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IMMOBILIZATION OF A QUARTERIZED POLYMERWITH IMMOBILIZED TRANSITION METAL IONS

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Poly-4-vinylpyridine was almost quantitatively quaternized with benzyl chloride in an aqueous ethanol solution, followed by crosslinking before and after immobilization with transition metal ions (Ni, Mn). The obtained samples were studied by physicochemical methods (scanning electron microscope (SEM), x-ray phase (XPA), infrared spectroscopy (IR) analysis. The aim is to use quaternized, cross-linked and immobilized samples as an effective sorbents and catalysts in many chemical processes.

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1. Introduction

The studies of interaction of synthetic polymers with transition metal ions have attracted much attention from scientists. This is due both to theoretical aspects that take into account the impact of the transition metal on the conformation of the polymer chain, and for applied aspects related to the creation of new specific ions for the extraction of a strictly defined metal from the mixture, the creation of new polymer catalysts, etc.

Most of the work on the interaction of metal ions with macromolecules of cross-linked polymers is devoted to the study of equilibrium in a polymer-ligand-metal mixture. It can be considered firmly established that the interaction of transition metal ions with polymer ligands can be described in terms of chemical equilibrium. Depending on the chemical structure of the polymer and the type of transition metal ion, the equilibrium can be shifted both towards the formation of the reaction product - polymer - metal complex, and towards the interacting components.

For a number of systems, a polymer transition metal ligand ion, for example, for systems: poly-4-vinylpyridin-Ni and poly-4-vinylpyridin-Mn, the processes of cooperative binding of a metal ion with a polymer chain are observed. The reason for the cooperative binding, most likely, is the conformational changes in the ligand macromolecules that occur during its interaction with the complexing agent. Nevertheless, in the literature, issues related to the change in the properties of the polymer chain during its interaction with the complexing agent have not yet been considered sufficiently deeply. But precisely this question is of great importance for the description of the properties of polymer-metal complexes. Nevertheless, in the literature, issues related to changes in the properties of the polymer chain during its interaction with the complexing agent have not yet been considered sufficiently deeply. But this issue is of great importance for the description of the properties of polymer-metal complexes.

Polymer-metal complexes formed under the conditions of cooperative binding of a complexing ion are individual compounds and should be considered as a new class of ionic polymers. The properties of these compounds differ significantly from the properties of the initial component of the reaction and are largely due to the metal content, as well as the conformation and configuration of the polymer ligand in the particle of the polymer-metal complex.

The most obvious difference in the properties of linear polymers and particles of polymer-metal complexes with their participation is manifested in reactions with chemically complementary macromolecules. In the case of the interaction of polymer - metal complexes with

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polymer anions, triple polymer-metal complexes are formed, the stability of which with respect to the action of low molecular weight electrolytes and the pH of the solution increases compared to polyelectrolyte complexes formed by the same chemically complementary pair without the participation of transition metal ions. The exceptional simplicity of obtaining polymer - metal complexes makes them very promising for a number of technological processes, for instance, for flocculation and stabilization of colloids, and the complexation process of a polymer molecule with transition metal ions should be considered as an effective way to modify the properties of linear macromolecules.

The fact that polymer - metal complexes are a special class of polymer compounds poses new challenges for researchers: a description of the molecular characteristics of these new polymer compounds, such as molecular weight, particle sizes, compositional heterogeneity, etc. as a function of the content of metal ions in a polymer-metal complex particle.

In this regard, the present work is devoted to the study of the characteristics of particles of quaternized, cross-linked polymer - metal complexes formed as a result of cooperative binding of metal ions of nickel and manganese with chains of poly-4-vinylpyridine [1-9].

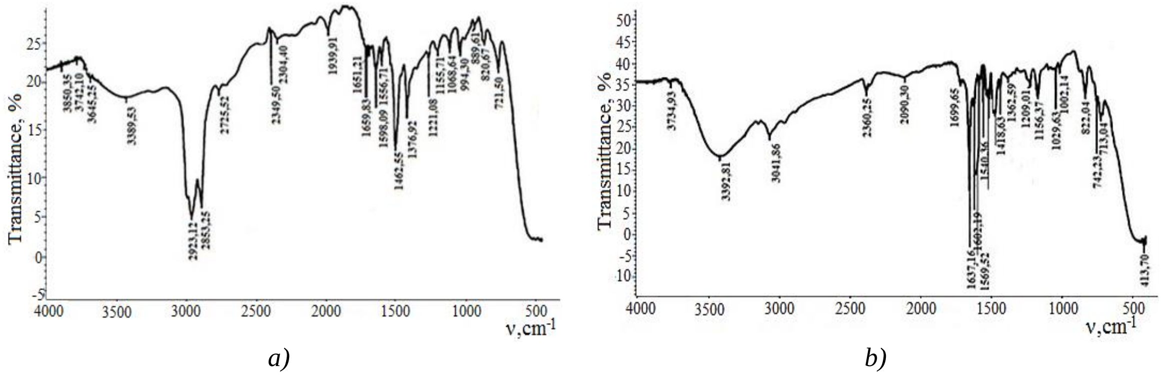
2. Experiment

First of all, the polymer was initially left in a water-ethanol solution during 24 hours to swelling to obtain quaternized samples. The water-organic environment has its own structural features that make a certain contribution to the process of obtaining the complex. The interest in such environments is due to both the need to solve a number of practical problems and the need for a detailed understanding of the processes occurring in such systems, to some extent modeling biological objects. Poly-4-vinylpyridine samples have obtained during reaction were partially quaternized with benzyl chloride. Solutions of polymer with a concentration of 1 g / 100 ml were heated to 60°C and benzyl chloride was added at this temperature in amounts of 10-60% by weight of the dissolved polymer. After 6 hours stirring, poly-4-vinylpyridine samples quaternized to various degrees were obtained. The quaternized polymer was precipitated with 0.1N NH4OH solution, washed with diethyl ether from excess benzyl chloride and dried under vacuum at 400 °C to constant weight [10].

3. IR spectroscopic

To determine the number of pyridine functional groups that revealed in the quaternization reaction, the IR spectroscopic (FTIR spectroscopy Nicolefisio VSA IR) method was used.

An analysis of the spectra showed that the spectra of vinyl pyridines have bands of bending vibrations at 1598.09 cm-1, which belong to free pyridine groups (Fig. 1 a). The analytical band for quaternized pyridine groups is shown at the 1637.16 cm-1, which is absent in the IR spectra of poly-4-vinylepyridine (Fig. 1 b).



a) *b)*

Fig. 1. IR spectra: a) poly-4-vinylpyridine; b) the quaternary salt of poly-4-vinylpyridine.

In addition, we calculated the optical density of the bands in the spectra of partially quaternized samples of poly-4-vinylpyridines and from the calibration graphs were determined the true content of quaternized pyridine groups. It was found that the true content of quaternized pyridine groups in the range from 70 to 90% respectively of the amount of benzyl chloride taken.

Then, to obtain immobilized metal-polymer complexes, ethanol solutions of partially quaternized samples of poly-4-vinylpyridine with a concentration of about 5% were added 0.1N water-ethanol, taken in a 1:1 ratio, solutions of transition metal salts Ni and Mn ($MnCl_2 \cdot 4H_2O$; $NiCl_2 \cdot 6H_2O$). Following, redox agent $NaBH_4$ was added to the obtained solutions in the amount of metal taken in the salt composition. Then, until by the completely precipitation of the metal polymer complexes we added there 0.1 N NH_4OH solution. After that, the precipitated complexes were washed with water to remove excess metal ions and dried under vacuum at a temperature of 40°C.

It could be seen, from the IR spectrum at 1663.24 sm^{-1}, there is an intense absorption band corresponding to the analytical band of the metal-polymer complex (Fig. 2).

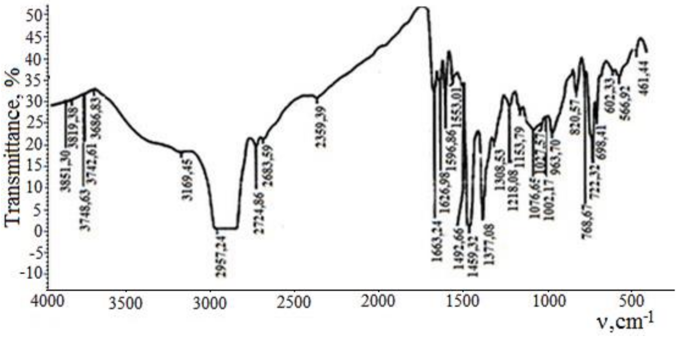


Fig. 2. IR spectrum of metal-polymer complex.

3.1. X-Ray diffractrometer

X-ray phase analysis (X-ray diffraction analysis on a D2-Phaser "Bruker" apparatus) showed that poly-4-vinylpyridine (P4VP) having an amorphous structure after crosslinking with N, N'-methylenebisacrylamide (MBAA) occurs in the structure the change (Fig. 3 a P4VP, Fig. 3 b P4VP and MBAA) and the degree of crystallinity increases.

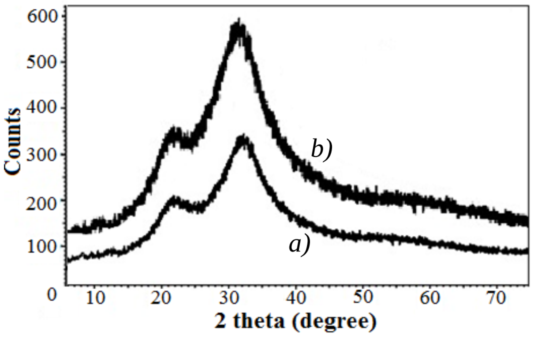


Fig. 3. Diffraction patterns of a) poly-4-vinylpyridine; b) P4VP and MBAA.

The crystallinity with respect to the homopolymer varies between 13-21%, and this is due to a change in structure or compaction of the structure as a result of crosslinking of the polymer. In addition, the structure of the obtained cross-linked metal-polymer complex was studied by X-ray phase analysis (Fig. 4, 5).

It was found that at low contents of metal in the polymer-metal complex (PMC) it was observed decreasing in the size of the polymer clew, that is, metal ions are an intermolecular cross-linker with respect to the polymer, and an increase in the composition of the polymer-metal complex leads to the association of already formed compact particles of PMC, as a result, inter macromolecular complexes are formed in which metal ions are inter macromolecular cross-linkers.

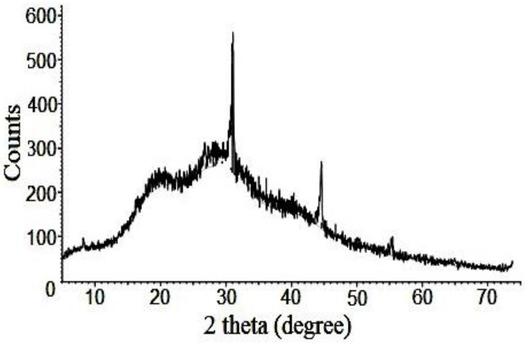


Fig. 4. X-ray diffraction pattern of the P4VP/Mn^0 complex.

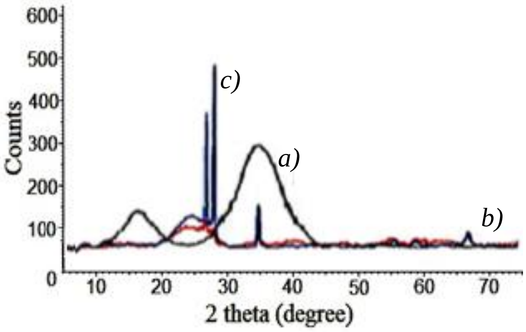


*Fig. 5. Diffraction patterns: a) P4VP; b) P4VP/Ni^0 (Ni^0 content of 5%);
c) P4VP/Ni^{2+} (Ni^0 content 30%).*

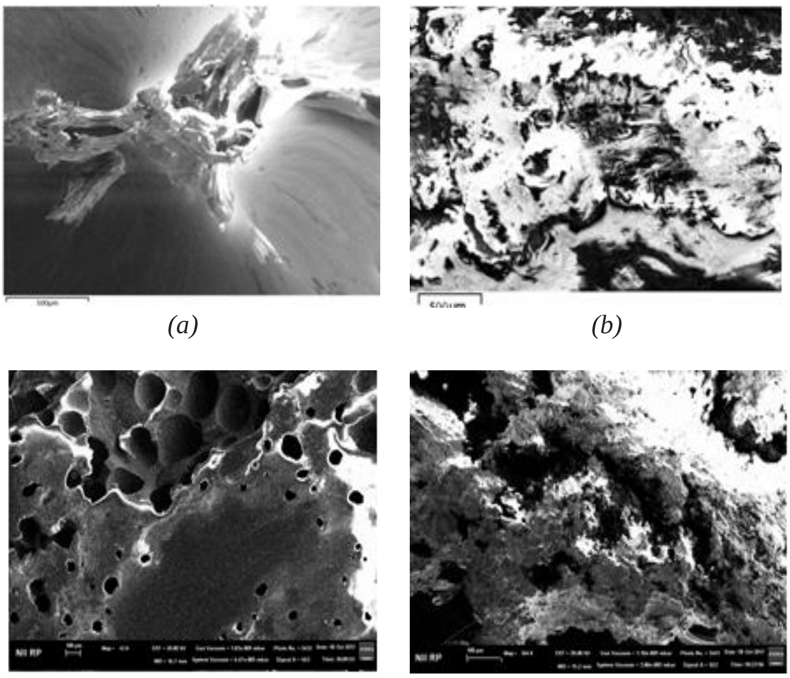
It should be noted that the process immobilization of metal to polymer carried out in two ways: adding metal salts solution before and after a crosslinking agent. To obtain cross-linked complexes, samples of poly-4-vinylpyridine were ground and dissolved in methanol, 8-10% solutions were prepared, and cross-linking agent N, N'-methylenebisacrylamide was added to the solutions. The grinding and mixing operation was carried out within 1-3 minutes in a ball vibratory mill with a ball diameter of 0.8 cm. The particle size of the crushed mixture was in the range 0.05-0.1 mm. From the crushed mixture were pressed tablets with a diameter of 8 mm and the thickness of 0.2-0.4 mm. The tablets were heated during 2-3 hours in ampoules at the temperature of 120-130°C.

Study of poly-4-vinylpyridine samples before and after such processing, which carried out under model conditions without the addition of a cross-linking agent, showed that their viscosity does not change as a result of this operation.

3.2. Scanning electron microscopy

Also, to study the morphology of the polymer and to clarify the changes in the structure, the obtained samples were studied by scanning electron microscopy (Sigma VP (Carl Zeiss Jena) SEM. Based on the data obtained, it was found that the structure of the non-cross-linked P4VP (Fig. 6, a), in contrast from a cross-linked sample (Fig. 6, b) is more chaotic. On SEM images the cross-linked polymer is formed the network-like structure, which leads the polymer to a more ordered structure.

The use of a redox agent (NaBH4) leads to the reduction of the metal to zero valency in the presence of a polymer, thereby the latter is immobilized by nanoparticles of the reduced metal and this is observed in Fig. 6 (c, d), that is, a structural change occurs and various phases form . As can be seen from the figures, the probable domains have the shape of a sphere, the sizes of which vary within 3-5 microns. More smaller and depending on the phase difference of the particles are Mn^0 and Ni^0 with a size of 15-20 nm. Since these parameters of the nanoparticles are ultrafine, this indicates the equable distribution of metal nanoparticles on the polymer surface.


(a) (b)

(c) (d)

Fig. 6. SEM structure: a) a non-cross-linked P4VP; b) cross-linked P4VP; c) P4VP/Mn^0; d) P4VP/Ni^0.

Conclusions

Thus, according to the data obtained and the studies carried out, it is considered logical to further use the above samples as sorbents and catalysts in many chemical processes. We investigated the catalytic properties of these samples in the oxidation of C_6-C_8 alkanes and hydrogenation of aromatic hydrocarbons (in particular benzene) under moderate conditions and obtained results that will be reported.

References

[1] A. D. Pomogailo, V. N. Kestelman, Metallopolymer Nanocomposites (Springer, Berlin Heidelberg, 2005).

[2] D. Wohrle, A. D. Pomogailo, Metal Complexes and Metals in Macromolecules (Wiley-VCH, Weinheim, 2003).

[3] V. A. Kabanov, A. A. Efendiev, Pure Appl. Chem. **54**, 2077 (1982).

[4] A. A. Efendiev, Macromol. Symp. **186**, 165 (2002).

[5] L. S. Molochnikov, E. G. Kovaleva, A. A. Zagorodni, Yu. M. Sultanov, M. Muhammed, A. A. Efendiev, Polymer **44**, 4805 (2003).

[6] R. A. Galimov, A. A. Gaifullin, T. H. E. Kharlampidi, Oxidation of alkanes to synthetic fatty acids. (Study guide. Kazan: KSTU, 2007, 140 p).

[7] V. A. Osyanin, Yu. N. Klimochkin, Oxidation of alkanes and cycloalkanes (Samara STU, 2006, 90p).

[8] Qi-Hu Qin, Hui Na, Chunyu Zhang and others, Journal of Nanoscience and Nanotechnology **15**(5), 3909 (2015).

[9] Li-Ping Jiang, Xu-Yang Zhou, Qiu-Fei Huang and others, Acta polymerica sinica **7**, 845 015).

[10] E. B. Amanov, Complexing polymer sorbents based on vinylpyridines tuned to sorbed ions. Diss. Cand. chemical Sciences. Baku: ITPT an AZ.R. 1984, pp. 29-33.