

Electrosynthesis of Polymer Complexes of Some Metals with Vinylimidazole

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Abstract—The possibility of electrochemical synthesis of polymer complexes on the basis of 1-vinylimidazole was demonstrated. Vinylimidazole was found to undergo polymerization in the course of electrolysis in the presence of $K_2S_2O_8$. At low current densities, polymer films were formed on the electrode surfaces, while at high currents, powders were obtained. The composition and structure of the polymer complexes were established by IR spectroscopy and elemental and thermogravimetric analysis.

Keywords: electrosynthesis, polymer complexes, 1-vinylimidazole, electrical conductivity

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Metal complexes of nitrogenous heterocycles, in particular azoles, exhibit high pharmacological activity and are involved in key life processes. Imidazole derivatives are important in medical chemistry. For example, 2-methylimidazole is used as a raw material in the production of antibacterial preparations. A number of mixed-ligand metal complexes of imidazole derivatives have been synthesized [1, 2]. The complex formation of imidazole derivatives with different metal cations has been studied [3–5]. In such complexes, imidazole and its derivatives behave as monodentate ligands coordinated through the nitrogen atom. A lot of patents have been devoted to the chemical synthesis and biological activity of metal complexes of azoles [6–10]. Some of the synthesized metal complexes have shown antibacterial activity [10]. Furthermore, poly(vinylimidazole) complexes can be used for modeling hemoproteids, polymeric hemochromes, etc. [11, 12].

Synthetic polymer metal complexes can find application in catalysis and electronics [13]. Studying the electrosynthesis process allows one to gain insight in the features of complex formation of metal cations with polymeric ligands [14]. In order to simplify the process, expand a number of vinylimidazole polymer complexes, and also to explore some issues of complex formation, in this work we investigated the possibility of electrochemical synthesis of polymeric iron, cobalt,

nickel, zinc, and copper vinylimidazole complexes. Typically, such metal polymers are prepared by chemical polymerization or copolymerization of metal-containing monomers. However, during chemical (co)-polymerization, metal elimination can occur [15]. Direct electrochemical synthesis allows more favorable conditions for the formation of polymer complexes [16–22].

We made use of the electrochemical method to synthesize polymer complexes of a series of metals with 1-vinylimidazole. It was found that the electrolysis of aqueous or aqueous-ethanolic solution of 1-vinylimidazole in the presence of $K_2S_2O_8$ as polymerization initiator on Fe, Co, Ni, Zn, or Cu anodes at current densities j of 1–20 mA/cm² formed polymer metal 1-vinylimidazole complexes in preparative yields. The synthesized complexes are brown, violet, yellow, gray, and white complexes. The polymer cobalt, nickel, zinc, and copper complexes are insoluble in water and most organic solvents, probably, because of their cross-linked structures [23].

It was found the metal contents of the synthesized polymer complexes depend on the current density, as well as the concentration and molar ratio of the starting components. According to the results of elemental and thermogravimetric analysis, the complexes formed at $j = 5–15$ mA/cm² contained, per one metal atom, two

molecules of 1-vinylimidazole and different numbers of bound water molecules which are difficult to remove. At low current densities ($j < 5 \text{ mA/cm}^2$), a thin colored film is formed on the electrode surface, and this film hinders approach of further 1-vinylimidazole molecules to the metal surface and release of metal ions into the solution. The film mechanically separated from the electrode surface cracks during drying, as in the case of vinyltetrazole [24].

The synthesized polymer complexes were characterized by IR spectroscopy. Comparison of the IR spectra of the complexes with those of poly(vinylimidazole) shows that the stretching vibration bands of the C=C and C=N bonds of the imidazole ring at 1495 and 1506 cm^{-1} are shifted red (2–6 cm^{-1}), as well as deformation and out-of-plane vibration bands at 800–1150 cm^{-1} are shifted red. The intensity of the bands is almost the same. These observations suggest that the imidazole ring is involved in coordination with metals, and the main role in this coordination is played by the imidazole N³ atom. Coordination occurs via the lone electron pair of the latter atom and the vacant orbital of the metal [25]. However, the other imidazole nitrogen atom, too, can be involved in coordination.

The IR spectra of the complexes contain no deformation and stretching (980 and 1650 cm^{-1}) vibration bands of the C=C bond, implying lack of residual monomer in the monomer.

The synthesized polymer complexes are thermally stable. The TGA curves show that the thermal degradation of the polymer complexes occurs in stages (first at 90–180°C and second at 200–350°C). The weight loss at the first stage is 7–8 wt %, which, according to calculations, correspond to one bound water molecule per polymer unit. Actually, water is the only product released during heating from 120 to 180°C. It should be noted the complexes change color on heating in the range 140–170°C, but after cooling the color is recovered, i.e. the complexes are thermochromic.

The electrophysical characteristics of the synthesized polymer complexes were also studied. The specific bulk electrical conductivity (σ) of the polymer complex is 3.2×10^{-12} – $5.6 \times 10^{-13} \text{ } \Omega^{-1} \text{ cm}^{-1}$, which is characteristic of dielectrics.

Thus, polymer complexes of 1-vinylimidazole were synthesized by the electrochemical dissolution of a series of metals (iron, cobalt, nickel, zinc, and copper). At low current densities ($j < 5 \text{ mA/cm}^2$) we observed formation

of colored polymer films on the surface of the electrodes, while at high current densities we obtained powders were obtained with quantitative yields.

EXPERIMENTAL

The IR spectra were measured on Specord M-80 and Bruker Vartek spectrometers in KBr pellets. Thermogravimetric analysis was performed on a Paulik–Paulik–Erdey MOM derivatograph at a heating rate of 5 deg/min. Isothermal heating was performed in evacuated (10^{-2} torr) and sealed glass ampules for 1 h. The ampules were placed in an oven preheated to a required temperature, which was maintained to an accuracy of $\pm 2^\circ\text{C}$. After heating had been complete, the ampules were cooled to room temperature, opened, and their contents were analyzed. The specific electrical conductivities of complexes pressed into KBr pellets at 14–15 MPa were measured with an ITs-34 ohmmeter using a silver amalgam paste as a conductive substrate.

Preparative electrolysis was performed in 50–100-mL glass electrolyzers with a jacket using a P-5872M potentiostat or a TES-23 galvanostat. Plates made of Fe, Co, Ni, Zn, or Cu served as an anode, and glassy carbon or platinum plates served as a cathode. 1-Vinylimidazole was synthesized by the procedure in [26].

Poly[bis(vinylimidazolato)iron(II) hydrate]. An electrolytic cell 70 mA in capacity was charged with a solution of 1 g (10.6 mmol) of 1-vinylimidazole and 0.25 g (0.01 mol) of potassium persulfate in water. Electrolysis was performed under stirring at $j = 12 \text{ mA/cm}^2$ on 4- cm^2 iron for 1.2 h. A brown-colored polymer complex formed in the bulk of the solution. The precipitate was filtered off, successively washed on the filter with hot water and diethyl ether, and dried at 80–100°C to constant weight. Yield per azole 82%. Found, %: C 44.23; N 22.18; Fe 20.87. $[(\text{C}_5\text{H}_6\text{N}_2)_2 \cdot \text{Fe} \cdot \text{H}_2\text{O}]_n$. Calculated, %: C 45.80; N 21.37; Fe 21.37. Bound water (by TGA): found 7.2%; calculated 6.87%.

Poly[bis(vinylimidazolato)cobalt(II) hydrate] was obtained in a similar way from 1 g (10.6 mmol) of 1-vinylimidazole and 0.25 g (0.01 mol) of potassium persulfate. Electrolysis was performed on 3- cm^2 cobalt plates for 2 h. Yield per azole 79%. Found, %: C 44.12; N 22.67; Co 20.78. $[(\text{C}_5\text{H}_6\text{N}_2)_2 \cdot \text{Co} \cdot \text{H}_2\text{O}]_n$. Calculated, %: C 45.28; N 21.13; Co 22.26. Bound water (by TGA): found 7.3%; calculated 6.79%.

Poly[bis(vinylimidazolato)nickel(II) hydrate] was obtained in a similar way from 1 g (10.6 mmol) of 1-vinylimidazole and 0.25 g (0.01 mol) of potassium

persulfate. Electrolysis was performed on 4-cm² nickel for 1.4 h. Yield per azole 83%. Found, %: C 43.92; N 22.36; Ni 21.46. [(C₅H₆N₂)₂·Ni·H₂O]_n. Calculated, %: C 45.28; N 21.13; Ni 22.26. Bound water (by TGA): found 7.1%; calculated 6.79%.

Poly[bis(vinylimidazolato)zinc(II) hydrate] was obtained in a similar way from 1 g (10.6 mmol) of 1-vinylimidazole and 0.25 g (0.01 mol) of potassium persulfate. Electrolysis was performed on 4-cm² zinc plates for 1.5 h. Yield per azole 89%. Found, %: C 43.81; N 20.18; Zn 23.15. [(C₅H₆N₂)₂·Zn·H₂O]_n. Calculated, %: C 44.22; N 20.66; Zn 23.98. Bound water (by TGA): found 7.2%; calculated 6.6%.

Poly[bis(vinylimidazolato)copper(II) hydrate] was obtained in a similar way from 1 g (10.6 mmol) of 1-vinylimidazole and 0.25 g (0.01 mol) of potassium persulfate. Electrolysis was performed on 5-cm² copper for 1.2 h. Yield per azole 90%. Found, %: C 43.92; N 20.10; Cu 22.85. [(C₅H₆N₂)₂·Cu·H₂O]_n. Calculated, %: C 44.44; N 20.74; Cu 23.70. Bound water (by TGA): found 7.3%; calculated 6.7%.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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