

Guest-host Phenomena in Macromolecule–Metal Complexes

Ayaz Efendiev

Institute of Polymer Materials of Azerbaijan National Academy of Sciences,
Samed Vurgun Str.124, Sumgait, 373204, Azerbaijan Republic

Summary: A new principle of design of complexing polymer sorbents and macromolecule-metal complex catalysts with memory to sorbing metals and catalyzing substrates in other words "hosts" able to recognize "guests" was developed. Polyvinylpyridines of different structure, polyethyleneimine and polyethylenepolyamine were selected for preparation of such sorbents and catalysts. Polymer sorbents and catalysts prepared using this principle exhibit guest-host phenomena and demonstrate significantly improved sorption and catalytic properties.

Introduction

Molecular recognition is widely spread in nature. Selection of substrates by enzymes, selective binding of antigens by antibodies, recognition of hormones by their receptors and reading of genetic code play a great role in biological processes. Application of these phenomena to chemical reactions is an important field of research called "guest-host chemistry". For example there have been described specific adsorbents prepared by forming silica gels in the presence of pre-chosen substances^[1-3]. To explain the mechanism of specificity the author proposed different hypotheses on "imprints", "matrices", "traces". Adsorption specificity of such silica gels is easily lost during subsequent treatment 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 corresponding substrate^[4]. Wulff described "molecular imprinting" of multiple organic functionality in organic polymers^[5].

We have developed a new principle of design of complexing polymer sorbents and metal polymer complex catalysts with memory to sorbing metals and catalyzing substrates, in other words "hosts" able to recognize "guests", i.e. the substrates for which they have been designed^[6-8]. The principle is based on the use of memory of polymer composition and consists in conformational prearrangement of macromolecules of noncrosslinked complexing polymer to a favorable for sorbing metal or catalyzing

substrate position followed by intermolecular crosslinking. 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.

Similar procedure was later used by other researchers for preparation of polymers able to separate mixture of ions and organic compounds^[9-12].

This paper summarizes our results on main regularities of synthesis of polyvinylpyridine (PVP), polyethyleneimine (PEI), polyethylenepolyamine (PEPA) based prearranged sorbents and catalysts exhibiting guest-host phenomena^[13-17].

Results and Discussion

The procedures of preparation of prearranged sorbents and polymer metal complexes are described in our earlier papers^[13-15].

Sorption properties of nonprearranged and prearranged for the uptake of copper, cobalt and nickel sorbents on the basis of partially (22-25% mass) quaternized with benzylchloride polyvinylpyridines are shown in Table 1 and Fig.1.

It can be seen that the prearrangement leads to a significant increase in sorption capacity and the sorption rate in comparison with the same sorbents prepared without such prearrangement. In each case we observe the higher increase with respect to metal for the ions of which they have been prearranged.

In case of nonprearranged sorbents the increase of the sorption rate is due to more rigid fixation of the spatial position of free hydrophobic and quaternized hydrophilic functional groups and in case of prearranged sorbents also due to more rigid fixation of the conformations optimum for the ion uptake. Further increase in the crosslinking degree alongside with fixation creates hindrance to diffusion of ions into the sorbent.

The next step was preparation and investigation of the sorbents on the basis of PEI and PEPA crosslinked with oligomer of epichlorohydrin and ammonia (ECHA). Sorption capacities of the obtained sorbents are given in Tables 2, 3.

It can be seen from the Tables 2 and 3 that conformational prearrangement of these sorbents also results in essential increase in sorption capacity.

The effect of improvement of sorption capacity is already achieved when the content of the metal in the initial complex with PEPA reaches a value of 2 meq/g and continues to

increase up to 4 meq/g. Further increase of the content of metal creates a problem for crosslinking the complex.

Table 1. Sorption capacity of the sorbents on the basis of partially quaternized polyvinylpyridines of different structure with crosslinking degree 15 % mass.

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

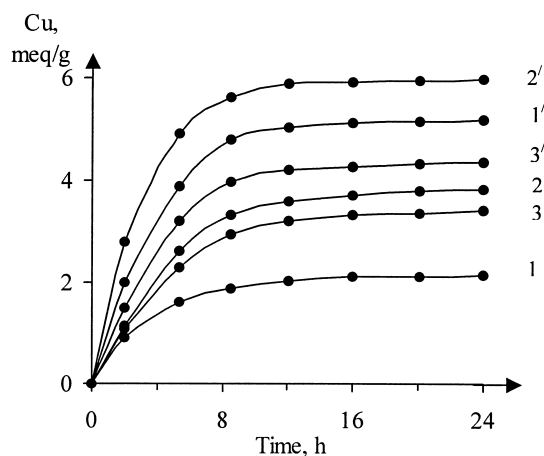


Figure 1. Kinetic curves of sorption of copper ions by nonprearranged (1-3) and prearranged (1'-3') poly-4-vinylpyridine based sorbents with various degrees of crosslinking, % mass : 2 (1'), 5 (1), 10 (2'), 15 (2), 15 (3'), 25 (3).

We studied complexes of copper with low molecular models of PEPA based sorbents in solution and with complexing polymers and their prearranged analogues by means of ESR method^[17].

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

Crosslinking degree, % mass	Sorption capacity, meq			
	Nonprearranged		Prearranged	
	Cu	Ni	Cu	Ni
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 capacity of nonprearranged (0) and prearranged (2,3,4) sorbents with various ratio of PEPA and ECHA.

Ratio PEPA: ECHA, % mass	Content of metal in initial complex, meg/q	Sorption capacity, meq/g	
		Cu	Ni
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
1:1.6	0	2.8	1.6
	2	4.5	2.4
	3	7.5	3.2
	4	7.5	3.6

It has been shown that there are significant changes in structure of prearranged complexes compared with nonprearranged ones. The more copper is contained in initial complex to be crosslinked the closer the structure of the complexes to their low molecular models in solution and the more uniform they are.

Catalytic properties of nonprearranged and prearranged for copper sorbents on the base of PEPA were investigated. As an example reaction of oxidation of ethylbenzene was chosen. The products of the reaction are ethylbenzene hydroperoxide (EHP), methylphenylcarbinol (MPC) and acetophenone (AP). The procedure of oxidation reaction was described in our earlier paper^[15]. Results are presented in Table 4.

It can be seen that the prearranged for copper complexes demonstrate higher catalytic activity and selectivity with respect to ethylbenzene peroxide in comparison with the nonprearranged ones, obviously, due to more uniform structure of the active centers.

Table 4. Oxidation of ethylbenzene in the presence of nonprearranged and prearranged copper complexes with PEPA and ECHA based polymer (concentration of catalyst – 1g/l, content of copper – 1,7meq/g).

Catalyst	Yield, % mass			Conversion, % mass	Selectivity with respect to EHP, % mol
	EHP	MPC	AR		
Nonprearranged	3,4	2,1	5,0	10,6	31,0
Prearranged	6,4	2,9	9,0	18,3	35,0

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 catalyst of the structure of active centers favorable for hydrocarbon substrate.

We carried out hydrogenation of allyl alcohol using poly-4-vinylpyridine complexes with nickel prearranged for allyl alcohol and for the reaction product – propyl alcohol.

The procedure of preparation of the complexes and the hydrogenation reaction was described earlier^[14].

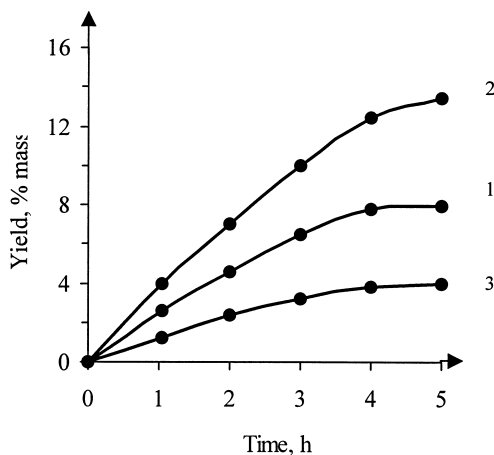


Figure 2. Kinetic curves for hydrogenation of allyl alcohol into propyl alcohol in a presence of nonprearranged /1/ and prearranged for allyl alcohol /2/ and propyl alcohol /3/ complexes of nickel with poly-4-vinylpyridine based polymers (concentration of the catalysts – 1,4g/l, content of copper – 4 meq/g).

Kinetic curves for hydrogenation of allyl alcohol to propyl alcohol are given in Fig.2.

It can be seen from the Figure that the rate of hydrogenation in a 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 that in a presence of nonprearranged complexes due to blocking of active centers from complexation with allyl alcohol.

Conclusion

A new principle of preparation of 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 to a favorable for sorbing metal or catalyzing substrate position followed by fixation of optimum conformations by intermolecular crosslinking. As a result "guest-host" phenomena between the crosslinked polymers and the substrates are realized and these, in turn, lead to essential improvement of basic sorption and catalytic properties of prearranged sorbents and catalysts.

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