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ORIGINAL PAPER

Voltammetric investigation of polyelectrolyte-Cu(II) complexes

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Abstract The complexation behaviours of poly(*N*-vinylcarbazole) (PNVCz), poly(acrylic acid) (PAA) poly(itaconic acid) (PIA) and their copolymers, synthesized by using different initial monomer compositions, with Cu(II) ions were investigated by the voltammetric technique. Their solutions were prepared in THF-water mixture according to the water-insoluble nature of PNVCz and its copolymers. The polymeric ligand-Cu(II) interactions, i.e. complex formations were studied as a function of copper ion concentration and copolymer composition. It was observed that although the cyclic voltammogram (CV) of Cu(II) alone in THF-water mixture was characterized by one redox wave, which has an irreversible nature, it became more reversible in the presence of polymer. Further, the CV results indicated the presence of two different electron transfer mechanisms, depending on the $n_{\mathrm{COOH}}/n_{\mathrm{Cu(II)}}$ ratio and the carboxyl content of the copolymers.

Keywords Poly(N-vinylcarbazole) · Poly(acrylic acid) · Poly(itaconic acid) · Poly(N-vinylcarbazole-co-itaconic acid) · Cu(II)-polymer complexes · Voltammetric investigations

1 Introduction

It is known that metalloproteins, performing the most important functions of living organisms, contain metal ions (Cu(II), Fe(II), Mn(II), Co(II) etc.) in their structures. The formation of polyelectrolyte complexes therefore has been widely investigated over the last decades. Furthermore, polymer-metal complexes have been tested in various technological areas such as the recovery of metal ions from industrial fluids and waste water along with their biological importance [1–16].

The complexation of synthetic water soluble and hydrophilic polymers with transition metal ions such as Cu(II), Co(II), Ni(II) and Zn(II), giving transition metal ion complexes in aqueous solution has been extensively investigated [17]. In order to improve the complexing ability of polymeric ligands with metal ions, it is necessary to design new complexing agents, which are constituted from the copolymeric structures of suitable monomers [18].

Although carbazole derivatives have been studied as photoreactive [19, 20], electroluminescent [21], organic thin film transistors [22], light emitting diodes [23–25], photorefractive polymers [26] and sensor electrode [27], there has been little search on their polymer-metal complexes [28–30].

Various characterization techniques such as UV-visible, FT-IR, NMR, ESR, viscometry etc. have been applied to investigate the structures of polymer-metal complexes and to prove their existence [31]. The application of voltammetric methods on polyelectrolyte-metal systems, consisting of the measurement of the diffusion properties of the electroactive component, is relatively recent. Although voltammetric analysis of polymer-metal systems is complex, the results obtained have been successfully interpreted [32–34].

In this study, copolymers of *N*-vinyl carbazole (NVCz) with acrylic acid (AA) and itaconic acid (IA) were chosen as water-insoluble polymeric ligands. The carboxyl groups joined into the polymeric structures have high binding ability to the polymer chains while the presence of hydrophobic-bulky carbazole units attached to the copolymer

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backbone increase the complexing efficiency of carboxyl ligands due to the dilution effect and, in turn, decrease the dimerization of the adjacent carboxyl groups.

2 Experimental section

The monomers, acrylic acid (AA, Fluka), itaconic acid (IA, Fluka) and *N*-vinylcarbazole (NVCz, Aldrich), which were used to synthesize the copolymers of NVCz, were used as received. Tetra butyl ammonium tetrafloroborate ($TBABF_4$, Fluka) was used as supporting electrolyte in the voltammetric measurements. Cupper(II) chloride ($CuCl_2 \cdot 2H_2O$; Riedel-de-Haen), THF and 1,4-Dioxane (Merck products) were used without further purification while the initiator, α,α′-azobisisobutylonitrile (AIBN; Merck), was recrystallized from methanol.

Four different feed mole ratios of NVCz were used to prepare the random copolymers of NVCz with water soluble and weakly-acidic comonomers (AA and IA). Copolymerization reactions were carried out in 1,4-Dioxane with AIBN (1.0×10^{-3} mol L^{-1}) at 50 °C under nitrogen atmosphere. The compositions of these copolymers were determined by UV and FTIR spectroscopic techniques. The product of the monomer reactivity ratios ($r_1r_2 \approx 0.20$) supported the idea that the NVCz-AA and NVCz-IA systems follow a random distribution of monomeric units. Homopolymers of AA and IA were synthesized using AIBN (1.0×10^{-3} mol L^{-1}) in 1,4-Dioxane and potassium persulphate (KPS) in water as initiators under identical experimental conditions. The synthesis, separation, purification and characterization methods have been described elsewhere [35]. However, voltammetric investigation of Cu(II) complexes has not been reported anywhere.

Dried samples of PIA, PAA and their copolymers with NVCz were added to a THF-water (92.3/7.7; v/v %) solvent mixture and stirred for 24 h at ambient temperature. For the preparation of polymer-metal complexes the polymer solutions at 1 gL^{-1} concentrations were mixed with $CuCl_2 \cdot 2H_2O$. The original pH of the solutions was nearby 3.7. The polymer to $CuCl_2 \cdot 2H_20$ mole ratios, i.e. $r = n_{\text{polymer}}/n_{\text{metal salt}}$ were changed from 50 to 4 ($n_{\text{COOH}}/n_{\text{Cu(II)}}$ = 50; 12.5; 6.67; 5 and 4), where n_{polymer} and $n_{\text{metal salt}}$ are the mole number of ligands and Cu(II) ions per mL of solutions, respectively. In order to follow the effect of copper concentrations, this ratio was used as $n_{\text{Cu(II)}}/n_{\text{COOH}}$.

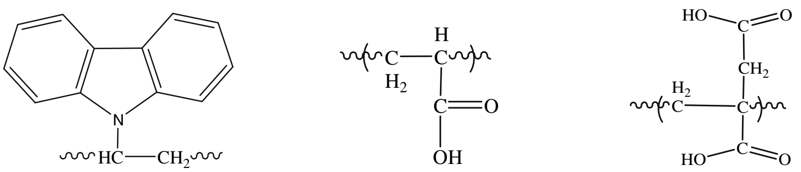
Cyclic voltamograms of polymer/Cu(II) solutions were obtained at a scan rate 100 mV s^{-1} between +900 and –800 mV, by using a Model POS 73 Wenking potentiostat and Kipp-Zonen recorder. The scan number was chosen as 5. The working and counter electrodes were Pt wire. In all cases the reference electrode was Ag/AgCl. 0.1 M $TBABF_4$ was used as the supporting electrolyte. All experiments were carried out at room temperature by purging N_2 for 30 min before the measurements.

3 Results and discussion

The chemical structures of PAA, PIA and PNVCz are shown in Scheme 1. The complexing properties of PAA and PIA are related to the carboxylic acid groups. Although PAA bears only α-carboxyl group ($pK_a = 4.25$), PIA has two ionizable groups with different pK_a ($pK_1 = 3.85$ and $pK_2 = 5.45$) values at every second carbon, which is connected by a methylene group to the backbone chain [36]. These carboxyl groups can dimerize by formation of intermolecular and intramolecular hydrogen bonds. Free radical homopolymerizations of AA and IA are propagated by vinyl groups. In the case of IA, chain transfer to the monomer because of the presence of allylic hydrogens in the molecular structure results in the production of PIA chains with low molecular weight (M_v = 3,400 g/mol) [35, 37].

The homopolymer of NVCz was also synthesized by free radical polymerization and a white product was obtained which was p-type semi-conductive with photoconductive and insulating character. In addition, NVCz can be polymerized by chemical and electrochemical oxidation of the ring to give a conductive polymer [37].

It is known that PNVCz is soluble in common organic solvents like benzene, toluene, chloroform and THF [37]. Although PNVCz and its copolymers synthesized in this work could also be dissolved in THF, their response to



PNVCz (M_v =122000g/mol) PAA (M_v =54500g/mol) PIA (M_v =3400g/mol)

Scheme 1 Chemical structures and molecular weights of polymers PNVCz (M_v = 122,000 g/mol), PAA (M_v = 54,500 g/mol), PIA (M_v = 3,400 g/mol) voltammetric measurements was fairly poor. Therefore water, chosen as a second solvent, was added to THF to improve the CV response.

The interaction of PAA, PIA, PNVCz and their copolymers with Cu(II) ions in THF-water mixtures (92.3/7.7; v/v %) were investigated by cyclic voltammetry. The reason for chosing this volume percent was critical since it was the limiting value of water content in the mixture, just before the phase separation. Further, it should be noted that when all polymer solutions without metal salt were scanned in the potential range chosen for this work no signal was observed.

Firstly, CVs of Cu(II) solutions corresponding to various metal ions to ligand mole ratios in the absence of polymeric ligands were obtained. Typical voltammograms of 9.75×10^{-6} and 3.05×10^{-5} mol L^{-1} Cu(II) solutions ($n_{Cu(II)}/n_{COOH}$ = 0.08 and 0.25, respectively) are shown in Fig. 1a and b. Although Cu(II) solutions show two cathodic peaks that correspond to successive electron transfer reactions of Cu(II) and Cu(I) and their corresponding anodic peaks on the reverse scan in aqueous media for the CVs of Cu(II) solutions indicated above, only one reduction (E_{pc} = –160 and –460 mV for 0.08 and 0.25, respectively) and one re-oxidation peak (E_{pa} = 740 and 900 mV, for 0.08 and 0.25 respectively) in THF-water mixture were observed [38]. Comparison of the peak potential differences, ΔE, suggest that reversibility of the redox reaction decreases with increase in copper concentration (Table 1). Further, increase in current with increase in copper concentration supports a copper related one step two electron transfer mechanism.

Similar experiments were also carried out in the presence of homopolymers and copolymers. The CVs of the Cu(II)-polymer solutions at 0.08 and 0.25 mole ratios of Cu(II) ion to ligand for PAA and PIA homopolymers and their copolymers containing 80 and 20 mol% NVCz in the initial compositions of polymerization solutions, i.e. the feed compositions, are given in Figs. 2–7. Further, the cathodic peak current intensities of the solutions of PIA, PNVCz and their copolymers were plotted against the mole ratio of metal ion to polymeric ligand (Fig. 8). As can be seen from all the CVs and the I_{pc}-$n_{Cu(II)}/n_{COOH}$ plot the current intensities for solutions containing the polymeric ligand increase with increase in copper concentration and, their values are different from the I_p values of copper solution. This is likely due to the differences between the diffusion coefficients of free and bound metal ions. On the other hand, the peak currents of PNVCz homopolymer have the lowest values because of the nonionic-molecular structure of NVCz units.

Table 1 Dependence of peak currents and potentials of Cu(II) solutions to the mole ratios of $n_{Cu(II)}/n_{COOH}$, in the case of the absence of polymeric ligand

$n_{Cu(II)}/n_{COOH}$	I_{pa} (mA cm^{-2})	I_{pc} (mA cm^{-2})	E_{pa} (mV)	E_{pc} (mV)
0.02	21	11	580	50
0.08	38	22	740	–160
0.15	51	33	765	–160
0.20	60	43	815	–410
0.25	76	66	900	–460

In order to gain further information about diffusion coefficients, CVs of polymer-Cu(II) complexes were obtained at different scan rates. Figure 9 shows the CVs of P(NVCz-co-AA), containing 60.0 mol% of AA in the feed. From these voltammograms diffusion coefficients were calculated according to the Randles-Sevcik equation [39].

$$I_p = 2.69 \times 10^5\ n^{3/2} A\ C\ D^{1/2}\ \upsilon^{1/2}$$

(where I_p is the maximum current intensity (A), n is the number of electrons involved in the electrochemical process, A is the electrode area (cm^2), D is the diffusion coefficient ($cm^2\ s^{-1}$), c is the concentration (mol cm^{-3}) and

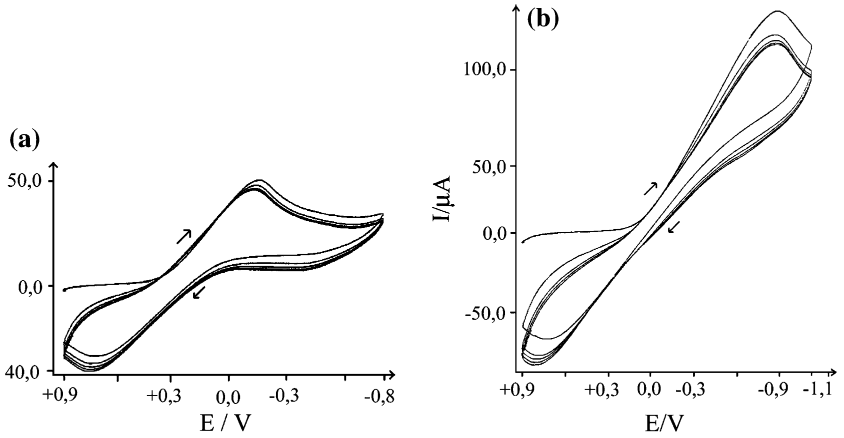


Fig. 1 (a) CV of 9.75×10^{-6} mol L^{-1} Cu(II) in THF-water mixture containing 0.1 M $TBAPF_6$ (Scan rate = 0.1 Vs^{-1}; pH = 4). (b) CV of 3.05×10^{-5} mol L^{-1} Cu(II) in THF-water mixture containing 0.1 M $TBAPF_6$ (Scan rate = 0.1 Vs^{-1}; pH = 4)

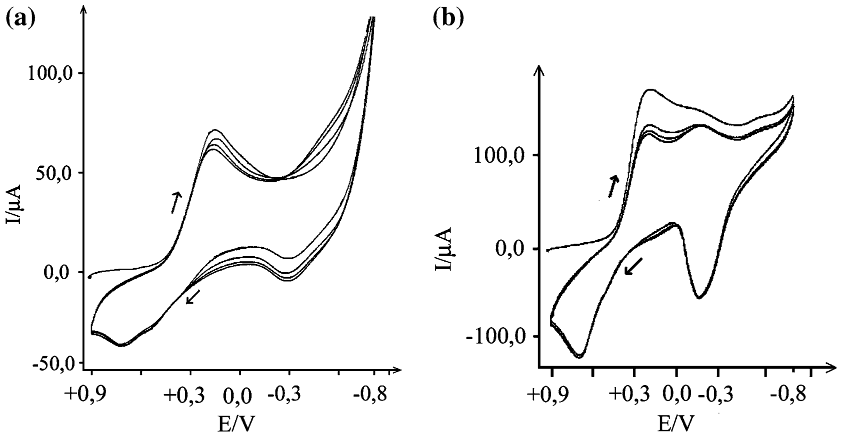


Fig. 2 (**a**) CV of PIA in THF-water mixture containing 0.1 M TBAPF$_6$ (n_{COOH}/$n_{\mathrm{Cu(II)}}$ = 12.5; Scan rate = 0.1 Vs^{-1}; pH = 4). (**b**) CV of PIA in THF-water mixture containing 0.1 M TBAPF$_6$ (n_{COOH}/$n_{\mathrm{Cu(II)}}$ = 4.0; Scan rate = 0.1 Vs^{-1}; pH = 4)

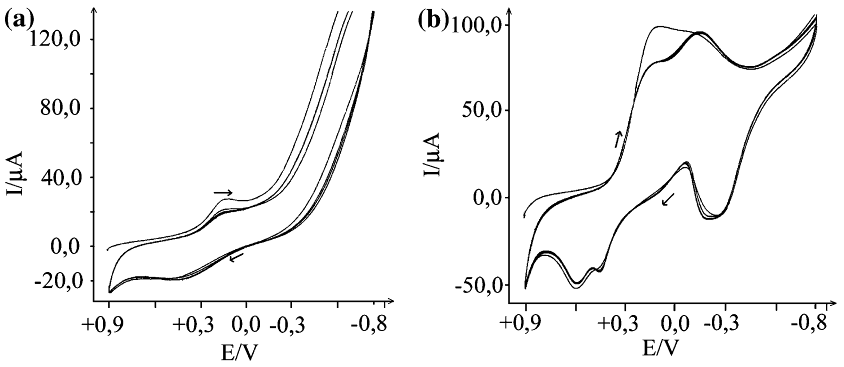


Fig. 3 (**a**) CV of PAA in THF-water mixture containing 0.1 M TBAPF$_6$ (n_{COOH}/$n_{\mathrm{Cu(II)}}$ = 12.5; Scan rate = 0.1 Vs^{-1}; pH = 4). (**b**) CV of PAA in THF-water mixture containing 0.1 M TBAPF$_6$ (n_{COOH}/$n_{\mathrm{Cu(II)}}$ = 4.0; Scan rate = 0.1 Vs^{-1}; pH = 4)

υ(is the scan rate (V s^{-1}). Diffusion coefficients were obtained from the graphs of log I_{p} versus log υ, which indicated a linear relationship with a regression coefficient higher than 0.997. The results are summarized in Table 2.

The decrease in the current and diffusion coefficients with increase in ionizable comonomer contents supports the formation of polymer-metal complexes in the solutions.

In summary, the results indicate that in the presence of polymeric ligands the reversibility of redox reactions increases and an additional anodic peak appears at a more negative potential (E_{pa} = –180 mV) than the conventional peaks of copper in the absence of polymeric ligand (Figs. 2–7). The conventional cathodic and anodic peaks around +160 and +620 mV for IA containing polymers and +200 and +550 mV for AA containing polymers, respectively, result from redox reactions of the species in the solution, while the symmetrically shaped ones at –115 and –120 mV observed in the second cycle and the anodic peak around –180 mV correspond to the reaction of species adsorbed on the electrode surface. The concentration dependence of these solutions and adsorption peaks are different from each other and their shapes and intensities are significantly related to the ratio of Cu(II) ion mole number to those of the carboxyl groups and the carboxyl contents of the copolymers (Figs. 8, 10a, b). In addition, conventional redox peaks (+160; +620 and +200; +550 mV for NVCz-IA and NVCz-AA copolymers, respectively) obey the Randles-Sevcik equations and peak currents are linearly proportional to the concentration, as mentioned above (Table 1). However, the adsorption peaks (–115; –120; –180 mV) are not linearly proportional to the copper concentration and the –COOH content does not necessarily result in an increase in current (Fig 10a, b).

The CV results can be summarized by the following complexation mechanisms:

In the case of PAA–Cu(II) complexes, it is assumed that for low Cu(II) concentration, complexation occurs mainly in the solution phase, because of the absence of an adsorption peak. The polymeric ligand—Cu(II) complexes are produced from the species in the solution by a one step complexation mechanism:

$$\left.\begin{array}{r}\mathrm{Cu(II)} + \mathrm{polymer} \rightarrow [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{sol}} \\ {[\mathrm{Cu(polymer)}]^{+2}_{\mathrm{sol}}} + 2\mathrm{e} \rightarrow \mathrm{Cu}^0 + \mathrm{polymer}\end{array}\right\}(\text{Mechanism I})$$

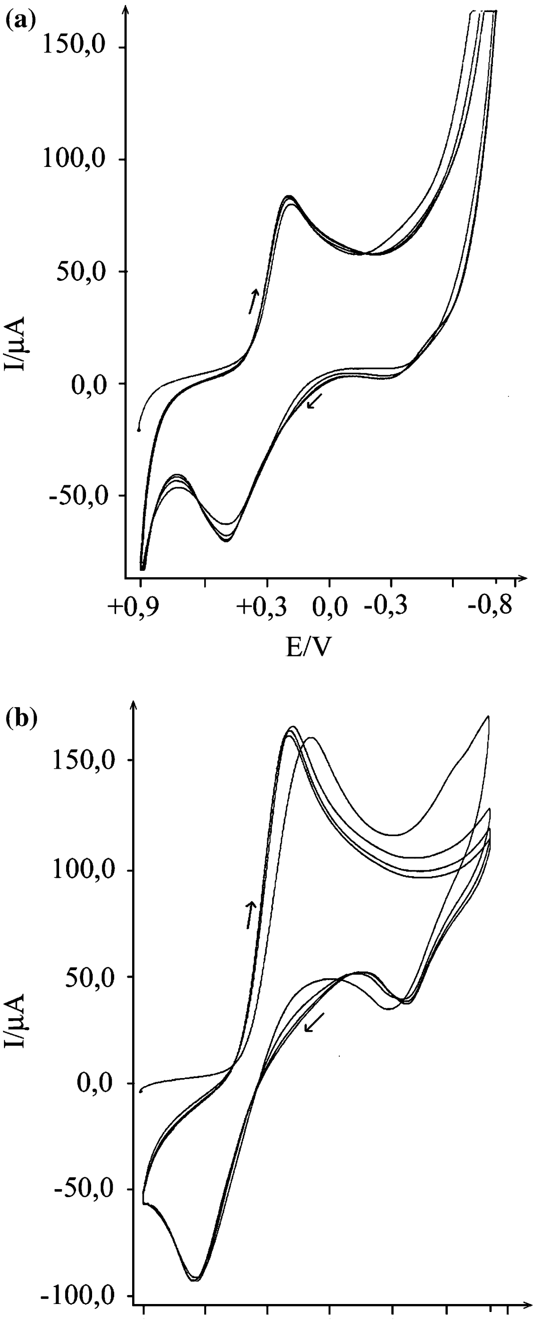


Fig. 4 (**a**) CV of P(NVCz-co-IA) (80.0 mol% of IA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 12.5; Scan rate = 0.1 Vs^{-1}; pH = 4). (**b**) CV of P(NVCz-co-IA) (80.0 mol% of IA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 4.0; Scan rate = 0.1 Vs^{-1}; pH = 4)

For PIA–Cu(II) complexes at high $n_{COOH}/n_{Cu(II)}$ ratios, complexation develops on the electrode surface by adsorption of Cu(II) and PIA in the solution,

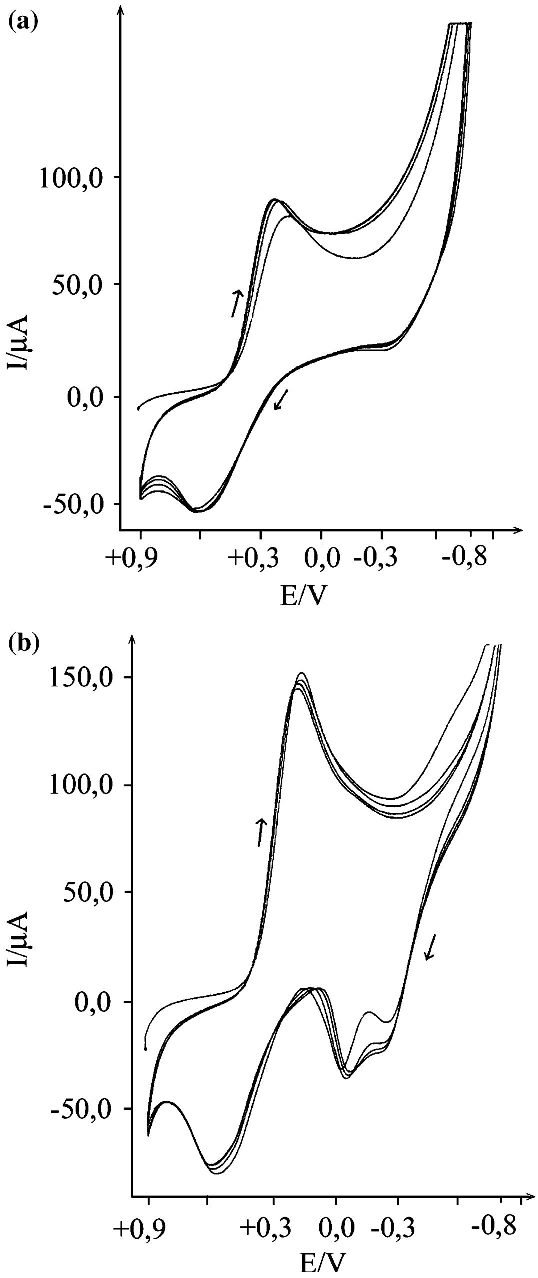


Fig. 5 (**a**) CV of P(NVCz-co-IA) (20.0 mol% of IA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 12.5; Scan rate = 0.1 Vs^{-1}; pH = 4). (**b**) CV of P(NVCz-co-IA) (20.0 mol% of IA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 4.0; Scan rate = 0.1 Vs^{-1}; pH = 4)

$$\left.\begin{array}{r}\mathrm{Cu(II)} + \mathrm{polymer} \rightarrow [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{ads}} \\ [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{ads}} + 2\mathrm{e} \rightarrow \mathrm{Cu}^0 + \mathrm{polymer}\end{array}\right\}(\text{Mechanism II})$$

For both homopolymers (PIA and PAA) at low $n_{COOH}/n_{Cu(II)}$ ratios (i.e. at high copper concentrations), [Cu(polymer)]$^{2+}$ complexes formed in the solution phase

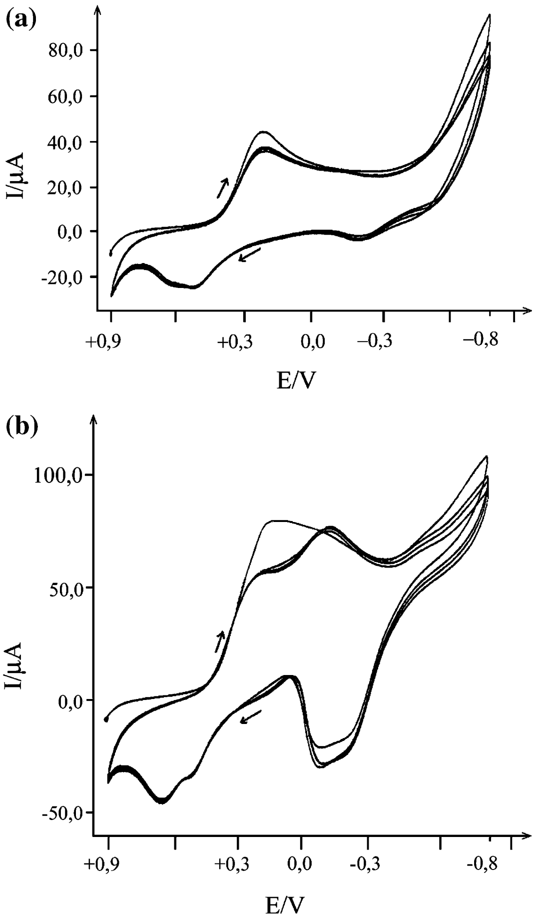


Fig. 6 (**a**) CV of P(NVCz-co-AA) (80.0 mol% of AA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 12.5; Scan rate = 0.1 Vs^{-1}; pH = 4). (**b**) CV of P(NVCz-co-AA) (80.0 mol% of AA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 4.0; Scan rate = 0.1 Vs^{-1}; pH = 4)

diffuse to the electrode and then complex formation follows the combination of Mechanisms I and II:

$$\left.\begin{aligned} \mathrm{Cu(II)} + \mathrm{polymer} &\rightarrow [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{sol}} \\ \mathrm{Cu(II)} + \mathrm{polymer} &\rightarrow [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{ads}} \end{aligned}\right\}$$

$$\left.\begin{aligned} [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{sol}}{+}2\mathrm{e} &\rightarrow \mathrm{Cu}^0 + \mathrm{polymer} \\ [\mathrm{Cu(polymer)}]^{+2}_{\mathrm{ads}}{+}2\mathrm{e} &\rightarrow \mathrm{Cu}^0 + \mathrm{polymer} \end{aligned}\right\}$$
$$\times\ (\text{Mechanism I and II})$$

The presence of both the cathodic and anodic peaks I–II and a new anodic peak at more negative potential (around –200 mV) and their increase with Cu(II) concentration support the mechanisms suggested above.

In the case of the copolymers at low Cu(II) concentrations ($n_{COOH}/n_{Cu(II)}$ < 12.5) both IA and AA copolymers show one step two electron transfer for all copolymer compositions. The absence of a desorption peak indicates that Mechanism (I) is dominant. For polymeric ligand-Cu(II) complexes prepared by the concentrated Cu(II) solutions containing P(AA-co-NVCz) and P(NVCz-co-IA) copolymers, Mechanisms I and II occur together, depending on the copolymer compositions.

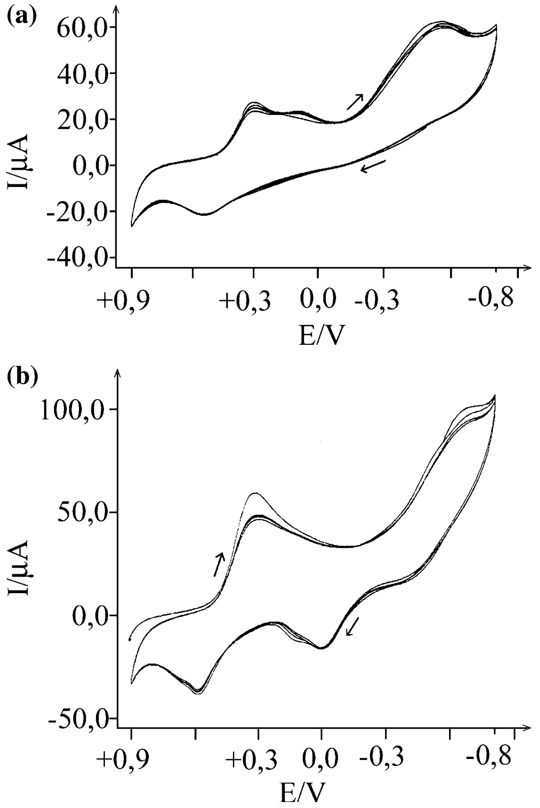


Fig. 7 (**a**) CV of P(NVCz-co-AA) (20.0 mol% of AA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 12.5; Scan rate = 0.1 Vs^{-1}; pH = 4). (**b**) CV of P(NVCz-co-AA) (20.0 mol% of AA in the feed) in THF-water mixture containing 0.1 M TBAPF$_6$ ($n_{COOH}/n_{Cu(II)}$ = 4.0; Scan rate = 0.1 Vs^{-1}; pH = 4)

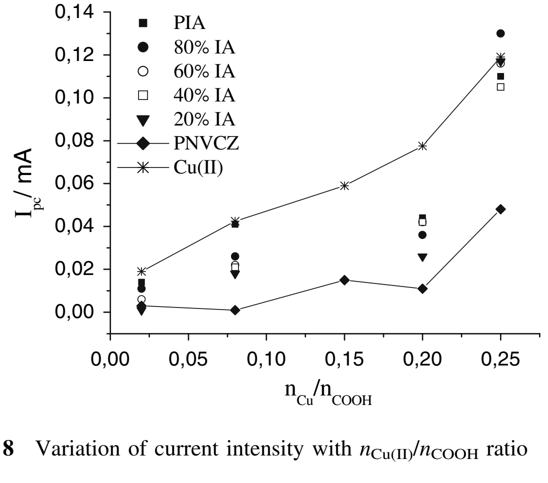


Fig. 8 Variation of current intensity with $n_{Cu(II)}/n_{COOH}$ ratio

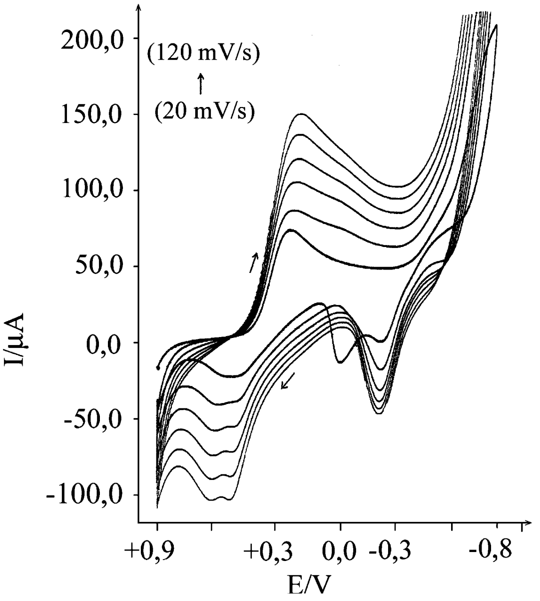


Fig. 9 CV of P(NVCz-co-AA) (40.0 mol% of AA in the feed) in THF-water mixture containing 0.1 M $TBABF_4$ as supporting electrolyte (Scan rate: (**a**) 120 mVs^{-1}, (**b**) 100 mVs^{-1}, (**c**) 80 mVs^{-1}, (**d**) 60 mVs^{-1}, (**e**) 40 mVs^{-1}, (**f**) 20 mVs^{-1})

Table 2 Diffusion coefficients of Cu(II) solutions in the absence and presence of polymers

Sample (mol% of AA)	Diffusion coefficient ($cm^2\ s^{-1}$)
PAA	1.29×10^{-7}
P(NVCz-co-AA; 80)	9.28×10^{-7}
P(NVCz-co-AA; 60)	4.43×10^{-7}
P(NVCz-co-AA; 40)	2.31×10^{-7}
P(NVCz-co-AA; 20)	1.98×10^{-8}
$CuCl_2{\cdot}2H_2O$	7.2×10^{-6}

4 Conclusions

The complexation mechanisms with Cu(II) ions of PAA, PIA, PNVCz and their copolymers were studied in non-aqueous media (dioxane, THF and THF/water mixture) by means of voltammetric methods. CV measurements show that both the nonaqueous medium and the presence of anionic polymeric ligands modify the electrochemical behaviour of Cu(II) in aqueous medium. Further, the voltammograms obtained at different $n_{Cu(II)}/n_{COOH}$ ratios for all homopolymers and copolymers synthesized in this work indicate that the polymer-Cu(II) complexations are not produced only in the solution but also on the electrode surface depending on the copolymer composition.

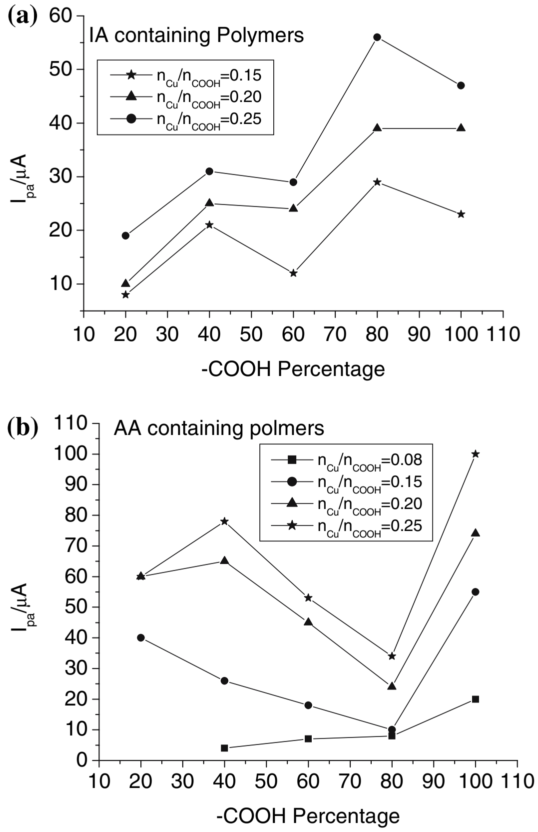


Fig. 10 (**a**) Variation of current intensity of anodic adsorption peak (I_{paII}; around –200 mV) with the feed composition of NVCz/IA copolymers, for different $n_{Cu(II)}/n_{COOH}$ ratios. (**b**) Variation of current intensity of anodic adsorption peak (I_{paII}; around –200 mV) with the feed composition of NVCz /AA copolymers, for different $n_{Cu(II)}/n_{COOH}$ ratios

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