

CHEMICAL MODIFICATION AS A METHOD OF SYNTHESIS OF ORGANOMETALLIC POLYMERS

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Presently extensive material about synthesis and investigation of the properties of transition metal π -complexes with the use of individual structurally different aromatic compounds as ligand remains collected.

A rapid development of high-molecular compounds chemistry has been accompanied by preparation of a number of new aromatic oligomers and polymers. In this connection it seems reasonable to use those high-molecular transition metallic π -complexes.

Oligo- and polyarylenes of different structures, olygo- and polyphenylenalkyls, oligophenplenacetylenes, oligohydroxyphenylenalkyls and their allyl derivatives, etc., were used as the initial aromatic polymer matrices, while transition metals (Cr, Mo, W, Fe, Co) and their low-molecular complexes as initial metals.

Organometallic oligomers and polymers have been synthesized by the following methods :—

1. Thermal polycoordination of carbonyl metals with polymeric matrices.

2. Vapour-phase interaction of atomic metals with oligomers and polymers.

3. Replacement of ligands in low-molecular complexes by macromolecular ligands/matrices.

As a rule all these reactions proceed with high yields. The structures of the macromolecular complexes obtained were confirmed by means of IR, NMR, YX, XP spectrometries, mass-spectroscopy and other techniques. In certain cases, besides the formation of macromolecular complexes, in some cases the systems of the clusters type were also obtained.

With the polymeric formation with metal-intense paramagnetic properties, catalytic activity appears. Iron-containing oligomers and polymers are capable of reversible one-electron reduction.

The nature of polymeric ligands, exerts a pronounced effect on the behaviour of the complexes being synthesized. The majority of carbonyl-containing metaloligomers and polymers are reactive and thermoreactive products and under the conditions widely used now in thermal treatment of plastics they can be converted into three-dimensional products due to splitting of the CO-groups.

Key Words : Organometallic Polymers; π -Complexes; Synthesis; Transition Metals

MUCH information on synthesis and properties of π -complexes of transition metals has been accumulated in which individual aromatic compounds of different structures are used as ligands.¹⁻³

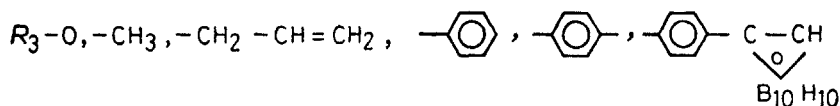
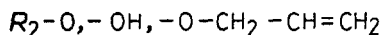
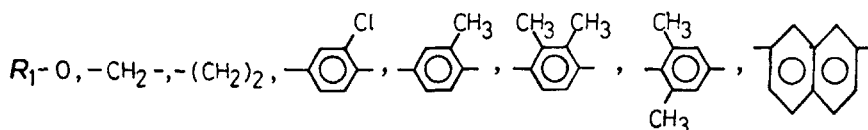
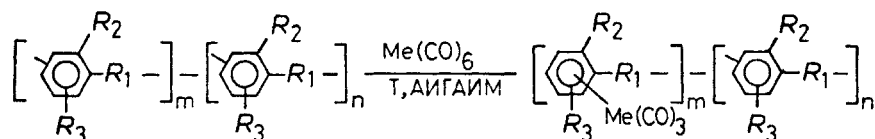
On the other hand, rapid development of chemistry of high molecular compounds has resulted in the preparation of novel aromatic oligomers and polymers.^{4,5} Therefore, it is of interest to use such high molecular compounds as ligands for the synthesis of macromolecular complexes of transition metals.

The presence of phenyl rings in the main macrochain of high molecular compounds is responsible for their high stability due to the possibility of conjugation, whereas vacancies in the *d*-levels of transition metals favour in a number of cases the appearance in the polymers of a high catalytic activity, electric conductivity, and other interesting and specific properties.

However, it should be noted that only few papers are devoted to using high-molecular compounds as ligands for synthesis of π -arene complexes.⁶⁻⁸

As initial aromatic matrices we used oligoarylenes, oligophenylenealkyls, oligophenyleneacetylene, oligoxyphenylenealkyls and their derivatives,^{9,10} polyphenylenesulphides, and other compounds, and as initial metals—transition metals Cr, Mo, W, Co, Fe, Ni, and others and their low-molecular π -complexes.

Using a great number of polymers as macroligands, it seemed expedient to us, on the one hand, to follow the ability of each of them to form bonds with metals and, on the other hand, to study the effect of the nature of such ligands on some properties of the macromolecular complexes being prepared.



Note: The words in Russian refer to diglyme.

The following methods were used for synthesis of organometallic oligomers and polymers:—

1. Polycoordination of carbonyls of metals with phenyl rings of polymeric matrices.
2. Vapour-phase interaction of atomic metals with oligomers and polymers.
3. Ligand exchange in low molecular aromatic complexes for macromolecular matrices.
4. Phenylation reaction.

As is known, arenecarbonyl derivatives ("semi-sandwich" complexes), especially typical for VI B group metals, are considered to be the most widespread type of arene derivatives of the transition metals. Such π -complexes are mainly obtained by polycoordination of metal carbonyls, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$ and individual compounds of the aromatic nature.¹

Upon interaction of many oligomers and polymers of the polyarylene type with carbonyls of the VI B group metals at 120–140 °C in diglyme as a coordinating solvent, we synthesized the whole series of partially or completely soluble macromolecular π -complexes (M.M. from 1000 to 5000) in yield up to 65 per cent with a metal content up to 15 per cent according to the scheme :

The structures of the synthesized π -complexes were confirmed by IR, NMR, UV, and mass spectrometry and by other methods. In particular, in the IR spectra of the majority of the prepared compounds, a shift of the CO band of the initial carbonyl to a low-frequency region (1880–1970 cm^{-1}) and splitting of the band into two components are observed. (This is a specific feature of the spectra of arenemetaltricarbonyl complexes containing the stretching vibration bands of carbonyl ligands)¹. The introduction of different substituents into the benzene rings of the matrices and even a replacement of metal atoms does not exert any substantial influence on the shift of these frequencies.

The results of comparative studying the NMR spectra of the initial oligomers and soluble fractions of the synthesized compounds on nuclei of H atoms and NMR ¹³C have shown that, contrary to the signals of arene rings in the initial oligomers, the signals of protons of the arene rings in the complexes undergo an upfield shift which is typical of the resonance signals of the protons of the phenyl rings bonded to (CO), fragments *via* π -coordination. In this case, along with the resonance signals of carbon atoms in free arene rings the signals of π -coordinated benzene rings and the resonance signals of carbon atoms in carbonyl ligands are also observed.¹¹

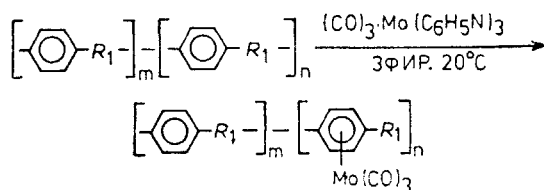
The evaluation of the properties of macromolecular complexes, in particular, the analysis of the metal content in them has shown that the initial polymers can be arranged in the following sequence with respect to their ability to coordination : oligo- and polyarylenes obtained by the reaction of oxidative dehydropolycondensation < oligoxyphenyls and their allyl derivatives, oligophenylenealkyls < oligophenylacetylenes < oligoarylenes obtained by polycyclotrimerization.

Probably, the ability of oligo- and polyarylenes under study to interact with metals of carbonyls of the VIb subgroup depends to a great extent on the spatial accessibility of the phenyl rings contained in their macromolecules. Evidently, this ability is more pronounced in the case of polyarylenes. The substituents of nucleophilic and electrophilic nature present in the benzene rings of polyarylenes strongly influence the reactivity of the polymers.

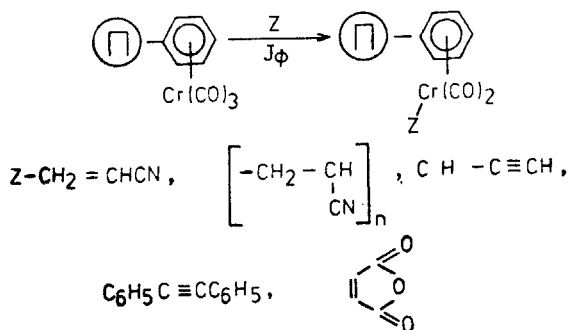
The use of oligomers with donor substituents (for instance, one or two methyl groups in *para*- and *meta*-positions) and of a ferrocenyl group allows one to obtain complexes with a higher content of metal than in the case of acceptor substituents.

It is noteworthy that the formation of tungsten and especially of molybdenum complexes under these conditions is observed only in individual cases. Mainly, insoluble products in low yields are formed. Apparently, macromolecular molybdenum complexes, similarly to their low-molecular analogs, cannot withstand a high reaction temperature and decompose even in the course of their preparation.

Therefore, to synthesize molybdenum-containing oligoarylenes, we used the exchange reaction of pyridine ligand in tris-pyridine-tricarbonylmolybdenum complex with a macromolecular arene¹², proceeding under mild conditions according to the scheme :



Irradiation of synthesized macromolecular π -complexes of the VI B group metals in an UV region is accompanied with a substitution of Π and *n*-donor (for instance, maleic anhydride) for one of the three CO-group remaining at the metal atom :



Note : C H - C \equiv CH, Read for C₆H₅ - C \equiv CH,

The study of properties of the prepared oligomers and polymers containing metaltricarbonyl fragments has shown that complexation of macromolecular matrices with metals results in that their paramagnetic properties become much more pronounced (*g*-factor of such compounds is close to that of a free electron and concentration of lone spins is within the range from 10 to 10^{20} per gram), catalytic activity appears, and so on.

The nature of polymeric ligands, in its turn, exerts a pronounced effect on the behaviour of the complexes being synthesized.

For instance, due to a stabilizing effect of the polymeric matrices, the bond of the metal with the phenyl rings in macromolecular complexes becomes, apparently, much stronger than in their low-molecular analogs. The majority of the prepared compounds are reactive and thermoreactive products and under the conditions widely used now in thermal treatment of plastics they can be converted into three-dimensional products due to splitting of the CO-groups and formation of the "sandwich" type structures.¹³

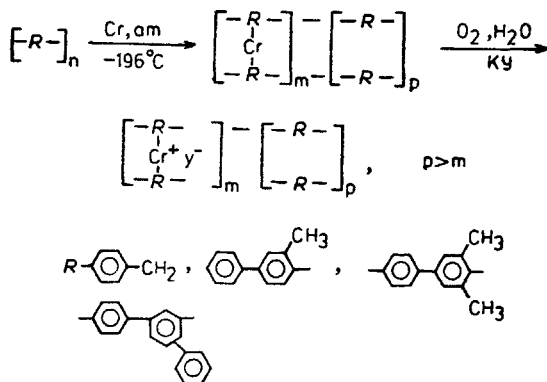
The mass losses of thermally treated samples under dynamic conditions (up to 900 °C) are about 3 times smaller than mass losses of the initial thermoplastic oligophenyls and amount to 17-20 per cent.

The direct interaction of vapours of metals in an atomic state with polymeric matrices recently discovered by Ozin, Francis, and Awl¹⁴⁻¹⁹ can be considered as the simplest method of synthesizing organometallic polymers of the "sandwich" type. The authors used mostly polymers containing phenyl rings in a side chain as macromolecular ligands. Organometallic polymers possessed some interesting properties but, as a rule, they were studied only by spectral methods in the course of synthesis.

We aimed our efforts at increasing the number of ligands (polymers of the polyarylene type) and tried to study in greater detail the properties of the prepared products. Macromolecular complexes were synthesized in the steady-state reactor.¹⁰ Metal, in particular chromium, was evaporated from a basket made of a tungsten wire. Simultaneously a polymer solution (5-10 per cent) in diglyme was fed into the reactor. The obtained complexes were separated as polycations. As a counterion use was made of iodine.

Polycations, containing up to 13 per cent of metal, soluble in polar solvents and having a molecular mass of from 1500 to 6000 were prepared in about 20 per cent yield according to the scheme :

The structure of synthesized macromolecular π -complexes was confirmed by IR, RFS, UV, X-ray electron spectroscopy and other methods of analysis. For instance, the study of NMR signals has shown that the absorption line of the samples is characterized by the value of the *g*-factor equal to that of bisarene-chromium, namely, 1.986.²¹

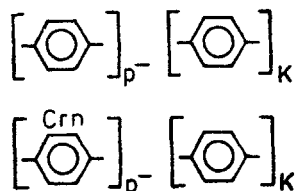


The spectra recorded by X-ray electron spectroscopy reveal the signal of electrons with a bond energy in the region 574.4eV typical of $2p^{3/2}$ electrons of chromium atom coordinated with aromatic nuclei.²²

The prepared macromolecular π -complexes of chromium,²³ similarly to their low-molecular analogs, are capable of one-electron reduction.

The polarogram of the samples revealed one cathodic wave within the potential region from -0.5 to -1.5V (DMF as a solvent and LiClO_4 as background electrolyte). The reduction of a polycation is observed in the region of a higher negative potential (-0.93V) than in the case of its low-molecular analog (-0.78V). This may be attributed to the formation of more stable complexes due to conjugation when polymeric matrices are used.

It should be noted that upon interaction of vapours of metal with solid polymeric matrices in the case of no solvating effect of the solvents, along with macromolecular π -complexes whose yield attains only 6 per cent, chromium-containing polymeric systems are mainly formed (up to 75 per cent) with Cr content from 5 to 6 per cent having the following structure.²⁴



In the X-ray electron spectra of the prepared compounds, the 575.5eV component is present which corresponds to the M-M bond.²²

Electron-microscopic investigations of the films obtained from benzene solutions of such systems is much more uniform than the structure of macromole-

cular π -complexes. Inside the polymeric matrix there are regions with a high electron density which may point to the formation of the aggregates of metal of the cluster type 10–20nm in size. In the formation of metallic structures polymeric matrices also participate. On separate selections they are clearly oriented and form chains consisting of 3–5 particles with a length not exceeding 800nm.

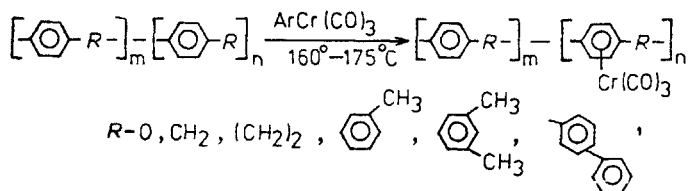
It is noteworthy that structural features typical for freshly prepared samples are retained after keeping the samples for several months at room temperature in the light which confirms the stability of the prepared system. Under the action of ultrasound (21kHz, exposure time 5 and 10min) the stability is retained.

To control the sizes of metallic aggregations in polymeric matrices, we made an attempt to atomize chromium in presence of nitrogen. As is known, in several cases cluster particles with preset sizes were obtained in an inter medium. We succeeded in preparation of polymeric systems with a narrower distribution of cluster particles (from 3 to 10nm) in the presence of small amount of nitrogen.

Upon interaction of polyphenylsulphide with $\text{Fe}_3(\text{CO})_{12}$ the prepared systems contain, along with macromolecular π -complexes, aggregation of α -iron and up to 15 per cent of highspin bivalent iron whereas no carbonyl groups are present.

After the corresponding thermal treatment, the materials are characterized by conductivity $E^{20} - 4 \cdot 10^{-4} \text{ (cm ohm)}^{-1}$.

The ability of arenemetaltricarboxyl complexes and their high-molecular analogs to retain differently organic ligands in the course of thermal treatment (see p. 263) was used by us for preparing chromium-containing oligomers via thermal exchange of arene in benzenechromiumtricarboxyl with oligoarylenes which made it possible to widen synthetic routes of obtaining organometallic polymers.

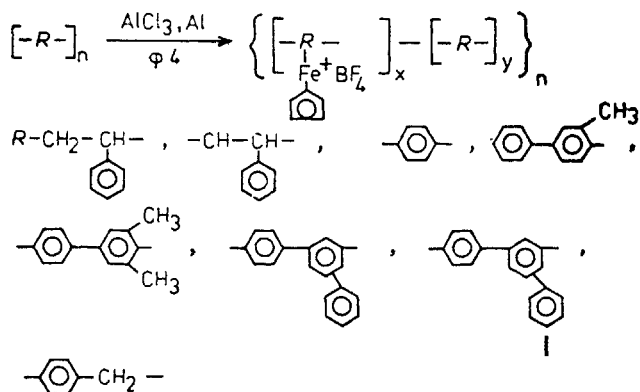


The method of mutual exchange of arene ligands of low-molecular complexes is rather widespread.^{25–28}

If however, this method is applied for synthesizing macromolecular complexes, the process, in contrast^{25–26} becomes non-equilibrium because of a higher stability of the M-C bond and is mainly directed towards the formation of organometallic polymers.

Besides the mutual exchange of arene ligands in complexes, there are many publications on substitution of CPD-rings, for instance, the substitution of phenyl rings for CPD-rings in ferrocene.^{29–35}

One could expect that in the case of using macromolecular matrices of the oligoarylene and polymer types the process can follow the scheme :



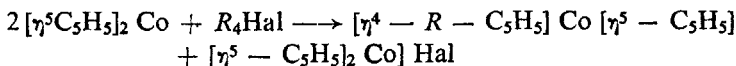
As a result, partially soluble products are prepared in yields up to 65–70 per cent with iron content up to 17 per cent.

In the IR spectra of the synthesized compounds, a wide band is observed in the $1030-1120\text{cm}^{-1}$ region typical of $B\pm_4^-$ anion and a set of bands which, by analogy with low-molecular complexes, can be assigned to π -bonded cyclopentadienyl and benzyl rings, respectively. The signals of CPD protons in the prepared macromolecular π -complexes, similarly to their low-molecular analogs, are shifted downfield to a greater extent than the corresponding signals in the ferrocene spectrum. In this case as one might expect, along with the signals of protons of non-coordinated benzene rings (in optimum, one ironcyclopentadienyl group for each two elementary unit), there are signals of the protons shifted upfield as compared with the first signals and belonging to the signals of coordinated benzene rings.

The polarogram of synthesized macromolecular complexes, similarly to that of their low-molecular analogs reveal two cathodic waves the first of which corresponds to reversible one-electron reduction of cations.

Leonova and others³⁷ have developed a simple preparative method of synthesizing organometallic polymers by grafting π -complexes of transition metals, in particular, cobaltocene to high-molecular matrices (phenylation of cobaltocene).

The method is based on the ability of cobaltocene to interaction with organic halides.³⁸

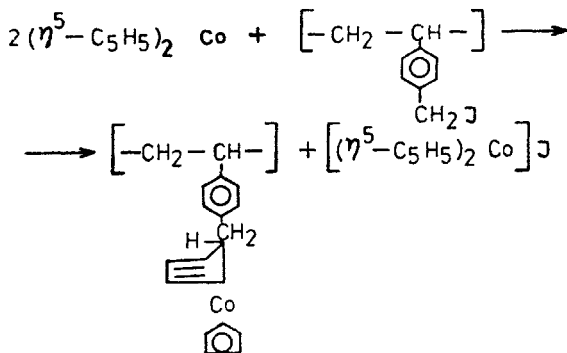


where R is alkyl, acyl, and so on.

As is known, the reactivity of the C-Hal bond increases from Cl_2 to I_2 .³⁹ The authors have shown that this process goes readily when polymers of the different structures containing a C-Hal bond are used as macromolecular ligands.

The reaction was studied for polychlorocyan and halogenized copolymers of styrene with divinylbenzene or with p-xylylenedichloride.

Evidently, one should assume that cobaltocene can be grafted to polymers of the oligoarylene type containing halide atoms. In this case of iodomethylated copolymer of polystyrene, the process of alkylating cobaltocene can be presented as follows :



The completion of substitution of the $(\eta^5 - C_6H_5) Co(\eta^4 - C_5H_5)$ fragment or iodine depends on the reaction time and the ratio of the reagents.

It is noteworthy that copolymer in which iodine is only partially substituted with π -complex can be repeatedly treated with cobaltocene and as a result, an optimum introduction of the cobaltocene fragment can be attained.

Cobaltocene-containing polymers, like cobaltocene,⁴⁰ possess a catalytic activity; they catalyze reactions of cyclo- and polycyclotrimerization, and others.

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