STUDIA UBB CHEMIA, LX, 1, 2015 (p. 7-17)
(RECOMMENDED CITATION)

UV-VIS AND FLUORESCENCE INVESTIGATION OF SOME POLY(ACRYLIC) GELS

MIHAI TODICA[a*], RAZVAN STEFAN[b], CORNEL VIOREL POP[a], IONEL PAPUC[b], OANA STAN[a] and LOREDANA ELENA OLAR[b]

ABSTRACT. Poly(acrylic) gels, (PAA), with polymeric concentrations 0.5, 1 and 1.5%, in aqueous state and neutralized with triethanolamine, (TEA), were investigated by UV-VIS and fluorescence methods. Such gels are suitable to obtain biocompatible matrices for some medical drugs. The aqueous gel with 1% PAA concentration shows an important absorption at 214 nm. At 1.5% PAA concentration the absorption increases and the peak shifts slowly to 212 nm. The absorption increases after neutralization and the maximum of absorbance shifts to 200 nm. Excitation of aqueous gels at 250, 270 and 290 nm is followed by two important fluorescence transition centered at 320 and 405 nm. The position of the fluorescence peaks is influenced by the polymeric concentration and by the neutralization. The UV-VIS and fluorescence investigations indicate some conformational changes determined by the neutralization.

Keywords: *poly(acrylic) gels; UV-VIS and fluorescence; neutralized gels*

INTRODUCTION

The development of intelligent medical pharmaceuticals requests the use of biocompatible matrices able to ensure a controlled delivery rate of the active substance, [1]. Some polymers, like the Poly(acrylic), (PAA), are suitable for this purpose. This polymer has a good stability and it is well accepted by the majority of living tissues. However the polymeric matrix obtained directly by polymerization has an acid character that is undesired for medical application. To prevent any repulsion reaction from the tissues this polymer is neutralized with triethanolamine, (TEA). Often this polymer it is used

[a] *"Babes-Bolyai", University, Faculty of Physics, 1 Kogalniceanu str, RO-40047 Cluj-Napoca, Romania. * Corresponding author*: *mihai.todica@phys.ubbcluj.ro*
[b] *USAMV, Departments: I Preclinic and III Paraclinic, Cluj-Napoca, Romania*

for the preparation of medical gels for skin disease treatment or skin care. Good mechanical properties are required in these situations. The polymeric matrix must be enough flexible to allow the organic motions of the body, must ensure good adherence to the skin, and must be removed simple after the complete delivery of the drug. Some of such properties are enhanced after neutralization, due to the cross linking effect induced by the TEA. Other benefic effect of neutralization is the increase of the viscoelastic properties of polymeric matrix, [2]. During the therapy these gels are frequently exposed voluntarily or involuntarily to UV or sun radiation. Under the action of these radiations modification of the local conformation of the polymeric matrix can occurs. In these situations it is important to know the response of such matrices, (the absorbance and the effect of neutralization), to the UV-VIS radiations. Moreover, it is possible to initiate the delivery of the active substance, or the excitation of some luminophors included in the drug by irradiation of the system with a specific radiation. In this case the investigation of the fluorescence properties of the polymeric matrix is suitable. In our work we investigated these aspects for some aqueous PAA gels, before and after neutralization with TEA. Such studies represent a first step towards the preparation of polymeric matrix with controlled release of the active substance.

RESULTS AND DISCUSSION

The absorption of the UV-VIS radiation is determined mainly by the transition of the electrons from a full bonding or non-bonding orbital into an empty anti-bonding orbital, [4, 5]. The spectral domain of absorption depends on the molecular particularities of the samples. In the pure PAA the most important absorption is observed around 207 nm, and it is determined mainly by the $\pi \rightarrow \pi^*$ transition of the carbonyl groups, [6]. In ours systems we expect to observe this transition with some modifications, due to the presence of water and TEA. In order to disclose the contribution of each component to the total absorbance, we analyzed the components separately and then in combination each to other. The pure PAA shows a maximum of absorption at 212 nm, with the amplitude 1.9 a.u, after that the absorbance decreases progressively in the domain 250-700 nm. For pure TEA the absorbance reach its maximum at 200 nm, with the amplitude 3.86 a.u, and then the absorbance decreases almost sharp until 250 nm, and remains almost constant in the domain 250-700 nm, (Fig. 1). The absorption spectra of the gels have almost the same shape as the spectrum of the pure polymer. An important peak is observed at 212-214 nm then the absorbance decreases progressively in the domain 250-700 nm, like in the case of pure

PAA. However some differences appear between the pure components and the gels. For instance the absorbance of the gels is less intense than the absorbance of pure PAA, but increases with the concentration of the polymer. The amplitude of the absorption peak of pure PAA is 1.9 a.u. (Fig. 1), the amplitude of 1% gel is 0.29 a.u. and the amplitude 1.5% gel 0.53 a.u. (Fig. 2). Note that the measurements were done in the same conditions in order to perform quantitative analyze. So we can conclude that the absorbance of the gels increases with the concentration of the polymer, with asymptotic tendency to reach the absorbance of pure polymer. Other modification concerns the position of the absorption peak. At 1.5% PAA concentration the absorption peak appears at 212 nm, as in the case of pure PAA, but at 1% PAA concentration the absorption peak shifts slowly to 214 nm, (Fig. 2).

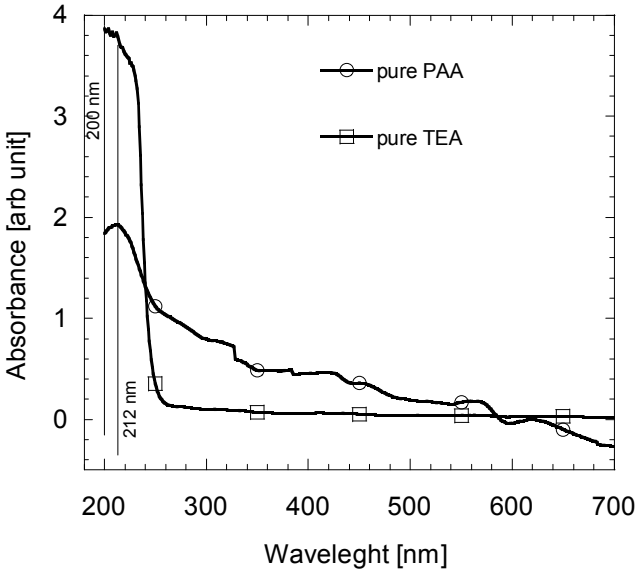

Figure 1. The UV-VIS absorption spectra of pure PAA and TEA

These differences are caused by the difference in water content of these systems. The samples with great polymeric concentration are characterized by high absorbance, and the peak is observed at 212 nm, whereas at great water concentration the peak shifts towards 214 nm and its amplitude diminish. As first conclusion we note the dependence of the amplitude and position of the absorption peak of the gels in function of the

polymer concentration, [7]. More important changes of the amplitude and position of the absorption peak appear after neutralization. At a given concentration of the polymer, i.e. 1%, the absorbance of the neutralized sample is greater than the absorbance of the aqueous gel, (0.56 for neutralized sample and 0.29 a.u. for aqueous gel). This increase is determined by the presence of neutralizer in the system

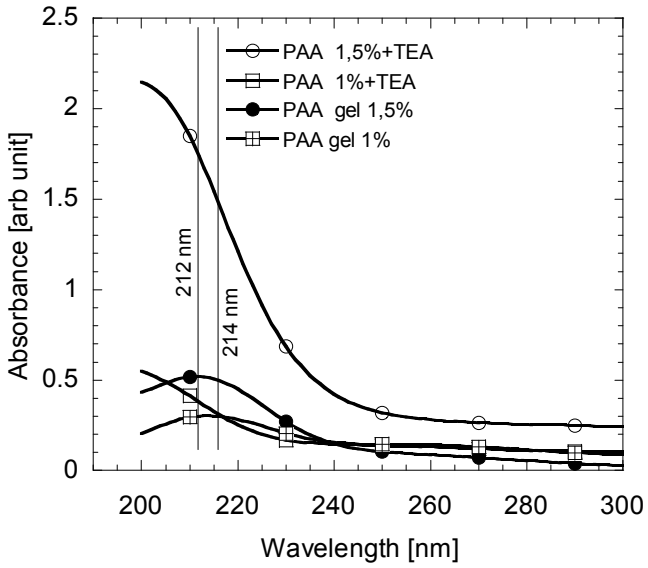

Figure 2. The UV-VIS absorption spectra of PAA gels with concentrations 1% and 1.5% in aqueous and neutralized state

As shown previously the neutralizer has absorption greater than the polymer. When the concentration of polymer, (respectively the TEA), increases, (i.e. 1.5% PAA), the absorbance increases at 2.16 a.u. with the tendency to reach the absorbance of pure TEA, (3.86 a.u.). In this sample the quantity of TEA is greater than in the sample 1%, because the ration PAA/TEA is all the times 1/1.5 constant. Other modification is the shift of the position of the absorption peak from 212 nm towards 200 nm, (Fig. 2). This shift is determined by the presence of TEA, for which the absorption peak appears at 200 nm. As conclusion, after neutralization the absorbance of the gels increases due to the presence of neutralizer, [8].

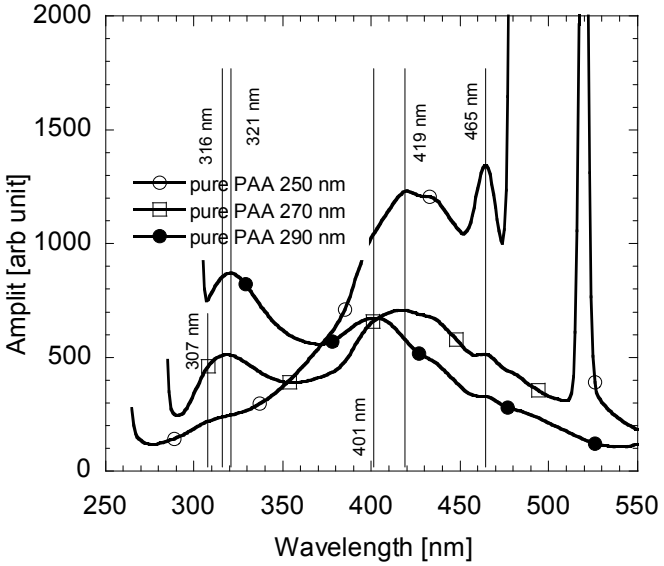

Figure 3. The fluorescence spectra of pure PAA at different excitation wavelengths

In the fluorescence experiments the electrons are excited from theirs initial state to a high energy level by irradiation with a source of light with well defined wavelength. The return to the initial state can be realized directly between the two energy levels by emission of one photon with the same energy that those of the exciting radiation, or by intermediate state. In this last case the transitions are accompanied by the emission of two photons with energy smaller than those of the exciting photon. These transitions are identified in the fluorescence spectra by the apparition of two emission peaks situated at wavelengths higher than the wavelength of the exciting photon, [9]. Although the excitation is made all the time at the same wavelength, the position of the intermediate state is not all the time the same, that results in the broadening of the spectrum. When the excitation frequency changes, the mechanism of fluorescence emission remains the same, but the position of the energy levels excited changes as well as the position of the peaks in the fluorescence spectrum. Analyze of these changes gives information about the structure of the atoms involved in the excitation process, [10, 11].

We analyzed first the pure components. The spectrum of pure PAA excited at 250 nm shows two clear peaks, a sharp one with high amplitude at 465 nm, and a large one at 419 nm with smaller amplitude. A weak shoulder can be seen at 307 nm, (Fig. 3). That means three transitions with different probabilities of apparition, the most probable corresponding to the lowest energy, (465 nm). At 270 nm excitation the first two peaks remains at the same wavelength but theirs amplitudes are smaller compared with the peaks observed at 250 nm excitation. In addition the rapport of amplitudes of these peaks is changed compared with the similar situation observed at 250 nm excitation. The first one became smaller and appears rather as a shoulder, whereas the second one has greater amplitude. A third peak appears at 316 nm. It represents the shoulder observed previously at 307 nm, but now it is well defined and shifts towards higher wavelengths. At 290 nm excitation the peak at 465 nm diminish again but remain at the same wavelength, the second peaks shifts to 401 nm and its amplitude diminish very few. The third peak increases substantially and shifts to 321 nm, (Fig. 3). That means a change of

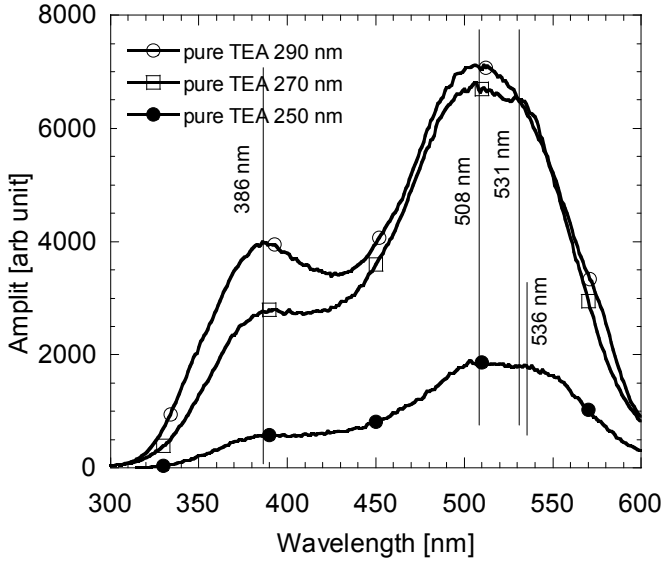

Figure 4. The fluorescence spectra of pure TEA at 250, 270 and 290 nm excitation wavelengths

the position of intermediate energy levels, as well as a change of the probabilities of these transitions. Now the transitions at high energy, (316 and 321 nm), become favorites.

The spectrum of pure TEA excited at 290 nm show two clear peaks with different amplitudes, a small one at 386 nm and a higher one at 508 nm. The high amplitude at 508 nm shows that the fluorescence transitions at low energy are favorites. At 270 nm excitation the spectrum has almost the same shape as at 290 nm, with the difference that the amplitude of the peak at 386 nm diminish slowly, and the peak at 508 nm reaches one shoulder at 531 nm. At 250 nm excitation the amplitude of the peak 386 nm diminish again and the second peak became broad with two shoulders at 508 and 536 nm, (Fig. 4). The presence of the peaks at 386 and 508 nm in all spectra indicates two fluorescence transitions that are less influenced by the energy of the excitation photons. The apparition of the 531 nm shoulder at 270 nm excitation, which become more evident and shifts slowly to 536 nm at 250 nm excitation, indicates a third fluorescence transition which is more probable at higher energy excitation.

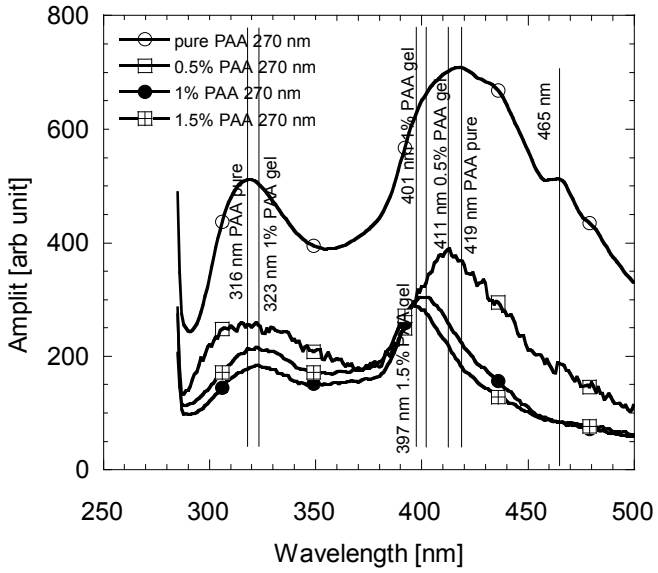

Figure 5. The fluorescence spectra of pure PAA and aqueous gels with concentrations 0.5, 1 and 1.5% excited at 270 nm

The fluorescence spectra of aqueous gels, before neutralizations, are almost similar to those of the pure polymer. We analyzed only the excitation at 270 nm, being the situation which provides the most useful details for discussion. All the samples contain two clear peaks as the pure polymer, a small peak around 316 nm and a higher one around 419 nm, but theirs amplitudes and positions depend on the polymeric concentration, (Fig. 5). At 0.5% polymeric concentration the first peak appears at 316 nm like in the

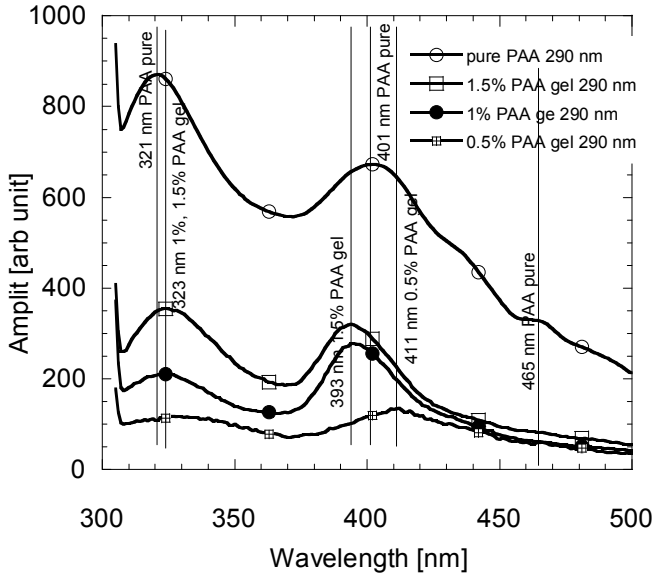

Figure 6. The fluorescence spectra of pure PAA and aqueous gels with concentrations 0.5, 1 and 1.5% excited at 290 nm

case of pure PAA, but its amplitude is much smaller than those of the pure polymer. This behavior can be explained taking into account the small quantity of polymer in this gel. The second peak appears at 411 nm, instead 419 nm as for pure PAA. When the polymeric concentration increases, (i.e. 1.5%), the first peak shifts slowly to 323 nm and the second one shifts towards 397 nm. The ratio of the amplitudes of these peaks remains almost the same for all the concentrations, and shows that the fluorescence transition at low energy, (419-397), is more probable. At 290 nm excitation, the shape of the spectra is not dramatically changed compared with the shape of spectra

recorded at 270 nm excitation. The spectra contain two major peaks around 320 and 410 nm. The first peak appears at 323 nm for samples 1% and 1.5% and shifts towards 330 nm and decreases substantially in amplitude for concentration 0.5%. The second one appears at 393 nm for samples 1% and 1.5% and shifts towards 411 nm for concentration 0.5%, (Fig. 6). We can observe that there are not dramatically changes compared with the situation observed at 270 nm excitation.

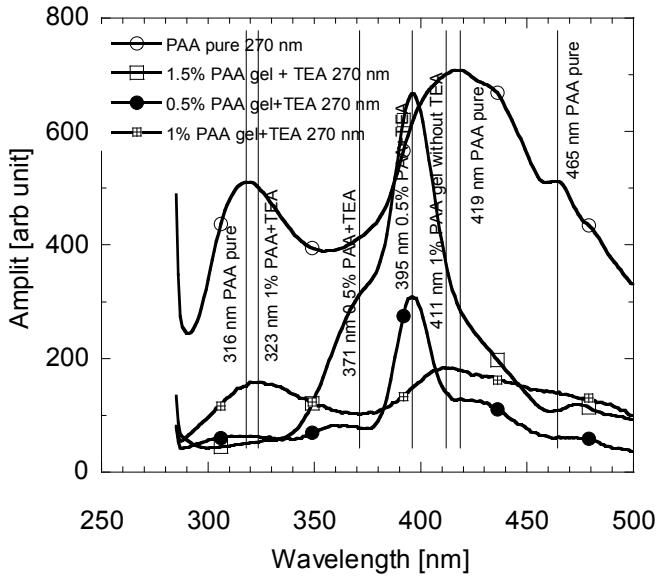

Figure 7. The fluorescence spectra of pure PAA and of neutralized gels with the polymeric concentration 0.5, 1 and 1.5%.

After neutralization the fluorescence spectra of samples show some differences compared with the un neutralized samples. At 270 nm excitation, for the sample with 1.5% polymeric concentration, we can observe a shoulder at 371 nm and a peak at 395 nm, (Fig. 7). The same sample without TEA shows peaks at 323 and 397 nm, (Fig. 6). The pure TEA show peaks at 386 nm. Practically the peak at 397 nm is assigned to the polymer and it is less influenced by the neutralization. The shoulder at 371 nm can be regarded as the peak of TEA, shifted from 386 to 371 nm. At 1% polymeric concentration the spectrum shows two peaks at 323 nm and 411 nm, (Fig. 7). The same sample, before neutralization, shows peaks at 323 and 401 nm, (Fig. 6).

We can observe that only the second peak was influenced by neutralization. At 0.5% concentration we can observe a well defined peak at 395 nm, (Fig. 7). In the un neutralized sample this peak appears at 411 nm, (Fig. 6). We can observe also two shoulders at 360 and 428 nm, which can be regarded as superposition of the peaks of pure TEA and PAA, (TEA at 386 and 508 nm, and PAA at 316 and 465 nm).

CONCLUSIONS

The UV-VIS spectra of the PAA and pure TEA contain maxima of absorption at 212 nm respectively at 200 nm. The absorbance of aqueous gels, before neutralization, increases with the concentration of the polymer and the peaks of absorption shift slowly towards higher wavelengths when the water concentration increases. The absorbance of the neutralized sample is greater than the absorbance of the aqueous gel and shift from 212 nm to 200 nm. The fluorescence spectra of pure PAA and pure PAA excited at different wavelengths contain peaks with amplitudes and positions depending on the frequency of excitation. This behavior is correlated with the modification of the intermediate atomic levels involved in the fluorescence emission, and with the modification of the transition probability from these levels. The spectra of gels, before neutralization, are almost similar to those of pure PAA, indicating low effect of water into the structure of the polymer. The neutralization reaction induces some modification of the electronic molecular structure, effect correlated with the modification of the position of the fluorescence peaks in the domain 395-415 nm.

EXPERIMENTAL SECTION

The PAA is a polymer with great affinity towards the water. The gel can be obtained by mixing the powder polymer, in solid state, with water. We use PAA with molecular mass 104400 g/mol which was mixed with distilled water, at room temperature, during 4 hours, until a homogeneous gel is obtained. The concentrations of the polymer in the solutions were 0.5%, 1% and 1.5% g/g. At higher concentration of polymer it is not possible to obtain homogeneous gels, [3]. The aqueous gels were neutralized with TEA in the proportion 1.5/1 g/g TEA/PAA. At this ratio base/polymer the PH of gel is about 6.5-7. The UV−VIS investigation was done with Jasco V−670 system with scan speed 200 nm/min, UV−VIS bandwidth 2 nm, and NIR bandwidth 8 nm. The fluorescence investigation was done with Jasco SP6100 system.

REFERENCES

[1]. M.K. Chun, C.S. Cho, and H.K. Choi, *Journal of Applied Polymer Science,* **2001**, 79. 1525.

[2]. C. Tiu, J. Guo and P.H.T. Uhlherr, *Journal of Industrial Engineering and Chemistry* **2006**, 12, 5, 653.

[3]. M. Todica, C.V. Pop, Luciana Udrescu, Traian Stefan, *Chimese Physical Letters*, **2011,** 28, 12, 128201-1

[4]. B. Stuart, "Polymer Analysis", John Wiley and Sons, Chichester, **2002**, chapter 5.

[5]. M. Rubinstein, and R. Colby, "Polymer Physics", Oxford University Press, Oxford, **2002,** chapter 5.

[6]. M. Todica, T. Stefan, S. Simon, I. Balasz, L. Daraban, *Turkish Journal Of Physics*, **2014**, 38, 2, 261.

[7]. M. Todica, L. Udrescu, "Metode experimentale in fizica polimerilor", Presa Universitara Clujeana, **2013**, chapter 4.

[8]. M. Navaneethana, K.D. Nishab, S. Ponnusamya, C. Muthamizhchelvana, *Materials Chemistry and Physics*, **2009**, 117, 443.

[9]. Joseph R. Lakowicz, "Principles of Fluorescence Spectroscopy", Springer, **2006**, chapter 3.

[10]. S. Garabagiu, C. Pestean, R. Stefan, *Journal of Luminescence*, **2013**, 143, 271.

[11]. M. Baia, S. Astilean, T. Iliescu, "Raman and SERS Investigations of Pharmaceuticals", Springer-Verlag Berlin, Heidelberg, **2008**.