Electrophysical properties of metal nitrate complexes with polyacrylamide

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The electrophysical characteristics of metallopolymers obtained by spontaneous polymerization of complexes of Er, Ca, and UO_2 nitrates with acrylamide were investigated. The conductivity (σ) at direct current was measured (10^{-5} to 10^{-6} Ohm^{-1} cm^{-1}), and its alterations during the polymerization were observed. The conductivity of the metallopolymers obtained depends essentially on the voltage applied during the polymerization and the component ratio in the original mixture. It is concluded that the conductivity is ionic in character. The conductivity and the electret properties discovered depend on the moisture content of the samples.

Key words: acrylamide, metal nitrates, complexes; polymerization, polyacrylamide; conductivity.

The presence of a metal ion chemically bound to a polymeric matrix predetermines a series of interesting properties of metal-containing polymers (MCP), among which the electrophysical properties should be distinguished.[1] In principle, the existence of the metal ion in the polymer may favor the appearance of electroconductivity, however, almost all of the MCP are insulators. Polyethynylferrocene is an exception, which can be classified as a semiconductor on the basis of its specific conductivity (σ = $10^{-12}\div10^{-10}$ Ohm^{-1} cm^{-1}).[2] Metal polyacrylates also possess semiconductive properties under certain conditions. For example, varying the temperature and the metal content in the polymer results in the alteration in the conductivity of Cu^{II} polyacrylate over a wide range (10^{-6}—10^{-1} Ohm^{-1} cm^{-1}, see Ref. 3). For Cr^{III} polyacrylate σ changes in the range $2.4\cdot10^{-9}$—$6\cdot10^{-10}$ Ohm^{-1} cm^{-1} at 90 °C depending on the metal content.[4]

High conductivity of metal-containing polymers can be achieved only with the use of doping admixtures, such as dichlorodicyanoquinone, tetracyanoquinodimethane, and iodine.[5—7] In these cases, σ is 10^{-4}—10^{-3} Ohm^{-1} cm^{-1}.

Previously, we have studied the spontaneous polymerization of acrylamide complexes (AAm-complexes) of metal nitrates and the dielectric properties of the polymers obtained.[8] The present work is devoted to the investigation of some of the electrophysical characteristics of the products of spontaneous polymerization measured using direct current.

Experimental

Acrylamide (AAm) was purified by recrystallization from hot benzene and $Ca(NO_3)_2\cdot4H_2O$, $Er(NO_3)_3\cdot6H_2O$, and $UO_2(NO_3)_2\cdot6H_2O$ (chemically pure and pure for analysis) were used without any additional purification. The reason for the choice of these metal salts was that under the conditions of spontaneous polymerization they easily polymerize over a short time (no more than 60 min) at room temperature with a wide range of component ratios in the original mixture.[9]

The samples were prepared by the known procedure,[10] according to which a mixture of thoroughly powdered AAm and metal nitrate was stirred in a mortar until a homogeneous mass was obtained. The water of crystallization was liberated and then the reaction mixture solubilized, which attests to the formation of a complex. The mixture prepared was placed in a test tube 12—15 mm in diameter with electrodes (10×10×0.2 mm) of sheet stainless steel. The electrodes were fixed by Teflon spacers so that the distance between them was ~10 mm, while the total volume of the system was 1 cm^3. Spontaneous polymerization was performed at a constant temperature in the range 20—60 °C, which was maintained (within 1 °C) by a water thermostat. When the reaction mixture was placed into the test tube, the electrodes were connected to the measuring circuit. The first measurement of the conductivity of the system was performed 3—5 min after mixing of the reaction system (this was taken into account for the correction of all of the time dependences of σ or kinetic curves of the changes of σ during polymerization).

The current in the circuit of the sample was measured with the use of a standard scheme by the voltage drop on a standard resistance. The current was registered by a high-ohmic amplifier of direct current and a two-coordinate self-recorder or by the indications of a digital voltmeter.

The changes in the sample conductivity during spontaneous polymerization was monitored using the same standard scheme. The current was measured under a constant applied voltage (in order to exclude probable effect of nonlinear dependence of current on voltage during polymerization). In the series of experiments, the applied voltage varied in the range 2—40 V. For comparison, voltage in the control experiment was applied only in the moments of current registration, *i.e.*, each 30 s, the duration of the measurement was 2 s (here we mean pulse voltage).

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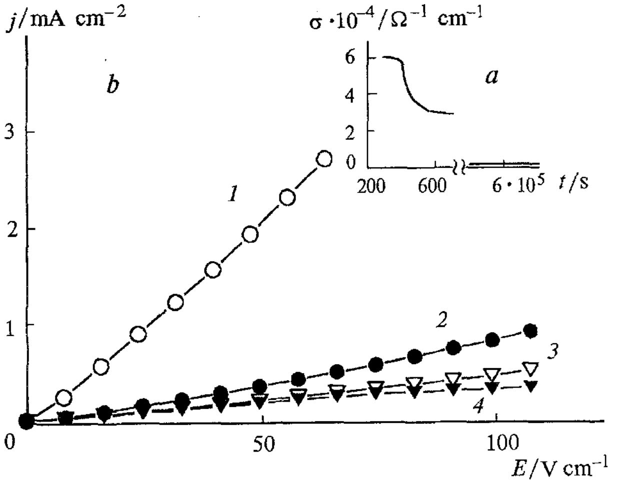

Fig. 1. Changes in the sample conductivity during polymerization (*a*) and voltaic characteristics (*b*) of the samples polymerized under different applied voltages: 20 V (*1*); 10 V (*2*); 5 V (*3*); 10 V, pulse voltage (*4*).

The procedure for the measurement of σ using direct current was chosen mainly because it made it possible to unambiguously compare results obtained for samples of different configurations under different conditions.

Results and Discussion

The curve of the change in sample conductivity during polymerization (Fig. 1, *a*) almost coincides with that of the kinetic dependence of the heat release measured by isothermal calorimetry.

For most cases, an abrupt decrease in σ (5—20-fold) is observed 5—6 min after the beginning of polymerization compared with the values 10^{-3}—10^{-4} Ohm^{-1} cm^{-1} obtained for the original sample. The degree of polymerization reaches 80 % during this time,[11] which attests to the efficient binding of the charge carriers at the initial stage of the process. Then the conductivity changes considerably more slowly, reaching 10^{-4}—10^{-6} Ohm^{-1} cm^{-1} after tens of minutes. The current density decreases respectively from several units of mA cm^{-2} to tenths of mA cm^{-2}.

When the samples obtained are stored for several days at room temperature and atmospheric pressure, the conductivity decreases by an average of one more order of magnitude, to 10^{-5}—10^{-6} Ohm^{-1} cm^{-1}, and then remains almost unchanged. Thus, the final σ value is 1—2 % of that registered at the beginning of the polymerization.

The experimental data (Fig. 1, *b*) attest that the voltaic characteristics of the samples depend on the voltage applied during polymerization (the measurements were performed after the storage of the samples for a week under the conditions described above). As can be seen from Fig. 1, *b*, the conductivity of the samples obtained at lower voltages are smaller, and may vary fivefold; it should be mentioned that this effect has not been described previously.

The ratio of the components of the original mixture substantially affects σ at the initial stage of polymerization (about 30 min). This dependence for the mixture AAm—$Ca(NO_3)_2 \cdot 4H_2O$ polymerized at 60 °C and applied voltage 5 V is presented in Fig. 2. It can be seen that σ of the system decreases as the metal content decreases (down to concentrations 1 : 10). When the content of $Ca(NO_3)_2$ in the original system is lower, the amount of water of crystallization is insufficient to solubilize the components. Therefore, 1—3 cm^3 of H_2O must be added to the system so that the reaction can occur. This causes an increase in σ up to values comparable with the conductivity at a higher content of metal. Then the polymeric structure of the sample is formed, and the dependence mentioned ceases to exist.

The conductivity in the systems studied can be classed as ionic, in which the charge carriers are formed during electrolytic dissociation of metal salts. This is confirmed by the strong dependence of σ on the presence of moisture: after short storage of a sample in an atmosphere of saturated water vapor at room temperature, an abrupt increase (up to three orders of magnitude) in σ is observed compared with that measured at 20 °C and 40 % moisture. On the other hand, the removal of water from the sample by evacuation results in a decrease in σ by several orders of magnitude (Fig. 3). As can be seen from Fig. 3, prolonged storage (for several months) of this sample at reduced humidity results in a slight increase in σ, but it does not reach a value comparable with the original value. Moreover, the value of σ is not recovered even after storage of the sample in a moist atmosphere.

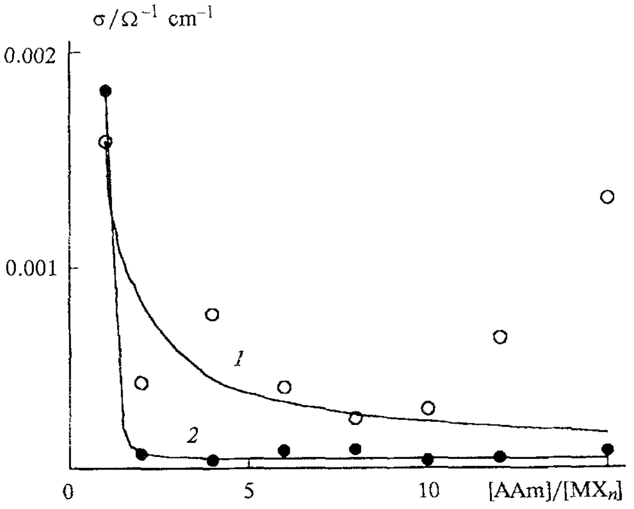

Fig. 2. Dependence of conductivity on the ratio of the components in the mixture 5 min after the beginning of polymerization (*1*) and 40 min after the beginning of polymerization (*2*).

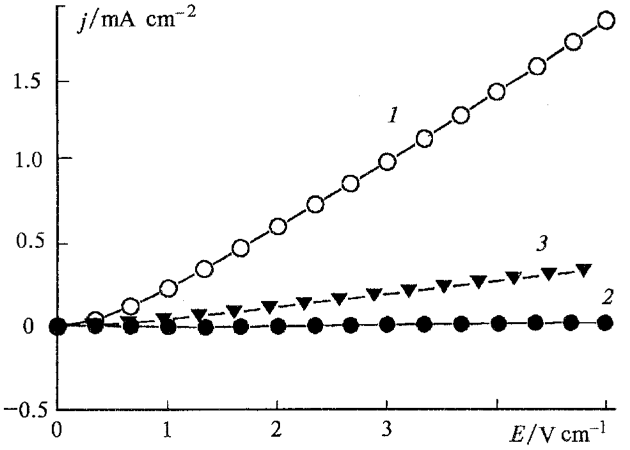

Fig. 3. Voltaic characteristics of the samples at different humidity of the medium: (*1*) the sample in the normal atmosphere (40 % moisture); (*2*) "dry" evacuated sample; (*3*) sample after prolonged storage in a sealed vessel.

The difference between the values of σ measured with direct and alternating current is further evidence in favor of the ionic mechanism of conductivity.[8]

In addition, the samples were found to possess electret properties (conservation of residual charge) which also depend on the moisture content in the sample. In the experiment described above, after brief storage of the sample in an atmosphere of saturated water vapor, the duration of the increase in the potential difference is ~15 s, followed by its slow decrease to the original value (over several minutes).

The estimation of the value of the bulk charge of the samples from the discharge current on a series of standard resistances gives a value on the order of 0.001 C cm^{-3} at current densities 10^{-4} A cm^{-2}.

The temperature in the range 20—60 °C and the nature of metal do not noticeably affect the value of σ.

Thus, the metal-containing polymers obtained by spontaneous polymerization of metal nitrate complexes with acrylamide possess interesting electrophysical characteristics, *viz.*, noticeable electroconductivity and electret properties. They should be classed as organic semiconductors based on the value $\sigma = 10^{-5} \div 10^{-6}$ Ohm^{-1} cm^{-1}. It is essential that, unlike metal-filled polymers, the conductivity is achieved at considerably lower bulk concentration of the metal. The electret properties of the samples are sufficiently reproducible, and their sensitivity and response times measured with respect to water vapor meet the requirements for sensor elements.

One might expect that this combination of properties will make it possible to successfully use these polymeric materials, for example, to create sensors of the moisture content in the atmosphere.

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