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Catalytic activity of molecular imprinted vinylpyridine/acrylonitrile/divinylbenzene terpolymers with guanidyl ligands-Cu(II) inside the active centres

Summary — A series of novel molecularly imprinted catalysts was prepared by suspension polymerization of acrylonitrile. *N*-vinylpyridine and divinylbenzene in the presence of Cu(II) ions and various templates: acetophenone, dibenzoylmethane, 4-methoxybenzyl alcohol or 4-hydroxyacetophenone. To improve the catalytic properties, the catalysts were additionally modified inside the active centres by indirect aminolysis of nitrile groups using ethylenediamine and thiourea/ethyl iodide. The catalytic activity of initial samples as well as the modified ones was tested in the model oxidation of hydroquinone to *p*-benzoquinone using hydrogen peroxide. The catalysts prepared with Cu(II) ions and 4-methoxybenzyl alcohol as the template exhibit the highest activity. In spite of low modification degree, catalysts with guanidyl ligands inside the active centres show higher reaction yield and selectivity than unmodified samples.

Key words: molecular imprinted polymers, guanidyl ligands, Cu(II) ions coordination, hydroquinone oxidation.

AKTYWNOŚĆ KATALITYCZNA TERPOLIMERÓW Z ODCISKIEM MOLEKULARNYM WINYLOPIRYDYNA/AKRYLONITRYL/DIWINYLOBENZEN Z LIGANDAMI GUANIDYLOWYMI-Cu(II) W CENTRUM AKTYWNYM

Streszczenie — Nowe katalizatory z odciskiem molekularnym otrzymano metodą polimeryzacji suspensyjnej mieszaniny monomerów: 4-winylopirydyny (VP), akrylonitrylu (AN) i diwinylobenzenu (DVB) rozcieńczonej cykloheksanolem oraz zawierającej jony Cu(II) i wzorce. Jako związki wzorcowe tworzące odcisk molekularny wybrano acetofenon (AF), dibenzoilometan (DBM), alkohol 4-metoksybenzylowy (MBA) oraz 4-hydroksyacetofenon (HAF) (tabela 1). Ich aktywność katalityczną oceniano na podstawie wyników reakcji utleniania hydrochinonu (H_2Q) do *p*-benzochinonu (Q) nadtlenkiem wodoru (stężenie $5{,}4 \cdot 10^{-2}$ mol/l) (schemat A). Analizując widno UV-Vis obliczano stopień przereagowania hydrochinonu (L_{H2Q}), wydajność reakcji (Y_Q) i jej selektywność ($S_Q = Y_Q/L_{H2Q}$). Największą aktywność wykazuje katalizator, w którym zastosowano większe stężenie wzorca MBA (tabela 3). Dodatkowo terpolimery modyfikowano w reakcji aminolizy grup nitrylowych etylenodiaminą i transformowano grupy aminowe do guanidylowych tiomocznikiem w jodku etylu (tabela 4). Mimo małych stopni transformacji katalizatory zawierające skoordynowane przez jony Cu(II) grupy, mające w otoczeniu ligandy guanidylowe są selektywniejsze od katalizatorów z terpolimerów niemodyfikowanych (tabela 3).

Słowa kluczowe: polimery z odciskiem molekularnym, ligandy guanidylowe, koordynacja jonów Cu(II), utlenianie hydrochinonu.

The number of papers focused on the syntheses of molecularly imprinted polymers (MIP) has grown significantly during the last few years, which is connected with their important roles as functional polymers or in enzymes and antibodies biomimicry [1—10]. Most of publications present few main areas of MIP applications: sensors, capillary electrochromatography, enantiomeric separation, solid-phase extraction and catalysis. MIPs are tailor-made polymers characterized by high selectivity for a target molecule dependent on polymerization procedure. Imprinted polymers can be synthesized following three different imprinting approaches: using the non-covalent, the covalent or the semi-covalent binding between single template molecule or template molecule-metal complex and functional monomers matched to ensure specific interactions [1, 4, 8]. After syntheses these

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templates are removed from the polymer giving shape-complementary imprint responsible for the recognition specificity of MIP. Some imprinted polymers, mostly applied in catalysis, are modeled as the enzyme-like systems with central metal ion coordinating polymer ligands inside the active centre [1, 6, 7]. A nature of this metal ion and its interactions with functional groups within the imprint determine activity and selectivity of the designed catalysts.

In our previous works we proved that the aminoguanidyl groups present in mimic catalysts without imprint increased their catalytic activity more than amino or guanidyl ones [11—13]. Catalytic properties of these samples were tested in the model reaction of hydroquinone (H_2Q) oxidation to *p*-benzoquinone (Q). The oxidation of phenol derivatives may be also used to investigate unmodified MIP system [14].

T a b l e 1. Monomers and diluents in suspension polymerization mixture

Substrates	Symbol of substrate	Composition of polymerization mixture for MIP samples						
		MIP-A	MIP-B[a)]	MIP-C	MIP-D	MIP-E	MIP-F	MIP-H
Acrylonitrile, cm^3	AN	20.3	20.3	20.3	20.3	20.3	40.5	20.3
Divinylbenzene, cm^3	DYB	4.6	4.6	4.6	4.6	4.6	9.1	4.6
4-vinylpyridine, cm^3	VP	2.3	2.3	2.3	2.3	2.3	4.6	2.3
Acetophenone, cm^3	AF	2.6	2.6	—	—	—	—	—
Dibenzoylmethane, cm^3	DBM	—	—	2.5	—	—	—	—
4-methoxybenzyl alcohol, cm^3	MBA	—	—	—	0.4	2.8	—	—
4-hydroxy acetophenone, cm^3	HAF	—	—	—	—	—	5.7	—
Cyclohexanol, cm^3	CH	22.4	22.4	25	24.6	22.2	49.3	25
Cu(II) acetate, g	CuA	2.0	2.0	2.0	2.0	2.0	2.0	—
Benzoyl peroxide, g	NB	0.7	0.7	0.7	0.7	0.7	1.4	0.7

a) VP contained small amount of poly(vinylpyridine).

The aim of this work is to demonstrate that the formation of functional groups inside imprinted catalysts increases their catalytic activity due to appearance of the additional binding with substrates and improvement of environmental conditions. To create template-complementary cavities a new group of imprinting molecules, phenol mimics with hydroxyl or keto groups has been chosen.

EXPERIMENTAL

Materials

As monomers to syntheses of imprinted polymers 4-vinylpyridine (VP), acrylonitrile (AN) and divinylbenzene (DVB) were applied. As the imprinting molecules acetophenone (AF), dibenzoylmethane (DBM), 4-metoxybenzyl alcohol (MBA) or 4-hydroxyacetophenone (HAF) have been chosen. Cu(II) acetate (CuA), benzoyl peroxide (NB) as initiator and cyclohexanol (CH) have been also used.

All specified materials were purchased from Sigma-Aldrich. VP was purified by distillation prior to use and other chemicals and solvents were of analytical grade. As the oxidation substrate hydroquinone (H_2Q) from Aldrich (99 % GC) was chosen.

Preparation of imprinted polymers

Molecularly imprinted polymers were prepared by suspension polymerization. First, the functional monomers VP, AN, and DVB were mixed with Cu(II) ions, cyclohexanol and one of the compounds playing the role of template (AF, DBM, MBA or HAF). After adding the initiator NB an organic phase was suspended in 1.0 wt. % of poly(vinyl alcohol) (PVA) with solution containing sodium chloride. The compositions of polymerization mixtures are specified in Table 1. The mixture was purged with gaseous nitrogen then polymerization was carried out at temperature ranged from 60 to 95 °C for 10 h with stirring at 240 rpm. Obtained beads of 0.1—0.25 mm diameter were washed with acetone and 1 M HCl solution repeatedly until colorless solution was seen. Non-imprinted blank sample (MIP-H) was prepared using the same procedure.

Functional guanidyl groups on the surface of MIP were introduced during two-step aminolysis of nitrile groups with ethylenediamine and transformation by thiourea/ethyl iodide mixture [15]. MIP samples modified with ethylenediamine are denoted by addition of letter E after slash mark to the symbol of unmodified sample. The samples modified in the second step to guanidyl groups are marked with addition of letter G.

Preparation of catalysts

Sorption of Cu(II) ions was performed using batch method [16, 17]. The resins were swollen in distilled water then placed in 20 cm^3 of CuA solutions ($1 \cdot 10^{-1}$—$1 \cdot 10^{-4}$ M) in acetate buffer of pH = 5.0 and shaked at room temperature for 48 h. Next the loaded samples were separated.

Oxidation reaction

Catalysts swollen in 20 cm^3 of H_2O_2 solution ($5.4 \cdot 10^{-2}$ mol/dm^3 in acetate buffer of pH = 5.0) were placed in polyethylene flasks. The mixture was purged with gaseous nitrogen then 20 cm^3 of $4 \cdot 10^{-3}$ mol/dm^3 of H_2Q aqueous solution [16, 17] was added. The Cu(II) to substrate ratio was 1:10. The entire mixture was shaken (350 cycles/min) in water bath at 35 °C for 80 min. Samples were taken at given time intervals and diluted with distilled water.

Methods of testing

The water and dioxane regains (g/g) were measured using centrifugation technique (5 min, 3000 rpm).

The amino groups content (Z_{NH2}) was analyzed according to the modified Colella-Siggia method described in [18]. Nitrogen content was checked by elemental analysis.

Sorption of Cu(II) (mmol/g) by MIP sample was calculated from the difference of Cu(II) concentration in solution before and after sorption. The Cu(II) concentration in solution was determined by atomic absorption spectrophotometry (AAS) using AAS-30 Perkin Elmer Aanalyst 100.

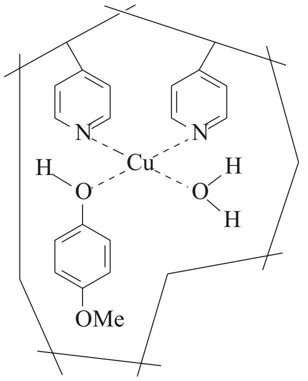
The oxidation degree of substrate (L_{H2Q} in %) and the yield of product (Y_Q in %) were defined as a decrease in substrate concentration and increase in product concentration, respectively, with relation to the initial substrate concentration. The concentrations of unreacted substrate and a product, which was *p*-benzoquinone (Q) were determined by UV-Vis spectrophotometry using Jasco 570c spectrophotometer at λ = 289 nm, and λ = 246 nm, respectively. The selectivity of product (S_Q in %) was defined as a ratio of product concentration and the reacted substrate concentration.

RESULTS AND DISCUSSION

The formation of MIP structure during polymerization takes place in good solvatation conditions. According to the monomer and diluents composition (AN, VP, DVB, cyclohexanol) the solubility parameters have being estimated at about 23 $MPa^{1/2}$. The influence of the template, making up the 5 wt. % of polymerization mixture, is negligible; moreover the solubility parameters of imprinting molecules are about 22 $MPa^{1/2}$ [19—21]. The conception of modeling of these systems was based on the interaction between Cu(II) ions, nitrogen atoms of VP molecule and hydroxyl or ketone groups of the template molecule, which determinate only the shape of cavities formed. AN has been chosen according to its ability to formation with divinyl comonomers the rigid and stiff structures. In our previous works we stated that porous copolymer AN/DVB consisted of oriented agglomerates with pores between them. The pore diameter was determined by degree of crosslinking and the nature of diluents [20—23]. Second active monomer VP is commonly used in MIP modeling, because of its high reactivity and possibility of binding with metal ion [24].

The crosslinking agent DVB is the most universally used in the syntheses of functional polymers, due to the high stability of created polymers formed. In all our MIP samples the concentration of DVB was constant — 10 wt. % in the relation to monomer mixture. The rigid structure of MIP is necessary for creation of stable, template-compatible cavities responsible for effective substrate recognition and binding. On the other hand, DVB introduces hydrophobic interactions between polymer and substrate, increasing sorption properties unfavourable in catalytic applications. To neutralize this effect the crosslinking monomer can be changed to more hydrophilic one *e.g.* 1,1,1-trihydroxymethylpropane trimethacrylate (TMPMA) [14] or additionally the polymer can be functionalized to make it more hydrophilic [25].

As the templates, the structural analogue of *p*-benzoquinone (Q) or the transition state analogue (TSA), having the ketone or alcohol character and dissolving in cyclohexanol have been searched (AF, DBM, MBA or HAF). Only one of these templates — DBM in complex of Co(II) ions was applied by Mosbach [24] to form the imprints inside the pyridine copolymers. In our syntheses, Cu(II) ions coordinating pyridine nitrogen and template oxygen of selected compounds form the imprints in polymer [Formula (I)]. The blank sample MIP-H was synthesized without template complex. The compositions of the monomer mixtures were similar in all cases (Table 2).



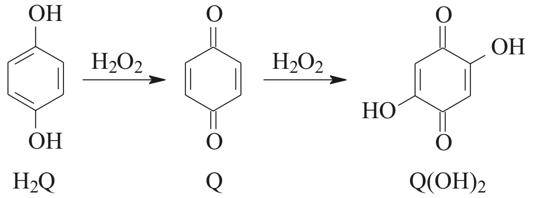
(I)

T a b l e 2. Characteristic of imprinted polymers obtained

Parameters	MIP-A	MIP-B	MIP-C	MIP-D	MIP-E	MIP-F
Nitrogen concentration, mmol/g	4.0	4.3	4.8	5.2	6.6	9.5
Water regain, g/g	0.56	1.46	1.14	1.52	1.73	1.14
Dioxane regain, g/g	2.1	2.77	2.57	2.59	2.25	0.98

Table 2 presents the characteristics of polymers' samples. The sample MIP-C obtained from the monomer mixture containing DBM has an irregular shape and soft gel structure and therefore it is not further analyzed. The other samples are rigid spheres with diameter of 0.1—0.25 mm. The nitrogen concentrations in all MIP samples are lower than nominal values in both nitrogen containing monomers, which probably results from the extraction of linear polyacrylonitrile with diluents after syntheses and the inhibiting influence of copper ions. The small yield of AN copolymerization is characteristic for suspension polymerization of this monomer [26]. Higher content of nitrogen characterizes only the sample MIP-H prepared without a template. Dioxane regain is higher than water one because of ability of this solvent to penetration the gel structure of MIP whereas water mainly fills the pores. The water and dioxane regains are various for individual samples according to their pore volumes. In our earlier investigations of AN/DVB structure we have shown that the shape of pores is forced by the diluent added to cyclohexanol (in the ratio 1:9) [22]. The MIP-A and MIP-B samples were obtained from the monomer mixtures diluted with AF. In case of MIP-B, pyridine monomer solution contained the small amount of homopolymer which might also imprint its shape increasing the pore volume. Comparison of the water and dioxane regains of MIP-A and MIP-B confirms this fact. Sample MIP-B shows extreme porosity indicating macromolecules imprint. The porous structure of MIP-D and MIP-E samples are formed by the same MBA template, but its amount in MIP-D monomer mixture is smaller than in MIP-E one. The water regain of MIP-D is the same as of MIP-H, what means that the small amount of alcohol did not change significantly the structure of beads. The highest water regain characterized the sample MIP-F modified with HAF.

Catalytic activity of samples was tested in the reaction of H_2Q oxidation to Q by H_2O_2. The Cu(II) ions were introduced into polymer beads in CuA solution (concentration $1 \cdot 10^{-2}$ or $5 \cdot 10^{-3}$ M, pH = 5.0). In disadvantageous conditions the next step of oxidation is possible (Scheme A) and the selectivity (S_Q) of reaction decreases. Catalytic activity is determined by two parameters as the loss of H_2Q (L_{H2Q}) and yield of Q (Y_Q). In our investigations on model H_2Q oxidation [11—14, 16, 17] we have proved that estimation of catalytic activity only on the basis of oxidation degree (L_{H2Q}) was insufficient as it published in *e.g.* [27]. Due to possibility of further oxidation of Q during the reaction it is necessary to measure also the increase in Q concentration and calculate the reaction selectivity [16].



Scheme A. Oxidation reactions of hydroquinone

Table 3. Catalytic activity of imprinted catalysts with Cu(II) ions

Catalyst	Cu(II) mmol/g	Time min	L_{H2Q}, %	Y_Q, %	S_Q, %
MIP-A	0.14	10	2.4	—	—
		30	21.8	14.6	67
		60	22.4	18.2	81.1
		80	24.1	20.6	85.4
MIP-B	0.11	10	3.4	—	—
		30	5.5	—	—
		60	5.6	—	—
		80	3.6	—	—
MIP-D	0.12	10	15.6	12.2	78.7
		30	21.0	20.0	95.2
		60	28.3	20.7	73.0
		80	32.4	20.0	61.6
MIP-E	0.17	10	41.2	29.5	71.4
		30	63.0	47.7	75.8
		60	73.7	52.6	71.3
		80	77.5	50.9	65.1
MIP-F	0.17	10	25.6	18.7	72.9
		30	67.4	26.5	39.3
		60	65.3	36.6	56.1
		80	71.5	40.0	55.9
MIP-A/G	0.04	10	33.9	19.2	56.5
		30	42.6	24.9	58.4
		60	56.3	25.3	45.0
		80	53.3	27.7	52.0
MIP-B/G	0.06	10	19.7	15.4	78.2
		30	18.8	18.2	96.8
		60	24.4	20.9	85.8
		80	22.7	22.2	97.8
MIP-D/G	0.09	10	28.4	21.7	76.4
		30	40.9	31.7	77.5
		60	46.8	32.5	69.4
		80	43.6	34.1	78.2

L_{H2Q} — oxidation degree, Y_Q — reaction yield, S_Q — reaction selectivity.

The catalytic activity of MIP-A with the imprint of AF is low, after 80 min only 24 % of H_2Q reacted. Sample MIP-B obtained from polymerization mixture containing poly(vinylpyridine) does not have the catalytic activity (Table 3). In all cases the lower oxidation degree determines increase in reaction selectivity. The samples imprinted with MBA, even with very small amount of the template (MIP-D), are characterized by higher catalytic activity than MIP-A, modified by AF. The increase in MBA concentration results in optimal catalytic activity (MIP-E). The oxidation reaction rates (V_o) observed for different imprinted catalysts are shown in Fig. 1. The rate is the highest for MIP-E sample and S_Q during the

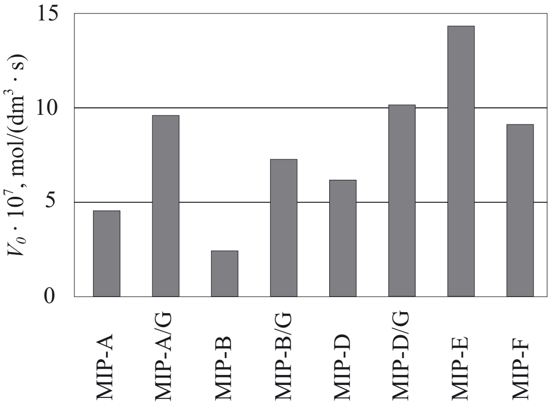


Fig. 1. Oxidation rates (V_0) of imprinted polymers samples for catalysts with and without guanidyl ligands (after 10 min)

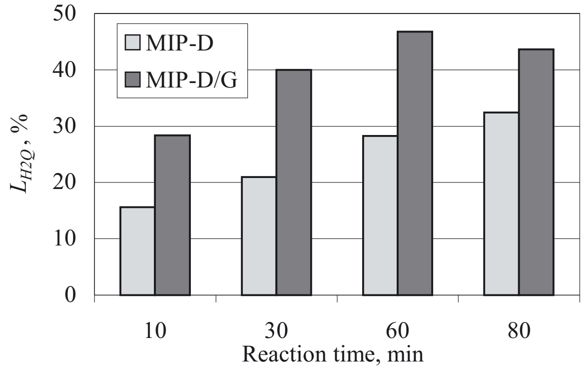


Fig. 2. Comparison of the oxidation degree during the oxidation of H_2Q (L_{H2Q}) for catalysts samples with (MIP-D/G) and without (MIP-D) guanidyl ligands

oxidation reaction (10—80 min) remains at the same level (about 70 %) (Table 3). Somewhat lower catalytic activity and S_Q than of MIP-E characterize MIP-F imprinted with HAF and additionally selectivity decreases during the reaction time (Table 3). It is the result of the subsequent oxidation of Q (Scheme A). It should be assumed that MBA is the best template for model reaction oxidation of H_2Q to Q. The MIP-H without the imprint also reveals the catalytic activity ($Y_Q = 28.1$ %), but its S_Q is considerably lower *e.g.* 36.9 %.

As it results from our previous investigations on enzyme-like catalysts with aminoguanidyl ligands, catalytic activity depends not only on specificity of metal complex inside the active centre but also on the environment formed by free functional groups [16].

In order to increase the catalytic activity of obtained MIP catalysts we transformed active centres environments as well. Small degree of nitrile groups modification to guanidine ones on the surface does not change the shape of imprints, but exchanges the hydrophobic interaction to hydrophilic and creates better environmental conditions similar to enzymatic ones. Modification was carried out as two-step aminolysis of nitrile groups with ethylenediamine and subsequent transformation with thiourea/ethyl iodide mixture [15]. The concentrations of amino and guanidyl groups are small (Table 4) and water regain does not change significantly, even though the hydrophilic groups have been introduced.

The samples modified with ethylenediamine did not have the catalytic activity. In spite of low guanidyl ligands concentration, the catalytic activities of modified samples (MIP-A/G, MIP-B/G and MIP-D/G) increase satisfactorily in comparison to the initial MIP without modification (Table 3, Fig. 2). S_Q value of the modified samples is higher than without transformation and increases during the reaction time, which indicates the favourable influence of environment created by amino groups. The oxidation rate after 10 min is of the same level for the samples MIP-A/G, MIP-B/G, MIP-D/G, MIP-F, and is higher than for unmodified samples MIP-A and MIP-B (Fig. 1). The same correlation was observed earlier for MIP samples crosslinked with trimethylolpropane trimethacrylate after introduction of aminoguanidyl ligands [25]. From the EPR investigation [25, 28] it follows that the guanidyl groups do not take part in Cu(II) ions coordination, but like the amino acids (Arg, His, Glu, Asp) in enzymes give the best environment conditions. At neutral pH the EPR parameters for modified samples ranged from: $A_{II} = 163 \cdot 10^{-4}$ cm^{-1}, $g_{II} = 2.325$ (for N2O2 complex type) to $A_{II} = 170 \cdot 10^{-4}$ cm^{-1}, $g_{II} = 2.308$ (for N3O type), which is close to Cu(II) coordination of pyridine ligands [29] and different from Cu(II)-guanidine parameters [28].

Despite advantageous influence of additional ligands within the active centres, the modification procedure is very long and inconvenient.

CONCLUSION

Catalysts prepared using molecular imprinting technique with Cu(II) ions and 4-methoxybenzyl alcohol as the template exhibits the highest activity. Introduction of guanidyl ligands in two-step reaction, even in low con-

Table 4. Characteristics of imprinted polymers with ethylenediamine or guanidyl groups

Parameters	Ethylenediamine groups			Guanidyl groups		
	MIP-A/E	MIP-B/E	MIP-D/E	MIP-A/G	MIP-B/G	MIP-D/G
Water regain, g/g	1.26	1.44	1.11	1.05	1.14	1.14
Dioxane regain, g/g	2.1	2.77	2.57	1.64	2.12	1.93
Z_{NH2}, mmol/g	1.09	0.94	2.28	0.35	0.65	1.06

centration, increases the reaction yield and selectivity. Catalytic activity depends on MIP compositions, its structure and the specificity of metal complex inside the active centre but also on the complex environment formed by free groups.

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Received 17 VII 2007.