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Spectroscopic and thermal studies on acrylic acid copolymers in interaction with uranyl cations

Summary — Two acid copolymers derived from acrylic acid and itaconic acid *i.e.*, poly(AA-co-IA) (7:2 molar ratio) or from the same acids and a small amount of *N*-vinylpyrrolidone *i.e.*, poly(AA-co-IA-co-NVP) (7:3:2 molar ratio) were prepared by standard free-radical polymerization in aqueous solutions to be further used in preparation of complexes with uranyl ions. FT-IR and ¹H NMR spectroscopy, thermogravimetric and relative viscosity measurements were used to characterize the resulting copolymers (PA-B, PA-T). Their polycomplexes with uranyl acetate, in aqueous solution and solid state (PA-Baq, PA-Taq and PA-Bss, PA-Tss, respectively), were analyzed by pH measurements, luminescence spectroscopy, FT-IR spectroscopy and thermal analyses for the latter ones.

Key words: water soluble copolymers, radical polymerization, uranyl cation, polymer complexes, luminescence.

BADANIA SPEKTROSKOPOWE I TERMICZNE KOPOLIMERÓW KWASU AKRYLOWEGO I ICH KOMPLEKSÓW Z KATIONEM URANYLOWYM

Streszczenie — Metodą polimeryzacji wolnorodnikowej prowadzonej w wodzie zsyntetyzowano dwa kopolimery. Jednym z nich był kopolimer binarny kwasu akrylowego (AA) i itakonowego (IA), tj. poli(AA-ko-IA) (PA-B), w którym stosunek monomerów wynosił AA:IA = 7:2, a w drugim terpolimer AA, IA oraz *N*-winylopirolidonu (NVP) połączony w stosunku molowym AA:IA:NVP = 7:3:2, tj. poli(AA-ko-IA-ko-NVP) (PA-T). Otrzymane kopolimery charakteryzowano za pomocą metod spektroskopowych (FT-IR, ¹H NMR), analizy termicznej (termogravimetria, skaningowa kalorymetria różnicowa) (rys. 2—4), a także wyznaczono lepkość ich roztworów wodnych. Przygotowano kompleksy obu kopolimerów z kationem uranylowym w postaci roztworów wodnych (PA-Baq i PA-Taq) oraz w postaci krystalicznej (PA-Bss i PA-Tss). Badano wpływ stężenia na pH roztworów wodnych kopolimerów oraz odpowiednich roztworów polikompleksów (rys. 1). Otrzymane polikompleksy badano również metodami analizy termicznej (rys. 5), FT-IR (rys. 2 i 3) oraz spektroskopii luminescencyjnej (rys. 6—10).

Słowa kluczowe: kopolimery rozpuszczalne w wodzie, polimeryzacja rodnikowa, kation uranylowy, kompleksy polimerowe, luminescencja.

Complexation of different metal ions with organic molecules containing appropriate functional groups continue to be of great interest since the new formed structures could find attractive applications in the biological and technological fields. Among them, much attention has been dedicated to the interactions of long chain organic polyacids with metal ions, in order to be further used in wastewater treatment, catalysis or preparation of highly absorbing materials [1—4]. It is generally accepted that the understanding of these electrostatic interactions (-COOH/metal cation) and the factors that govern them could offer a more clear perspective on some aspects of physics and chemistry involved in biological processes, for instance, binding of Ca²⁺ with the carboxylic moiety from proteins may affect blood clot-

ting and nerve cell transmission [5]. Also, ordered supramolecular architectures achieved *via* a combination of metal ions with polycarboxylate monolayers are the results of the metal ion-carboxylic acid interaction mentioned above [6]. It has been shown that the syntheses of inorganic nanoparticles (Co, Ni, Ag) with polymeric carboxylic acids provides materials with unique properties which can be used in the modern field of nanotechnology [7—9].

As it has been demonstrated, poly(acrylic acid) (PAA) is a good candidate for the formation of metal complexes among polyacid and divalent, trivalent or tetravalent metal ions, which stability depends on many factors including the syntheses conditions, the polymer structure, temperature, solvent type, concentration, pH, ionic strength [10]. Other researchers have investigated the complexation properties of PAA with metal ions using

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different techniques like ultrafiltration, ion exchange, ion selective electrode potentiometry, and in a few cases, the fluorescence spectroscopy of lanthanide and actinide or uranium species in aqueous solutions [11–14]. The reasons of the last approach were the advantages of the application of polyelectrolytes in complexation and migration of radionuclides (uranium) that are used for easy recovery of the uranyl ions from aqueous systems.

In an attempt to understand the interactions between some water-soluble acrylic acid copolymers and metal ions released of inorganic glass powders, frequently used in the formulations of improved glass-ionomeric dental restorative materials [15], we initiated a study to examine the final complexes characteristics in aqueous solutions and in solid state by specific techniques including luminescence spectroscopy. Previously, our work was focused on the development of new polymeric fluorophores with pyrene, stilbene, anthracene units in a polyurethane or acrylic backbone that can be particularly useful in the design of chemosensors and not only [16–21].

Herein, we report the preparation of poly(acrylic acid-*co*-itaconic acid) (AA-*co*-IA) and poly(acrylic acid-*co*-itaconic acid-*co*-*N*-vinyl pyrrolidone) (AA-*co*-IA-*co*-NVP) copolymers, and the formation of complexes with uranyl ions. The uranyl ions were used to probe the ion binding properties of polyacids by observation of the fluorescence behavior in solution and solid state including quenching experiments.

EXPERIMENTAL

Materials

Acrylic acid (AA), itaconic acid (IA) and 1-vinyl-2-pyrrolidone (NVP) (Aldrich Chemical) of analytical pure grade were used as monomers. Ammonium persulfate [(NH₄)₂S₂O₈, Aldrich Chemical] was used as a polymerization initiator. Uranyl acetate dihydrate [UO₂(CH₃COO)₂ · 2H₂O, Merck] was employed for polymer complexation.

Copolymer syntheses

Radical copolymerizations to prepare poly(AA-*co*-IA) (PA-B) and poly(AA-*co*-IA-*co*-NVP) (PA-T) were run in water, in a nitrogen atmosphere, in the presence of ammonium persulfate as initiator (8.7 wt. % with respect to the amount of monomers) at temp. 95–100 °C for 6–7 hours. Molar ratios of monomers used in syntheses were AA:IA = 7:2 for the binary copolymer, and AA:IA:NVP = 7:3:2 for terpolymer. Copolymers were isolated by a standard freeze-drying technique. Polymer solutions in methanol were precipitated with a large excess of diethyl ether to purify the synthesized copolymers. The materials were collected by filtration and dried in vacuum for two days at room temperature.

Polycomplex preparations

The polymer/UO₂²⁺ aqueous solutions and solid complexes were prepared according to the literature data [22]. The poly(AA-*co*-IA) · UO₂²⁺ (PA-Baq) and poly(AA-*co*-IA-*co*-NVP) · UO₂²⁺ (PA-Taq) aqueous solutions were prepared *via* the addition of copolymer solutions in different concentrations to aqueous solutions of (CH₃COO)₂UO₂ · 2H₂O in 0.001 mol/L concentration. Copolymer solutions concentrations used in polycomplexes preparation varied in the range 0.0001–0.01 mol/L. The resulting reaction mixtures were obtained in molar ratios *n*, where *n* is the ratio between the molar concentration of copolymer and uranyl acetate solutions. Photoluminescence and pH investigations were performed at room temperature within 10 min after the mixing of the solutions to avoid the precipitation of the resulting polycomplexes, and pH to 5 to prevent the hydrolysis of UO₂²⁺.

The solid complexes of poly(AA-*co*-IA) · UO₂²⁺ (PA-Bss) and poly(AA-*co*-IA-*co*-NVP) · UO₂²⁺ (PA-Tss) were prepared by mixing of equal volumes of aqueous solutions of the two copolymers, in 0.2 mol/L concentrations, with (CH₃COO)₂UO₂ · 2H₂O aqueous solutions in 0.001 mol/L concentration. The yellowish precipitates were centrifuged, washed with distilled water several times, and dried in vacuum to constant weight.

Measurements

Viscosities of water solutions (0.5 g/100 mL) were measured using an Ubbelohde suspended level viscometer at 25 ± 0.1 °C. Thermal stability was investigated at 50–800 °C in an air at a heating rate 10 °C/min using a thermogravimeter Q-1500D System (F. Paulik, J. Paulik, Erdey). Differential scanning calorimetry (DSC) analyses were done using a Mettler DSC 112E Instrument, at heating and cooling rate of 10 °C/min. Data reported are from the second heating-cooling cycle. The temperature at the midpoint of the corresponding heat-capacity jump in the second heating cycle was taken as glass transition temperature (*T_g*).

The FT-IR spectra were recorded using a Bruker Vertex 70 Fourier transform infrared spectrometer, using KBr pellets. ¹H NMR spectra were recorded using a Bruker AC 400 instrument, at room temperature with deuterium oxide as a solvent.

Wide-angle X-ray scattering measurements were performed using a Bruker AXS-D8 Avance X-ray diffractometer, using CuK_α radiation (λ = 1.54 Å) at 36 KV and 30 mA. The measurements were performed at 2θ in the range 5°–60°.

A Perkin-Elmer Model LS 55 luminescence spectrophotometer was used to measure the fluorescence intensities of UO₂²⁺ polycomplexes in aqueous solutions. The fluorescence emission spectra of the polycomplexes were also, performed in solid state using a front surface

accessory for measuring the intensity of the fluorescence from a powder sample in a cell. The fluorescence spectra were recorded upon illumination with UV light (310 nm) for all carboxylate compounds. Uranyl luminescence in polycomplexes was readily quenched by *N,N*-diethylaniline. The luminescence quencher was added *via* a micro-syringe to the sample cuvette, and its concentration referred to the analytical value in the whole volume.

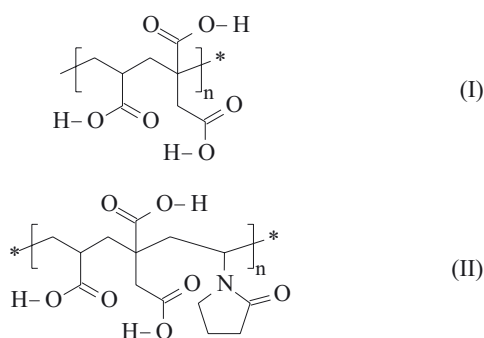
RESULTS AND DISCUSSION

Viscosity

The relative viscosities of water solutions of synthesized copolymers PA-B and PA-T were determined being 0.21 and 0.25 g/dL, respectively.

Structure

The structures and the compositions of copolymers, PA-B and PA-T [formulas (I) and (II)] were confirmed by FT-IR and ^1H NMR spectroscopy, according to the data



reported in the experimental section. The ^1H NMR spectrum of PA-B shows signals $\delta = 1.7\text{--}2.56$ ppm and $\delta = 2.6\text{--}2.9$ ppm related to protons of CH_2 and CH groups, respectively. In PA-T spectrum the signal $\delta = 1.4\text{--}2.2$ ppm indicates the protons of CH_2 group, while signals $\delta = 3.3$ ppm and $\delta = 3.96$ ppm indicate the protons of $\text{CH}_2\text{-N}$ and CH-N groups, respectively. A careful analysis of the NMR spectra shows that the compositions of the acrylic acid copolymers for PA-B and PA-T are AA:IA = 7:2 and AA:IA:NVP = 7:3:2, respectively. The second copolymer in our study was selected because the presence of a small amount of NVP modified PA-B structure maintaining its stable aqueous solutions. In this way the acid groups become more available for salt-bridge formation, what is useful in the development of biomaterials with improved mechanical properties [15]. Tethering of some of the acid groups or the introduction of *N*-pyrrolidone residues along the polymeric backbone could give more freedom and lessen the steric hindrance, which brings about a significantly enhanced $\text{-COO}^-\text{UO}_2^{2+}$ interaction. Within this context, the complexation of the both acidic copolymers with uranyl ions

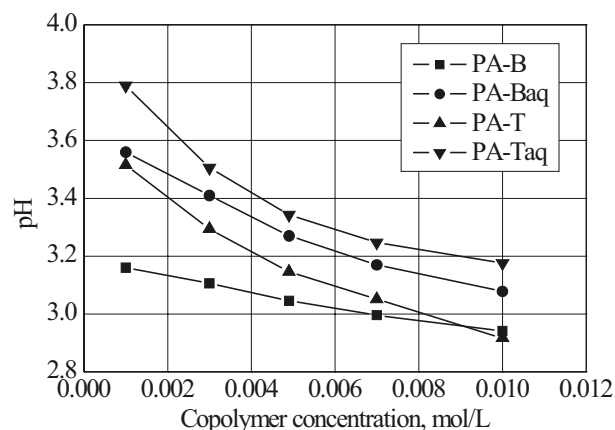


Fig. 1. Effect of the copolymer concentration on pH of aqueous solutions of PA-B, PA-Baq, PA-T and PA-Taq

was studied by potentiometry technique with the molar ratio method [23].

Figure 1 presents the variation of pH of the copolymers (PA-B and PA-T) and corresponding polycomplexes (PA-Baq and PA-Taq) in aqueous solutions, as a function of copolymer concentration. An increase in the polymer concentration led to a decrease in pH value, the saturation being remarked around 2:1 molar ratio of polymer/uranyl ions. Hence, the observed changes in pH upon mixing of the two solutions indicated that indeed the release of hydrogen ions into the medium occurred, as a result of the binding of uranyl ions by carboxylate groups of the copolymers. In fact, this should be attributed to the complexation of two repeating units of polymer with one uranyl ion *via* Coulombic interactions.

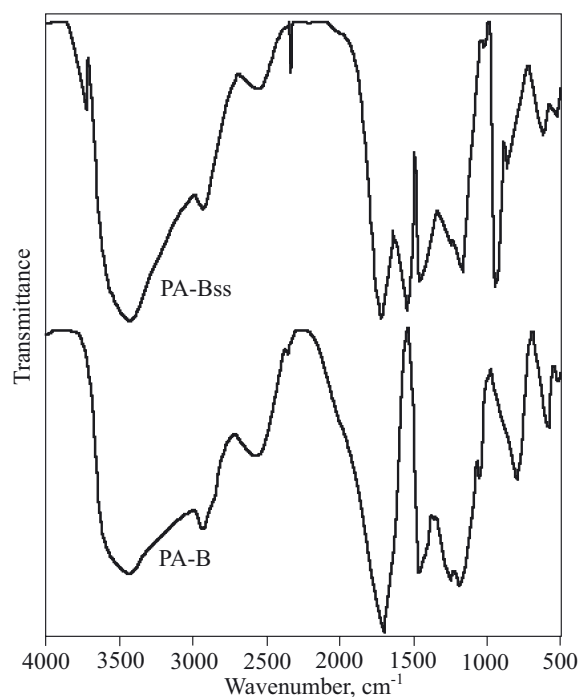


Fig. 2. FT-IR spectra of PA-B copolymer and its complex PA-Bss

The FT-IR spectra of copolymers (PA-B and PA-T) and their polycomplexes are presented in Figures 2 and 3. The purified copolymers exhibited strong absorption peaks at $3460\text{--}3440\text{ cm}^{-1}$ (O-H stretching vibration), $2960\text{--}2930\text{ cm}^{-1}$ (C-H stretching), $1725\text{--}1720\text{ cm}^{-1}$ (C=O stretching), $1500\text{--}1450\text{ cm}^{-1}$ (C-H stretching), $1425\text{--}1420\text{ cm}^{-1}$ (C=O stretching), and at 1190 cm^{-1} (C-H stretching). Other absorption bands characteristic to PA-T copolymer appeared at 1637 cm^{-1} , 1534 cm^{-1} and 1452 cm^{-1} (amide I, II and III, respectively), and 1170 cm^{-1} and 1092 cm^{-1} (C-N absorption). As compared the spectra of polycomplexes and the spectra of initial copolymers, the stretching vibration bands of the carboxyl group $\nu_{\text{asymm}}(\text{COO}^-)$ and $\nu_{\text{symm}}(\text{COO}^-)$ are shifted to

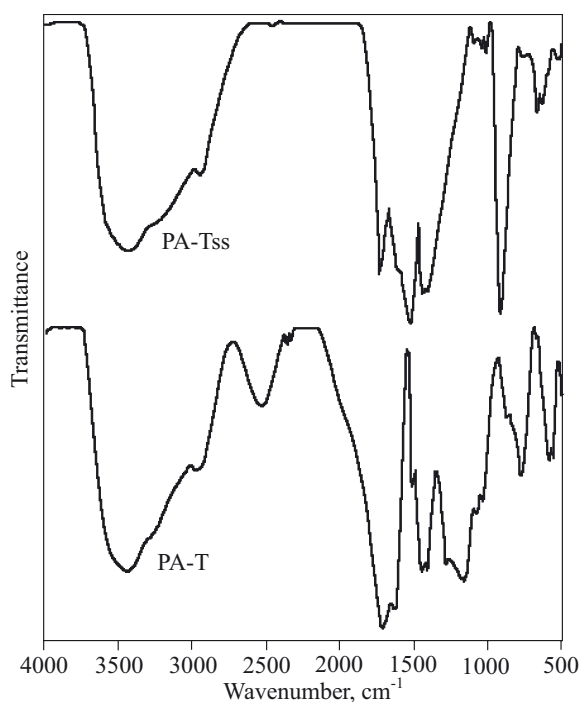


Fig. 3. FT-IR spectra of PA-T copolymer and the corresponding complex PA-Tss

lower frequencies ($1717\text{--}1715$ and $1412\text{--}1410\text{ cm}^{-1}$, respectively), due to the effect of coordination of the carboxyl groups with uranyl ions. The appearance of a new asymmetric vibration band at 1534 cm^{-1} attributed to COO^- is explained by the ionization of carboxylic groups from copolymer. A comparison of PA-B spectrum with that of PA-Bss indicates the presence of a broad band at 3500 cm^{-1} owing to the formation of polycomplex, as a proof of the presence of non-associated OH groups, resulted from the disturbance of PA-B/ H_2O association through complexation with uranyl ions. Also, in the FT-IR spectrum of PA-Bss the most important peak is characteristic to the linear $\text{O}=\text{U}=\text{O}$ stretching vibration at 932 cm^{-1} which confirms the existence of a specific interaction between the COOH groups from polyacid and uranyl ions.

Thermal behavior

The thermal behavior of the polyacids and polycomplexes was investigated by TGA and DSC methods. Figures 4 and 5 illustrate the TG and DSC curves for PA-T and PA-Tss, respectively, heated in an air at the rate $10\text{ }^\circ\text{C}/\text{min}$ from 20 to $600\text{ }^\circ\text{C}$. It has been observed that the

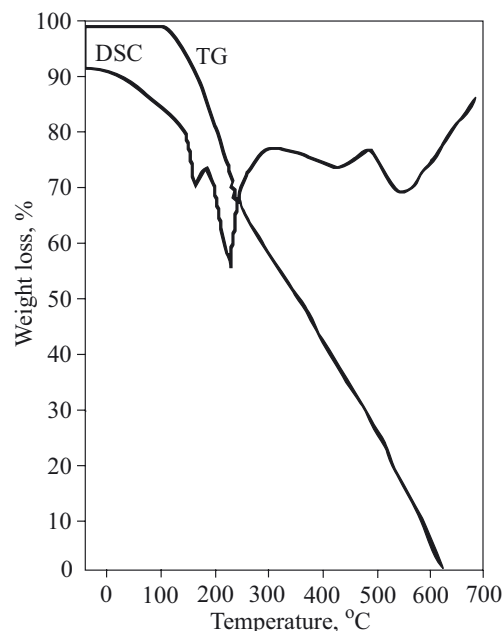


Fig. 4. TG and DSC curves of PA-T

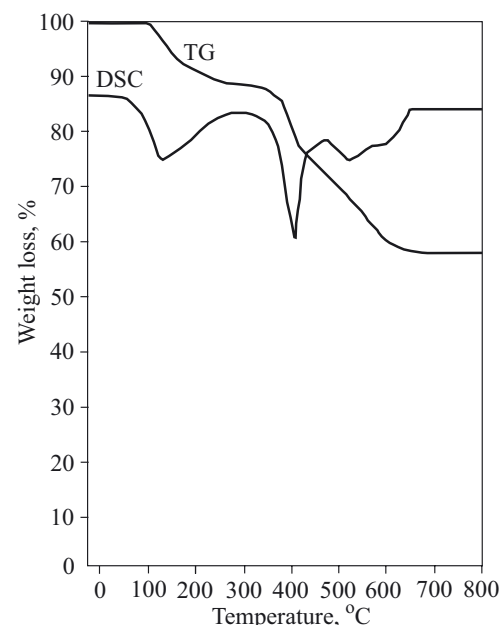


Fig. 5. TG and DSC curves of PA-Tss

thermal behavior of PA-T is characterized by a three-stage degradation process. The first region, in the range of $120\text{--}280\text{ }^\circ\text{C}$, is due to intermolecular and intramolecular anhydride formation with the consequent

decarboxylation of free carboxylic and anhydride groups (40 % weight loss). The second stage starts at 340 °C (32 % weight loss) and corresponds to a loss of NH₃ and H₂O by breaking of the pyrrolidone ring. The third region (> 475 °C) is usually attributed to main chain breakdown and the decomposition to carbon dioxide and volatile hydrocarbons.

In the case of PA-Tss polycomplex there are three steps of decomposition process on the thermogram. The first region (20–160 °C) corresponds to the elimination of the crystallization and coordination water from uranyl acetate, and dehydration water resulted by the cyclization of unbound carboxyl groups and anhydride formation (12.5 % weight loss). The noticeable endothermic effects (290–370 °C) in the DSC curve reflect the decomposition of the organic ligand and U₃O₈ formation (21.5 % weight loss). A small endothermic effect was also observed around 475 °C and it is ascribed to the start of decomposition of the polycomplex. In this case, the residual weight was about of 58 %, due to the presence of U₃O₈ product showing high thermal stability.

In the DSC curve, every copolymer showed a single distinct glass transition at $T_g = 76$ °C (PA-B) and at $T_g = 108$ °C (PA-T), while in the corresponding complexes (PA-Bss, PA-Tss) the glass transition could not be observed up to 160 °C, the onset of the first stage of thermal degradation. Therefore, T_g of the polycomplexes is supposed to be higher than their degradation temperature, and this is a clear indicative of a strong interaction between the uranyl ions and the above acid copolymers. Moreover, the amorphous natures of these polycomplexes are supported by the diffractogram patterns which presented a flat plateau all along the axis.

Fluorescence study

Information concerning the interaction between uranyl cation and every acid copolymer can be obtained from emission spectra of their complexes in solutions or solid state at room temperature. The emission spectra of UO₂²⁺ aqueous solution and PA-Baq polycomplexes at different values of n (molar ratios of PA-B:UO₂²⁺) are given in Figure 6. Thus, upon excitation at 310 nm, two peaks (490 and 515 nm) and a shoulder (540 nm) appear in the emission spectra of UO₂²⁺ aqueous solution. Obviously, the variation of the content of PA-B (0.0005, 0.001, 0.002, 0.004 or 0.006 mol · L⁻¹) added into uranyl acetate solution (0.001 mol · L⁻¹) led to a series of polycomplexes ($n = 0.5, 1, 2, 4, 6$). In the case of $n = 0.5, 1$ and 2 the spectra profiles are similar, but for $n = 4$ and 6 are rather different and blue-shifted about 10 nm. On the other hand, the fluorescence intensity is increasing and is accompanied by a blue-shifted emission about 10 nm, together with the formation of a new shoulder (460 nm). The most probable explanation is the removal of some coordination water molecules from uranyl acetate through the complex generation [11]. Under similar con-

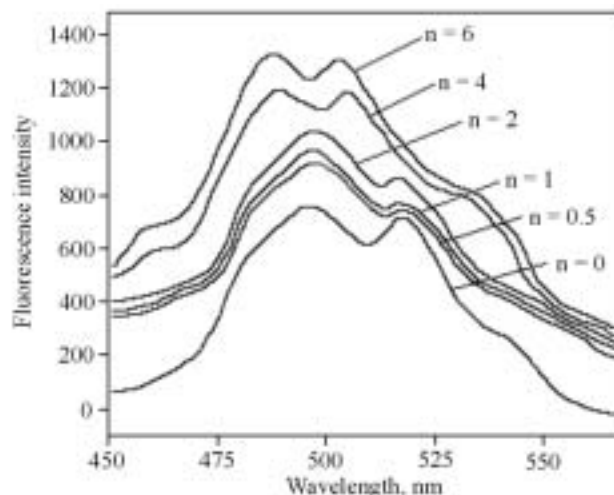


Fig. 6. Emission spectra of the aqueous solution of (CH₃COO)₂UO₂ ($n = 0$) and PA-Baq polycomplex at different molar ratios of PA-B and UO₂²⁺ (n)

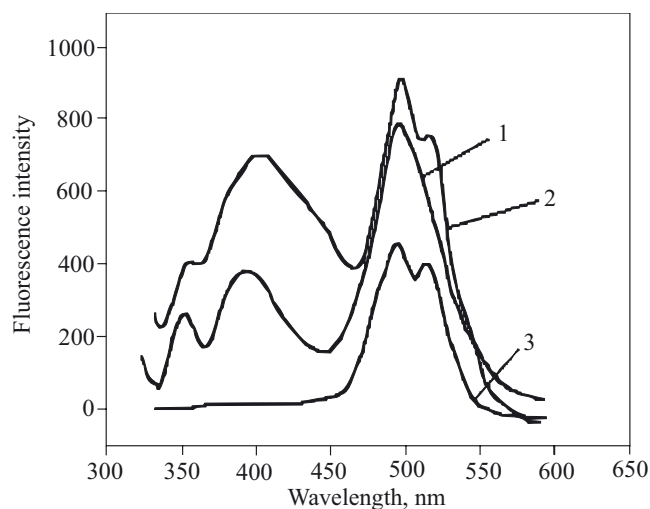


Fig. 7. Emission spectra of the aqueous solutions of complexes PA-Baq (1), PA-Taq (2) and aqueous solutions of uranyl acetate (3)

ditions, the fluorescence spectrum of PA-Taq complex shown in Figure 7, shows two maxima located at 500 and 510 nm. The comparative fluorescence spectra of the polycomplexes and starting fluorophore in the solid state are shown in Figure 8, where emissions at 500 nm (PA-Bss), 500 and 525 nm (PA-Tss), and at 525 nm (uranyl acetate) can be identified. It should be pointed out that the former complex showed a less structured emission in comparison to that observed in aqueous solution.

Our findings suggested that the complex structures formation occurred through a mechanism that imply two carboxylic groups and uranyl ion one coordinated by two water molecules, according to Scheme A.

Additional features of the fluorescence spectra of polymeric complexes in the presence of some electron donors should be noted, when is expected that the pho-

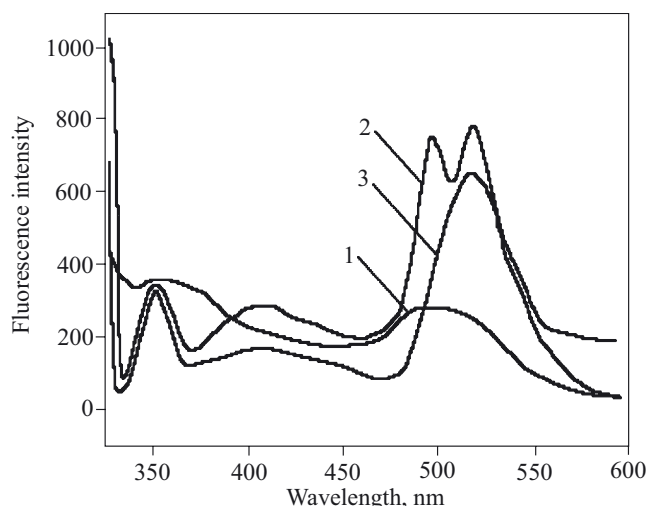
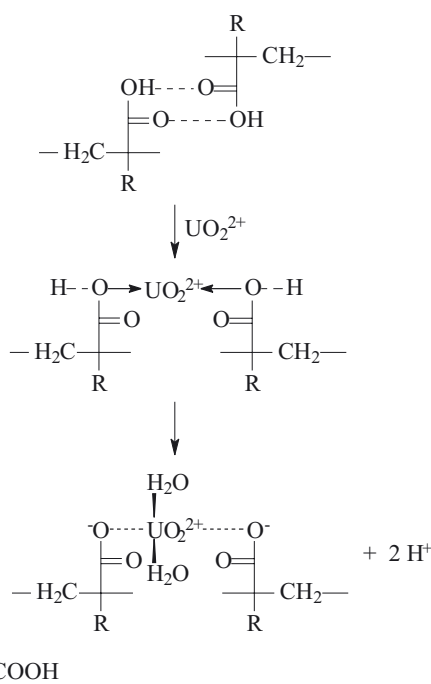


Fig. 8. Emission spectra of the polymer complexes PA-Bss (1), PA-Tss (2) and $(\text{CH}_3\text{COO})_2\text{UO}_2$ (3) in solid state



Scheme A. The mechanism of uranyl polycomplex formation

toexcited states of uranyl fluorophore would be quenched efficiently after the addition of *N,N*-diethyl-aniline (DEA) into an aqueous solution. Indeed, the fluorescence emission of polycomplexes (PA-Baq, PA-Taq) is quenched by DEA, and the corresponding intensity changes are given in the insets in Figures 9 and 10, as functions of quencher concentration. In both cases, one

Fig. 10. Photoluminescence quenching at room temperature of the uranyl ion from polycomplex PA-Taq by increasing concentration of DEA (a) and Stern-Volmer plot for the quenching of fluorescence intensity of this polycomplex (b)

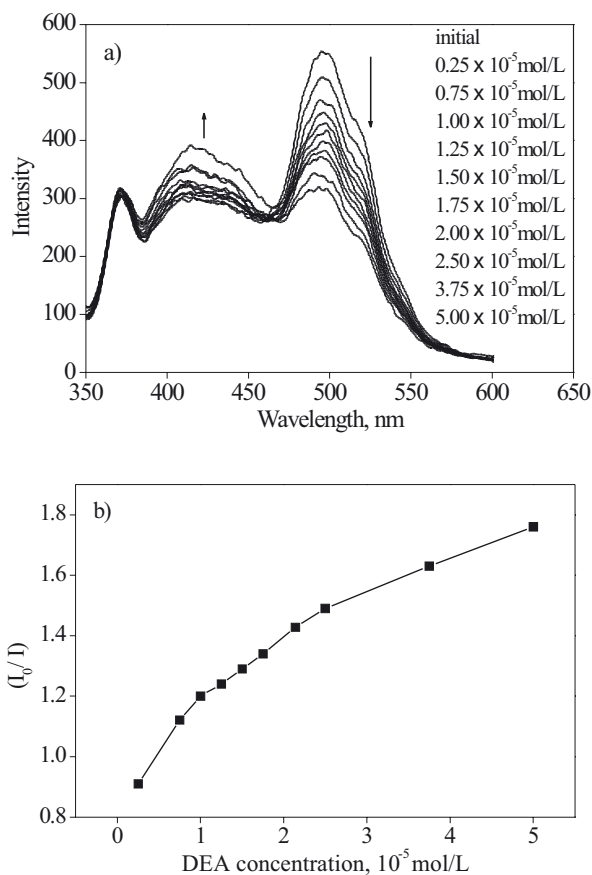
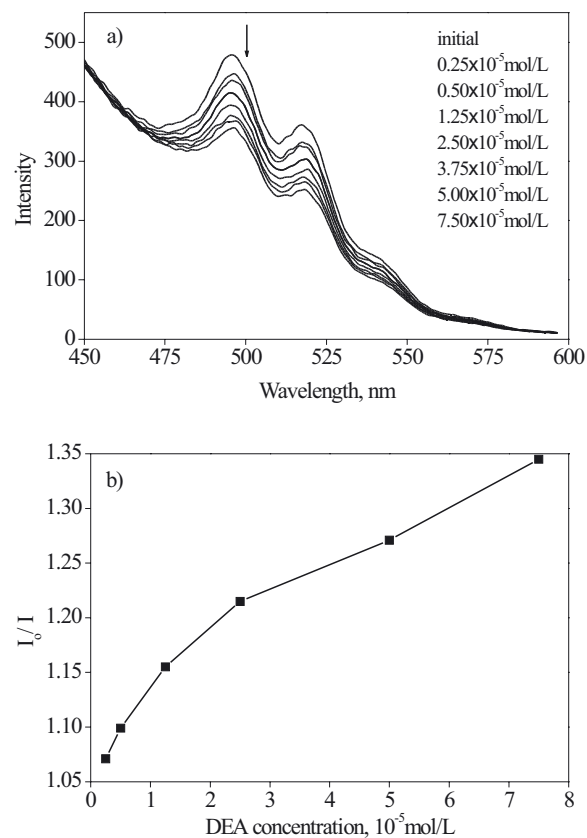


Fig. 9. Photoluminescence quenching at room temperature of the uranyl ion from polycomplex PA-Baq by increasing concentration of DEA (a) and Stern-Volmer plot for the quenching of fluorescence intensity of this polycomplex (b)



observes quenching, but for the same amount of amine (5×10^{-5} M) the extent of fluorescence quenching varies from 55 % (PA-Baq) to 20 % (PA-Taq). Such result may have originated from the different mobility of uranyl in solutions are an important effect on the quenching efficiency is predominantly connected to the chemical structures of the copolymers. Moreover, it is likely that the complexation limited the diffusion of the quencher, and thereby, the quenching is less efficient. The typical fluorescence behavior observed for the complexes studied herein is presented by the Stern-Volmer plot. As shown in Figures 9b and 10b, the Stern-Volmer plots for uranyl acetate, PA-Baq and PA-Taq are not perfectly linear, demonstrating thus that the electron transfer from DEA to the singlet excited uranyl ions could be in competition with a simple collisional deactivation of excited uranyl ion [24].

CONCLUSIONS

The mechanism of interactions between acrylic acid copolymers and uranyl ions in the aqueous solutions and in solid state, based mainly on strong Coulombic interactions, was confirmed by spectroscopic methods including fluorescence technique. The quenching by amine of the fluorescence emission of the synthesized polymeric complexes in the aqueous solutions may be used in sensor applications.

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