Digest Journal of Nanomaterials and Biostructures Vol. 9, No. 2, April - June 2014, p. 809 - 816

DEPENDENCE ON THE DYE'S TYPE AND CONCENTRATION OF THE EMISSIVE PROPERTIES OF ELECTROSPUN DYE-DOPED BEADED NANOFIBERS

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Luminescent polymer fibers were obtained by electrospinning solutions of 8% (in ethanol) polyvinylpyrrolidone (PVP) doped with three different dyes (coumarin 6, rhodamine 6G and sulforhodamine 101). Using the same parameters for the electrospinning process, nanofibers with diameters between 200 and 800 nm and different sizes and distributions of the beads were obtained as proven by scanning electron microscopy (SEM). We assessed the dependence of their emissive properties (intensity and wavelength) on the type of dye using photoluminescence (PL) spectra for the same concentration of the dopand dye (10^{-3}M). Moreover, employing 4 different concentrations for coumarin 6 and rhodamine 6G (from 10^{-3} to 10^{-6} M) we evaluated the dependence with the concentration of the dye on the emissive properties of the electrospun dye-doped PVP nanofibers.

(Received April 21, 2014; Accepted June 6, 2014)

Keywords: Electrospinning; Dye-doped beaded nanofibers; Electron microscopy; Luminescence

1. Introduction

Nanostructured materials present exotic properties that can lead to new applications and technologies. One example is constituted by polymers, materials intensively studied over a long term for which ultra miniaturization permitted their use in many domains.

In the last period polymer fibers attracted a lot of attention as building blocks of a wide range of products. From clothing, cosmetics or air conditioning filters to surgical masks, vascular grafts, and heart valves, polymer fibers are without a doubt part of many spheres of human life. Potential applications of polymer nanofibers are ranging from medicine as medical prosthesis, wound dressing, tissue engineering, drug delivery to electrical and optical sensors [1-11]. When producing fibers with diameters of nanodimensional sizes, both the surface area to weight ratio and surface area to volume ratio of fibers increase significantly. One technique used to produce nanometrical polymer fibers is the electrospinning process. Numerous review papers regarding the electrospinning has been published during the recent years [12-16]. There are presented both improvements of the process [17, 18] and properties of the nanofibers produced by electrospinnning [19, 20].

An emerging research area is the synthesis and characterization of polymer nanofibers with special optical properties [21, 22]. In this case, doping of the polymer is used to improve and tailor the optical features of the fibers [23]. Several types of dopands, including dyes, can influence the optical properties of doped polymer nanofibers. Dyes are currently used for applications in fields as varied as the coloring of textile fibers, medical imaging, lasers, photonic devices and organic light emitting diodes, their spectroscopic behavior in solutions being known. When used as dopants in polymer nanofibers, dyes can generate emission over the whole visible spectral region, with enhanced excitation efficiency and low excitation power operation [24, 25].

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Doping with dyes in order to produce fluorescent nanofibers may enable a number of new technologies. Dye-doped nanofibers have been utilized as nanometric light sources [26, 27] and also as subwavelength optical waveguides [28, 29].

In this context, we focussed on obtaining doped polymer nanofibers with enhanced and tailored optical properties. The aim of the paper was to produce dye-doped polymer nanofibers incorporating uniformly dispersed dyes using the electrospinning technique. The morfological properties of the electrospun dye-doped polymer fibers were evaluated using scanning electron microscopy (SEM). We were able to tailor the luminescent properties of the material by doping the polymer (polyvinylpyrrolidone) with different dyes (coumarin 6, rhodamine 6G and sulforhodamine 101). Furthermore, we evaluated the influence of the concentration of the dyes on the emissive properties of dye-doped polymer nanofibers using four different concentrations of rhodamine 6G and coumarin 6.

2. Experimental part

Solutions of 8% polyvinylpyrrolidone (PVP), with $(C_6H_9NO)_n$ chemical formula and Mw=1300000 molecular weight, were prepared by dissolving the polymer in ethanol. Three dyes were purchased from Aldrich and were used without further purification: coumarin 6 of 98% purity ($C_{20}H_{18}N_2O_2S$, Mw=350.44), rhodamine 6G Basic Red 1 of 99.9% purity ($C_{28}H_{31}N_2O_3Cl$, Mw=479,01), and sulforhodamine 101 of 98% ($C_{31}H_{30}N_2O_7S_2$, Mw=606.71). All samples were deposited by electrospinning on glass substrates of 2.5 cm x 2.5 cm.

The electrospinning technique (ES) is a simple method of producing polymer nanofibers. This process does not require complicated devices or high temperatures to produce solid fibers from solution. The ES setup consists of a needle (spinneret) connected to a high-voltage DC power supply (30kV Spellman SL300), a pump (New Era Pump System) and a grounded collector. A syringe contains the dye-doped polymer solution that is pumped from the needle tip at a constant rate (from 0.01 ml/h to 1 ml/h). The droplet that is formed on the tip of the needle is streched when a high voltage is applied and a polymer fiber is obtained. Various factors influence the formation of the polymer fibers: the polymer’s molecular weight and concentration, the electric potential, the flow rate, the distance between needle and grounded collector, and the ambient parameters (temperature, humidity and air velocity in the chamber). The variation of the ES parameters allows us the tailoring of the nanofibers’ morphological properties.

The characterization was performed in parallel with material synthesis. Thus, a ZEISS EVO 50 XVP scanning electron microscope (SEM) and a ZEISS AxioMat1 optical microscope (transmission and fluorescence) were used in order to evaluate the dye-doped polymer nanofibers from the point of view of structure and morphology. Prior to the imaging with the SEM, the samples were sputtered with a thin layer of gold. The photoluminescence (PL) evaluated using a FLS920 EDINBURGH INSTRUMENTS spectrofluorimeter (equipped with a 450 W Xe lamp and double monocromators in both excitation and emission) was used in order to characterize the optical properties of the dye-doped electrospun nanofibers.

3. Results and discussion

For the first set of measurements we prepared solutions in ethanol of 8% PVP doped with coumarin 6 (C 6), rhodamine 6G (Rh 6G) and sulforhodamine 101 (SRh 101) in concentrations of 10^{-3}M. To obtain comparable results for the nonwoven mats of nanofibers for which we further measured the emissive properties, we used the same set of parameters in the electrospinning process for all samples. Thus, at a flowing rate of the polymeric solution of 1 ml/h we applied a voltage of 20 kV at a distance between the electrodes of 15 cm.

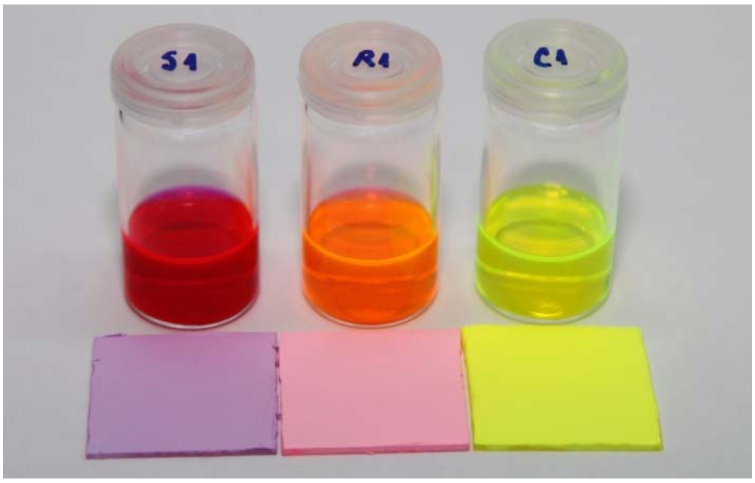

Fig 1. Images of solutions and electrospun samples collected on glass substrates for PVP doped with: a) SRh 101, b) Rh 6G and c) C 6.

The images of polymer solutions and their corresponding samples are presented in Figure 1. To allow an optimal evaluation of the optical properties of the nanofiber mats the glass substrates were covered by electrospinning until the complete obstruction of light, varying the electrospinning time from 15 minutes to 1 hour.

The morphologies of polymer nanofibers doped with different dyes were evaluated using scanning electron microscopy. In Figure 2 are presented the SEM images at different magnifications for PVP nanofibers doped with SRh 101 (Fig. 2a and b), Rh 6G (Fig. 2c and d), and C 6 (Fig. 2e and f). The medium diameters of the nanofibers vary from 800 nm to 200 nm, depending on the dopant dye, with larger values for the SRh 101 doped nanofibers and decreasing slightly for the Rh 6G and considerably for the C 6.

We can observe that we obtained the structure of “beads on string” for all the samples. Although all parameters of the electrospinning process had the same values and the concentration was 10^{-3} M for all dyes, different sizes and distributions of the beads were obtained. Thus, the number of beads formed on the nanofibers is small for the polymers with larger Mw (SRh 101 and Rh 6G) and increases greatly for C6 which has a smaller Mw.

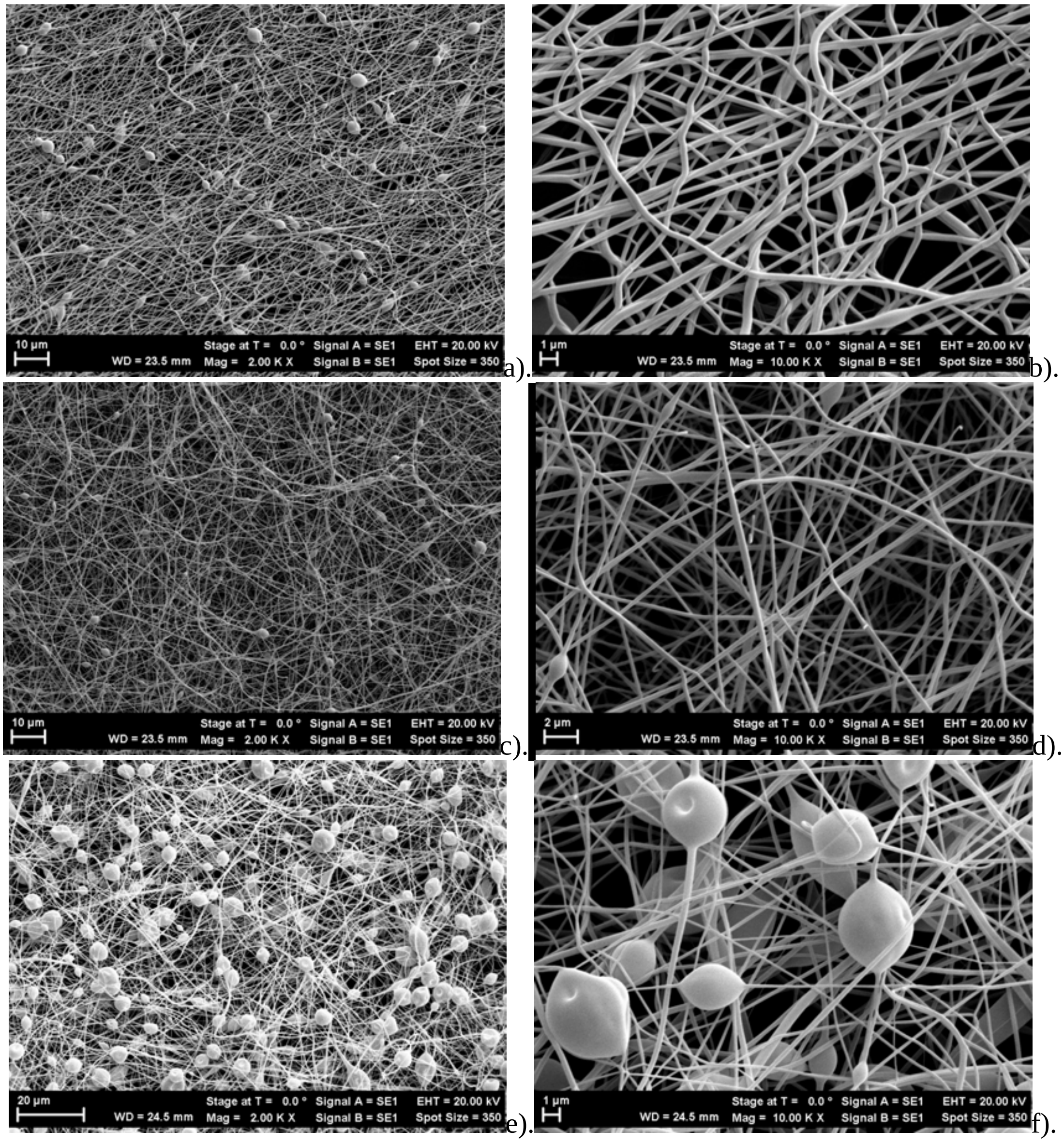

Fig. 2. SEM images (at two magnifications) of PVP nanofibers doped with: SRh 101 (a) and (b); Rh 6G (c) and (d); C 6 (e) and (f).

We further evaluated the emissive properties for the PVP nanofibers doped with different dyes. In Figure 3 are presented the emission spectra of PVP nanofibers doped with 10^{-3} M concentration of SRh 101, Rh 6G and C 6. For the SRh 101 doped PVP fibers we used an excitation wavelength of 560 nm and we obtained an emission band with a maximum around 615 nm. The Rh 6G doped PVP nanofibers show an intense emission peaking at approximately 572 nm when excited with 500 nm. The most intense luminescence is observed for the C6 doped PVP nanofibers which present a very intense emission with the maximum at 523 nm when using an excitation of 470 nm. Thus, we doped the PVP in the same concentration for each dye and we obtained different intensities for the luminescence.

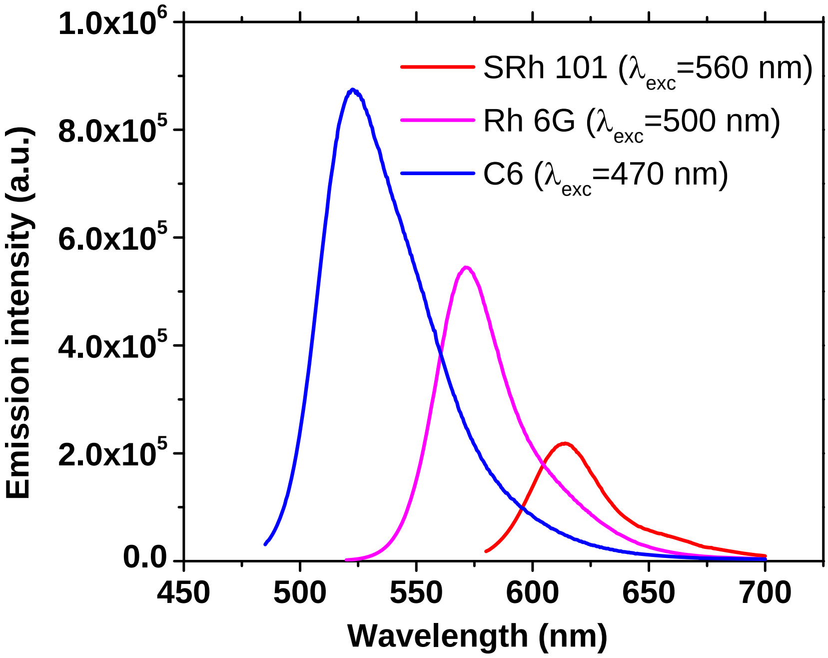

Fig. 3. Emission spectra of PVP nanofibers doped with 10^{-3} M concentration of sulforhodamine 101, rhodamine 6G and coumarin 6.

We also studied the influence of the concentration of the dye on the emissive properties of the PVP electrospun nanofibers. Thus, we examined the fibers produced by electrospinning from doped PVP solutions containing different concentrations of the same dye. Images of the polymeric solutions and the corresponding glass supports covered with electrospun nanofibers are presented in Figure 4 for PVP doped with Rh 6G in concentration of 10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M, respectively.

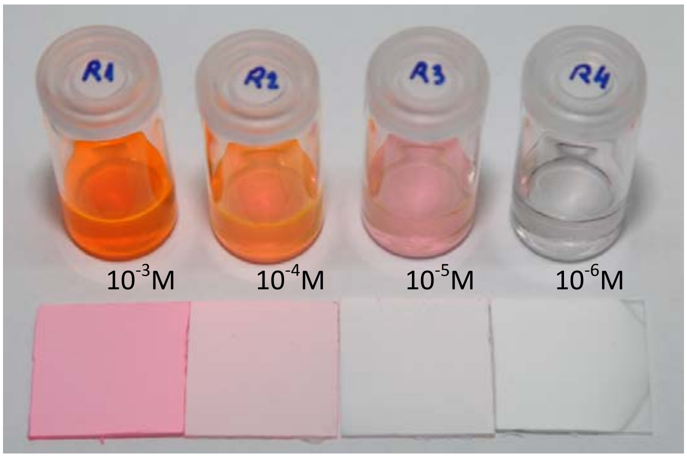

Fig. 4. Images of solutions and electrospun nanofibers collected on glass substrates for PVP doped with different concentrations of Rh 6G.

Figure 5 presents the emission spectra obtained for different concentration of Rh 6G doping in PVP nanofibers (10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M, respectively) under an excitation with 500 nm. The nanofibers were deposited uniformly on glass substrates using a fixed set of parameters for the electrospinning process.

There can be observed a uniform increasing of the intensities of the emission bands and a shift toward longer wavelength of the band’s maximum with the increasing of the dye concentration in the polymeric nanofibers. Thus, under an excitation of 500 nm we observed the emission maxima at 572 nm for 10^{-3} M, 565 nm for 10^{-4} M, 557 nm for 10^{-5} M and 555 nm for 10^{-6} M, with a difference of 17 nm between the emission peak of the most concentrated and the emission peak of the most diluted samples.

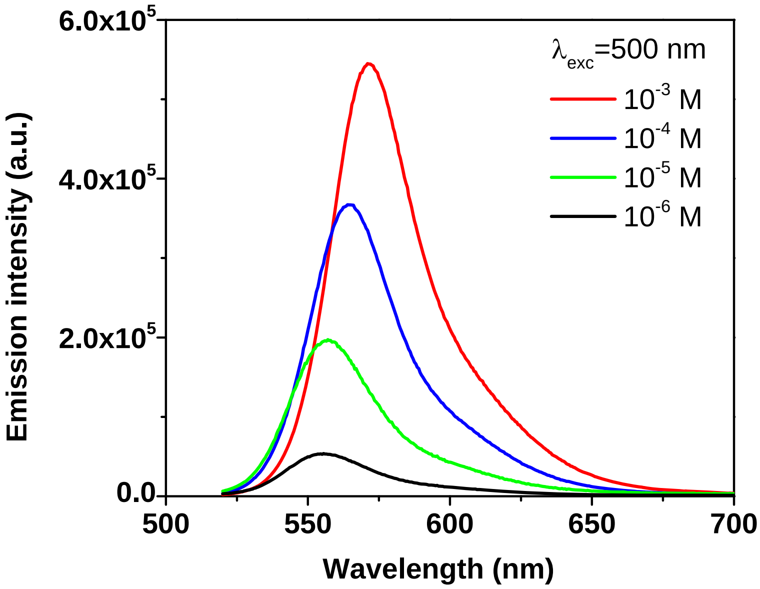

Fig. 5. Emission spectra of PVP nanofibers doped with different concentrations of rhodamine 6G (10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M).

In order to establish if the behavior is the same when we change the doping dye we used different concentrations of C6 (10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M) for the doped PVP solutions that were further electrospun on glass substrates using the same parameters for the electrospinning process as in the case of Rh 6G. The images of the C6 doped PVP solutions and their corresponding electrospun samples are presented in Fig. 6.

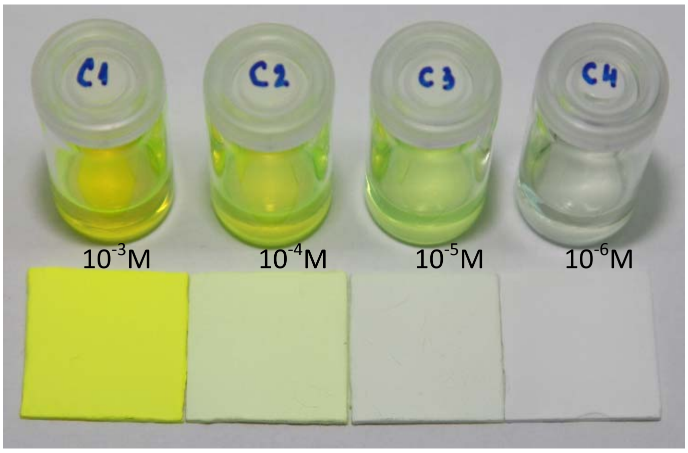

Fig. 6. Images of solutions and electrospun nanofibers collected on glass substrates for PVP doped with different concentrations of C 6.

Evaluation of the luminescent properties of the C6 doped PVP electrospun nanofibers showed us that the increasing of the intensities of the emission maximum with the increase of the dye's concentration is not as uniform in the case of C6 as in the case of Rh 6G. Figure 7 presents the emission spectra for 10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M concentrations of C6 in PVP nanofibers under an excitation with 470 nm. Thus, we observed the emission peaking at 523 nm for 10^{-3} M, 515 nm for 10^{-4} M, 507 nm for 10^{-5} M and 505 nm for 10^{-6} M, respectively. The shift towards longer wavelength of the emission maximum with the increasing of the concentration of the dye is 18 nm. For the SRh 101 doped PVP samples a similar behavior was observed.

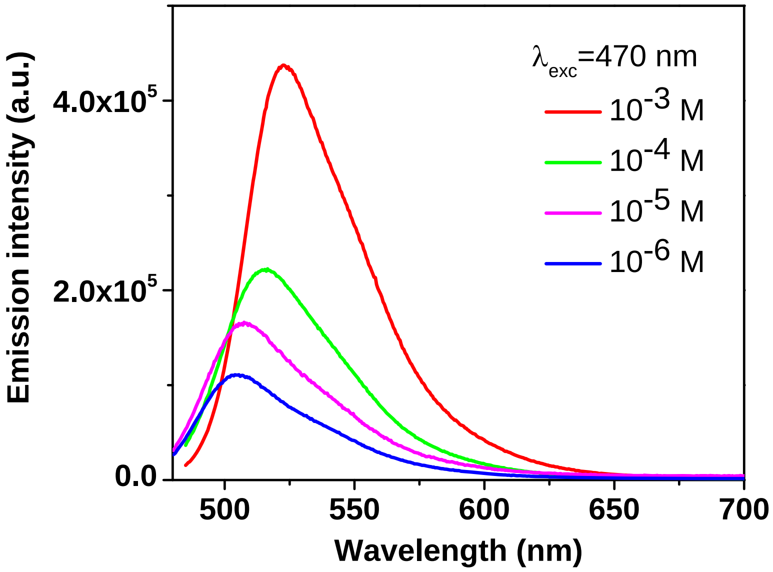

Fig 7. Emission spectra of PVP nanofibers doped with different concentrations of coumarin 6 (10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M).

In our opinion, while the morphology of the dye doped electrospun nanofibers depends on the molecular weight of the dye, the PL intensity depends on the dye's efficiency at a certain wavelength [30] and on the nature of the solvent [31]. Also, for C6 doped samples we observe a larger width of the PL bands. A possible explanation of this result can be linked to a smaller supplementary PL band that appears because of the protonated form of the dye, which was previously reported for coumarins [32].

4. Conclusions

We produced electrospun polyvynilpyrolidone (PVP) nanofibers doped with different dyes (sulforhodamine 101 and rhodamine 6G which have strong emissions in the orange-red spectral domain and coumarin 6 which presents a very strong emission in the green-blue region of the visible spectrum). Using the same parameters for the electrospinning technique we obtained nanofibers with the "beads on string" morphology and diameters between 200 nm and 800 nm. For the same concentration of the dye we observed a direct dependence between the dye's molecular weight and the fibers' diameters (larger for sulforhodamine 101 and rhodamine 6G and smaller for coumarin 6). Instead, the diameters and number of the beads are indirect proportional with the molecular weight of the dyes (smaller for sulforhodamine 101 and rhodamine 6G and larger for coumarin 6). The evaluation of the luminescent properties showed that for the same concentration of the dye in the polymeric solutions (10^{-3} M) we obtain a higher intensity for the emission peaking at smaller wavelength (523 nm for coumarin 6), and the value decreased with the increasing of the peak's wavelength (572 nm for rhodamine 6G and 614 nm for sulforhodamine 101). There is a similar behavior for both rhodamine 6G and coumarin 6 doped PVP fibers when examining the influence of the dye's concentration. As expected, an increasing of the intensities of the emission band and a shift towards longer wavelengths (17 nm for rhodamine 6G and 18 nm for coumarin 6) appears with the gradually increasing of concentration from 10^{-6} M to 10^{-3} M.

Our studies demonstrate the possibility of obtaining completely organic and highly fluorescent materials for lasers, photonic and organic light emitting devices with tunable luminescence.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2011-3-0107.

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