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Lifetime of Violet 1 Dye Doping the Polymer Nanostructured Optical Fibers and Thin Films for Biomedical applications

Luay Hamid Sulaiman

Physics Department, College of Science, Mustansiriyah University, Iraq

E-mail: luayhamid@uomustansiriyah.edu.iq

Abstract

This study, the homemade electrospinning system was used to produce the [PMMA] polymer nanofibers doped with Violet 1 dye and also prepared polymer films. The fluorescence spectra showed the intensity of emission increase with concentration, the lifetime measured by using single-photon counting technique showed the lifetime increased with concentration increased until the concentration reach (0.5×10^{-3}) [M] then it drops exponentially to reaches to (2 nsec). Also, lifetime measured in low temperature. This study showed in low concentration, the self-absorption dominated, whereas at high concentration the internal quenching dominated.

1. Introduction

There are exotic properties nanostructured materials, which are lead to amazing applications and technologies. Some example is related to constitute by materials; polymers were studied intensively for ultra-miniaturization that may be able to apply in any field. In the last period, the fibers of polymer attracted considerable attention as basic construction unit of a wide range of industrial products, from cosmetics or clothing, air filters of conditioning to vascular grafts surgical masks, and also heart valves. On these basis polymer fibers is part of our daily basis, scientific and industrial life. Nano polymer fibers with diameters about (50-100) nm to a micron have potential applications of are deals from the biomedical application as tissue engineering, medical prosthesis, drug delivery, wound dressing, to optical and electrical sensors (ph., mechanical bending, pressure, temperature, pH, and more many sensors). There are many processes to products polymer nanofibers, but one process that simple is electrospinning processes. The electrospinning technique is the best-known technique to preparation micro and Nanofiber polymer that used in different applications such as medical, industrial, and others,[1,2,3]

Electrospinning discovered in the early 20th century. It was known at that time electrostatic spinning; now it becomes a common technique denominator to prepare all type of fiber in the range microfiber to nanofibers. In the last years, there are different developments for this technique and also the relation between electrospun and electrospinning. Electrospinning is an efficient and versatile method that produced long nanofibers by using a suitable system with the proper high electric field. Electrospinning technique is the best development of electrospraying because of the two technique beads on the same mechanism, electrical and physical mechanisms. The difference between them is electrospinning produced continuous fibers with the same shape, but in electrospraying were produced a small droplet [4].



Nano or microfibers can be produced from different solutions polymeric or melts using polymer in electrospinning process because the electrical, mechanical and chemical properties of the polymer are desirable, the polymer has high chemical resistance and sometimes high conductive material with good tensile strength. This property makes the fiber formed by electrospinning processes is ultrahigh fibers quality, and there are large areas of application in, communication as optical fiber, drug transfer delivery system, and their application potential in areas like filtration, and biomedical application is binding bones and tissue scaffolds, or protective textiles [5].

More essential properties of the polymeric fiber which make these fibers attractive, small pores size high active surface area and the possibility of 3D producing structures, which increased the nanofibers interesting the nanofibers production by this process influenced by polymer solution viscoelastic and electrostatic force. The polymer solution with different concentrations plays an important behavior role in formation fiber in the processing by electrospinning system. As classified, i: at low concentration, the polymeric particles micro could be formed because the solution at this concentration, electrospray happen not electrospinning refereeing to the viscosity is low, and the surface tensions are high [6], i: When concentration becomes a little higher, a mixture of nodes and fibers will be formed [7], iii: When used appropriate concentration, there are nanofibers can be formed and be obtained [8], iv: In very high concentration, there are not Nanoscale fibers, appears ribbons in microscale and helix-shaped of the fiber [9].

In electrospinning, that is an important parameter is an electrical charge that may be uncompensated or excess charge in both ions negative or positive. The number of both ions, negative or positive is the same and equal in the solution then is electrically neutral, but the solution contains ions and charged molecules.

This study finds that there is an essential excess in the presence of ions created in the interface of the surface separating the collector and polymer container moving electrons into the polymeric solution from the collector creates an increase negative ions in polymeric solution. Electrons moving to leave the solution in the container leave the solution have more positive ions exceeding to negative ions, the created, ions move by convective and diffusive processes [10].

2. Processing parameters

The crucial parameter affected by electrospinning processes is applied voltage. There is a threshold voltage which must exceed for the charged polymer or solution jets that ejected from the Taylor cone. Drop shape approached the cone, which Taylor described early [11,12] and then charged electrically of the solution emanated jet from the nozzle where the applied electric field was deforming to that shape. The emanated jet takes a path which is starting a straight segment. The emanated jet diameter in the straight segment monotonically decreased with the drop away from the nozzle. Each segment of the stream jet detainee most of its graded reduced velocity, but suddenly moved outward radially at a comparison velocity as the electrical development instability of bending. The polymer solution jet moved and elongated continually like coiled that carried out because of electrical forces of the charges. Then finally stream jet as thin fluid solidified to a nanofiber.

When the voltage reached the threshold, at this point, the formation of the fiber occurs. The solution must be changed with the applied electric field and starting the process of the electrospinning, and this effect studied with different parameters by Reneker et al. [12] which concluded that the applied voltage has no significant effects on the diameter of the fiber on polyethylene oxide using electrospinning process. Another study from Zhang et al. [13] predicting that with high voltage there is more ejection of polymer but with the large diameter of the formation output fiber and also its morphology by using poly(vinyl alcohol) (PVA) dissolved by water. The feed or flow rate of the ejected polymer from the nozzle is another parameter that affected when the polymer or any solution of the material conversion rate and velocity of the jet sample are affected directly. A slower rate there is enough time to take the place of the solvent to evaporate. A minimum flow rate as possible must be present. The high rate also studied, but the produces fibers be large diameters [14].

The selected distance between the tip and collectors must be optimization to get an excellent time to evaporate the solvent from the solution polymer at this distance to form proper morphology of the fiber.

The other parameters, such as the fiber diameter and temperature, also the effect of humidity and morphology, are essential. In increasing the temperature yield of fibers with less diameter, but the solvent of the solutions completely dry with lower humidity. In the other side, when the humidity of the ambient was high, the small pores appear on the surface of the fiber.



Figure 1. Photographic picture of nanofibers produced in this study before exposure by 530 nm laser and after (result in this study).

An electrospinning setup in general consists of many components high voltage power supplied in kV range, a glass container with 0.4 mm nozzle and grounded metal collector hold glass substrate. In a typical electrospinning process, the high voltage applied to the diameter of the fibers lies between 50 and 500 nm [15].

When the diameters of polymer fiber materials shrunk from micrometers e.g. 10–100 μm to submicron or nanometers e.g. (10–10⁻³) to 10–10 m, there appear several amazing characteristics such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 10³ times of that of a microfiber), flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. The different application of electrospun illustrated in figure (2).

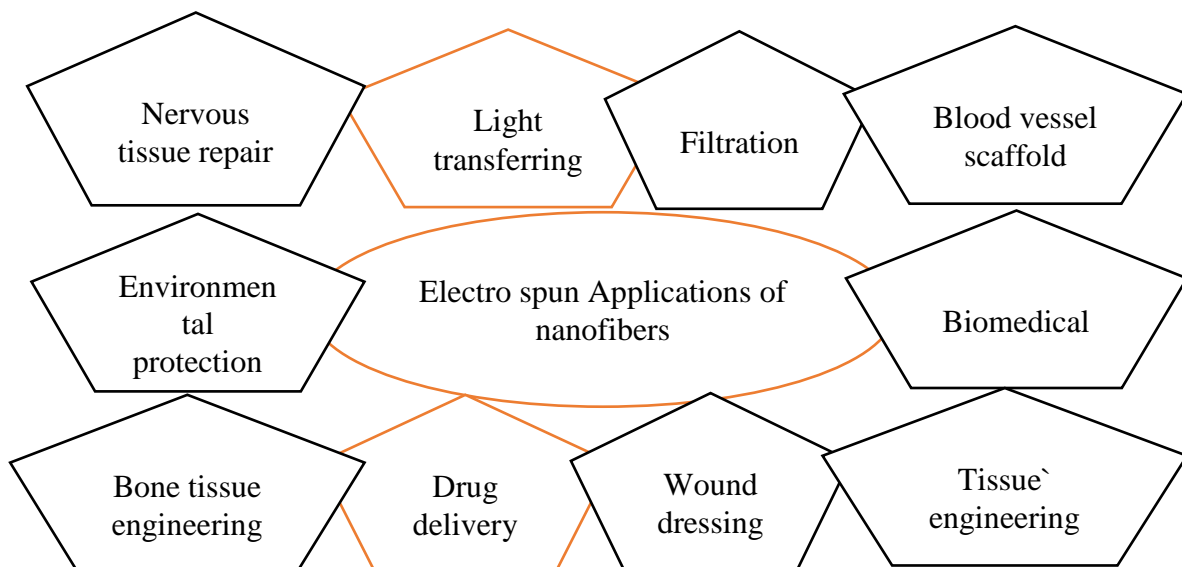


Figure 2. Applications of electrospun fibers in different sectors (as this study collected).

One of the major areas of research in the biomedical application is a drug delivery where electrospinning fibers support help to the therapeutic agent is enveloped in fibers. In addition, electrospun fibers maintain the integrity and efficacy of the drug molecules due to light treatment standards. In this research we try to highlight the importance of electrospinning generally in biomedical field applications, namely tissue engineering and regenerative medicine. Also the polymer fibers were doped with laser dye to obtain the possibility of transferring the light beam into the tissues

to conduct the desired handling by using different concentrations to control the lifetime of doping lasing compounds as it is important parameter in this matter.

In this study, homemade electrospinning system is used, PMMA polymer dissolved in two solvent ethanol and methanol, this solution doped by Violet 1, spectroscopic study result presented.

3. Experimental part

The homemade electrospinning system in molecular and laser group was composed of glass container of U-shape used as pump polymer container with capillary head needle size (22 to 25) corresponding the inner diameter which the polymer fiber flows from it in small diameter (0.3 to 0.5) mm accelerated by applied high-voltage supplied used as applied potential, from high power supply of 0 to 10 kV. The grounded rectangular collector from aluminum (100x150) mm. This collector located in different height distance (15 to 25) cm apart from a tip of the needle (nozzle). The measured relative temperature and humidity by a property system inside the chamber of the electrospinning. These parameters keep constant at 28°C and 22% respectively.

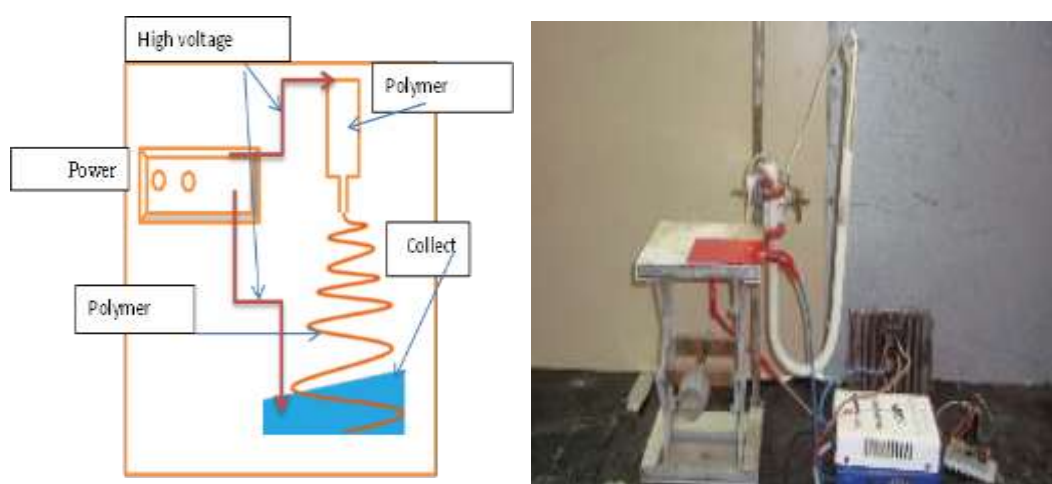


Figure 3. Represent the homemade electrospinning system.

A typical spectrometer system used in this study consist of one-meter Monochromator which is suitable to determine the fluorescence emission and by used green laser with the second harmonic with wavelength 530 nm and Hamamatsu IP 28 photomultiplier tube with the spectral response (400- 680 nm) connected to the computer.

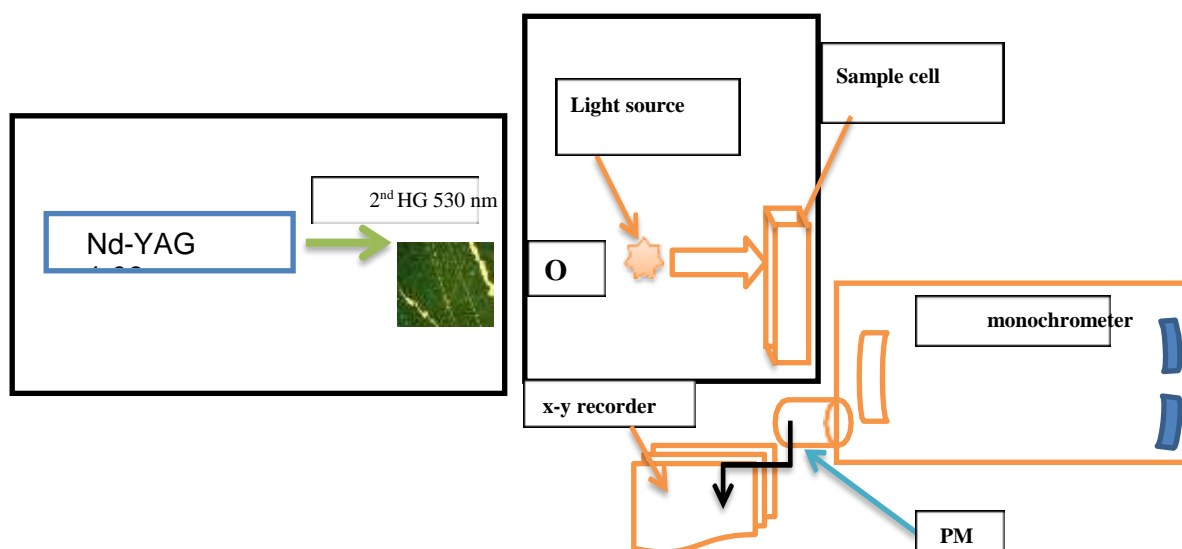
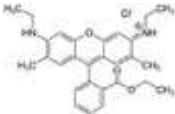
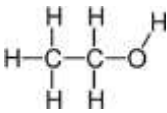


Figure 4. Block diagram of the spectrometer.

The chemical materials used in this study summarized in the table (1). The laser dye solutions that prepared for use to prepared by dissolving the amount of Violet 1 in ethanol & methanol by using the appropriate amount of solvent and Violet 1 and then mixed with PMMA polymer solution.

Table 1. Summarized chemical materials.

Name	Molecular weight	Molecular STRUCTURE	Purity	Molecular shape	Supplied from
Violet 1 or (Rhodamine 6G)	479.017 g/mol	$C_{28}H_{31}N_2O_3Cl$	As reserved without any purification		LAMDA PHYSK
Ethanol	46.069 g/mol	CH_3CH_2OH or C_2H_6O	Spectroscopy standard		
methanol	32.042 g/mol	CH_4O or CH_3OH	Spectroscopy standard	H_3C-OH	
Chloroform		(CH_3CCl_3)	spectroscopic grade		Philip Harris chemical company UK

The single-photon counting technique is also used to study the lifetime of the studied molecules, Figure (5) shows the block diagram of the main component of this system.

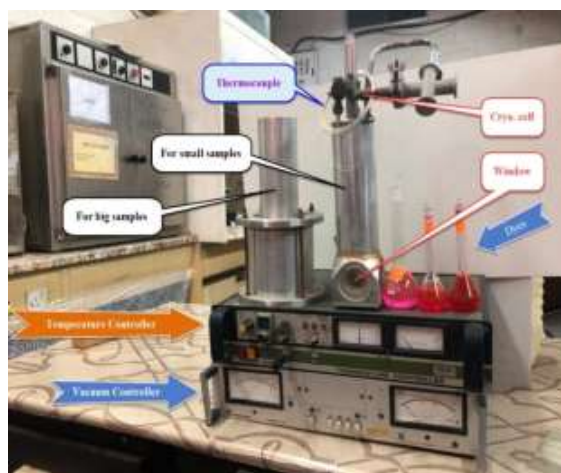


Figure 5. Block diagram of the single-photon counting technique used in this study.

4. Results and discussions

In this study, [PMMA] polymer was doped by Violet 1 and Preparation of two forms of samples. One of the samples thin films prepared by using spin coating system and the other nanofibers were prepared using the homemade electrospinning system. The fluorescence emission of liquid samples was recorded in Figure (6) with different concentrations range (10^{-1} to 10^{-6}) [M], from this figure note that the intensity of the fluorescence increases with decreasing concentration, this behavior appears because at high concentrations, the molecules are affected by each other and this causes to compete for the fluorescence emission and low emission intensity. However, it observed that the intensity of fluorescence in solid-state nanofibers and thin films, nanofibers are higher than that of films also notes a narrowing in width of fluorescent spectra of the fibers relative to the films, i.e. less FWHM in fiber than thin films. This behavior appears because the absorption cross-section of polymer doped Violet 1 nanofibers much more than polymer thin films doped with Violet 1 dye.

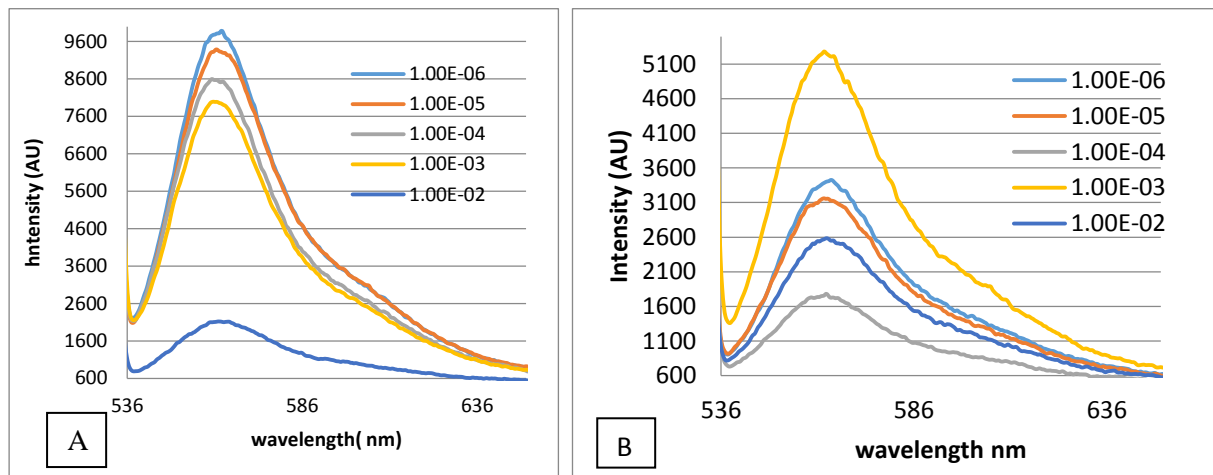


Figure 6. Fluorescence spectra of Violet 1 doped polymer, A- nanofibers and B- thin films at 310 °K

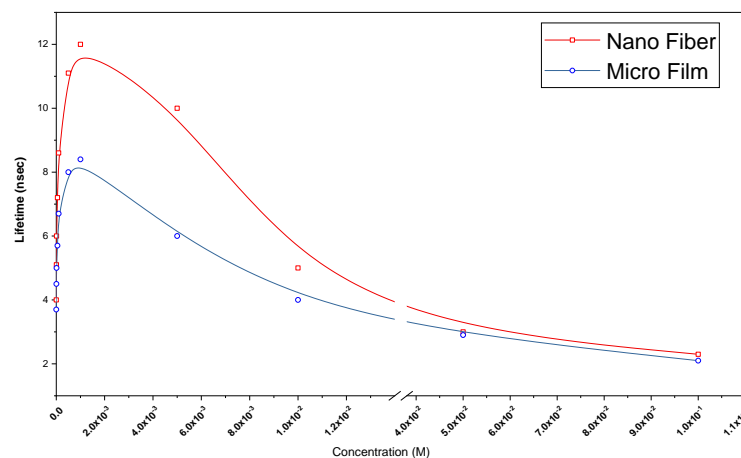


Figure 7. The relation between the lifetime and concentrations of Violet 1 dye doped polymer thin films at 310 °K.

Table 2. The relation between concentration and relative quantum yield of Violet 1dye doped polymer thin films and nanofibers at 310 °K.

The concentration of quantum yield of Violet 1dye [M]	The relative quantum yield of Violet 1dye nanofiber	The relative quantum yield of Violet 1dye thin films
0.000001	0.930232558	0.860465116
0.000005	1.186046512	1.046511628
0.000010	1.348837209	1.162790698
0.000050	1.76744186	1.395348837
0.000100	2	1.558139535
0.000500	2.581395349	1.860465116
0.001000	2.790697674	1.953488372
0.005000	2.209302326	1.627906977
0.010000	1.860465116	1.395348837
0.050000	0.930232558	0.674418605
0.100000	0.534883721	0.488372093

Figure (7) presented how lifetime with different concentrations for Violet 1dye doped polymer thin films samples and nanofibers prepared by electrospinning system. This figure shows that the lifetime at low concentrations (1×10^{-6} [M]) was (3.9 nsec), and it increases with concentration increasing until the concentration reaching 0.5×10^{-3} [M] where lifetime becomes as high as possible (12 nsec), but then it drops rapidly when concentration increases until (1×10^{-1} [M]) the lifetime reach minimum value (2 nsec.). Two factors cause this behavior; the 1st because the overlapping between the absorption and fluorescence spectra of the R6G this behavior maybe lead to the self-absorption, i.e., the emitted photon may be absorbed again internally by the other Violet 1dye molecules more than once. While the 2nd the internal quenching which leads to reducing the lifetime rapidly because increasing the no. of molecules in volume unit i.e. increasing of concentration. It also observed that the fluorescence lifetime of the nanofibers Violet 1dye doped polymer sample behaved as in fluorescence lifetime of the thin films Violet 1dye doped polymer samples. At high concentrations Violet 1dye it observed that the lifetime became in the same range values because the density of Violet 1dye molecules in unit volume becomes high which lead to an increase in internal competing in photophysics processes of Violet 1dye molecules. In table (2) the relative quantum yield of two samples presented by doping the natural lifetime of dye 4.3 nsec [9].

5. Conclusions

The photophysics processes Violet 1dye doped polymer affected by the type of samples preparing and consequently, the fluorescence emission and lifetime. In nanofibers, the cross-section of absorption is significant compared to thin films and liquid phase dye-doped polymer. The diameter of nanofibers produced by electrospinning system may have different diameters, the height of the tip to the collector, and the value of the high voltage must be taken into account. Also the relative quantum yield of the lasing compounds affected by photophysics processes in the same manner.

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