Electrochemical investigation of complexation of polymer ligands containing 2,2´-biquinolyl fragments with Ni^{II} ions in solution

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Polyamic acids containing biquinolyl (biQ) fragments in the polymer backbone are capable of coordinating with Ni^{II} ions to form two types of coordination units: with one or two biQ ligands in the Ni coordination environment. The relative number of $[Ni(biQ)_2]^{2+}$ coordination units in the polymer chain increases with an increase in the concentration of the biQ fragments in solution and with a decrease in the conformational rigidity of the polymer. The synthesis of the nickel complexes with the polymer ligands can be carried out using both Ni salts and the electrochemical dissolution of the Ni anode.

Key words: electrosynthesis, soluble Ni anode, biquinolyl, Ni polymer complexes.

Among a variety of chemical reactions, catalytic processes are often characterized by the highest efficiency. However, requirements imposed on modern catalysts become more and more rigorous. The catalysts should be highly active, stereoselective, recyclable, correspond to requirements of "green chemistry," *etc.*[1] Various types of polymers can serve as a basis for the development of catalytic systems. Polymers are usually less expensive and more technological than inorganic crystalline materials. They represent a unique possibility to combine in one material high thermomechanical and catalytic properties. Polymers are very convenient for the preparation of hybrid materials, because the polymer chain allows one to introduce functional groups and active sites of diverse nature. The variation of the polymer chain structure makes it possible to perform "fine tuning" of the necessary parameters and properties, thus creating prerequisites for the preparation of materials of specified properties. The anomalously low entropy of polymers make them susceptible to various effects, which allows one to manufacture "controlled" polymer-based systems. The specific features of polymers listed above cause prospects and urgency of the problem of design and synthesis of new efficient catalysts based on polymers of various types.

Interest in the obtaining of nickel-containing polymer systems is due to the wide use of the nickel complexes in catalysis (see, *e.g.*, Refs 2—6 and literature cited therein) and electrocatalytic transformations.[7—9] It seems very attractive to change the expensive Pt- or Pd-containing catalysts by the cheaper Ni complexes without substantial loss of activity. In the most cases, the nickel complexes with phosphine-containing or bipyridyl ligands are used. The scope of the reactions is rather wide, but the carboxylation reactions of various aryl halides[10—15] and the reductive homo- and cross-coupling of aryl[8,16—20] and hetaryl halides or chlorophosphine[21—26] are most studied. The reactions are carried out under mild conditions in an undivided electrochemical cell at the reduction potential of the nickel complex. A soluble anode (Mg, Zn, or Fe) is often used for the suppression of side processes. Electrolysis is usually carried out in dimethylformamide or *N*-methylpyrrolidone; however, there are works using protonic solvents (alcohols[27] or water[28]) and ionic liquids.[29,30]

At the same time, the phosphine-containing catalysts are not optimal from the ecological point of view in spite of their high efficiency, because the reactions products are often contaminated with toxic phosphorus compounds. In the case of other homogeneous catalysts, the problem of their separation from the reaction products also appears. As was already mentioned above, the use of polymer catalysts can be one of the routes to solve this problem.

We have synthesized recently new polymers of polyamic acid type (PA) containing biquinolyl (biQ) fragments in the main chain capable of coordinating with transition metal ions .[31]

The choice of polymers is caused by the striving for the study the influence of various structural factors (confor-

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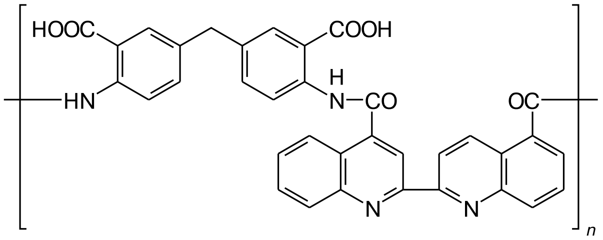
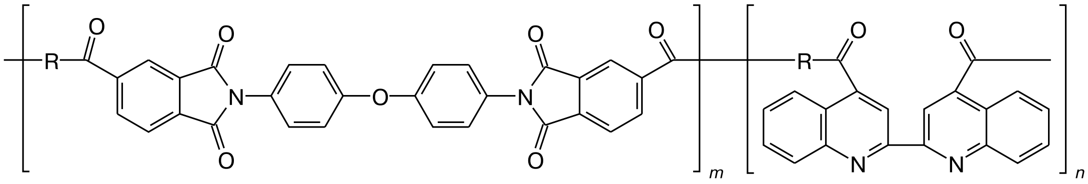


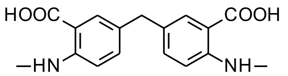
PA^I



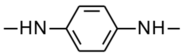
PA^II, PA^III

PA^II: R = R^1; **PA^III**: R = R^1 or R^2; m : n = 8 : 2

R^1 =



; R^2 =



R^1 : R^2	Yield of **PA^III** (%)
90 : 10	10
80 : 20	20
70 : 30	30

mational rigidity of the polymer chain, a number of coordinating units, and their steric and electronic properties) on the structure of the coordination units formed. We have earlier shown[32,33] that polymers **PA^I**, **PA^II**, and **PA^III** can serve as convenient polydentate ligands for the formation of the Cu^{I} (see Ref. 32) and Pd^{II} polymer complexes. The study of the catalytic activity of the obtained metallopolymer systems showed that the copper-containing complexes are efficient catalysts of the aerobic electrocatalytic oxidation of aliphatic alcohols[34] and amines[35] to carbonyl compounds. Palladium complexes exhibit a high catalytic activity in the cross-coupling reactions at the palladium content lower than 0.05 mol.% and they are capable of recycling.[33,36,37]

This work is a continuation and further development of these studies. The task was to study the complexation of the aforementioned polymers with Ni^{II} ions in solution by cyclic voltammetry (CV) and MALDI-TOF mass spectroscopy aimed at developing new nickel-containing polymer systems for the subsequent use in catalysis and electrocatalysis. To determine the composition of the coordination units formed in the polymer, we also used the model low-molecular-weight ligand, dihexyl 2,2´-biquinolyl-4,4´-dicarboxylate (biQ(COOHex)$_2$), which made it possible to use the MALDI-TOF method. A comparison of the properties of the polymer complexes and complexation processes involving low-molecular-weight ligands makes it possible to reveal the influence of the polymer chain on the redox properties of the nickel-containing coordination units.

Experimental

N-Methylpyrrolidone (NMP) (Aldrich) was dehydrated over calcium hydride and distilled, collecting the fraction with b.p. 80 °C (7 Torr).

Acetonitrile (pure grade) was stirred for 12 h over calcium hydride, distilled, then refluxed for 2 h with P_2O_5, and again distilled, collecting the fraction with b.p. 81—82 °C under atmospheric pressure.

The electrochemical oxidation and reduction potentials were measured using an IPC-Win digital potentiostat—galvanostat connected to a personal computer. Voltammograms were detected by the CV method at the stationary platinum electrode at various potential sweep rates with 0.05 *M* n-Bu_4NBF_4 as a supporting electrolyte in *N*-methylpyrrolidone at 20 °C in a 10-mL electrochemical cell. Oxygen was removed from the cell by purging it with dry argon. Electrolysis was carried out using a P-5827 M potentiostat in a 10-mL electrochemical one-compartment cell. The working electrode (anode) was a Ni wire of 1 cm in length with a diameter of 2 mm containing at least 99.99% nickel. A platinum wire served as an auxiliary electrode. The reference electrode was a saturated silver chloride electrode (its potential *vs* Fc/Fc$^+$ is 0.48 V in NMP). The measured potential values were recalculated taking into account ohmic losses.

The MALDI-TOF spectra were recorded on a Bruker Daltonics Autoflex II instrument with a frequency of laser radiation of 337 nm on the cryogenic 9-nitroanthracene matrix.

The mass spectra with sputtering ionization in the electric field were detected on a Finigan LCQ Advantage mass spectrometer. The temperature of heating of the capillary was 150 °C, the electric potential was 4.5 kV, the feeding rate of the mobile phase was 10 μL min^{-1}, nitrogen was a sputtering and drying gas, and acetonitrile (Merck) with an addition of 1% water (Acros Organics) served as a solvent and a mobile phase.

Electrochemical synthesis of $[Ni^{II}(PA)_2][BF_4]_2$ complexes. The Ni wire was dissolved under the galvanostatic conditions ($I = 1 \cdot 10^{-3}$ A) in 10 mL of a 10^{-3} *M* (as calculated respectively to the biQ fragments) solution of PA in NMP in the presence of 0.05 *M* *n*-Bu_4NBF_4 and 10 μL ($5.5 \cdot 10^{-4}$ mol) of H_2O. The process was stopped after passing electricity of 1.1 F per 1 mole of the biQ fragments. Complexation was monitored by the appearance of peaks corresponding to the $Ni^{2+/0}$ reduction at the potentials of −390 and −650 mV for **PA^{I}** and −360 and −640 mV for **PA^{II}**. Water (5 mL) was added to the obtained solution. The precipitate that formed was filtered off, washed with CH_3CN, and dried at 90 °C. For **PA^{I}** 4.8 mg of the precipitate were obtained (80%), and 5.6 mg (76%) were obtained for **PA^{II}**. According to the atomic absorption analysis data, the Ni content in the precipitate is 4.85% for **PA^{I}** and 0.75% for **PA^{II}** (the calculated Ni content for the formation of the $[Ni(biQ)_2]^{2+}$ coordination units is 4.14% for **PA^{I}** and 0.73% for **PA^{II}**).

Electrochemical and mass spectrometric studies of the Ni^{II} complexation with $biQ(COOHex)_2$ in solution. Dihexyl biquinolyldicarboxylate $biQ(COOHex)_2$ (5.1 mg, 0.01 mmol) was dissolved in CH_3CN (10 mL), and galvanostatic electrolysis with the nickel anode ($I = 1 \cdot 10^{-3}$ A) was carried out. The process was stopped after an electricity of 1.6 F per 1 mole of the biQ fragments was passed. Complexation was monitored by the appearance of peaks corresponding to the $Ni^{2+/0}$ reduction in the formed complexes $[(biQ(COOHex)_2)_2Ni]^{2+}$ and $[biQ(COOHex)_2Ni]^{2+}$ at the potentials of −300 and −620 mV, respectively. The obtained solution was analyzed by the MALDI-TOF method, which showed molecular ions with *m/z* 1082 $(biQ(COOHex)_2)_2Ni)^+$ and 570 $(biQ(COOHex)_2)Ni)^+$.

Results and Discussion

An important criterion of complexation in solution is the change in the electrochemical potential of the $Ni^{2+/0}$ redox transition compared to that of the initial nickel salt and the shift of the reduction potential of the ligand in the presence of the ion of the complexing agent. Therefore, the first stage of investigations was the study of the electrochemical reduction of the polymer ligands and their low-molecular-weight analog using cyclic voltammetry.

Investigation of the redox properties of the low-molecular-weight polymer ligands. The voltammogram (Fig. 1) of a $biQ(COOHex)_2$ solution in acetonitrile exhibits four reduction peaks, which are well consistent with the literature data for 2,2´-biquinolyl.[38] The reduction proceeds as a consecutive transfer of four electrons and is accompanied by protonation.

The CV curves observed for polyamic acids (**PA^{I}**, **PA^{II}**, and **PA^{III}**) in solution are similar. The CV curve obtained for **PA^{III}** is presented in Fig. 2 as an example. The first reduction potentials of all polymers are close to the reduction potentials of the low-molecular-weight analog (Table 1); however, for **PA^{II}** and **PA^{III}** they are somewhat shifted to the anode region relative to **PA^{I}**, since the molecular units in **PA^{II}** and **PA^{III}** manifest the acceptor properties.

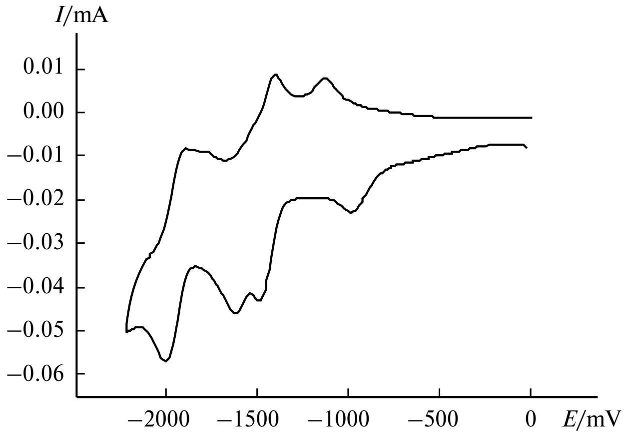


Fig. 1. CV curve for a 1 *mM* solution of $biQ(COOHex)_2$ (Pt, 0.05 *M* Bu_4NBF_4, CH_3CN, 100 mV s^{-1}, *vs* Ag/AgCl/KCl).

Electrochemical study of the complexation of the polymer ligands and their low-molecular-weight analog with Ni^{II} ions. Salt $NiCl_2$ or the Ni anode were chosen as a source of Ni^{II} ions. A one-compartment cell was used for the electrochemical synthesis of the complexes. The dissolution of the nickel anode was carried out in the galvanostatic mode. In the both cases, a criterion for complexation can be the shift of the $Ni^{II/0}$ formal potential value upon the addition of the nitrogen-containing ligand. The peak potential of $NiCl_2$ reduction in NMP is −1.17 V (*vs* Ag/AgCl/KCl). The dissolution of the Ni anode in the same solvent with 0.05 *M* Bu_4NBF_4 results in the appearance of an intense peak of the Ni^{II} ions reduction at the close potential value (−1.15 V). The addition of the low-molecular weight ligand $biQ(COOHex)_2$ to a solution containing the Ni^{II} ions results in the appearance of two new peaks at the potentials of −300 and −620 mV.

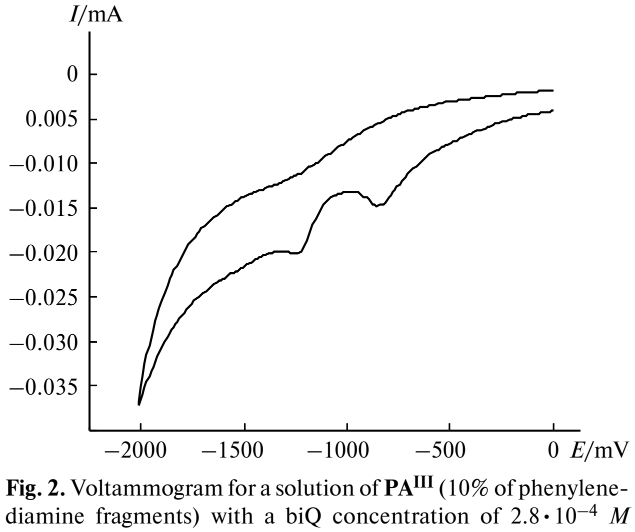


Fig. 2. Voltammogram for a solution of **PA^{III}** (10% of phenylenediamine fragments) with a biQ concentration of $2.8 \cdot 10^{-4}$ *M* (0.05 *M* Bu_4NBF_4, NMP, Pt, 100 mV s^{-1}, *vs* Ag/AgCl/KCl).

Table 1. Reduction potentials of biQ(COOHex)$_2$, various polyamido acids, and their nickel complexes (NMP, 0.05 *M* $Bu^n{}_4NBF_4$, Pt, 100 mV s^{-1})

Redox-active sites	$-E_p$/mV			
	biQ(COOHex)$_2$	**PA^{I}**	**PA^{II}**	**PA^{III}** (10%)
biQ	910, 1360, 1490, 1860	960, 1300	900, 1250	890, 1250
$[Ni(biQ)_2]^{2+/0}$; $[NibiQ]^{2+/0}$	300, 620	390, 650	360, 640	350, 640

The dynamics of changing the voltammetric pattern upon the addition of $NiCl_2 \cdot 6H_2O$ in various molar ratios to biQ(COOHex)$_2$ in acetonitrile is shown in Fig. 3. As can be seen, the addition of an equimolar amount of nickel chloride to a solution of biQ(COOHex)$_2$ shifts the reduction peaks of the ligand to the anode side. This shift of the reduction potentials of biQ(COOHex)$_2$ possibly indicates that the complexation with Ni^{II} decreases the electron density on the ligand; *i.e.*, the σ-donor properties of biQ(COOHex)$_2$ are more strongly manifested than the reciprocal d—π-binding Ni—ligand. Along with this, the addition of nickel chloride to the solution results in the appearance of two new (compared to the curve for the free ligand) peaks at the potentials of –300 and –620 mV. The new peaks correspond, most likely, to the Ni$^{2+/0}$ reduction in the formed complexes $[Ni(biQ)_n]^{2+}$ (n = 1, 2). Unfortunately, it is difficult to estimate the amount of Ni^{2+} ions remained uncomplexed from the voltammetric data, because the reduction potential of the Ni^{2+} ions lies in the same region as the first reduction peak of the biQ ligand.

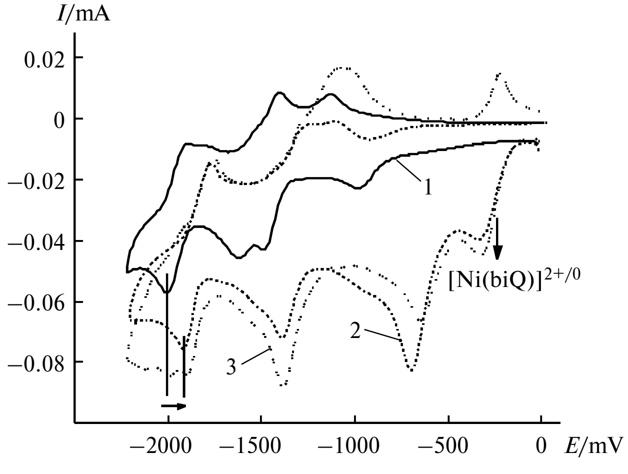


Fig. 3. Voltammograms for solutions of 1 *mM* biQ(COOHex)$_2$ (*1*), 1 *mM* biQ(COOHex)$_2$ and 1 *mM* NiCl$_2$ (*2*), and 2 *mM* biQ(COOHex)$_2$ and 1 *mM* NiCl$_2$ (*3*) (CH_3CN, 0.05 *M* Bu_4NBF_4, GC, 200 mV s^{-1}, *vs* Ag/AgCl/KCl).

To elucidate the composition of the formed complexes using the CV method, we studied solutions with various Ni : biQ(COOHex)$_2$ molar ratios (1 : 1 and 1 : 2) and the 1 *mM* concentration of Ni^{II}. It turned out that the addition of one more equivalent of biquinolyl (Ni : biQ(COOHex)$_2$ = 1 : 2) to the initial solution (with the ratio Ni : biQ(COOHex)$_2$ = 1 : 1) resulted in an increase in the peak current at –300 mV from 28 to 30 μA, which corresponds to an increase in the concentration of the complex from $4.0 \cdot 10^{-4}$ to $4.3 \cdot 10^{-4}$ mol L^{-1}. On the contrary, the peak current at E = –620 mV decreases from 41 to 36 μA, which corresponds to a change in the concentration from $6.0 \cdot 10^{-4}$ to $5.7 \cdot 10^{-4}$ mol L^{-1}. The peak at –620 mV disappears completely in a large excess of the ligand. It should be mentioned that the voltammetric curves were detected several times in each case of mixing the reactants in order to achieve the stationary pattern. Thus, the CV data suggest that the peak at a potential of –300 mV corresponds to the reduction of the Ni^{II} complex with two biquinolyl-containing ligands, whereas the peak at –620 mV corresponds to $[Ni(biQ)L_n]$ (n = 2—4) complex containing only one biquinolyl ligand, and the remaining coordination sites are occupied by the solvent molecules.

An analogous tendency is also observed for solutions of the polymers in the presence of Ni^{II} ions. The addition of more than twofold excess of **PA^{I}** or **PA^{II}** polymers (based on the molar amount of the biQ fragments) to a solution containing Ni^{II} ions and the dissolution of the Ni anode in the presence of these polymers in the solution result, in both cases, in the appearance of a new redox pair at the potential of –0.39/–0.23 (**PA^{I}**) and –0.36/0.21 V (**PA^{II}**) in the voltammogram (Fig. 4).

The addition of water to the obtained solution leads to the precipitation of slightly greenish polymer nickel complexes. The yields and current efficiencies for the nickel

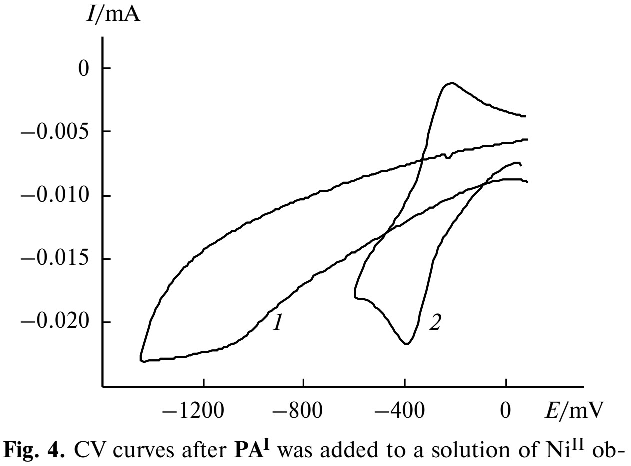


Fig. 4. CV curves after **PA^{I}** was added to a solution of Ni^{II} obtained by the dissolution of the Ni anode: the initial solution of Ni^{II} (*1*), the ratio Ni^{II} : biQ = 1 : 2 (*2*), NMP, Bu_4NBF_4 0.05 *M*, Pt, 100 mV s^{-1}, *vs* Ag/AgCl/KCl.

Table 2. Preparative yields (%) and current efficiencies for the polymer Ni complexes* and the elemental analysis data for these complexes

Complex	Preparative/Current		Content of Ni (%)	
	yield	efficiency	exp.	theor.
$[Ni(\mathbf{PA^I})_2][BF_4]_2$	80	76	4.85	4.14
$[Ni(\mathbf{PA^{II}})_2][BF_4]_2$	76	72	0.75	0.73

* Conditions: Ni anode, 1.05 F per mole of biQ, NMP, 0.05 *M* Bu_4NBF_4, $5 \cdot 10^{-4}$ *M* polymer.

complexes obtained by the dissolution of the Ni anode in the presence of polymer ligands $\mathbf{PA^I}$ and $\mathbf{PA^{II}}$ are listed in Table 2 along with the atomic absorption analysis results for the complexes. It is seen that the experimental and theoretical values calculated for the $[Ni(biQ)_2]^{2+}$ coordination units are well consistent.

To reveal the possibility of formation in the polymer of the Ni-containing coordination units with one biQ fragment in the Ni^{II} ion coordination environment (other coordination sites can be occupied by solvent molecules, for example, NMP or CH_3CN), we carried out the voltammetric study of solutions with various Ni : biQ molar ratios. If the dissolution of the nickel anode is carried out in the presence of polymer $\mathbf{PA^I}$, two reduction peaks at the potentials of −390 and −650 mV, which are close to those observed earlier for the low-molecular-weight complexes (see Table 1), appear in the CV curve (Fig. 5).

Upon the subsequent addition of $\mathbf{PA^I}$ (to the Ni : biQ ratio of 1 : 2), the peak at −390 mV increases and the peak at −650 mV decreases as it was observed in the case of the low-molecular-weight biquinolyl-containing ligand. The Ni^{II} complexes containing $\mathbf{PA^{II}}$ are reduced at the potentials of −360 and −640 mV. A similar tendency of changing in the peak currents is observed upon the subsequent addition of $\mathbf{PA^{II}}$ to a solution of Ni^{2+}. The Ni^{II} complexes with $\mathbf{PA^{III}}$ are formed much more slowly than those with $\mathbf{PA^I}$ and $\mathbf{PA^{II}}$ due to the greater conformational rigidity of the polymer $\mathbf{PA^{III}}$ ligand. For instance, for $\mathbf{PA^{III}}$ (20%) the voltammetric curve reaches the stationary state only 1 h after mixing of the reactants (ratio biQ : Ni = 2). In the polymers with the greater conformational flexibility ($\mathbf{PA^I}$ and $\mathbf{PA^{II}}$), the number of coordination units $[Ni(biQ)_2]^{2+}$ gradually increases and the number of $[Ni(biQ)L_2]^{2+}$ decreases with an increase in the number of the biQ fragments. In the case of $\mathbf{PA^{III}}$ (10%), the coordination units $[Ni(biQ)L_2]^{2+}$ remain even in an excess of the biQ fragments, whereas the number of the $[Ni(biQ)_2]^{2+}$ sites is low. Almost no complexation is observed for $\mathbf{PA^{III}}$ (30%) even 1 h after the end of electrolysis.

Since the Ni polymer complexes were synthesized for their subsequent use in catalysis, it was of interest to study the possibility of immobilization of these polymer systems on the graphite electrode surface. Polymer $\mathbf{PA^{III}}$ (10%) was immobilized on the surface of the graphite tissue by impregnation with a solution in NMP with the biQ concentration equal to 10^{-6} mol L^{-1} and subsequent drying under reduced pressure at 80 °C. Thus treated graphite tissue was used as a cathode in electrosynthesis, and a nickel wire served as an anode. Nickel was dissolved in the galvanostatic mode at a current value of 1 mA, passing the amount of electricity necessary for the generation of a 1.5-fold excess of Ni^{II} ions over the biQ fragments. The obtained solution was left for 30 min, after which the graphite tissue was taken out, washed with acetonitrile, dried, and studied using voltammetry (Fig. 6).

As can be seen from Fig. 6, the electrosynthesis on the electrode surface results in the formation of $[Ni(biQ)L_2]^{2+}$ coordination units, which are stable upon multiple potential cycling. Therefore, we may hope that this graphite surface can successfully be used in catalysis and electrocatalytic transformations. We found that no $[Ni(biQ)_2]^{2+}$

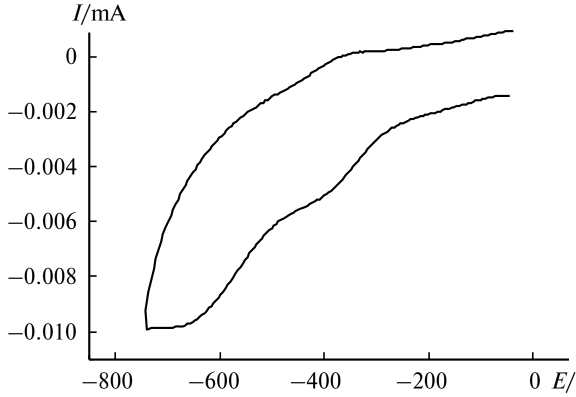


Fig. 5. Voltammogram for a solution containing 1 *mM* Ni^{II} (dissolution of the Ni anode) and 1.5 *mM* biQ ($\mathbf{PA^I}$) (0.05 *M* Bu_4NBF_4, NMP, Pt, 100 mV s^{-1}, *vs* Ag/AgCl/KCl).

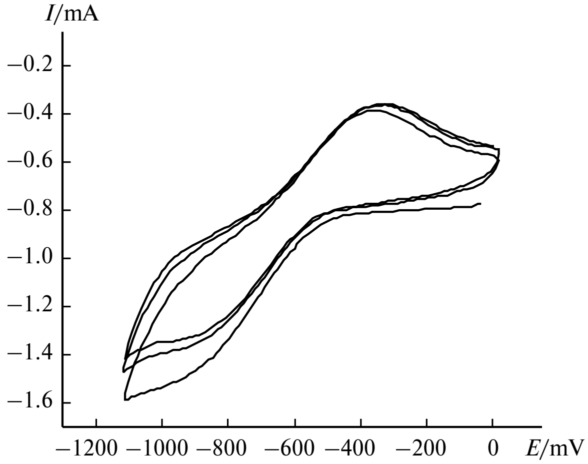
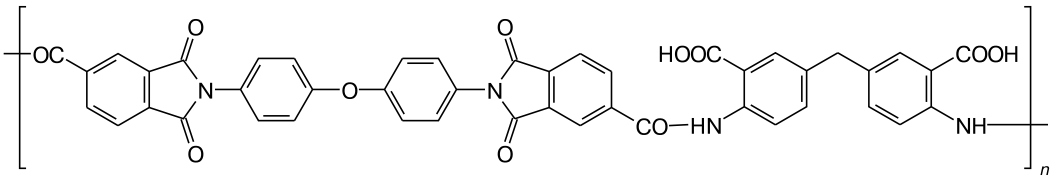


Fig. 6. CV curve for the Ni—$\mathbf{PA^{III}}$ complex (10% phenylenediamine fragments) immobilized on the graphite electrode (CH_3CN, 0.05 *M* Bu_4NBF_4, 100 mV s^{-1}, *vs* Ag/AgCl/KCl).



PA^IV^

coordination units were formed when the polymer was immobilized on the graphite surface, which can also be favorable for catalysis. This indicates that the immobilization of the polymer restricts its conformational mobility, thus favoring the formation of the $[Ni(biQ)L_2]^{2+}$ coordination sites. A similar situation was observed earlier during the study of Cu-containing polymers of analogous structure.[32,34]

To be finally convinced in the complexation of Ni^{II} ion precisely with the biQ fragments of the polymer chain rather than with, *e.g.*, carboxyl groups, we synthesized polymer $\mathbf{PA^{IV}}$ having the same functional groups (carboxyl, amide, ester) in the main chain as other polymers, but containing no biQ fragments. As it should be expected, no complexation with Ni^{II} ions occurs in this case. This is indicated by the absence of any new reduction peaks in the curve of a solution containing Ni^{2+} ions and $\mathbf{PA^{IV}}$ polymer, except for the reduction peak of the initial salt.

Investigation of the complexation of the low-molecular-weight ligand $biQ(COOHex)_2$ with Ni^{II} ions by the MALDI-TOF method. Solutions of the low-molecular-weight ligand with various Ni : biQ molar ratios were studied to determine the composition of the formed nickel complexes by the MALDI-TOF method in the presence of 9-nitroanthracene as a matrix. Mixtures of $NiCl_2$ and $biQ(COOHex)_2$ in the ratios 2 : 1, 1 : 1, and 1 : 2 in acetonitrile were prepared. In all cases, the spectral study of the obtained solutions showed three peaks:

$m/z = 513$ ($M^{+\cdot} = [biQ(COOHex)_2]^+$),
$m/z = 605$ ($M^{+\cdot} = [NibiQ(COOHex)_2]Cl$), and
$m/z = 1082$ ($M^{+\cdot} = [Ni(biQ(COOHex)_2)_2]$.

The MALDI method is not quantitative; however, the tendency for changing the ratio of the formed complexes can qualitatively be monitored by the relative peak intensities. The tendency agrees with the data obtained by the CV method: with an increase in the amount of the ligand the amount of $[Ni(biQ(COOHex)_2)L_n]Cl_2$ complex in a solution decreases and the amount of $[Ni(biQ(COOHex)_2)_2]Cl_2$ increases.

The ESI-MS study of solutions containing Ni^{II} and $biQ(COOHex)_2$ in the ratios 2 : 1 and 1 : 2 showed peaks of molecular ions corresponding to the complexes with one biQ ligand in the coordination sphere of nickel ($[Ni(biQ(COOHex)_2)(CH_3CN)Cl]^+$ (m/z =646)) and with two ligands ($[Ni(biQ(COOHex)_2)_2]^+$ ($m/z = 1082$)). In addition, the ion of complex $Cl_2(CH_3CN)Ni—\mu\text{-}biQ(COOHex)_2—Ni(CH_3CN)Cl_2$ was observed ($m/z = 852$), in which bipyridyl acts as bridging ligand and is coordinated with two Ni^{II} ions. However, this complex ion is present in very small amounts.

Thus, the studies performed indicate that polyamic acids containing biquinolyl fragments in the main chain are capable of coordinating with Ni^{II} ions to form coordination units of two types: with one or two biQ ligands in the coordination sphere of the Ni^{II} ion. The relative number of $[Ni(biQ)_2]^{2+}$ coordination units in the polymer chain increases with an increase in the concentration of biQ units in solution and with an increase in the conformational mobility of the polymer. The nickel complexes with the polymer ligands can be synthesized both using Ni salts and by the electrochemical method (by the dissolution of the Ni anode).

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