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The Main Approaches for Description of the Topochemistry of Macromolecular Metal Complexes

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Summary: The topochemistry of the distribution of metal complexes on macromolecule ligands is studied on an example of macrocomplexes obtained by the interaction of transition metal compounds (MX_n) with functional groups of the grafted layer (PE-gr-polyallylamine, PE-gr-polyacrylic acid, PE-gr-poly-4-vinylpyridine, etc.). Three main types of macrocomplexes are found out: **I** – isolated complexes ($\bar{r} \geq 15$ Å); **II** – the aggregations of cluster types (complexes of paramagnetic metals unbounded chemically between each other) ($\bar{r} \leq 7$Å). **III** – clusters with a strong exchange interaction (exchange-bound clusters caused by chemical bonds of complexes similar to polynuclear complexes). The ratio and distances between complexes of differen types as well as their possible role in catalytic processes are estimated and discussed.

Introduction

A main usage of macromolecular metal complexes is a catalysis. A best way consists in a combination of the advantages of homogeneous and heterogeneous catalysts and the removal of their shortcoming.[1] Though the aim does not achieved so far, the intensity of researches in this direction does not diminished. The many factors influence the catalytic properties of polymer-immobilized metal complexes. Some important characteristics of immobilized catalysts are functional groups distribution and accessibility, the uniformity of their bonding properties, and similar features for anchored metal complexes that give rise to active centers under the of a cocatalyst. All the above characteristics and their response to reaction conditions reflect the latent properties of immobilized catalysts and have been coined the term „topochemistry of macromolecular metal complexes“.

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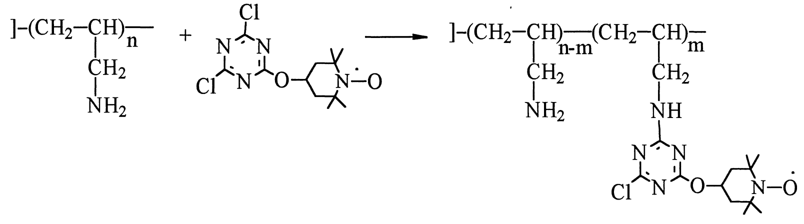
Topochemistry of the functional layer of polymer carriers

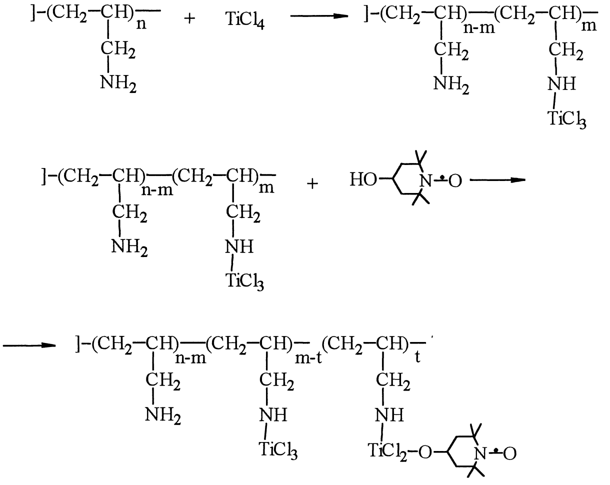
In the eighties we elaborated the principal new type of macroligands. They allow to carry out a reaction center into the surface or localize it in thin surface of the inert polymer. These are polyethylene (PE), polypropylene (PP), copolymer of ethylene with propylene (CPP), polystyrene (PS), and others, the surface of which is functionalized by gas phase grafted polymerization of corresponding monomers (allylic alcohol, allyl- and diallylamine, acrylic acid, 4-vinylpyridine, etc.).[2] For example, in the case of PE these products are denoted as PE-grafted-poly-diallylamine (PE-gr-PAlAm), PE-grafted-poly(4-vinylpyridine) (PE-gr-P4VPy), PE-grafted-poly(acrylic acid) (PE-gr-PAA). The degree of grafting was ranged from 1 to 10 wt.%, the tickness of grafted layer was 100-300 Å. To determine the accessibility of functional groups for the reaction with transition metal compounds (MX_n) as well as study topochemistry of metal complexes formed the method of spin labels was used which earlier was in wide use in analysis of various biological[3], polymeric[4] and other objects.[5] Spin-labeling of macroligands in the case of PE-gr-PalAm with using of stable 2,2,6,6-tetramethyl-4-(2′-oxy-4′,6′-dichlorotriaxine)piperidine-1-oxyl nitroxyl radicals ($R^{\cdot}$) can be presented by following scheme:[6]



The calibrating curve of the parameter of Δ - $\bar{r}$ (where $\Delta = d_l/d - (d_l/d)_0$ and d_l/d is the ratio of total intensities of end and middle components of EPR spectra[6] (for our systems $d_l/d = 1.76 - 0.036\ A_{||}$)) was used for determining the effective distances ($\bar{r}$) between iminoxyl radicals onto polymers. It turned out that $\bar{r} = 25 \div 35$ Å for PE-gr-PAlAm-$R^{\cdot}$ system at varied concentration of the fixed radical. At the considerable increasing of the fixed $R^{\cdot}$ (ten times) the average distance between them are decreased only in 10 Å. Take into account the real surface of macroligands such state is possible only if ‚chromatographing“ of $R^{\cdot}$ into ‚deep“ layer of the functional cover occurs. By other words, grafted layer is ‚friable‘ and all its functional groups are pactically accessible for the interaction. The $R^{\cdot}$ radical takes up layer-by-layer position, the number of the layers is about 10.

Topochemistry of diamagnetic complexes fixed into polymers

The same method can be also used for spin-labeling diamagnetic metal complexes bounded with polymer. This can be illustrated on an example of the interaction of $TiCl_4$ with PE-gr-PaAlAm:[6]



A minor portion of the immobilized metal complexes is involved in clusterlike aggregations that effectivelly bond stable nitroxyl radicals by coordinationn of the $-N-O^{\cdot}$ fragments. The effective distances between radicals are less than 10-12 Å in such aggregations. The portion of the bonded metal complexes involved in aggregations is considerably greater for titanium-containing polymers. The remaining portion of the immobilized complexes is uniformly distributed along the grafted functional layer as isolated complexes that covalently bond to the radicals $R^{\cdot}$. It was shown that metallation of the functional covering makes the polymer more accessible for spin-labeling. Besides metallation of the functional covering has a considerable effect on the dynamic behaviour of the polymer matrix.

The study of topochemistry of polymer-bond paramagnetic complexes

These complexes provide the most information about topochemistry. Cu^{2+}, V^{4+}, Mn^{2+}, and other ions are mostly used as paramagnetic centers and the main methods for studying are magnetochemistry and ESR. Thus, the temperature dependence of the magnetic susceptibility (χ^{-1}) of the Cu^{2+} complexes fixed onto PE-gr-PAA[7] shows that in all cases there is a ‚break' in the curve of $\chi_M^{-1} = f(T)$ (Figure 1).

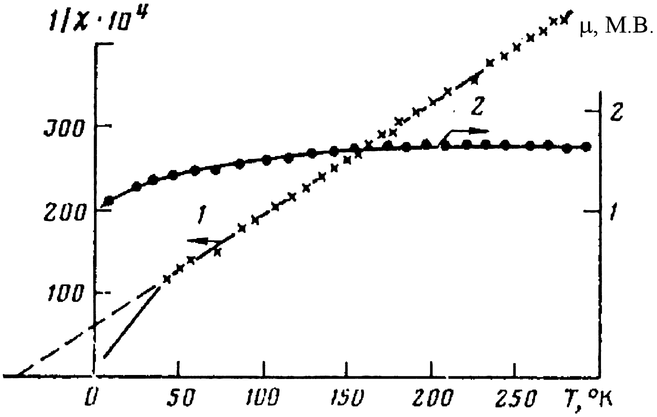


Figure 1. Temperature dependence for χ^{-1} (1) and μ_{ef} (2) for PE-gr-PAA-Cu(II) (0.4 mmole/g).

The Weiss constant (θ) is equal to 50K. This can be explained by the presence of two types of bond complexes of Cu^{2+}: i) isolated complexes (their behaviour obeys Curie law) and ii) complexes aggregated to clusters with the antifferomagnetic exchange:

$$\chi_{exp} = \chi_{isol} + \chi_{exch} \qquad (1)$$

The content of copper in complexes of these types is estimated by the equation:

$$\bar{C}_{total} = \bar{C}_{isol} + \bar{C}_{bond} \qquad (2)$$

The experimental data show that already at the concentration C_{total} = 0.1 mmole/g more half of copper ions is localised in cluster aggregations. More detailed information can be obtained using ESR. With increasing of the $\bar{C}_{total}$ the form of ESR spectra is changed (Figure 2): a wide asymmetrical singlet is appeared and grows.

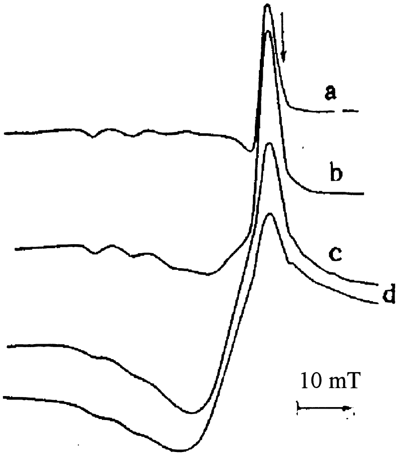


Figure 2. Change in the form of the ESR spectrum (77 K) of Cu(II) complexes on PE-gr-PAA with increasing mean cupric ion concentration; mmole/g, 0.03 (a), 0.08 (b), 0.15 (c), 0.23 (d). The arrow represents g = 2.0036.

The width of the signal is monotonically increases. The average value of the g-factors ($\bar{g}$ = 2.16 ± 0.02) agrees with the $\bar{g}$ –factors of isolated complexes of Cu(II), and the width (ΔH) corresponds to the total length of the spectra of latters. These facts indicate the closeness of structures of copper centers responsible for both types of the spectra. Increasing of the width of the singlet signal with $\bar{C}_{total}$ points to an existance and grow of dipol-dipol interactions between copper ions. The experimentally observed dependence of on ΔH $\bar{C}$ is linearly approximated[8] with a coefficient slope of $(9.7 \div 2.3) \cdot 10^{-20}$ Gs cm^3:

$$\Delta H = \Delta H_0 + A\,\bar{C} \qquad (3)$$

Using the ESR data the content of copper in dipol-dipol bond aggregations.with respect to $\bar{C}_{total}$ is estimated. It was shown that already at the concentration more than 0.15 mmole/g almost all copper was bounded into aggregations, its local concentration was $(6.0\pm40.6)\cdot10^{20}$ cm^{-3}.[7]

Thus, one can imagine the following distribution of copper in the grafted layer. There are isolated complexes with effective distance $\bar{r}_{isol} \geq 15$ Å (**I** type). A part of copper is in cluster-like aggregations with $r_{aggr} \leq 7$ Å, in which the complexes are not bounded chemically (**II** type). Finally, the considerable part of copper is bounded into clusters with strong exchange (exchange-bond clusters of **III** types) caused by chemical bonds of the complexes between each other.

This topographic pattern has most probably the general character for any macroligands and any metal complexes. We have confirm it in the case of V(IV) complexes bounded with PE-gr-P4VPy by the donor-acceptor bond.[9] As shown in Figure 3, parallel with well-resolved 8-component signal, the wide signal of the same g-factors is appeared and grows with increasing of the content of VCl_4.

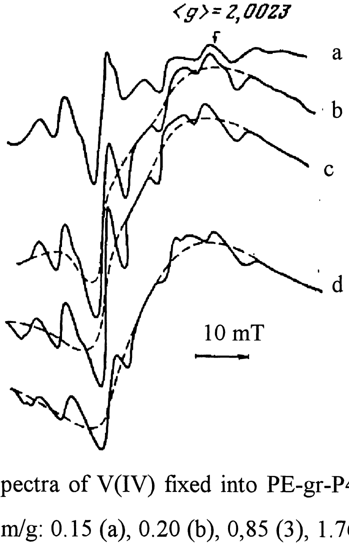


Figure 3. ESR spectra of V(IV) fixed into PE-gr-P4VP (5 wt.%). The content of V(IV)·10^4, g-atom/g: 0.15 (a), 0.20 (b), 0,85 (3), 1.76 (4),

Probably, this is a spectrum of the same complexes broaded by the dipol-dipol interactions. The width of hyperfine structure lines remains also costant with increasing of the VCl_4 content; the spectra are anisotropic. Taking into account the thickness of the grafted layer (grafted of 5 wt.% of 4-vinylpyridine) already at the least concentration of VCl_4 ($0.15\cdot10^{-4}$ mole/g) the distribution of V(4+) is characterized by following data. The content of isolated bond complexes of V(4+) $\overline{C}_{isol} \leq \delta H/A_{min} \approx 2\cdot10^{-4}$ g-atom cm^{-3}, $r_{isol} \geq 22$ Å, $r_{clust} \geq 6.8 \div 9$ Å. Since at the distance of ~ 7-9 Å the energy of dipol-dipol interaction is much less than kT, one can assume that not dipol-dipol interactions but a spatial organization of metal ions is important for the formation of cluster aggregations. It is likely that cluster aggregations arise around metal ions bounded two polymer chains. This can enhance a probability of bonding of other metals near it. The further studies are necessary for understanding the main reasons.

Conclusion

The distribution of polymer-bond metal ions are not homogeneous. Even at the low concentrations of bounded complexes the formation of three types of complexes is observed.

– isolated complexes ($\overline{r} \geq 15$ Å)

– the aggregations of cluster types (complexes of paramagnetic metals unbounded chemically between each other) ($\overline{r} \leq 7$Å)

- clusters with a strong exchange interaction (exchange-bound clusters caused by chemical bonds of complexes as polynuclear complexes)

It is likely that the size of macromolecule segments bounded the complexes are enough great, and their slow motions are not able to average the local environment of complexes. Besides, the complexes **I**, **II**, and **III** are very dynamic, in principle, their ratio can be altered depending on both the concentration of metal complexes and the conditions of their bonding with polymers (temperature, nature of solvents, the swelling degree of polymers, etc.). The topochemistry pattern can be considerably altered when a reducion (for example, Ti(4+) → Ti(3+), V(4+) →

V(3+), etc.) or an oxidation of metal ions proceeds in the course of their binding with functional groups of polymers. Besides, at introducing of other metals into systems other variants of the distribution of metal complexes are also possible.Thus, at additional introducing of Pd(II) into PE-gr-PAA-Cu^{2+} system via vacant functional groups the ESR spectra of Cu(II) does not change even at the following reduction Pd(II) → Pd_0.[10]

The peculiarity of topochemistry of the macrocomplexes influence essentially their catalytic properties. As a rule, the extremal dependence of the specific catalytic activity on the surface density of bond metal complexes in all catalytic processes (for example, polymerization, hydrogenation, oxidation, etc.).[1] However their kinetic behaviour correlates with neither $\bar{C}_{isol}$ or $\bar{C}_{clust}$ of the complexesn and requires the further studies.

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[1] A. D.Pomogailo, «Catalysis by Polymer-Immobilized Metal Complexes», Gordon @Breach, Amsterdam 1998.

[2] D. A. Kritskaya, A. D. Pomogailo, A.N. Ponomarev and F.S. D‘yachkovskii, *J. Appl. Polym. Sci.*, **1980**, *25*, 349; *J. Polym. Sci., Polym. Symp.*, **1980**, 23.

[3] G. I. Likhtenstein, *Method of Spin Labels in Molecular Biology,* Nauka, Moscow 1974 (in Russian).

[4] A.M. Vasserman and A.L. Kovarskii, *Spin Labels and Probes in Physicochemistry of Polymers,* Nauka, Moscow 1986 (in Russian).

[5] S. S. Eaton and G. R. Eaton, *Coord. Chem. Rev.* **1978**, *26*, 207.

[6] N. M.Bravaya and A. D. Pomogailo, *J. Inorg. Organomet. Polym.*, **2000**, *10*, N1.

[7] A.T. Nikitaev, A. D. Pomogailo, N. D. Golubeva and I.N. Ivleva, *Kinetika i Catalis,* **1986**, *27*, 709 (in Russia).

[8] O. Ya. Grinberg, A.T. Nikitaev, K. I. Zamaraev and Ya. S. Lebedev, *Zh. Strukt. Chim.,* **1969**, *10, 230.*

[9] A. D. Pomogailo, A.T. Nikitaev and F.S. D‘yachkovskii, *Kinetika i Catalis,* **1984**, *25*, 166 (in Russia).

[10] A. D. Pomogailo and N. D. Golubeva, *J. Inorg. Organomet. Polym.,* (in press).