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Design of Enzyme-like Complexing Polymer Sorbents and Metal-Polymer Complex Catalysts with Memory to Substrates

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Summary: A new principle of design of enzyme-like complexing polymer sorbents and metal polymer complex catalysts has been developed. The principle is based on the use of memory of polymer composition and consists in conformational prearrangement of macromolecules of noncrosslinked complexing polymer favorable for sorbing metal ions and/or catalyzing substrate position followed by intermolecular crosslinking. It has been shown that prearranged polymer sorbents and catalysts demonstrate significantly improved sorption and catalytic properties.

Keywords: catalysts; complex; enzymes; polymer; sorbent

Introduction

Advantages of biological catalysts are explained by extremely high level of organization of chemical transformations therein, and the fact that this organization is achieved at the macromolecular level. Hence tremendous activity and selectivity is existing in biological catalysts. The principles of enzyme action are based on molecular recognition of catalyzed substrates. In general, molecular recognition is widespread in nature. Substrates' selection by enzymes, recognition of hormones by their receptors, selective binding of antigens with antibodies, and genetic code reading play an extremely important role in biological processes. Adaptation of these principles to chemical reactions is an important field of research.

We have developed a new principle of design of enzyme-like complexing polymer sorbents and metal polymer complex catalysts with memory to sorbing metals and catalyzing substrates. The principle is based on the use of memory of polymer composition and consists in purposeful conformational prearrangement of macromolecules of noncrosslinked complexing polymers favorable for sorbing metal and/or catalyzing a specific substrate position. Subsequent intermolecular crosslinking preserves these conformations. After removal of template substrate from the crosslinked polymer the system might ''keep in mind'' the state when macromolecules were bound with molecules of substrate. This should lead to a decrease of activation energy of the sorption process and as a result to an increase of sorption capacity, rate and selectivity of the metal ions uptake, as well as catalytic activity and selectivity of the crosslinked metal polymer complexes.

The idea of conformational prearrangement would not appear doubtful if we take into consideration some literature data. For example, a number of papers have been published in which specific silica gels with increased adsorption selectivity with respect to pre-chosen substances were described.[1–3] Such adsorbents were prepared by forming silica gels in a presence of adsorbing substance. To explain the mechanism of adsorption the authors proposed hypotheses on ''imprints'', ''matrices'' or ''traces''. However, adsorption specificity of silica

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gels prepared in such a way is easily lost during subsequent treatment, washing, drying and even storage of the gels, obviously because so called ''imprints'' or ''traces'' have not been chemically fixed in the gels.

Studying the macromolecular models of enzymes Kabanov put forward the principle of preparation of polymers with tertiary structure optimized for sorption of a corresponding substrate.[4] Wulff described ''molecular imprinting'' of multiple organic functionality in organic polymers.[5] The author of this paper in collaboration with Kabanov and Orujev developed a principle of preparation of complexing polymer sorbents with macromolecules favorably prearranged for sorption of metal ions followed by fixation of optimum for particular metal conformations by intermolecular crosslinking.[6–8] A similar principle was also used for preparation of polymers able to separate mixture of ions and organic compounds.[9–12]

The general procedure for preparation of prearranged complexing polymer sorbents and macromolecule-metal complex catalysts consists in interaction of noncrosslinked polymer with metal ions to be sorbed or substrates to be catalyzed in rather dilute solution, i.e. under conditions when macromolecules are still mobile enough. The second step is fixation of the structure of the active centers by intermolecular crosslinking. The third step is removal of the template substrate from the crosslinked system.

The removal of the template should be done in such a way so as to prevent catastrophic destruction of the polymer structure. As a result, crosslinked complexing sorbents or macromolecule-metal complexes with conformations advantageous for the template substrate are produced where the sorption process is practically not hindered by the elastic forces due to the distortion of the polymer chain. This, in turn, results in the thermodynamically favorable sorption of metal ions forming certain coordination structures and leads to a significant increase in sorption capacity, rate and selectivity of the uptake of the metal ions, catalytic activity and selectivity of macromolecule-metal complexes.

This paper summarizes our results on main regularities of design of enzyme-like polymer sorbents and metal-polymer complex catalysts with memory to substrates based on polyvinylpyridines of different structure (PVP), branched polyethyleneimine (PEI) and linear low molecular polyethylene-polyimine (LLM PEI).

Experimental

Poly(4-vinylpyridine), poly(2-vinylpyridine) and poly(2,5-methylvinylpyridine)

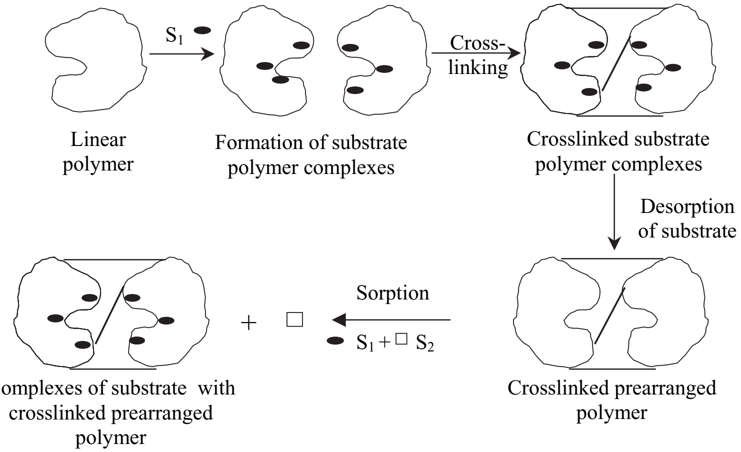
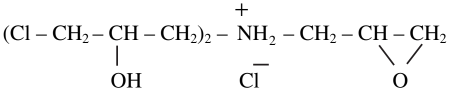


Figure 1.
Scheme of synthesis of polymers prearranged for complexation with a substrate.

have been prepared by radical polymerization of the corresponding monomers (“Merck“) which were purified by double distillation in vacuum. Polymerizations were carried out at 60 °C in vacuum-sealed (10^{-4} torr) ampoules containing 30% mass solution of the corresponding vinylpyridines in toluene, and 1% of isopropylbenzene hydroperoxide was used as an initiator. The polymers precipitated from toluene solution in a form of white flakes which were twice reprecipitated from ethanol solution by diethyl ether and dried in vacuum at slightly elevated temperature. Partial quaternization of the samples was carried out using 20–30% mass of benzylchloride in methanol solution at 60 °C. MM of the prepared polymers were in the range of 100 000–150 000 g/mol.

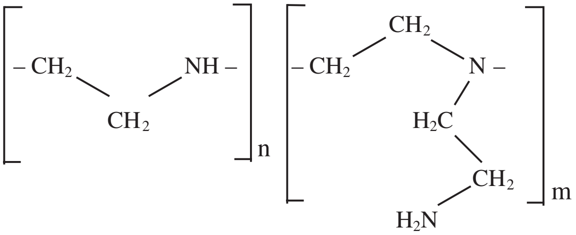
PEI (“BASF”) with MM 100 000 g/mol was in the form of 50% mass aqueous solution. LLM PEI with MM 275 g/mol was obtained from Nizhniy Tagil Plant of Plastics (Russia). The structure of LLM PEI can be represented in Scheme 1.

The oligomer of epichlorohydrin and ammonia (ECHA) was obtained by stirring 1 mole of ammonia (12.5% mass aqueous solution) with 2 moles of epichlorohydrin at 65–70 °C for 2 hours. ECHA has the following structure:

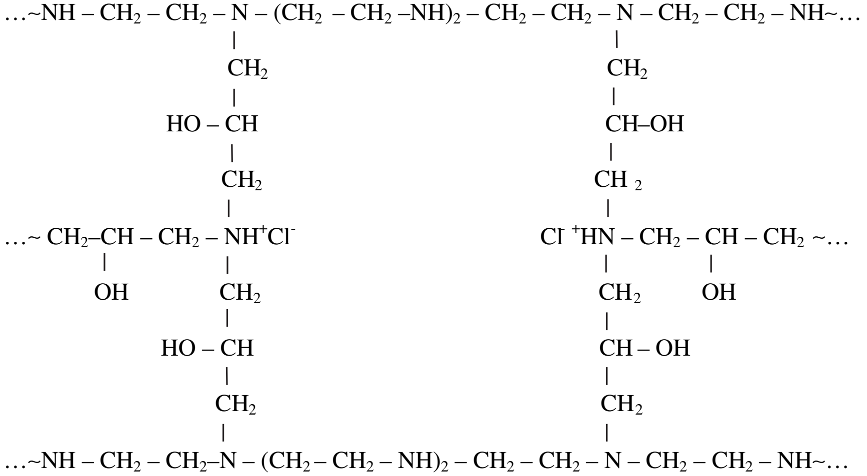


Other reagents were of analytical grade.

Prearranged complexing sorbents were synthesized by adding 0,1 N aqueous or water-ethanol solution of $CuCl_2$, $NiCl_2$ or $CoCl_2$ to ethanol or aqueous solution of PVP, PEA or LLM PEI with concentration about 5% mass.



Scheme 1.



Scheme 2.

Complexes of PVP and PEI were crosslinked using N,N′–methylenediacrylamide as a crosslinking agent. Complexes of LLM PEI were crosslinked using ECHA. LLM PEI crosslinked with ECHA might be represented in Scheme 2.

Polymer–metal complex catalysts prearranged for a substrate were prepared by mixing noncrosslinked complexes with an excess of a substrate to be catalyzed in ethanol solution followed by rapid freezing and removal of the solvent and the substrate by freeze drying before crosslinking.

The procedures of preparation and investigation of prearranged sorbents and polymer metal complexes were described in our earlier papers.[13–15] Sorption properties and catalytic activity of the catalysts were studied using standard techniques.

Results and Discussion

Nonprearranged polymers and polymers with active centers prearranged for sorbing metals or catalyzing substrates have been prepared. In case of nonprearranged polymers macromolecules containing active centers are crosslinked and subsequently used as sorbents or catalysts. Such sorbents or catalysts do not exhibit high selectivity with respect to a desired substrate, and different substrates might be sorbed on active centers with small degrees of preference.

In case of prearrangement noncrosslinked macromolecules containing active centers react with substrate in solution, and the system is prearranged to a minimum free energy where the sorbing substrate is built in. In other words, active centers are formed where the built-in substrate has been already taken into account as the element of the structure. Such optimum for this particular substrate structure of the active centers is fixed by means of intermolecular crosslinking. This remains after removal of the substrate from the crosslinking system. After removal of the substrate from the crosslinked polymer the system ''remembers'' the state when macromolecules were bound with a sorbing substrate more preferable for the sorbent or catalyst crosslinked in a presence of this substrate. This, in turn, reduces activation energy of substrate sorption on active centers and improves the sorption properties of complexing polymer sorbents and catalytic properties of metal-polymer complex catalysts.

Sorption capacities were determined, and kinetics of sorption on prearranged sorbents were investigated. For comparison we also investigated the sorption properties of nonprearranged sorbents.

Prearranged sorbents on the base of vinylpyridines were prepared and investigated. Samples of poly(4-vinylpyridine), poly(2-vinylpyridine) and poly(2,5-methylvinylpyridine) with quaternization degrees of 22–25% have been prearranged for the uptake of copper, cobalt and nickel ions. Sorption capacities of the sorbents are given in Table 1.

It can be seen from the Table that the prearrangement of PVP based sorbents

Table 1.
Sorption capacities of the sorbents on the base of partially quaternized polyvinylpyridines of different structures with crosslinking degree of 15% mass.

Polymer	Sorbent	Sorption capacities/meq/g		
		Cu^{2+}	Co^{2+}	Ni^{2+}
Poly(4-vinylpyridine)	Nonprearranged	3.55	0.86	0.84
	Prearranged for Cu^{2+}	5.85	1.11	0.88
	Prearranged for Co^{2+}	5.51	1.39	0.78
	Prearranged for Ni^{2+}	5.60	0.94	1.10
Poly(2-vinylpyridine)	Nonprearranged	1.46	0.14	0.12
	Prearranged for Cu^{2+}	2.11	0.33	0.36
Poly(2,5-methyl-vinylpyridine)	Nonprearranged	1.23	0.31	0.22
	Prearranged for Cu^{2+}	5.14	0.39	0.30

leads to a significant increase in sorption capacity in comparison with the same sorbents prepared without such prearrangement. In each case we observe a higher increase with respect to metals for ions of which they have been prearranged.

Earlier we studied noncrosslinked poly(4-vinylpyridine), poly(2-vinylpyridine) and poly(2,5-methylvinylpyridine) using NMR spectroscopy and calculated dipole moments of the fragments of their macromolecules (as model molecules of corresponding ethylpyridines were taken).[16] It was shown that according to the obtained results the sorption capacities of the sorbents on the base of different polyvinylpyridines decrease in the following order: poly(2,5-vinylpyridine) > poly(4-vinylpyridine) > poly(2-vinylpyridine). However it can be seen from the table that sorbents on the base of poly-2,5-methylvinylpyridine possess the lowest sorption capacity. It seems that steric hindrance caused by methyl group prevents orientation of functional groups in macromolecules of poly(2,5-methylvinylpyridine) to a position favorable for complex formation.

It is seen from Table 1 that due to prearrangement the sorption capacity of the sorbents on the base of poly(2,5-methylvinylpyridine) increases more significantly in comparison with the sorbents on the base of poly(4-vinylpyridine) and poly(2-vinylpyridine). This can be explained by the fact that prearrangement eliminates the steric hindrance caused by methyl groups.

The next step was the preparation and investigation of the sorbents on the base of PEI and LLM PEI. Sorption properties of the obtained sorbents are given in Tables 2 and 3.

Table 2.
Sorption capacities of sorbents on the base of PEI.

Crosslinking degree/% mass	Sorption capacity/meq/g			
	Nonprearranged		Prearranged	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
10	3.7	3.9	8.9	5.8
15	3.6	3.8	7.5	5.7
20	3.5	3.7	7.1	4.9

Table 3.
Sorption capacities of nonprearranged (0) and prearranged (2,3,4) sorbents with various ratios of LLM PEI and ECHA.

Ratio LLM PEI: oligomer/ % mass	Content of metal in initial complex/meq/g	Sorption capacity/ meq/g	
		Cu^{2+}	Ni^{2+}
1:1.0	0	4.0	2.0
	2	7.2	3.1
	3	8.2	3.8
	4	8.2	4.1
1:1.3	0	3.5	1.8
	2	5.8	2.9
	3	7.8	3.7
	4	7.8	3.9

It can be seen from the Tables 2 and 3, conformational prearrangement of the sorbents on the base of PEI and LLM PEI for Cu and Ni, respectively, also results an essential increase of the sorption capacity, the selectivity and the rate of the uptake.

The effect of improvement of sorption capacities is already achieved when the content of the metal in the complex with LLM PEI reaches a value of 2 meq/g and continues to increase up to 4 meq/g. Further increase of metal content creates a problem for crosslinking of the complex with ECHA.

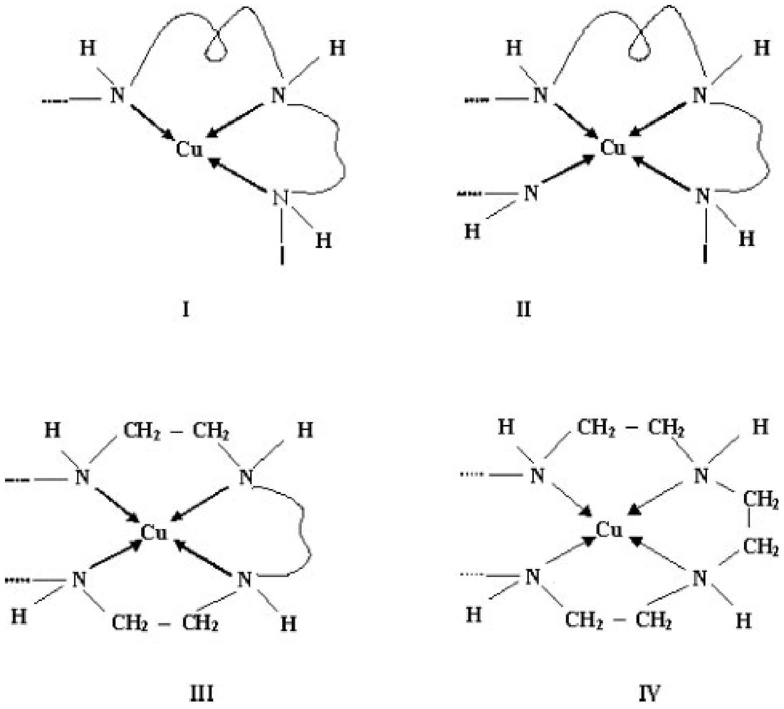
The improvement of the sorption properties of complexing polymer sorbents obviously is determined by a decrease, because of prearrangement, of the energy and entropy consumption required for conformational regrouping of the macromolecules segments on formation of a complex with metal. It was found that the efficiency of the prearrangement is determined both by the nature of the polymer itself (flexibility of the macromolecules and type of ligand group) and the nature of the metal undergoing complex formation (coordination number and geometry of the complexes formed).

However, it should be noted that the interrelation between the structure of the complexes and the efficiency of the prearrangement has not been practically studied. By formation of complexes of metals with complexing polymers, especially when they are crosslinked, distortion of the geometry of the complexes can be observed and, as shown in[9] even a transition from one form to another might take place. These issues are of a considerable interest for prediction of the sorption properties of complexing polymers and might be solved with the use of magnetochemical and spectral methods.

We studied complexes of copper with complexing polymers on the base of LLM PEI and their prearranged analogues by means of ESR method.[17] The ESR study of the effect of prearrangement of the sorbents on the type of formed complexes required a knowledge of the composition and conditions of existence of copper complexes in solution, since the formation of complexes of the same composition in the sorbent phase could be one of the criteria of the prearrangement. It has been shown that copper ions in solution forms four types of complexes (Figure 2).

Some parameters for ESR spectra of copper ion complexes formed with low molecular model compounds of the sorbents in solutions – LLM PEI and its mixtures with ECHA, ethylenediamine (EDA) and diethylenediamine (DEEDA) are given in Table 4.

Complex I is a triamine complex, and complexes II–IV are tetraamine complexes and differ in degree of distortion of the tetragon, which is characteristic for ethylenediamine complex. In complex II copper is bonded to four isolated amine groups, and in complex III – to two isolated ethylenediamine fragments. Characteristic feature of complex IV is the participation of four amine groups directly adjacent in the LLM PEI chain and connection to each other via three ethyleneamine bridges. Only one complex IV exists in aqueous solutions of LLM PEI and mixtures of LLM PEI and ECHA in alkaline medium.



I

II

III

IV

Figure 2.
Types of copper complexes formed in solution.

Table 4.
ESR spectra parameters of Cu complexes I–IV with low molecular model compounds of sorbents.

Low molecular model compound	pH	g_{II}	A_{II}x10/Tl	pH	g_{II}	A_{II}x10/Tl
		I			II	
LLM PEI	3–4	2.247	170	–	–	–
LLM PEI +ECHA	–	–	–	3	2.212	180
EDA [18]	–	–	–	–	–	–
DEEDA [19]	–	–	–	–	2.212	187

Low molecular model	pH	g_{II}	A_{II}x10, Tl	pH	g_{II}	A_{II}x10, Tl
		III			IV	
LLM PEI	4–5.5	2.262	178	5.5–12.5	2.203	160
LLM PEI +ECHA	4–5.5	2.203	179	5.5–12.5	2.202	160
EDA [18]	–	2.202	–	–	–	–
DEEDA [19]	–	–	–	–	–	–

When a condensation reaction occurs this does not generally result in a change of the structure of copper complex. For example, in case of a sorbent obtained after hardening of the mixture of LLM PEI and ECHA with the amount of copper ion of 4 meq/g of LLM PEI introduced during prearrangement only one complex with the parameters $g_{II} = 2.205$ and $A_{II} = 163 \times 10^{-4}$ Tl is formed. Parameters of ESR spectra for complexes of copper ions in a phase of sorbents on the base of LLM PEI with different degree of protonation (α) are given in Table 5.

It can be seen from the Table that the degree of protonation has a significant effect on the compositions of the copper complexes in both the prearranged and nonprearranged sorbent phases. When $\alpha \rightarrow 1$ complex II is formed in a phase of nonprearranged sorbent and when $\alpha \sim 0.4$ the complex is transformed into III or IV. Increase in the quantity of copper ions introduced on prearrangement in case of the protonated form of the sorbent leads to rearrangement of the complexes from inter-chain (content of copper ions 1 and 2 meq/g) to intra-chain (content of copper ions 3 and 4 meq/g) complexes. In the case of the partially protonated complex IV, which is characteristic for LLM PEI formed in solution, only the phase of the sorbent with a content of copper ions of 4 meq/g is formed. In this case the quantity of copper introduced on prearrangement reached a maximum value. This is why conformations most favorable for complex formation with copper ions which existed in solution, i.e. under conditions where the macromolecules with sufficient mobility are fixed. Thus, it might be expected that this sorbent would have the best sorption properties. In fact, as it is shown above, the sorbent with 4 meq/g of copper introduced on prearrangement had maximum sorption capacity.

Table 5.
ESR spectra parameters for complexes of copper ions in a phase of LLM PEI based sorbents with various content of copper in initial complex.

Content of copper ions in the initial complex, meq/g	g_{II}	A_{II}x10,/Tl	g_{II}	A_{II}x10/Tl
	$\alpha \rightarrow 1$		$\alpha \rightarrow 0(4$	
0	2.221	176	2.210	183
1	2.220	174	2.205	185
2	2.216	179	2.205	188
3	2.215	178	2.204	166
4	2.214	176	2.198	167

Accordingly, conformational prearrangement of polyethylenepolyamine based sorbents ensures that on subsequent bonding metal complexes are formed preferentially with structure identical to that of their low molecular analogues in solution, and the copper is more uniformly distributed within the bulk of the specimens compared to nonprearranged sorbents.

Table 6.
Oxidation of ethylbenzene in the presence of nonprearranged and prearranged copper ion complexes with LLM PEI and ECHA based polymer.

Catalyst	Yield/ % mass			Conversion/ % mass	Selectivity with respect to EHP/% mol
	EHP	MPC	AP		
Nonprearranged	3.4	2.1	5.0	10.6	31.0
Prearranged	6.4	2.9	9.0	18.3	35.0

It is be concluded that use of ESR spectroscopy when studying complexes of copper with polymer sorbents indicated significant changes in the structure of the complexes in such sorbents compared to nonprearranged ones. This allows to establish a correlation between the structure of the complexes and the sorption properties of the sorbents.

The prearrangement of the sorbents with copper ion contents of 2–4 meq/g of LLM PEI ensures a significant improvement in sorption and kinetic characteristics of the sorbents, as well as the preservation in the sorbent phase of the structure of the complexes existing in solution. When the quantity of copper introduced on prearrangement is small this structure is not maintained and the improvement of the sorption characteristics of the sorbents is less pronounced.

In all cases conformational prearrangement ensures that complexes are formed in the sorbent phase. The preferred structure of which is characteristic for their low molecular analogues in solution. This is especially important when using transition metal complexes with polymer sorbents as catalysts. This is a prerequisite for the formation of uniform active centers, which is an important condition for preparation of selective catalysts. With this point in mind catalytic properties of nonprearranged and prearranged for copper sorbents were investigated. As first example the reaction of oxidation of ethylbenzene was chosen. The products of the reaction are ethylbenzene hydroperoxide (EHP), methylphenylcarbinol (MPC) and acetophenone (AP). The reaction was carried out in a glass thermostatted reactor. Gaseous oxygen was used as an oxidizer at atmospheric pressure. The procedure of oxidation reaction was described in our earlier paper.[20] Nonprearranged and prearranged complexes of copper with LLM PEI and ECHA based polymer were used as catalysts. The catalysts were taken in the amount of 1g/l. The content of copper in both catalysts was the same – 1.7 meq/g. Results are presented in Table 6.

It can be seen that the prearranged complexes demonstrate higher catalytic activity and selectivity with respect to ethylbenzene peroxide in comparison with the nonprearranged ones.

An attempt has been made to a further increase of the catalytic activity of metal polymer complexes by means of formation and subsequent fixation in memory of the

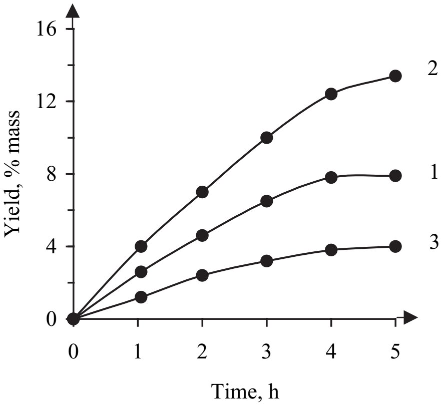


Figure 3.
Kinetic curves for the hydrogenation of allyl alcohol to propyl alcohol in the presence of nonprearranged /1/ and prearranged for allyl alcohol /2/ and propyl alcohol /3/ complexes of nickel with poly(4-vinylpyridine) based polymers.

catalyst with the structure of active centers favorable for hydrocarbon substrate. We carried out hydrogenation of allyl alcohol using poly(4-vinylpyridine) (PVP) nickel complexes prearranged for allyl alcohol and for the reaction product – propyl alcohol.

The procedure of preparation of nonprearranged and prearranged samples for allyl alcohol and propyl alcohol PVP-nickel complexes was described earlier.[14] Cross-linked PVP-nickel catalysts were taken in the amount of 1.4 g/l. The nickel content in all catalysts was 4 meq/g. Kinetic curves for hydrogenation of allyl alcohol to propyl alcohol in a presence of nonprearranged and prearranged for allyl and propyl alcohol PVP nickel complexes are given in Figure 3. It can be seen that the rate of hydrogenation in the presence of complexes prearranged for allyl alcohol is much higher in comparison with nonprearranged complexes. On the contrary, the rate of the reaction in a presence of complexes prearranged for propyl alcohol is lower than in a presence of nonprearranged complexes due to blocking of active centers from complexation with allyl alcohol.

Conclusion

The results obtained have demonstrated that conformational prearrangement of complexing polymers for sorbing metal ions and catalyzing substrates leads to an essential improvement of sorption properties of the sorbents and catalytic properties of the catalysts prepared on their base. It has been shown that effect of "memory" can also be used as an additional instrument for the investigation of the mechanism of catalytic reactions.

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[1] F.J. Dickey. *J.Phys.Chem.* **1955**, *59*, 695.
[2] R. Curti, U. Colombo, F. Glerici. *Gazz.Chem.Ital.* **1952**, *82*, 491.
[3] J. Morrisson, M. Worsley, D. Shay, G. Hadson.*Can.J. Chem.* **1959**, *37*, 1986.
[4] V.A. Kabanov. *Uspehi Chimii Fiziki Polimerov*, Chimia, Moscow, 1973, p. 283.
[5] G. Wulff. In: *Polymeric Reagents and Catalysts*, W.I. Ford, Ed., American Chemical Society, Washington, DC, **1986**, p.186.
[6] V.A. Kabanov, A.A. Efendiev, D.D. Orujev. *Auth. Cert.USSR 502, 907*, **1974**; *Bull.Inv.* **1976**, *N6*.
[7] V.A. Kabanov, A.A. Efendiev, D.D. Orujev. *J.Appl. Polym.Science.* **1979**, *24*, 259.
[8] A.A. Efendiev, V.A. Kabanov. *Pure and Appl.Chem.* **1982**, *54*, 2077.
[9] H. Nishide, J. Deguchi, E. Tsuchida. *Chemistry Letters*, **1976**, 169.
[10] S.N. Gupta, D.C. Neckers. *J.Polymer Science*, **1982**, *20*, 1609.
[11] B. Ekberg, T. Mosbach. *Tibtech*, **1989**, *7*, 92.
[12] Alvarez-Lorenzo.*Macromolecules*, **2000**, *N33*, 8693.
[13] A.A. Efendiev. *Macromol.Symp.* **1994**, *80*, 289.
[14] A.A. Efendiev, J.J. Orujev, E.B. Amanov, Yu.M. Sultanov, in: "Metal Containing Polymeric Materials", Plenum Publishing Corporation. New York, N.Y. **1996**, p.255.
[15] L.S. Molochnikov, E.G. Kovalyova, A.A. Zagorodni, Yu.M. Sultanov, A.A. Efendiev, *J.Polymer*, **2003**, *44*, pp. 4805–4815.
[16] A.B. Amanov, I.I. Sidorchuk, E.A. Agayeva, A.N. Shnulin, B.K. Abbasova, A.A. Efendiev. *Doklady Akademii Nauk Azerb.SSR*, **1986**, *42, N 3*, 48.
[17] V.A. Kabanov, L.S. Molochnikov, S.A. Ilichev, O.N. Babkin, Yu.M. Sultanov, J.J. Orujev, A.A. Efendiev. *Vysokomol.Soyed.* **1986**, *B 28*, 2459.
[18] G.P. Vishnevskaya, M.S. Shapnik, R.Sh. Safin.*Zh.-neorgan.khim.* **1981**, *26*, 5781.
[19] N.M. Kabanov, A.M. Kokorin, V.B. Rogacheva, A.B. Zezin. *Vysokomol. soyed.* **1979**, *A21* 209.
[20] A.A. Efendiev, J.J. Orujev, T.N. Shakhtakhtinsky, V.A. Kabanov, in: "Homogeneous and Heterogeneous Catalysis", *Proceedings of the Fifth International Symposium on relations between Homogeneous and Heterogeneous Catalysis*, VMU Science Press, Utrecht, The Netherlands, **1986**, p.717.