Preparation of Laser Dye-polymer Nanoparticles for Laser Luminescence Applications

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Abstract In present work a nanoform consisted of one of the famous dye known as rhodamine B was selected to add to the other selected polymer poly methyl methacrylate. Both rhodamine b and poly methyl methacrylate were mixed with different weight ratios. The absorption and emission curves were measured showing some noticed shift. This shift is interpreted in terms of the mixed ratios of the parent materials. Laser photoluminescence spectrum was measured showing some promising applications for this material.

1. Introduction

Luminescence, was introduced in 1888 by Q.C.Lum [1], is known as a cold body radiation which is a self-emission of photons under the effect of the spontaneous emission phenomena of a substance. Chemical reactions, electrical energy, subatomic motions or stress on a crystal can emit the photons as a lighting process. The luminescence phenomenon involves the following types:

1- chemiluminscence which is appeared as a result of such chemical reaction, like as:

    a- Bioluminescence, resulting from biochemical reactions in living cells;

    b- Electrochemiluminescence, resulting from an electrochemical reaction;

    c- Lyoluminescence, resulting from the dissolving a solid(heavily irradiated) in a liquid solvent;

    d- Cond luminescence; which is a light emission under the effect of heat.

2- Crystalloluminescence which is produced during the crystallization process.

3- Electroluminescence which appears when an electric current passes through a substance, like as: cathode luminescence, a result of a luminescence material being struck electrons.

4- mechanoluminescence, a result of a mechanical action on solid materials, which includes the following:

    a- Triboluminescence, generated when bonds in a material are broken when that material is scratched, crushed or rubbed;

    b- Fractoluminescence, generated when bonds in certain crystals are broken by fractures;

    c- Piezoluminescence, produced by the action of pressure on certain solid materials;

    d- sonoluminescence, a result of imploding bubbles in a liquid by sound.

5- Photoluminescence as a result of photon's absorption, including the following:

    a- Fluorescence, photoluminescence as a result of a singlet electronic relaxation (typical lifetime: nanoseconds);

    b- Phosphorescence, photoluminescence as a result of triplet – singlet relaxation (ms to hours);

    c- Raman emission, photoluminescence as a result of inelastic light scattering (ns).

6- Radio luminescence, as a result of bombardment by ionizing radiation.

7- Thermoluminescence, is the re-emission of absorbed energy when a substance is heated; like as: cryoluminescence which is the emission of light when an object is cooled (ex: wulfenite).

In general, photoluminescence process can be classified by various parameters such as the energy of the exciting photon with respect to the emission [1, 2]. Resonant excitation describes a situation in which photons of a particular wavelength are absorbed and equivalent photons are very rapidly re-emitted. This is often referred to as resonance fluorescence. For materials in solution or in the gas phase, this process involves the electrons but no significant internal energy transitions involving molecular features of the chemical substance between absorption and emission. In crystalline inorganic semiconductors where an electronic bond structure is formed, secondary emission can be more complicated as events may contain both coherent contributions such as resonant Rayleigh scattering where a fixed phase relation with the driving light field is maintained (i.e. energetically elastic process where no losses are involved), and incoherent contributions (or elastic modes where some energy channels into an auxiliary loss mode).

The latter originate, e.g., from the radiative recombination of excitons, Coulomb-bound electron-hole pair states in solids. Resonance fluorescence may also show significant quantum optical correlations [3-5].

More processes may occur when a substance undergoes internal energy transitions before re emitting the energy from the absorption event. Electrons change energy states by either resonantly gaining energy from absorption of a photon or losing energy by emitting photons. In chemistry-related description, one often distinguishes between fluorescence and phosphorescence. The former is typically a fast process, yet some amount of the original energy is dissipated so that re-emitted light photons will have lower energy than did the absorbed excitation photons. The re-emitted photons in this case is said to be red-shifted, referring to the reduced energy it carries following this loss (as the Jablonski diagram shows). For phosphorescence, electrons which absorbed photons undergo intersystem crossing ehere they enter into a state with altered spin multiplicity, usually a triplet state. Once the excited electrons is transferred into this triplet state, electron transition (relaxation) back to the lower singlet state energies is quantum mechanically forbidden, meaning that it happens much more slowly than other transitions. The result is a slow process of radiative transition back to the singlet state, sometimes lasting minutes or hours. This is the basis for "glow in the dark" substances.

Photoluminescence is an important technique for measuring the purity and crystalline quality of semiconductors such as GaN and InP and for quantification of the amount of disorder present in a system [6].

Time resolved photoluminescence (TRPL) is a method where the sample is excited with a light pulse and then the decay in photoluminescence with respect to time is measured. This technique is useful for measuring the minority carrier lifetime of III-V semiconductors like gallium arsenide (GAs.)

In the early years of the laser development, the laser was regarded by skeptics as "a solution looking for a problem". Eventually more and more "problems" were found, and lasers have unquestionably become an important part of the science and technology of our time, with applications ranging from medical to military.

Dye lasers are the most vesatile and of the most successful laser sources known today due to their significant contributions to basic physics, chemistry, biology and other fields. The first laser dye was reported in 1966 by Sorokin and Linkard at IBM's Thomas J. Watson Research center, Yorktown Heights, were the first to obtain stimulated emission from an organic compound, namely chloro-aluminum-phatholocyanine; which is an organomeallic.

Traditional laser technology utilizes a variety of inorganic materials to produce the required emission. Several different types of inorganic lasers have been developed to emit in UV, Vis. or IR regions of the EM spectrum. Though inorganic laser are of low cost and robust devices, they have some drawbacks. They emit only at very few specific wavelengths and in very narrow bands, whereas dye lasers cover the entire visible and near IR region and have far greater tenability compared to inorganic lasers. Dye lasers are contributing greatly to the progress in laser technology.

There are some requirements of dye molecules for effective performance which should have some characteristics like as:

- Strong absorption at excitation wavelength and minimal absorption at lasing wavelength; i.e. minimum overlap between absorption and emission spectra.
- High quantum yield (0.5-1.0);

- Good photochemical stability;
- A short fluorescence life time (5-10ns);
- Low absorption in the first excited state at the pumping and lasing wavelengths;
- Low probability of intersystem crossing to the triplet state; and
- Laser dyes have to be very pure since impurities frequently quench the laser output.

Therefore by appropriate dye selection it is possible to produce coherent light of any wavelength from 320-1200 nm.

Laser dyes are complex molecules containing a number of ring structures, which lead to complex absorption and emission spectra. The laser dyes can be categorized into different classes by virtue of their structures that are chemically similar. Common examples are Coumarines, Rhodamines, Xanthenes and Pyromethenenes. The structure and composition of the molecule has an important influence on spectral emission.

Liquid dye lasers are a coherent source of radiation with a wide tuning range and find many applications in various fields. However, these lasers cannot be used in certain applications due to the need for large volumes of organic solvents. The use of solid matrices containing laser dyes is an attractive alternative to the conventional liquid dye solutions. The first solid-state dye laser were reported in the late 1960's by Soffer and Mcfar land [8] and Peterson and Snavely [9]. They demonstrated stimulated emission from polymeric matrices doped with organic dyes.

However work on solid-state dye lasers was not pursued for aver a decade due to low lasing efficiencies and fast photodegradation of the dye. In recent years, significant breakthroughs have been achieved in the development of partical tunable solid-state dye laser [10-18].

The solid-state dye lasers [19, 20] have several advantages over the conventional liquid dye lasers. Along with the case of handling, these lasrs possess commercial advantages because of low cost of production and the safety of operation. Other technical advantages are compactness, manageability, versatility, lack of flammability and lack of toxicity. The flow fluctuation and solvent evaporation is considerably reduced in the case of solid-state dye lasers.

There are a number of materials which have been used as solid hosts for laser dyes such as polymers, porous glasses, organically modified silicates or silicate nano-compsites, polycom glasses (combination of polymer and sol-gel) [21-27].

Generally, the solid host materials suitable for use in solid-state dye lasers should have the following requirements. They should be highly transparent to the pump laser and dye laser wavelengths. They should be hard enough to undergo mechanical treatment such as diamond cutting, grinding and polishing as required by any optical material and materials should possess good thermal stability over a wide range of temperatures.

Polymeric matrices have some important advantages over other host materials because they are simple to prepare and cheap to produce. They possess high optical homogeneity, their chemical composition can be treated mechanically. Polymer based systems have limitations such as low damage threshold of the host material and limited lifetimes [28]. Polymers are poor thermal conductors and have large time of heat dissipation [29] from the focused pump laser spot to low heat boundary.

2. Materials and Methods

For obtaining dye-doped polymer composite, poly methyl methacrylate had been obtained firstly by free radical vinyl polymerization. It was prepared by mixing a volume ratio of water/ethanol of 70:30 as solvent and $K_2S_2O_8$ (0.05 M) as polymerization initiator; the solvent was mixed with the initiator at room temperature, and after being compiled, the initiator was dissolved in the solvent, then the methyl methacrylate monomers (MMA) were added. The total volume of the monomers to solvent is 10%. The polymerization was carried out at 55 ^{o}C on a hotplate at 70 ^{o}C for 4 hours, and the polymer was isolated by centrifugation at high speed (10,000 rpm) and washed successively with ethanol-distilled water mixture to remove any impurities such as residual monomer and initiator. The product was then dried in an oven at 55 ^{o}C for 24 hours. The white powder of PMMA with a M_w of 871829 g/mol and radius of gyration R_G of 342.25 nm (measured using static light scattering technique[30–33]) was obtained[34] as a product fig.(1).
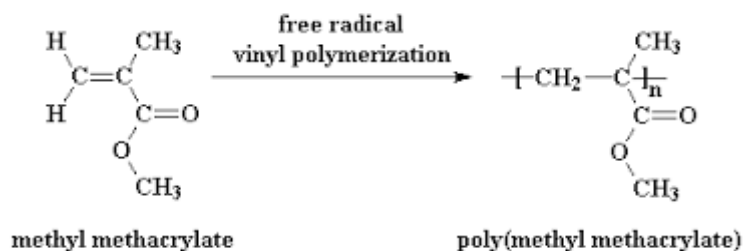
Figure 1: Scheme of MMA polymerization

Homogenous solutions of PMMA dissolved in DMF were obtained by magnetically stirring for 48 h at room temperature and after dissolution of the polymer, the dye was directly added into the solution and the stirring was continued for a further 10 min. The percentages of PMMA and RhB are illustrated in table (1).

Table 1: The percentages of PMMA and RhB is different samples

Sample	PMMA	RhB
A	4	1
B	2	1
C	3	2
D	1	1
E	2	3
F	1	3

The infrared (IR) spectra of samples in KBr discs were obtained by transmission Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were recorded between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. Absorption and emission spectrums were obtained by UV-VIS and fluorescence spectroscopies. The samples were dissolved in chloroform (lobal cheme Inc.) and the absorption spectrums were recorded in the range of visible light. Using an excitation source at 530 nm the emission spectrums were recorded between 540 and 750 nm.
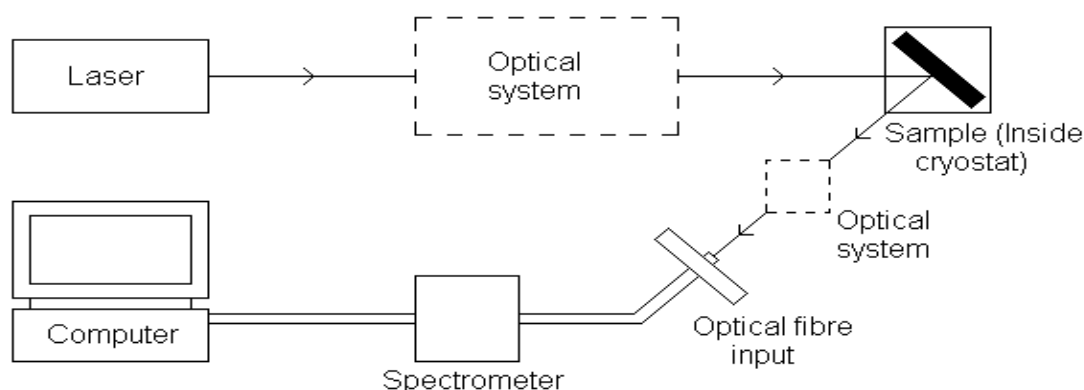

Figure 2: Typical construction of PL system

A laser tuned to a wavelength close to the band gap energy of the sample is directed onto the sample. This may be held in a cryostat to facilitate measurements being taken at low temperatures. Since measurements are taken continuously a He-Cd laser with wavelength 442nm was used as an excitation source. When the laser beam is incident on the sample, photoluminescence occurs and light is emitted from the sample at wavelengths dependent on the sample composition. The sample is oriented such that the reflected laser beam and the PL emission propagate in different directions.

The emitted light is directed into a fiber optic cable and then into a spectrometer. A filter may be placed in front of the fiber input to remove any incident laser light. Inside the spectrometer, a diffraction grating diffracts different wavelengths in different directions towards an array of photo-detectors that measure the intensity of each wavelength component. The digital information is interpreted by the computer, which can display a PL spectrum. The spectrum indicates the relative intensities of light of different wavelengths entering the detector fig(2).

3. Results & Discussion

FT-IR characterization:

The overall analysis of the spectra revealed that after the introduction of RhB into the PMMA, the vibrational bands became more intense and their shape sharpened compared to the corresponding bands of the pure PMMA fibers. Moreover, due to the presence of the RhB, the vibrational bands in the 3000–2800 cm^{-1} and the 1750–1400 cm^{-1} spectral regions were slightly shifted towards lower wavenumbers. Namely, these changes were the most visible in the case of the vibrational band at 1730, characteristic for the stretching of the C=O of PMMA, which was strongly increased and insignificantly blue-shifted to the wavenumber 1728 cm^{-1} after doping of the PMMA with RhB. Also, the band at 1695 cm^{-1} associated with C=O stretching of the pure RhB appears in the spectra of PMMA doped with RhB fig (3) [35].
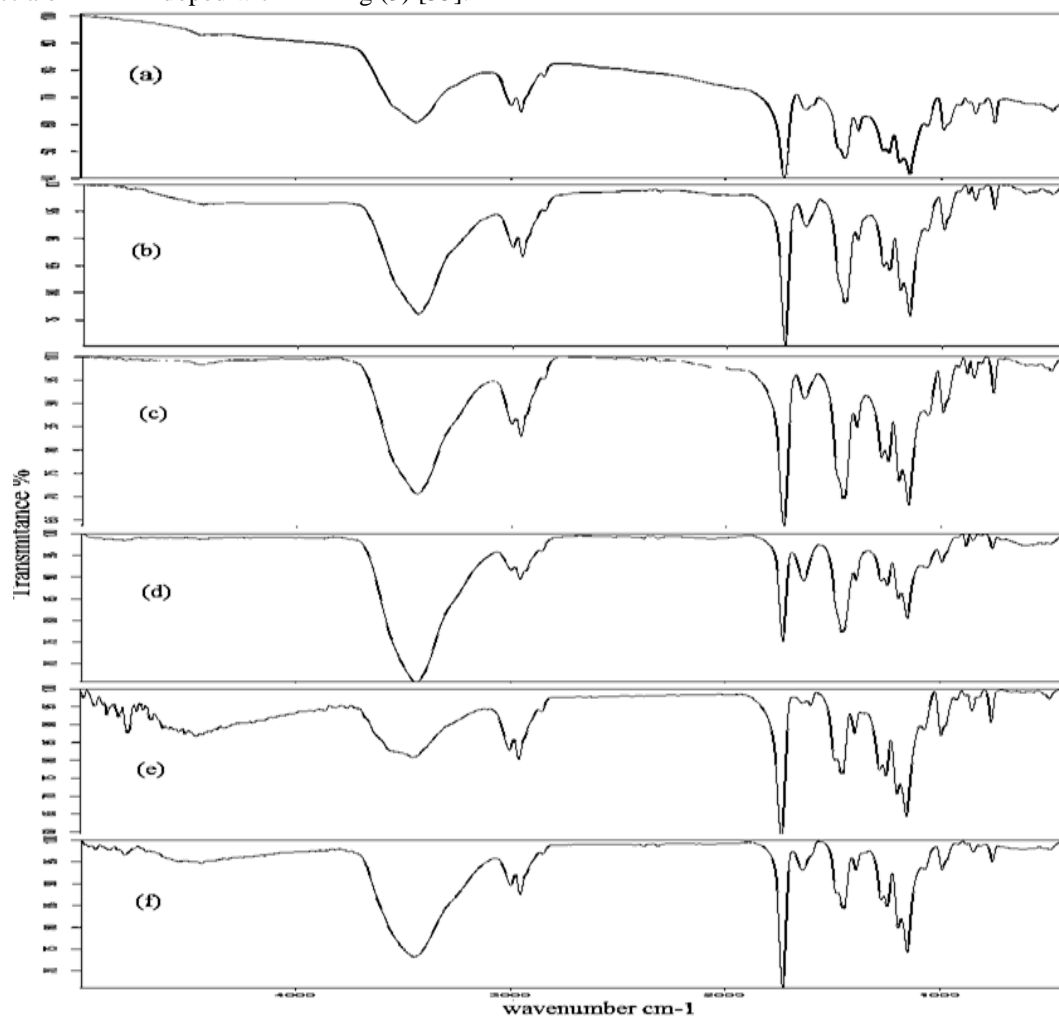
Figure 3: FTIR spectra of poly(methyl methacrylate) doped with different concentrations of RhB

UV-VIS and Fluorescence characterization:

UV absorption and fluorescence spectrums had been measured for each sample and for pure rhodamine b showing a red shift in the absorption spectrum for the samples from the absorption peak of pure rhodamine b fig.(4). a blue shift is also observed in the emission spectrum for the samples from the peak of pure rhodamine b fig.(5). Absorption and emission spectrums for sample a, b, c, d, e and f are shown in figure (6).
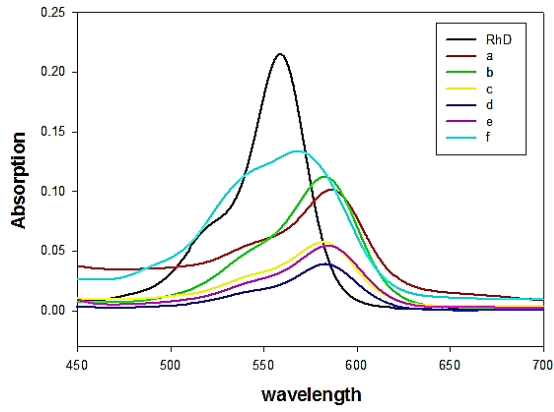
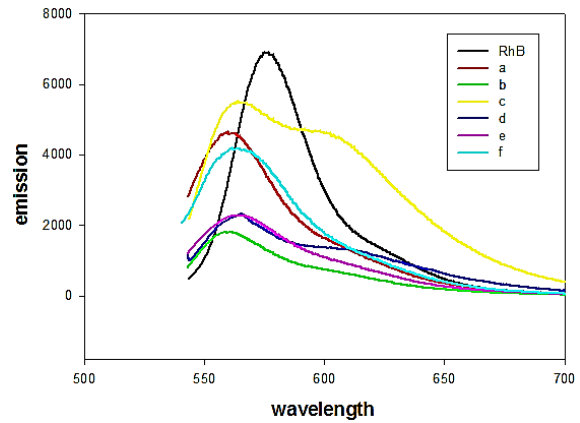*Figure 4: UV-VIS absorption spectrum for RhB and different samples*

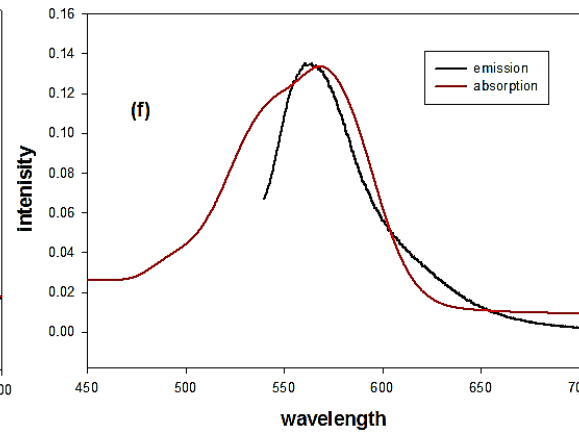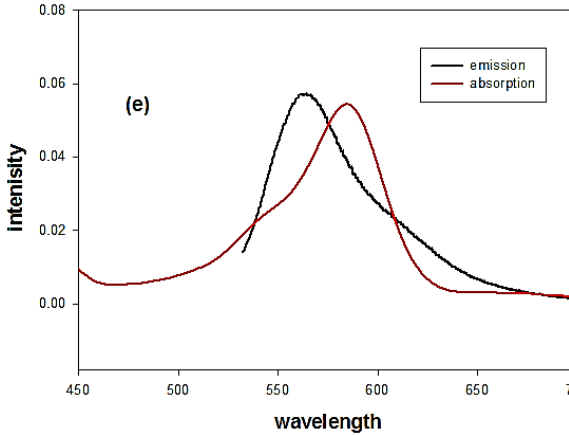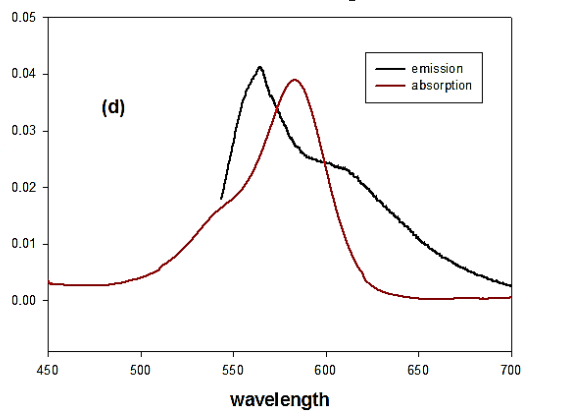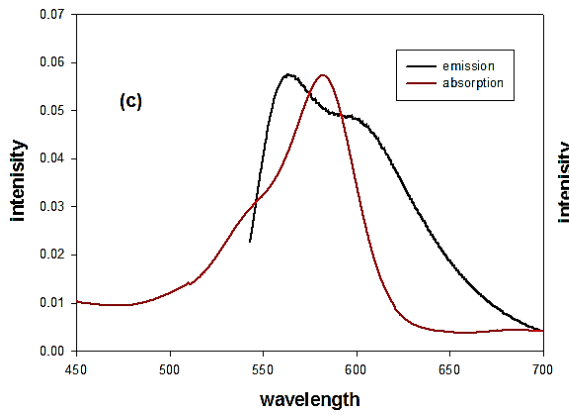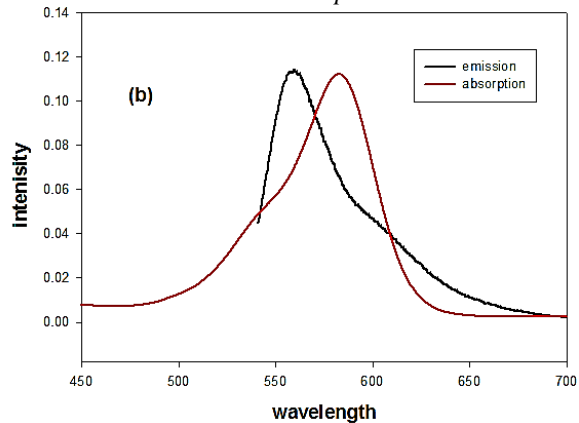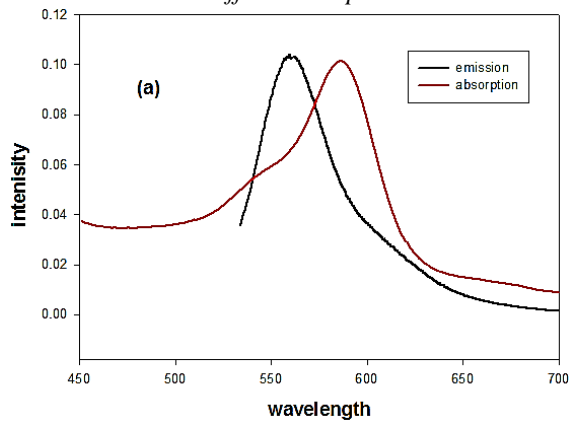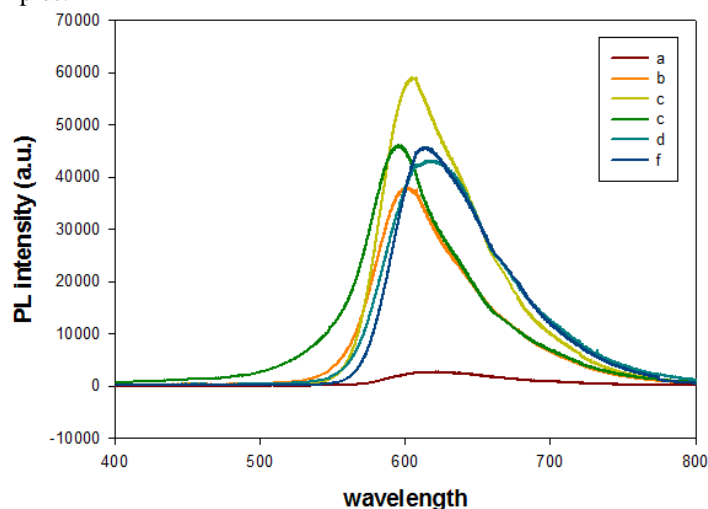*Figure 5: florescence spectrum for RhB and different samples.*

Figure 6: Emission and absorption spectrum for PMMA with different concentrations of RhB

Laser photoluminescence

Laser photoluminescence measurements had been applied to the samples with different concentrations of RhB at room temperature using a He-Cd laser (442 nm in wavelength) as the excitation light source. Fig(7) shows the PL spectrum for this samples.

Fig(7) laser photoluminescence spectrum for PMMA doped with different concentrations of RhB.

Table 2: Absorption, emission and PL peaks for different samples

Sample	Absorption (nm)	Emission (nm)	PL (nm)
a	586.5	559.5	620.5
b	583	560	601.5
c	582	563.5	605
d	584.5	564.5	595.5
e	585	561.5	618.5
f	568	561	613

4. Conclusion

Poly methyl methacrylate doped with different concentrations of rhodamine B has been synthesized and characterized with FTIR spectroscopy. UV-Vis absorption spectrum become broader and shifted to higher wavelengths (red shifted). While, fluorescence emission also has become broader and shifted to lower wavelengths (blue shifted). Laser photoluminescence examination has been performed and showing that this is a promising material and can be used in many photoluminescence applications.

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