions, and also redox reactions with participation of complexes having macromolecular ligands.

Usually the problem of the effect of the ligand on the reactivity of the M–L bond is treated as the effect of the coordination with the ligand on the catalytic activity of M^{n+}. The nature of the ligand is known to have a significant influence on the catalytic properties of the metal ions; a particularly marked influence is observed for enzymes and their models [64]. The nature of the ligand can

influence not only the reactivity of the metal-containing catalyst but also the mode of the reaction catalysed [65]. An explanation of the causes of the effect of the ligand on the catalytic properties of the complexes, including polymeric complexes, should be sought in the effect of several factors. The nature of the M–L bonds affects the donor–acceptor properties of the metal ion: an increase in the amount of ionic character of this bond entails an increase in the electron-accepting and a decrease in the electron-donating capacity of the metal; the formation of dative M←L bonds increases the charge of M, increasing thereby its electron-accepting capacity. It may be that in some cases ligands participate in the catalytic process itself. Thus in oxidation–reduction reactions there is a possibility of electron transfer via a ligand bridge; in some cases the coordinated ligands may form hydrogen bonds with the solvent, influencing thereby the mutual orientation of the reactants [65].

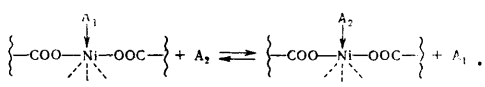
An attempt was made to employ complexes with ion exchangers (for example, resins based on polystyrene) containing iminodiacetic acid groups [66] as heterogeneous catalysts. The authors think that the advantages of using polymeric complexes for catalysis compared with low-molecular-weight complexes consist in the ease of separation of the catalyst from the reaction medium and, what is more important, in the fact that during the catalytic reaction very low but constant concentrations of metal ions in equilibrium with the polymeric complex are established:

$$\sim [fM] \rightleftarrows \sim [f^{n-}] + [M^{n+}] .$$

A review has already been devoted to the problem of using macromolecular complexes as heterogeneous catalysts for chemical reactions [67]. On the whole, one may conclude that, although certain macromolecular complexes do in fact show an enhanced catalytic activity compared with their low-molecular-weight analogues, nevertheless the employment of heterogeneous catalysts of this type is greatly impeded by diffusion phenomena, the inhomogeneity of the composition of the ligand, the non-uniform content of the metal, and similar factors complicating the study of the process.

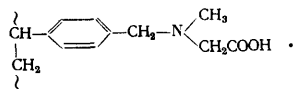
The capacity of such complexes to exchange ligands, which is based on the use of coordination vacancies in the transition metal incompletely saturated by the polymeric ligand, may be regarded as one of the effects of the reactivity of the metal–macromolecule coordinate bond.

Helfferich [68] was virtually the first to use for ligand exchange acidic cation exchangers in the nickel-form. Subsequently Latterel and Walton [69] showed that the nickel-forms of ion exchangers with carboxylic acid residues may be employed to separate many amines (A_1 and A_2):



Siegel and Degens [70] isolated aminoacids from their mixtures with the aid of sorption–desorption on the copper chelate complex of Chelex 100, [100] which consists of a polystyrene matrix with iminodiacetic acid groups. They also examined the reactivity of the Fe^{3+}-, Co^{2+}-, Ni^{2+}-, and Zn^{2+}-forms of Chelex 100 in relation to the sorption of amines, phenols, and also purine and pyrimidine bases, unsaturated hydrocarbons, sugars, peptides, humic acids, and other interesting natural compounds.

Hering and Heilmann [71] separated quantitatively glycine and β-alanine on poly-*N*-(*p*-vinylbenzyl)-*N*-methylaminoacetic acid in the nickel- and copper-forms (other metals were also employed):



Rogozhin and Davankov [72] obtained dissymetric complex forming ion-exchange sorbents of similar structure with optically active α-aminoacid groups. In many cases it proved possible to achieve a quantitative separation of the optical isomers by the chromatography of the ligands on these sorbents in the presence of complex-forming metal ions. Since their separation is based on stereoselective effects in the complex formation process, this method is an example of a new principle of the cleavage of racemates [72]. The sequence in which the ligands emerge from the chromatographic column is directly related to the stability of the complexes formed by them with participation of the stationary polymeric ligand. Therefore chromatography of the ligands may be employed in the study of the kinetics of labile mixed complexes [73].

We shall consider in greater detail how the reactivity of complexes with macromolecular ligands is reflected in their redox properties. All metal-containing redox polymers are obtained by combining a polymeric matrix with specific substances capable of oxidation and reduction. Three main classes of such compounds are distinguished [61], the coupling of which to the matrix involves (1) the formation of covalent bonds and is thus essentially irreversible, (2) the coupling is to some extent reversible and can involve some form of complex formation, (3) the substance being an oxidising or a reducing agent is linked to the polymeric matrix by adsorption forces, via the formation of clathrate compounds, etc. Since in the last class of compounds the metal atoms are linked to the polymer chain by forces weaker than those of covalent or coordinate bonds, we shall consider only the first two classes of metal-containing redox polymers.

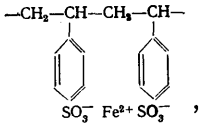
By combining ferrocene with diazotised poly-*p*-aminostyrene, Sansoni and Sigmund [74] obtained a polymer the apparent normal potential of which is 0.415 V and the redox capacity is 5.4 mequiv. g^{-1}. Fe^{II} and Fe^{III} polyvinylferrocenes have been reported [75]. Arimoto and Haven [76] oxidised the polymer (molecular weight of the order of 50 000) by suspending it in a solution of cerium sulphate, the polymer being gradually converted into a water-soluble pale blue Fe^{III} form, which can be reduced by any reducing agent to an insoluble yellow form containing iron(II). Partially sulphonated polyvinylferrocene is soluble in water and may be oxidised but the sulphonated molecule is unstable in the oxidised state and rapidly loses iron ions. Sansoni and Sigmund's ferrocene polymers [74] constitute essentially an example of the irreversible binding of a molecule with redox properties to a polymer already synthesised.

Examples of the formation of polycoordination compounds with the aim of synthesising redox polymers having reversible properties may be found in studies in which ion-exchange resins were saturated by inorganic cations. Thus Sansoni [74] also obtained oxidation–reduction cation exchangers by saturating Amberlite IR-120, Dowex-50, and Wofatit by the following redox systems: Fe^{2+}/Fe^{3+}, Sn^{2+}/Sn^{4+}, Ce^{3+}/Ce^{4+}, and Ti^{3+}/Ti^{4+}. Mills and Dickenson treated Duolite A-3 with a solution of copper sulphate until the resin became completely saturated and then with

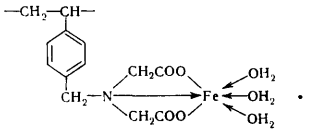
an excess of sodium hydrosulphite until the complete reduction of copper ions to the metal.

Similarly silver ions on Duolite A-2 resin were reduced by the same reagent to metallic silver; after such treatment the resin reacts with oxygen and eliminates it from liquid media [77].

M^n/M^{n+1} redox systems fixed in a suitable manner in a macromolecular matrix (the so called redoxites) or linked ionogenically to the ion-exchange resin (the so called redox ion exchangers) are of significant interest for preparative and analytical chemistry, since, when they are employed, the reduced (oxidised) substances are not contaminated by the reduction product of the reducing (oxidising) agent. The industrial application of systems of this kind was hindered for a long time by the fact that the usual reducing agents (Fe^{2+}, Sn^{2+}, and others) do not exhibit a high reducing capacity on ion-exchange resins. Hering [78] was the first to use for complex formation at a polymeric level the principle, familiar from inorganic chemistry, of a change in the redox potential of the metal ion following the addition of complex-forming agents or following a change in the pH (which in most cases is also explained by the formation of complexes with hydroxide ions). The formation of complexes of macromolecular ligands with metal ions can result in the formation of both reducing and oxidising agents, the reactivity of which greatly exceeds that of the free metal ions. We may quote a specific example of a change in the normal redox potential of the Fe^{2+}/Fe^{3+} system when it is combined with a resin containing iminodiacetic acid groups. According to Hering [78], the reducing capacity of Fe^{2+} increases markedly when the iron ions are not fixed on strongly acidic cation exchangers, which are capable of binding Fe^{2+} only in the ionic form, such as, for example,



but on resins of the type of Dowex-A-1 or Dowex-50W which are capable of complex formation:



The Fe^{2+}/Fe^{3+} oxidation–reduction system, the normal potential of which is +0.78 V, is known to be a weak oxidising agent. The normal potential of the Fe^{2+}/Fe^{3+} system on a resin containing iminodiacetic acid groupings may be calculated from the Nernst equation:

$$E = E_0 + RT/nF \lg C_{ox}/C_{red.} = +0{,}78 + (0.058 \cdot \lg 10^{-11}/10^{-6}) = +0.49\text{v}.$$

It is evident from the data presented that, when a polymeric matrix is employed, the weakly oxidising Fe^{2+}/Fe^{3+} system becomes a powerful reducing agent. The fact that the reducing capacity of the Fe^{2+}-form of the iminodiacetic acid resin is sufficient to reduce the oxygen dissolved in water merits particular attention [78]. When Ag^+ ions form complexes with the same Dowex-A-1 resin, the normal oxidation–reduction potential of the Ag^0/Ag^+ system shifts to positive values; thus the Ag-form of Dowex-A-1 resin is a more powerful oxidising agent than the Ag^0/Ag^+ system.

2. Reactions of a Coordinated Macromolecule

Little information has been published about the reactions of a coordinated macromolecular ligand, but the reactivity of coordinated low-molecular-weight compounds has now been investigated fairly widely. Thus there is a large number of specific examples of the effect of coordination on the reactivity of molecules, for example bidentate singly-charged ligands such acetylacetone, acetoacetic ester, aminoacid esters, salicylaldimines, etc. have been quoted in a review by Jones and Connor [79].

Since coordination leads to a redistribution of electron density in the ligand molecule and to a change of interatomic distances and valence angles, which entails a change in the polarity and strength of the bonds, it follows naturally that in the general case it cannot fail to influence the reactivity of the ligand. It is known that coordination usually, if not always, weakens the bonds (frequently those adjoining the coordinate bond) within the molecule and lowers the frequencies of the corresponding stretching vibrations. Such decrease of the frequency $\Delta\nu$ is determined by the acceptor capacity of the complex-forming cation, which is confirmed by the observed parallel variation of $\Delta\nu$ and the electron-accepting properties of cations, determined by an independent procedure [80]. During complex formation, coordination via the interaction of the unpaired electrons of the ligand and the free orbitals of the metals shifts the electron density of the ligand towards the metal, as a result of which the ligand becomes more electrophilic. The situation becomes more complicated when dative interaction with the reverse transfer of negative charge to the ligand contributes appreciably to the formation of the M→L bond; in the formation of such an M←L bond the effect of coordination extends to a large number of electrons and the antibonding orbitals of the ligand are involved in the binding, which entails a weakening of the bonds in the ligand.

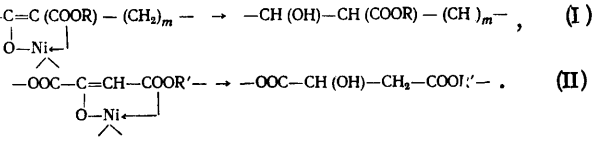
Siling and Gel'bshtein [65] quote the following references concerning the reactivity of ligands in complexes: (a) data on the chemical reactions of coordinated organic molecules (see, for example, Jones and Connor [79]); (b) infrared spectroscopy (see, for example, Nakamoto [80]); (c) data on the acid dissociation constants of the complexes and free ligands (see, for example, Grinberg [81]); (d) data on catalytic activity in reactions with participation of coordinated organic molecules (see, for example, Langenbeck [82]) or macromolecules [67].

The first attempts at investigation of the reactions of a coordination macromolecular ligand dealt with transesterification and hydrogenation. A study of the transesterification kinetics of acetoacetic ester and its copper complex showed [83] that transesterification with butanol takes place in both polar and non-polar solvents; the rate constants for the reaction and the activation energies and entropies were determined. However, the polymeric ligand (I) and the copper complex obtained on its basis have very low reaction rates.

The hydrogenation of polymeric ketoesters on a Raney nickel catalyst may be quoted as an example of reactions of a coordinated macromolecule which take place more effectively.

It has been shown [85] that macromolecular ligands of the β-ketoester type (I and II) can undergo hydrogenation in the coordinated (Ni^{2+}) state, being converted into poly-β-hydroxyesters; the reaction takes place with liberation of Ni^{2+} ions, probably in consequence of the breakdown of

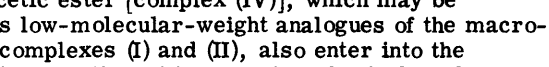
the resonance in the quasiaromatic ring of the coordination centre:



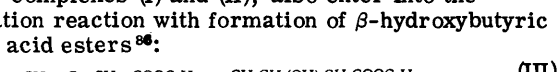
(I)

(II)

Nickel complexes of acetoacetic ester [complex (III)] and oxaloacetic ester [complex (IV)], which may be regarded as low-molecular-weight analogues of the macromolecular complexes (I) and (II), also enter into the hydrogenation reaction with formation of β-hydroxybutyric and malic acid esters[86]:



(III)



(IV)

It has been established that the hydrogenation of complexes (I)–(IV) under asymmetrising Akabori conditions (Raney nickel catalyst subjected to preliminary modification by an asymmetric compound) leads to optically active reaction products (Table).

Asymmetric hydrogenation of coordinated ligands of the ketoester type.

Initial ketoester and polyketoester complexes	Modifying agent (0.5 h, pH 5.1, 0°C)	Yield of hydroxy-ester or polyoxy-ester, %	$[\alpha]_{589}^{20}$
$(CH_3COCHCOOC_2H_5)_2Ni$	—	95	0.0
	L-glutamic or (+)-tartaric acid	92	−2.0
	—	100	0.0
$[-(CH_2)_m-COCH(COOC_2H_5)]_2Ni$	L-glutamic or (+)-tartaric acid	96	+1.2
	—	100	0.0
$(C_2H_5OOCCOCHCOOC_2H_5)_2Ni$	L-glutamic acid	98	−1.3
	—	100	0.0
$(-OOCCOCHCOOR')_2Ni$	L-glutamic acid	92	+8.6

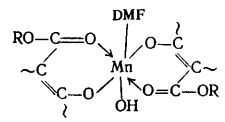
It may be supposed that in the hydrogenation of nickel complexes by hydrogen under pressure at an elevated temperature the initial complex breaks down with simultaneous (or subsequent) coordination of the substrate containing groups capable of chelation to the surface of the heterogeneous catalyst; this results in the formation of an intermediate mixed substrate–metal–modifying agent chelate. Such fixation of the conformation of the transition state and the steric limitation of the accessibility of unsaturated bonds to hydrogen lead to preferential formation of one of the optical isomers of polyoxyesters and hydroxyesters[87]. On the other hand, the hydrogenation of copper complexes of poly-β-ketoesters or acetoacetic ester does not lead to identified reaction products, only the decomposition of the complexes with liberation of the metal on the surface of the catalyst is observed[88]. The use of synthetic polymers as carriers for the active phase of the catalyst for non-stereospecific hydrogenation has been described by Sokol'skii and coworkers[89]. Thus palladium and platinum were deposited on poly(ethylene terephthalate) to be used subsequently in the hydrogenation of unsaturated alcohols (the reactivity of catalysts of this kind increased by a factor of 5–6 compared with palladium black). We attempted to employ the products of the asymmetric hydrogenation of (I) and (II) (above) as polymeric modifying agents in asymmetric induction from polymer to polymer[84]. It was shown that, like the Akabori catalyst[90], the metal-containing polymeric catalyst exhibits a definite stereospecific control in the hydrogenation of polymeric ketoesters.

In conclusion of the section on the synthesis of complexes with macromolecules and their chemical reactions, we may note that certain difficulties arise in the interpretation of these processes.

The steric factor plays an important role in the formation of complexes with macromolecules and their reactions. To calculate the energy of formation of low-molecular-weight complexes, formulae are employed in which account is taken of the radius of the complex-forming ion and the ligand[91] and it is assumed that the ligands approach closely the metal ion. On the other hand, in the formation of complexes with macromolecular ligands, the metal ions cannot in all cases approach the ligand owing to its large dimensions and the wide variety of its conformations. The so called critical ratios of the radii r_M/r_L or r_L/r_M make it possible to infer for low-molecular-weight compounds the highest coordination number n allowed by given steric factors[91], whereas for macromolecular ligands it is not always clear what value of r_L should be adopted.

A characteristic feature of a low-molecular-weight complex is a rigorous geometrical disposition of the functional groups of the ligand relative to the metal. On the other hand, for polymeric complexes the geometrical and stoichiometric relations may be significantly altered, which of course entails a change in the reactivity of both the coordinate metal–ligand bond and of the coordinated macromolecule. In polymeric complex compounds there is a possibility of the formation in the same macromolecule of coordination centres of various symmetries, frequently extremely strained, and, as shown by Tolmachev and coworkers[92], with various magnetic characteristics. Moreover, in complexes with bi- and poly-dentate macromolecular ligands part of the metal ions may be held by the usual Coloumbic forces without forming a coordinate bond and frequently retaining their counterions or forming 1 : 1 coordination centres (for example, instead of 1 : 2), such cases being quoted by Marinsky and coworkers[93] for the polymeric analogues of iminodiacetic acids.

A coordination number $n = 6$ is known to obtain usually for complex-forming metals. When 1 : 2 coordination centres are formed with macromolecular bidentate ligands, the residual vacancies in the complex-forming ion may be saturated, for example, by solvent molecules or by other ligands (the ligand exchange quoted above is based on this principle, p. 1089). As an example of the formation of a mixed macromolecule–metal–solvent complex, we may quote the coordination centre of the manganese complex of a poly-β-ketoester[59]:



Naturally the degree of coordination unsaturation of the centres cannot fail to influence significantly the reactivity of the given class of polymeric compounds.

Even these few examples show that the concepts adopted in the chemistry of low-molecular-weight complexes may be extended to macromolecular objects only when account

is taken of the fine structure of the macromolecular ligand and the polymeric complex formed from it. Therefore one of the tasks at the present stage of the investigation of the synthesis and chemical reactions of complexes with macromolecules is the accumulation and systematic arrangement of factual data in order to discover the specific features of this field.

V. FACTORS DETERMINING THE PROPERTIES OF VARIOUS TYPES OF POLYMER–METAL BONDS

To estimate the reactivity of any type of compounds, the following procedures have been employed [94]: (a) examination of various charge densities, bond orders, bond polarisibilities, etc. (b) determination of the energies of the reactants and the transition state. Only the second procedure is valid, since any treatment without taking into account the transition state is not sufficiently precise. Nevertheless up to the present time the procedure involving a comparative semiquantitative estimation of the reactivities of various compounds is still mainly used in the chemistry of organometallic compounds.

In discussions of the problems of the reactivity of organometallic compounds attention is concentrated on the behaviour of the C–M bond. Although the understanding of the nature of this bond is in fact most important for the understanding of the properties of the organometallic compound, other factors also play a certain role. These include certain steric characteristics of the organic substituent, the possibility of intra- and inter-molecular coordination with participation of the metal, effect of the solvent employed, etc. [94] These factors of course play a significant role also for polymeric organometallic compounds in which the multiplicity of chain conformations, solvation of the macromolecules, and interchain coordination may actually become of decisive importance in a particular reaction. To assess the properties and reactivities of organometallic compounds, the concept of electronegativity is sometimes employed [95]; nowadays it is believed that this criterion is neither a qualitative nor a quantitative characteristic of the chemical bond [96].

The main common factors determining the reactivity of organometallic compounds with a metal–carbon σ-bond, including polymeric organometallic compounds, are the nature of the metal and the stability of the organic cryptocarbanion.

One of the procedures whereby the nature of the metal–carbon bond in organometallic compounds may be inferred consists in the determination of the effective charges of the linked atoms. The effective charges may be calculated from the X-ray absorption spectra and frequently dipole moments are adduced to assess the effective charges and the electronegativities; sometimes the effective charges are determined from the ratio of the bond moment to the product of the elementary charge and the bond length [96]

Various methods have been employed to elucidate the problem of the relative stabilities of the carbanions of saturated low-molecular-weight hydrocarbons [97]. Thus the equilibria $RX + R'M \rightleftharpoons RM + R'X$ or $RMg + R'Hg \rightleftharpoons RHg + R'Mg$ have been investigated; a polarographic scale has been proposed for the determination of the CH acidity from the equation $\alpha E_{1/2} = f(pK_a)$ and the equilibrium ionisation constant of the CH acid has been used to assess the relative stability of the corresponding carbanion [97]. On the whole, one may assume that the higher is the acidity of the hydrocarbon, the greater the concentration of the charge in the corresponding carbanion, and the lower the nucleophilicity of the corresponding organometallic compound.

Unfortunately no studies on the determination of the effective charges of metals in polymeric metal-containing compounds or on the determination of the stability of macromolecular carbanions are described in the literature.

In the general case there are two limiting possibilities in the formation of bonds in complex compounds [98]: (a) formation of covalent bonds by utilising the unshared pairs of, for example, an oxygen-containing ligand; when two electrons are delocalised to an equal extent between two atoms, for example O and M, a negative charge is transferred to the metal (so that its resultant charge may actually become negative) with formation of a positive charge at the oxygen atom; (b) the ligand molecules are held around the metal ion by ion–dipole interaction forces only.

The true position for both low-molecular-weight and macromolecular complexes is intermediate between these two limiting mechanisms and in molecules of complex compounds the metal–ligand bond is to some degree covalent with unequal sharing of the electrons.

It is known [98] that the majority of transition metal complexes are of the type ML_4 or ML_6; the first usually has a square or tetrahedral form and the complexes of the second type are almost always octahedral (in polymeric complexes these postulates may not in fact hold, see p. 1091).

When a non-transition metal forms an octahedral complex, for example SnR_4X_2 by the reaction of triphenylstannated poly(vinyl chloride) with hydrogen chloride (p. 1088), the metal (tin) utilises one *s*, three *p*, and two *d* orbitals of the valence shell from which six sp^3d^2 hybrid orbitals oriented along the three coordinate axes are formed. In the formation of an octahedral transition metal complex, a similar hybridisation takes place, but here the *d* orbitals of the inner shell are employed. Thus, in the transition metals of the First Period (iron, nickel cobalt, and manganese), d^2sp^3 hybridisation involves only two 3*d*, one 4*s*, and three 4*p* orbitals. Many characteristic features of transition metal complexes are due precisely to the fact that a metal atom still has residual 3*d* orbitals not participating in the hybridisation and formation of valence bonds.

One may assume that the reactivities of both organometallic and complex compounds, including macromolecular complexes, are determined by the same factors—the nature of the metal and the nature of the organic component of the molecule. Probably, the most striking feature of the properties of coordination compounds is the coordination unsaturation of the metal due to the 3*d* or 4*f* vacant orbitals, as already stated above.

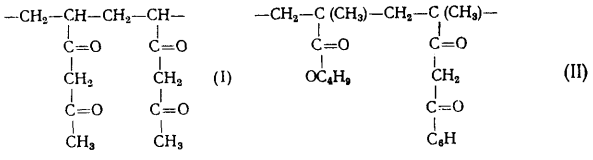
VI. CHARACTERISTICS OF THE CHEMICAL REACTIONS OF METAL-CONTAINING MACROMOLECULES DUE TO THEIR POLYMERIC NATURE

The field of chemical reactions in polymer chains is not at the present time simply the field of the synthesis of new macromolecular compounds which are difficult or even impossible to obtain by the polymerisation or polycondensation of low-molecular-weight substances. It is closely related to the problem of the reactivity of macromolecules and goes far beyond the framework of the concepts applied to it in the classical scheme of the individual branches of the chemistry of macromolecular compounds.

We shall examine the effect of the macromolecular nature of polymeric metal-containing compounds on their reactivity, following the classification of the characteristics of the reactions involving polymers proposed by one of the authors [99].

As already stated on p. 1085 the chemical modification of a polymer chain by substitution of lithium leads to the possibility of ionic grafting of a number of monomers on polylithiopolyethylene and polylithiostyrene. The study [100] of the kinetics of the anionic polymerisation of styrene and isoprene on these macromolecular initiators showed that in polar media the rate of polymerisation is higher than in the presence of the corresponding low-molecular-weight initiator (butyl-lithium): for the polymerisation of styrene on polylithiopolystyrene (PLPS), the ratio of the effective rate constants for chain propogation $k_{PLPS}/k_{C_4H_9Li}$ is 2.5 at 25°C and 3.9 at 10°C. The increase of the rate of polymerisation of styrene initiated by the macromolecular initiator ("live polystyrene") may be accounted for as due to the effect of the association of the growing polystyrene chains via intermolecular interaction between them, since they are formed in the immediate vicinity of one another owing to the presence of active centres in the same chain of the lithium-substituted polymer. In the microphase comprising such growing polymer chains the local concentration of the monomer may prove to be higher than its average concentration in the bulk phase (the concentration effect); the reaction takes place within such aggregate, which exhibits an enhanced selective permeability in relation to monomer molecules [16]. The effect of the polymeric nature of the system to be metallated influences the substitution of lithium in polystyrene compared with its low-molecular-weight analogue (toluene) [17] (p. 1083). In this case the so called chain effect is of decisive importance, namely the steric inaccessibility of the benzyl position in the polystyrene chain.

The formation of complexes between macromolecular ligands of the poly-β-diketone type with 3*d* transition metals is convenient for the demonstration of the change in the reactivity of a functional group owing to the chain effect. It was found that the effectiveness of the formation of coordination centres depends on the distribution of the complex-forming groups in the chain. Thus Fig. 6 shows the effectiveness of the binding of Ni^{2+} (expressed as a percentage) for two polymeric ligands: ligand (I) obtained by the polymerisation of methyl vinyl ketone with simultaneous acetylation and containing diketone groups in each unit and ligand (II) obtained by the ester condensation of poly(butyl methacrylate) with acetophenone and not necessarily containing diketone groups in each macromolecular unit:



(I) (II)

In the polymeric ligand (I) only 45% of the functional groups are employed for the binding of Ni^{2+} and this proportion remains constant regardless of the excess of Ni^{2+} ions in the medium [99]. On the other hand, in the polymeric ligand (II) up to 70% of the complex-forming groups are employed; in the presence of a small excess of ions the effectiveness of complex formation is low but increases with the concentration of the metal in solution.

Examination of the Stuart–Briegleb models shows that in the given case the chain effect is shown by the steric hindrance to the complex-formation process; with low-molecular-weight analogues, all the functional groups of the ligand are of course employed in the formation of the complex.

The chain effect was shown fairly notably in a comparative study of the stabilities (β_2) of the poly-β-ketoester (I) and acetylacetonate (II) complexes of the same metals [101]:

$\lg\beta_2$ for (I)	$\lg\beta_2$ for (II)	$\lg\beta_2$ for (I)	$\lg\beta_2$ for (II)
Mn^{2+} 7.10	Mn^{2+} 10.50	Ni^{2+} 7.55	Ni^{2+} 13.50
Co^{2+} 7.35	Co^{2+} 12.60	Cu^{2+} 8.00	Cu^{2+} 18.40

The defectiveness of the coordination centres formed, the distortion of the geometry of the coordination centres, and mixed complex formation with participation of the solvent (p. 1091) all lead to a greater lability of the L–M bond compared with the stoichiometric and geometrically regular acetylacetone complexes. One cannot exclude the possibility that this property of macromolecular and manganese complexes in fact makes them active‡, for example in the polymerisation of butadiene [67]: the corresponding acetylacetonates exhibit only a slight activity under these conditions.

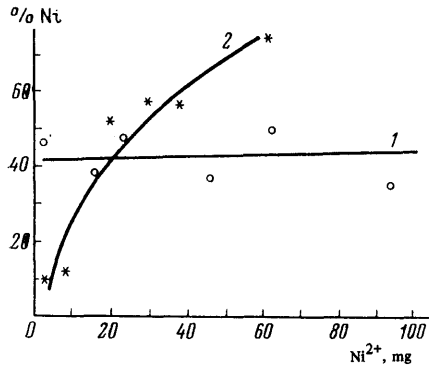
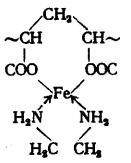


Figure 6. Effectiveness of the binding of Ni^{2+} (%) by polymeric ligands of types (I) (curve *1*) and (II) (curve *2*).

An interesting example of the influence of the concentration effect, which is a direct consequence of the presence of the polymer chain, on the catalytic activity of polymeric complexes in the decomposition of hydrogen peroxide was demonstrated by Kabanov et al. [102] They observed that, by virtue of the local concentration of H_2O_2

‡There is of course no direct relation between the thermodynamic stability constant of the complexes and their catalytic activity due to the homolytic splitting of the L–M bond; here it would be more correct to compare the thermal stabilities of the complexes and their activities; however, the K_{st} data presented may also be of definite interest.

in the vicinity of the coordination centres of the mixed iron(II) chelate with poly(acrylic acid) and ethylenediamine,



the catalase activity of the latter exceeds that of the low-molecular-weight analogue (Fe^{2+}, malonic acid, ethylenediamine) by several powers of 10.

The study of the interaction of copper(II) salts and polymethacryloyl-lysine by Moravetz et al. [103] showed that the polymer tends to form complexes even at a comparatively low pH, where the content of the complex in solutions of the monomeric analogue is low. This phenomenon may be understood if each spiral of the ligand macromolecule is regarded as a specific region of a concentrated solution of the polyaminoacid, which for this reason forms complexes effectively independently of the formation of 20-membered rings (the concentration effect). The concentration effect is shown in the fact that the macromolecular ligand behaves apparently as a more powerful complex-forming agent than its low-molecular-weight analogue.

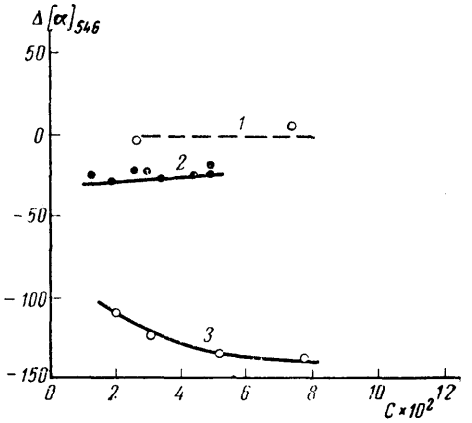


Figure 7. Dependence of the change $\Delta[\alpha]$ of a reaction mixture of triethylenediaminecobalt(III) and a polymeric anion on the concentration of the latter: 1) sodium acetate; 2) sodium polyacrylate; 3) sodium polymethacrylate.

Another consequence of the presence of the polymer chain is the conformation effect. Thus the study of optical rotatory dispersion in a system comprising a polymeric anion (polyacrylate, isotactic, syndiotactic, or atactic polymethacrylate, polyphosphate, polystyrenesulphonate) and an optically active cation $[Coen_3]^{3+}$ or $[Niphen_3]^{2+}$ showed that in such a system the nature of the polymeric ligand is more important. Fig. 7 shows that $\Delta[\alpha]$ falls with increasing polymethacrylate concentration but increases slightly as the concentration of polyacrylate rises, remaining unchanged in the presence of acetate. This is probably associated with different types of metal–polymeric ligand outer sphere interaction, which depends on the charge density along the chain and consequently on the chain–coil conformational transitions [104].

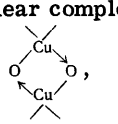
The configurational effect involving a change in the reactivity of the functional groups in the macromolecule compared with the low-molecular-weight ligands may be divided into several subtypes according to Plate's classification [99]. A striking example, where the presence of a group already involved in complex formation next to a free complex-forming group influences (unfavourably) the formation of the next coordination centre along the chain, is provided by the nickel complexes of polyacryloylacetone discussed above (p. 1093) (the so called "neighbour effect").

Another subtype of the configurational effect is shown in the influence of electrostatic interactions in the macromolecule on the rates of chemical reactions and on the equilibrium concentrations of the resulting complexes owing to the additional attraction (repulsion) of the reacting groups. The above example of the reaction of an optically active complex cation and a polyanion shows that not only the nature of the ionised groups but also the degree of their neutralisation is important [104].

Leyte and coworkers [105,106] observed the formation of mononuclear or dinuclear copper complexes in solutions of polymethacrylic acids as a function of the degree of neutralisation of the polymeric ligand; they expressed the binding of the Cu^{2+} by the polymeric acid in terms of the ratio

$$f = \frac{\text{equivalent concentration of ionised polymeric acid}}{\text{equivalent concentration of } Cu^{2+}}$$

When the charge of the polyelectrolyte was low ($f = 1.3$), the formation of the dinuclear complexes



in which, as in copper acetate, copper ions form a structure with D_{4h} symmetry having two polymeric ligands along the C_4 axis, was demonstrated with the aid of spectroscopic and static magnetic data.

With increase of the charge of the polyanion to $f = 3.3$, the dinuclear complexes dissociate into mononuclear species in which the central ion is surrounded in a distorted octahedron by polymeric ligands with negative charges. It is interesting that an analogous relation between the nature of complex formation with copper and the degree of neutralisation of a macromolecular ligand was observed by Japanese investigators [107] for polyglutamic acid.

The influence of different microstructures of the polymer chain on the rate of a chemical reaction with participation of the macromolecule, as happens in the formation of diastereoisomers in the chemistry of low-molecular-weight organic compounds, may be regarded as yet another consequence of the configurational effect.

The influence of the chain microstructure reduces in principle to the occurrence of a favourable (or unfavourable) disposition of neighbouring units in a transition state of known geometry. Complex-formation reactions with polymeric ligands of the acrylic and methacrylic types, for which there exist reliable methods whereby polymers microtactic to different degrees may be obtained, have been most thoroughly investigated. Moravetz et al. [103] were some of the first investigators to turn their attention to the dependence of the chelating capacity of polymethacrylic acid in relation to copper or magnesium ions on

its stereoregularity. They started with the hypothesis that, if complex formation involves neighbouring sections of the chain, the steric configuration of the latter should influence the stability of the complexes formed; on the other hand, when complex formation involves remote COOH groups, the complex formation equilibrium should be relatively insensitive to the configuration of the microligand. It was found that, in relation to Cu^{2+}, the isotactic polymer is three times more reactive than the syndiotactic polymer, whereas in relation to Mg^{2+} the opposite relation obtains:

k_b (isotactic)	k_b (syndiotactic)
13.4—18.0 Cu^{2+} (degree of ionisation 0.5-0.9)	1.6—6.1 (degree of ionisation 0.3-0.9)
9—14 Mg^{2+} (degree of ionisation 0.25-0.75)	15—24 (degree of ionisation 0.25-0.75)

$$k_b = [M_b^{2+}]/[M_f^{2+}](\overline{COO})_p ,$$

where M_b and M_f are the concentrations of bound (b) and free (f) cations and $(COO)_p$ is the concentration of ionised carboxy-groups in the polymer.

This is in fact understandable since copper ions form complexes with a definite geometry of the coordination centre, which are particularly stable when the ligand is the isotactic polymer, whereas magnesium ions form relatively unstable complexes with a less well defined geometry of the coordination centre; in the latter case the complexes of the syndiotactic polymer are actually somewhat more stable than those with the isotactic polymer.

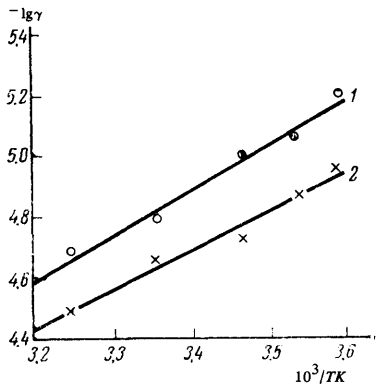
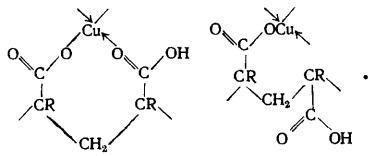


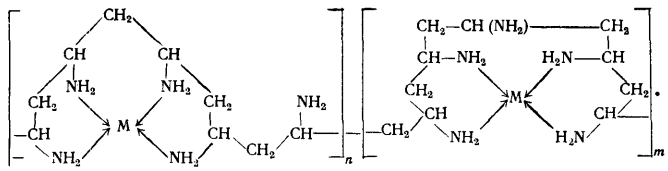
Figure 8. Kinetics of complex formation by isotactic (line *1*) and syndiotactic (line *2*) polymethacrylic acids with Cu^{2+}.

Geuskens et al. [108] re-examined the differences between the reactivities of polymethacrylic acid in relation to copper ions as a function of the microtactic character of the polymeric ligand chain:



Kinetic data show (Fig. 8) that in the temperature range 5–35°C isotactic polymethacrylic acid is more reactive than its syndiotactic isomer: the rate of complex formation involving the first-isomer is higher by a factor of 1.5 than for the second; the activation energies are 6 and 7 kcal $mole^{-1}$ respectively.

The polymeric nature of the macromolecular ligand is shown particularly clearly in the so called "synthetic muscle model"; in the chemistry of low-molecular-weight complexes there are simply no analogues. Teyssie et al. [109] investigated the formation of transition metal complexes of polyvinylamine and obtained complexes soluble in water over a wide range of pH and ionic strengths; with the aid of a wide variety of research techniques, they showed that the formation of complexes with Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} greatly influences the dimensions and shape of the polymeric ligand molecules:



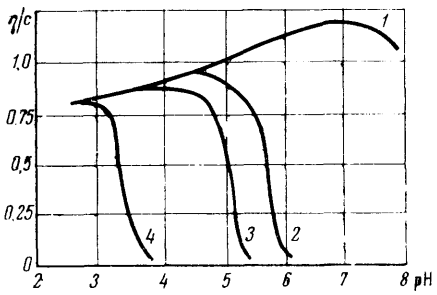
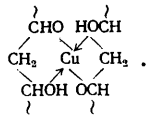


Figure 9. Variation of the viscosity of polyvinylamine solutions in complex formation with transition metal ions: 1) polyvinylamine; 2) Zn^{2+}; 3) Ni^{2+}; 4) Cu^{2+}.

The three condensed cyclic structures produced by complex formation give rise to very powerful contraction of the macroligand molecule, which has been clearly demonstrated by a viscometric technique (Fig. 9). The authors explain the colossal decrease of the viscosity of polyvinylamine solutions in the presence of 3*d* transition metal ions by a change in chain conformation during the complex formation step.

The work of Kuhn et al. [110] provides a still more unusual example of the effect of the polymer chain on complex formation. Employing the principle of reversibly contracting fibres already known from biochemistry, they showed that a partially neutralised and cross-linked copolymer of poly(vinyl alcohol) and polyacrylic acid contracts under the influence of a number of salts (Ca^{2+}, Mg^{2+}, Cu^{2+}) and is reversibly extended in the presence of EDTA; the reversible shift of the system is determined by the presence of the competing ligands poly(vinyl alcohol) and EDTA. We may note here that DNA and RNA nucleoprotein filaments also contract when the above

salts are added to the medium and become extended when a suitable complex-forming agent is introduced. The "contracting polymeric systems" of Kuhn [110] operating on the principle of complex formation and oxidation–reduction simultaneously are also extremely interesting. On treatment with Cu^{2+} ions, the gel of poly(vinyl alcohol) swollen in water (100% H_2O and 10% of the polymer) forms a coloured complex with simultaneous intense contraction of the gel fibres (recorded dynamometrically):



If the system is then acted upon by H_2/Pt, the central metal ion is reduced to Cu^+ and the coordination centre breaks down; the gel fibres are decolourised and resume their former dimensions. On the other hand, the effect of O_2/Pt leads to the oxidation of the metal ion to Cu^{2+}, complex formation, and the dyeing and contraction of the gel fibres (Fig. 10).

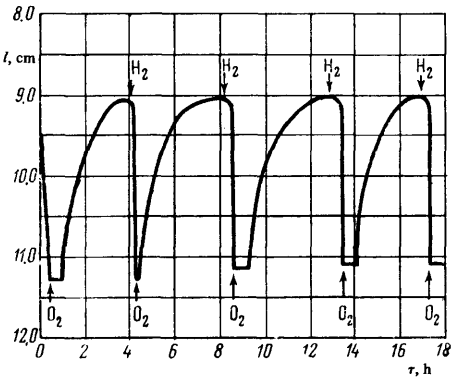


Figure 10. Variation of the length of a poly(vinyl alcohol) fibre on reversible oxidation–reduction in the presence of Cu^{2+} ions.

Kuhn's system has no analogies in the chemistry of low-molecular-weight compounds and is a striking example of the influence of the chain structure on the reactivity of the complex-forming molecule. We may note that Kuhn's system imitates the redox reactions of DNA complexes, for example with Fe^{2+} or Cu^{2+}, where the reduction of central atoms causes a weakening of the bonds between the complementary chains and its oxidation gives rise to the stabilisation of the two-tier conformation of DNA. [111]

All the findings described in this last section show that chemical reactions already known for low-molecular-weight analogues can be achieved on polymeric coordinated and non-coordinated ligands. At the same time the characteristics of the chemical reactions of macromolecules due to their polymeric nature are fairly remarkable, the effect of the polymeric chain on the reactivity of polymeric compounds of this type being most striking.

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