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Electrochemical Copolymerization of *N*-Vinylazoles with Acrylic Acid at Iron and Copper Electrodes

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Abstract—Possibility of electrochemical synthesis of polymeric coatings based on copolymers of 1-vinyl-1,2,4-triazole and 1-vinylimidazole with acrylic acid at iron and copper electrodes with aryldiazonium salt as initiator has been demonstrated. Dielectric properties of the so prepared polymeric coatings have been studied. Degradation of 1-vinylimidazole copolymers with acrylic acid has been slower than that of other acrylic acid copolymers.

Keywords: electrochemical copolymerization, polymeric coating, 1-vinyl-1,2,4-triazole, 1-vinylimidazole, acrylic acid

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Fabrication and testing of new physiologically active synthetic copolymers, especially biodegradable, is a topical issue of modern materials science. In this work we studied polymeric coatings based on 1-vinyl-1,2,4-triazole, 1-vinylimidazole, and acrylic acid prepared electrochemically at iron and copper electrodes. The starting monomers were chosen taking into account the biological activity of compounds containing di- and triazole cycles [1], and the known local anaesthetic and haemostatic action of acrylic acid polymers [2].

Quality of the prepared coating generally depends on the nature and state of the starting surface as well as on the initiator used. In particular, active free radicals capable of polymerization initiating can be conveniently produced via electrochemical reduction of aryldiazonium salts. Here we investigated the possibility of electrochemical synthesis of polymeric coatings based on the above-listed monomers in aqueous and aqueous-ethanolic solutions at iron and copper electrodes in the presence of aryldiazonium tetrafluoroborates (n-$RC_6H_4N_2^+BF_4^-$, R = H or CH_3).

Initiation of polymerization and polymer chains growth were preceded by adsorption of neutral monomer molecules and the electroactive compound at the electrodes, as evidenced by polarization and adsorption measurements [3, 4].

Basing on the monomer nature and certain further factors, different chemical processes can follow formation of the active adsorbed adduct at the electrode surface. In some cases, polymer chains grow at the electrode surface (heterogeneous polymerization), whereas if the adduct is not strongly bound at the electrode surface, it can pass into the surrounding solution (homogeneous polymerization). In the latter case the polymeric film is formed via precipitation from the solution.

For the systems studied in this work increasing the current density up to 15 mA/cm^2 resulted in higher yield of the coating (Fig. 1), but further increase of current density did not change the yield, and the coating quality turned poorer due to the influxes. Moreover, at higher current density side process of hydrogen evolution (water electrolysis) occurred at the cathode, thus additionally deteriorating the coating quality.

Similarly to the results shown in [5], in this work we observed the higher monomer conversion in the course of polymerization at copper electrode (Fig. 1, curve *2*).

The film formation started immediately after the energizing, the coating mass and thickness steadily increased to yield 5–45 μm thick film. The film growth

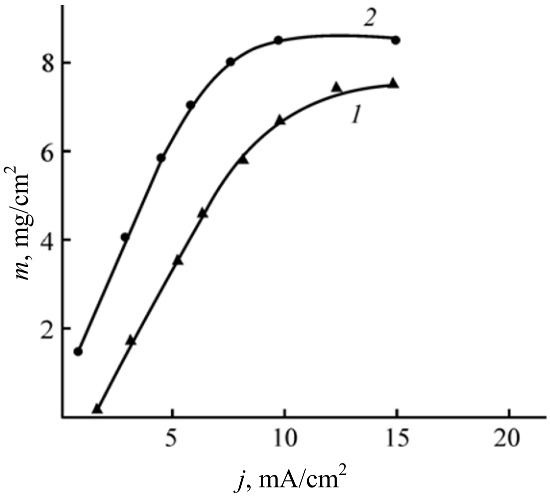

Fig. 1. Specific mass of polymer coating based on copolymer of 1-vinylimidazole with acrylic acid prepared with iron (*1*) and copper (*2*) electrode as a function of the current density. Polymerization duration 4 min.

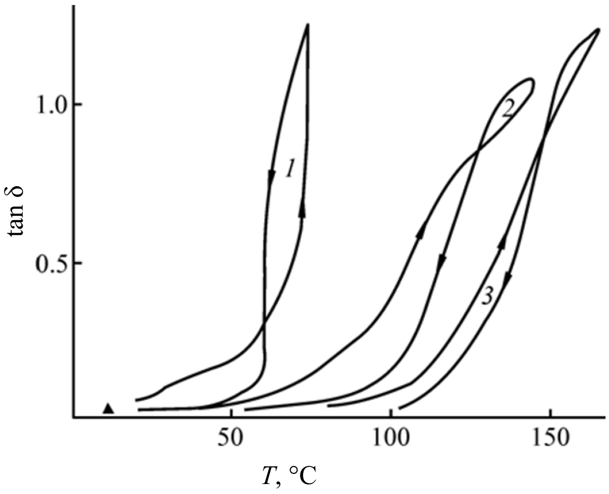

Fig. 2. Repeated cyclic measurements of dielectric loss factor as a function of temperature (↑ heating and ↓ cooling). 24 h maintaining at room temperature between the measurements. Figures at curves correspond to the cycle number.

was significantly slowed down 4–5 min after the polymerization start due to the blocking of the electrode surface by the polymer.

IR spectra of the so prepared films contained absorption bands with maxima at 870, 1140, 1215, and 1505 cm^{-1} (triazole cycle); 625, 670, 790, and 900 cm^{-1} (in-plane deformation of imidazole ring); 1070, 1275, 1410, and 1540 cm^{-1} (skeletal vibrations of the heterocycle [8, 9]); 2500–3000 cm^{-1} (OH, acrylic acid), 1710 and 1720 cm^{-1} (C=O, acrylic acid), as well as 1460 and 1470 cm^{-1} (methylene and methine groups). Disappearance of absorption band of vinyl group at 1650 cm^{-1} confirmed that polymerization occurred via opening of double C=C bonds.

Repeated measurements of dielectric losses as function of temperature revealed the strong effect of residual moisture on the position of the branch of dipole-segmental losses (Fig. 2).

Thermal treatment of the polymer allowed removal of the plasticizer (moisture); simultaneously, interaction of carboxylic groups of acrylic acid units was enhanced. The initially elastic coating turned brittle after heat treatment at 160°C. The moisture loss was confirmed by IR spectroscopy (the bands assigned to the bound water, at 3500–3600 cm^{-1}, weakened) and TGA data. According to TGA results, moisture loss occurred up to 280°C, the total mass loss being 8–10 wt % of the specimen.

Dielectric parameters of the sample became constant after the third heat treatment cycle: the traces produced at the third and the fourth cycles were identical. In particular, tan δ_{20} was decreased from 0.07 (cycle 1) to 0.03 (cycle 3), and the observed glass transition temperature was increased from 55–60°C (cycle 1) to 114–128°C (cycle 3). The observed hysteresis (Fig. 2) evidenced the fast elimination of the surface water, whereas the differences between the cycles were attributed to slow redistribution of residual water in the specimen volume. Dielectric permeability ε of the studied polymeric coatings was of 1.8 to 2.5.

Additional in vitro tests showed that the onset of destruction of iron electrodes coated with the copolymer based on 1-vinylimidazole and acrylic acid occurred at the 20th day of the experiment (as evidenced by the surrounding solution clouding and brown coloration). Thus, preliminary tests revealed that biodestruction of the studied copolymer was slower as compared to that of other known copolymers of acrylic acid.

EXPERIMENTAL

Polymeric coatings were produced in glass electrolysis cells without diaphragm in galvanostatic (*j* 1–15 mA/cm^2) or potentiostatic modes (room temperature; 1.5–2 cm^2 iron or copper plates as electrodes; aqueous or 1 : 1 aqueous ethanolic medium; 1 mol/L of the monomers; 5×10^{-2} mol/L of initiator). A TES-23 galvanostat was used as power source; potential was controlled with a PI-50.1 potentiogalvanostat equipped with a PR-8 device programmer. The coatings thickness was measured either by micrometric (ICh-10 MN) or magnetic (ITP) method.

1-Vinylimidazole, 1-vinyl-1,2,4-triazole, and the diazonium salt were prepared as described elsewhere ([8], [9], and [10], respectively). Acrylic acid was purified following the standard method described in [11].

IR spectra were recorded with “Specord UV-VIS” spectrometer (pellets with KBr or free films). Thermogravimetric analysis was performed using a MOM derivatograph (Paulik-Paulik-Erdey type, Hungary) at heating rate of 5 deg/min, under nitrogen atmosphere. Dielectric measurements were performed using a YaD-4 constant-temperature cell (electrodes diameter of 10 mm) equipped with a E7-4 alternating current bridge as described in [12].

Biological tests. Iron electrodes covered with a copolymer to be tested were immersed by third into a 50 mL beaker filled with blood plasma and monitored the surrounding solution appearance.

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