

# Electrochemical Synthesis of Polymer Complexes with Selected Metals Based on 1-Vinyl-1,2,4-triazole

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**Abstract**—A single-stage electrochemical synthesis of polymer complexes of Fe, Co, Ni, and Cu based on 1-vinyl-1,2,4-triazole has been elaborated. It has been found that 1-vinyl-1,2,4-triazole can be electropolymerized via the double bonds opening in the presence of potassium persulfate. At low current density, colored metal-polymer coatings have been formed at the surface of electrodes, and powders have been obtained at high current density. The composition and structure of the polymeric complexes have been elucidated by means of infrared spectroscopy, gas-liquid chromatography, elemental analysis, and thermogravimetric analysis.

**Keywords:** electrolysis, electropolymerization, polymeric complexes, 1-vinyl-1,2,4-triazole, heat resistance

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Azole-based polymeric metal complexes exhibit strong biological effects and are involved in key vital activities [1, 2]. Biological activity of the ligands in these complexes often differs from that of the free ligand. Metal ions in the complex become less toxic and are prone to catalyzing of various biochemical processes [1].

Many patents have been devoted to chemical synthesis of azoles complexes with metal ions [3–7]. Polymeric complexes based on 1-vinyl-1,2,4-triazole can be used in the development of models of hemoproteids and polymeric hemochromes [8, 9].

Metal-polymer complexes of azoles can be applied in catalysis [10]. Investigation of their electrochemical synthesis can clarify the features of the complex formation between metal cations and polymeric ligands [2, 11].

Polymeric complexes are usually prepared via chemical (co)polymerization of metal-containing monomers. However, this process can be accompanied by the metal elimination [12]. Electrochemical synthesis provides more favorable conditions for the preparation of polymeric complexes of azoles and their derivatives [2, 13–19].

The reports on chemical synthesis and investigation of structure of polymeric complexes based on 1-vinyl-1,2,4-triazole have been scarce [20–23]. Complex formation of poly-1-vinyl-1,2,4-triazole with Cu(II) has been studied by means of ESR spectroscopy and spectrophotometry [20]; structure of the polymeric complexes has been elucidated. Special features of the complex formation with polymeric ligands have been discussed in [21, 22].

Herein we present the data on electrochemical synthesis of polymeric complexes of iron, cobalt, nickel, and copper with 1-vinyl-1,2,4-triazole in aqueous and aqueous-ethanolic media. We found that the highest yield of the polymeric complexes was attained during electrolysis of aqueous of aqueous-ethanolic solution of 1-vinyl-1,2,4-triazole in the galvanostatic mode at current density  $j$  of 11–15 mA/cm<sup>2</sup> (the  $j$  1–25 mA/cm<sup>2</sup> range was probed) in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as electrolyte and polymerization initiator on Fe, Co, Ni, or Cu anode.

The synthesized polymeric complexes based on 1-vinyl-1,2,4-triazole were colored powders insoluble in water and such organic solvents as DMSO and DMF, similarly to the complexes with other ligands [2, 18].

The data of elemental and thermogravimetric analysis of the obtained compounds revealed the presence of two molecules of 1-vinyl-1,2,4-triazole and one to two molecules per a metal ion, depending on the metal nature. As in the case of 1-vinylimidazole [2], a colored film was formed at the electrode surface at low current density ( $j < 5 \text{ mA/cm}^2$ ), preventing the transport of more 1-vinyl-1,2,4-triazole molecules to the metal surface. The composition of the film and powder products was identical. The film detached from the electrode surface was cracked during drying, as described elsewhere [2, 18]. The plasticized metal-polymer films can be applicable in electronics.

IR spectra of the synthesized polymeric complexes revealed the shift of the bands to lower frequency by 2–5  $\text{cm}^{-1}$  in comparison with the spectrum of 1-vinyl-1,2,4-triazole. IR spectra of the polymeric complexes contained a series of the absorption bands assigned to stretching and deformation vibrations of the triazole ring ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$  1505,  $\nu(\text{C}-\text{N})$  1426,  $\nu(\text{N}-\text{N})$  1284, and  $\delta(\text{C}-\text{H})$  650. Intensity of the absorption bands practically was not changed in comparison with 1-vinyl-1,2,4-triazole, evidencing the triazole ring coordination with the metal ion. However, the intensity of the bands of torsion vibrations of the triazole ring (600–800  $\text{cm}^{-1}$ ) was changed, and the band at 635  $\text{cm}^{-1}$  almost disappeared upon coordination of the nitrogen atom with the metal. The spectra revealed smooth change in the said region for different metal complexes, suggesting the coordination with the nitrogen atom farthest from the substituent, as marked in [24].

IR spectra of the polymeric complexes did not contain the deformation and stretching bands of the vinyl  $\text{C}=\text{C}$  group (980, 1655  $\text{cm}^{-1}$ ), confirming complete polymerization via the double bond opening.

According to the TGA data, decomposition of the obtained compounds was multistage. The first stage occurred at 80–200°C, the mass loss being 7–14%, whereas the second stage occurring at 320–380°C led to the mass loss of 45–60%. The first stage likely consisted in elimination of bound water, as confirmed by isothermal heating of the complexes and analysis of the liquid decomposition products.

GLC analysis revealed that water was the only product of isothermal heating of the polymeric complexes at 130–190°C. It should be noted that the color of the complexes was changed during heating at 130–190°C (for example, the brown iron complex became colorless),

but the coloration was restored upon cooling to ambient temperature, as in the case of similar 1-vinylimidazole complexes [2], i. e. the obtained complexes were thermochromic.

Investigation of electrophysical properties of the obtained compounds showed the specific volumetric electroconductivity of  $\sigma$   $4.1 \times 10^{-11}$ – $5.6 \times 10^{-12} \Omega^{-1} \text{ cm}^{-1}$ , typical of dielectrics.

In summary, polymeric complexes based on 1-vinyl-1,2,4-triazole were obtained via electrochemical dissolution of a series of metals (Fe, Co, Ni, and Cu). Colored polymeric films were formed at the metal surface at low current density ( $j < 5 \text{ mA/cm}^2$ ), whereas powders were obtained with almost quantitative yield at high current density.

## EXPERIMENTAL

IR spectra were recorded using Specord M-80 and Bruker Vartek spectrometers (KBr pellets). Thermogravimetric analysis was performed using a MOM (Hungary) Paulik–Paulik–Erdey derivatograph (heating rate 5 deg/min). Isothermal heating of the specimens was performed using sealed vacuumed ( $10^{-2}$  Torr) glass ampoules during 1 h. The ampoules were put in a pre-heated oven, the temperature being maintained constant ( $\pm 2^\circ\text{C}$ ). Upon heating, the ampoules were cooled to ambient temperature and opened. The liquid decomposition products condensing in the cold part of the ampoule were analyzed by means of GLC using an LKhM-8MD chromatograph (detector: katharometer; column: 1.5 m  $\times$  3 mm, filled with AW HMDS + 10% Carbowax 20 M; carrier gas: helium, 50 mL/min).

Specific electroconductivity of the samples pressed at 14–15 MPa was determined using an ITs-34 ohmmeter using silver amalgam as the conductive support. Preparative electrochemical synthesis was performed in a 50–100 mL glass electrolyzer at 20–23°C using a P-5872M potentiostat or TES-23 galvanostat. Fe, Co, Ni, or Cu plate served as anode, and glass carbon or platinum plate was used as cathode.

1-Vinyl-1,2,4-triazole was prepared as described elsewhere [25].

**Poly[bis(1-vinyl-1,2,4-triazolato)iron(II) hydrate].** A 70 mL electrolytic cell was filled with an aqueous solution containing 1 g (10.5 mmol) of 1-vinyl-1,2,4-triazole and 0.27 (1 mmol) of potassium persulfate. Electrolysis was performed at stirring (only for the powder preparation) at the optimal current density

14 mA/cm<sup>2</sup> with 4 cm<sup>2</sup> iron anode during 1.4 h. Light brown powder was formed in the solution during the electrolysis. The precipitate was filtered off, washed with hot water and then with diethyl ether, and dried to constant mass at 80–100°C. Yield with respect toazole 85%. Found, %: C 37.12; N 32.24; Fe 22.26. [(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>·Fe·H<sub>2</sub>O]<sub>n</sub>. Calculated, %: C 36.36; N 31.89; Fe 21.21. Content of bound water: 7.6% (TGA), 6.82% (calculated).

**Poly[bis(1-vinyl-1,2,4-triazolato)cobalt(II) hydrate]** was prepared similarly from 1 g (10.5 mmol) of 1-vinyl-1,2,4-triazole and 0.27 (1 mmol) of potassium persulfate. Electrolysis was performed with 3 cm<sup>2</sup> cobalt anode during 2.3 h. Yield with respect toazole 81%, brown-red powder. Found, %: C 36.28; N 32.18; Co 22.89. [(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>·Co·H<sub>2</sub>O]<sub>n</sub>. Calculated, %: C 35.97; N 31.47; Co 22.06. Content of bound water: 7.3% (TGA), 6.79% (calculated).

**Poly[bis(1-vinyl-1,2,4-triazolato)nickel(II) hydrate]** was prepared similarly from 1 g (10.5 mmol) of 1-vinyl-1,2,4-triazole and 0.27 (1 mmol) of potassium persulfate. Electrolysis was performed with 4 cm<sup>2</sup> nickel anode during 1.6 h. Yield with respect toazole 87%, light blue powder. Found, %: C 36.42; N 31.50; Ni 23.16. [(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>·Ni·H<sub>2</sub>O]<sub>n</sub>. Calculated, %: C 35.99; N 31.50; Ni 22.00. Content of bound water: 7.3% (TGA), 6.75% (calculated).

**Poly[bis(1-vinyl-1,2,4-triazolato)copper(II) dihydrate]** was prepared similarly from 1 g (10.5 mmol) of 1-vinyl-1,2,4-triazole and 0.27 (1 mmol) of potassium persulfate. Electrolysis was performed with 5 cm<sup>2</sup> copper anode during 1.4 h. Yield with respect toazole 92%, light blue powder. Found, %: C 32.43; N 29.96; Cu 22.23. [(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>·Cu·2H<sub>2</sub>O]<sub>n</sub>. Calculated, %: C 35.99; N 31.50; Ni 22.00. Content of bound water: 7.4% (TGA), 6.75% (calculated).

#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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