Dye-Doped Polymer Laser Prepared by a Novel Laser Polymerization Method

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In this work, dye-doped polymer gain media samples of rhodamine-B in an ethylene glycol solvent with different concentrations has been added in a mixture with methylmethacrylate and 2-hydroxy ethylmethacrylate at volume 1:1. Copolymer has been prepared and synthesized by the Conventional Thermal Polymerization Method (CTPM) using an oven, and by our novel method called the Gamma Irradiation Polymerization Method (GIPM) using Cobalt-60 (^{60}Co). The absorption molar coefficients, absorption cross sections, fluorescence quantum yields, fluorescence life times, and emission cross sections were determined and calculated from the measured absorption and emission spectra. The efficiencies of the fabricated samples by both methods were measured and compared.

1. INTRODUCTION

Research on dye-doped polymer lasers (DDP) is currently an attractive and very active field. It can be used to provide a tunable range of laser wavelengths to cover electromagnetic spectra from UV through visible to infrared with high quantum efficiencies[1-8]. It has been reported that dye-doped polymer gain media can be polymerized by the Conventional Thermal Polymerization Method (CTPM) using an oven, in this method, a DDP laser is initiated by chemical initiators and solidified using an oven under a certain temperature[9-13], . As far as we know, there are no reports of a dye-doped polymer laser prepared by γ-ray irradiation.

The purpose of this paper is to study the photo-physical properties of dye-doped polymer laser samples prepared and polymerized by the Conventional Thermal Polymerization Method (CTPM) and the Gamma Irradiation Polymerization Method (GIPM) using Rhodamine-B dye. The photo-physical parameters comprising absorption molar coefficients, absorption cross sections, fluorescence quantum

yields, fluorescence life times, and emission cross sections are calculated from the measured absorption and emission spectra. The efficiencies of the fabricated samples by both methods are measured and compared.

2. EXPERIMENTAL

The samples were fabricated and synthesized using two methods of polymerization: *conventional thermal polymerization method* (CTPM) using oven and *γ-irradiation polymerization method* (GIPM) with a ^{60}Co γ-ray source.

The structural formulae of rhodamine B is depicted in Fig. 1, and the name of the copolymer is abbreviated as p(HEMA-MMA). The copolymers p(HEMA-MMA) are in an equal volume ratio. The dye was purchased from Radiant Co. without further purification. The dye rhodamine-B was dissolved in ethylene glycol (EG) and left in ultrasonic water bath for two hours. The dye used was highly pure (>99%) as the impurities lead to a decrease in lasing efficiency. This mixture then added to a 1:1 mixture of freshly purified HEMA monomer and MMA monomer solvent (The HEMA-MMA monomers used was also pure, washed repeatedly with aq NaOH 10% until free from inhibitors such as hydroquinone, then washed with distilled water, dried (CaCl$_2$) and fractionally distilled under reduced pressure in an all-glass apparatus sealed under nitrogen and stored at 0°C in dark). Varying the dye concentrations produces differently doped solid-state dye polymer samples.

In this work, two groups with dye concentrations of 5×10^{-5} mol/dm^3, and 1×10^{-3} mol/dm^3 were chosen for rhodamine-B. Each sample of the two groups was poured into a cylindrical glass mould. After careful deaeration by bubbling N$_2$ gas to remove oxygen, the initiators 2, 2-azo bis isobutyronitrile (conc. 0.015 g/l) were added and the moulds were sealed and then the polymerization for the first group was performed in an oven at 60^{0}C for about ten days. This process is called the Conventional Thermal Polymerization Method (CTPM). The polymerization for the second group was performed (without initiators) using the γ-ray (Gamma) Irradiation Polymerization Method (GIPM), in which samples were irradiated at 15^{0}C with a ^{60}Co γ-ray source.
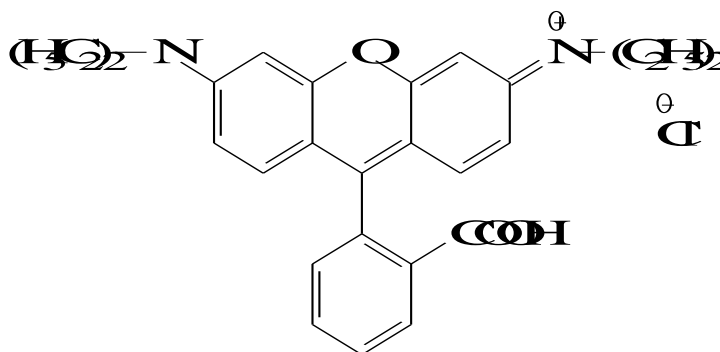

Figure 1. Chemical structures of rhodamine-B dye laser.

The irradiation dosage was 8 KGy (*full description of the GIPM method may be found in our USA patent* App. Pub: 20100234486 A1, *and detailed irradiation effects with the Dye-Doped Polymer laser will be described elsewhere*). Rods 12 mm in diameter and 20 mm in length were formed and optical quality surface was obtained by conventional girdling and polishing. These rods were sliced for both groups to produce discs with a thickness of 2 mm to be used for emission and absorption spectra measurements. The experimental setup for fluorescence and efficiency measurements is shown in figure 2. The pumping system performed using frequency-doubled Q-switched Nd:YAG laser provides 3 Hz, 5 ns of energy 50 mJ made of SolarLS, Belarus. The pump energy was rendered into a line image by a quartz cylindrical lens ($f = 150$ *mm*) and used to transversely excite the dye-doped polymer laser medium. The produced beam from dye-doped polymer laser medium pass through small telescope, filter, polarizer and then detected with sensor connected with Oscilloscope, and part of the beam reflected to fiber optic connected with monochromator and imaged in ICCD Camera.
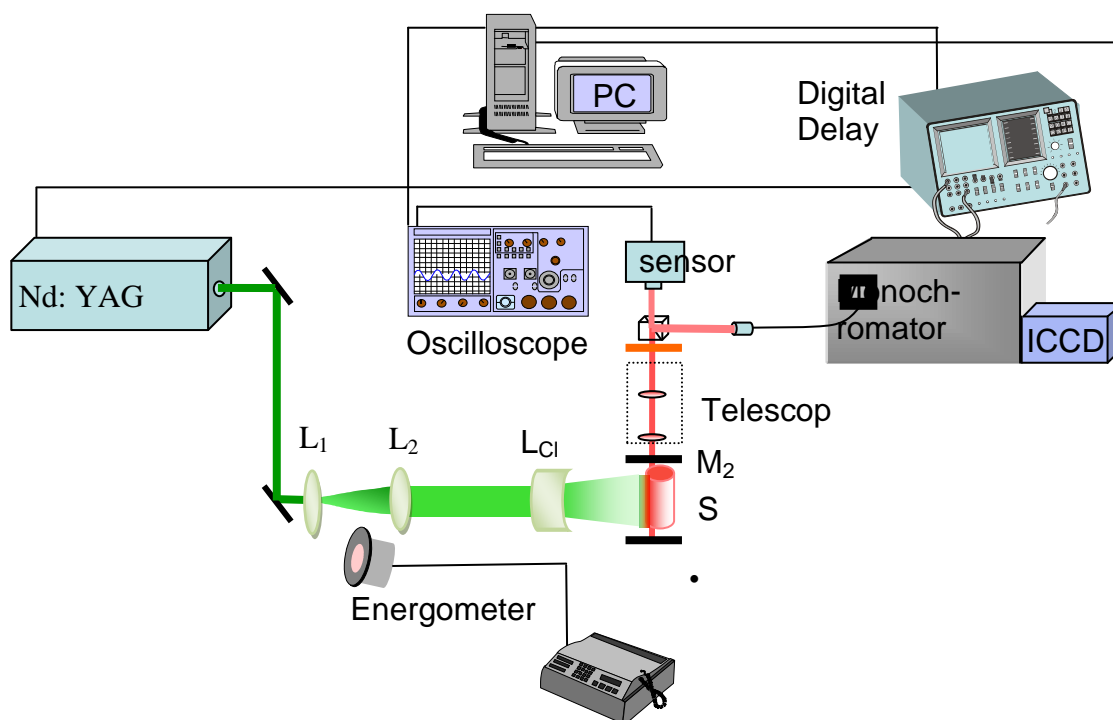

Figure 2. Schematic diagram of Dye-Doped polymer laser experimental setup.

3. RESULTS AND DISCUSSIONS

3.1 Absorption spectra

The absorption spectra of the sample in liquid state (sol(MMA:HEMA/EG)) before polymerization and two solid samples of p(MMA:HEMA/EG) prepared by CTPM and GIPM (with thickness of 2mm) were obtained in visible range, i.e. 400–700 nm.

Figure 3 shows the absorption spectra of the three hosted samples listed in table I, at a concentration of 5×10^{-5} mol/ dm^3. It can be seen from Fig. 3 that the optical spectrum of dye-doped

polymer is influenced noticeably by the nature of the host materials[14]. A red-shift of 5 nm in the absorption peak is observed for p(MMA:HEMA/EG) laser sample prepared by GIPM compared to CTPM. In addition, a 6-nm red-shift is seen for the absorption peak of p(MMA:HEMA/EG) laser sample prepared by CTPM when compared to that hosted by sol(MMA:HEMA/EG) laser sample. Therefore, the difference in the absorption peak between the p(MMA:HEMA/EG) laser samples prepared by GIPM and that hosted in sol(MMA:HEMA/EG) is around 11 nm. The observed red-shifts are attributed to the change in the refractive index of the host materials [9,13,15].

Table I: Refractive index values of host materials.

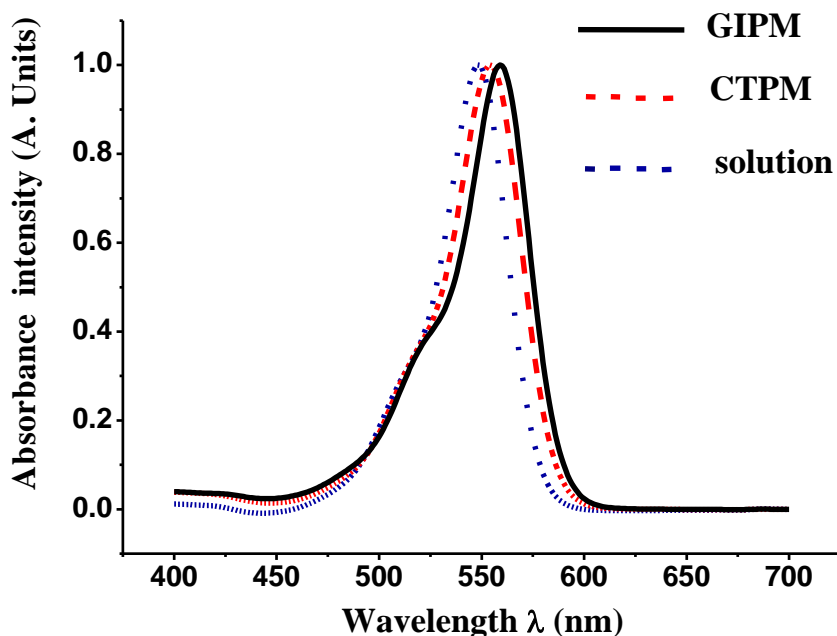| State	Host Medium	Solvent	Dye Laser	Polymerization Method	Refractive Index
Solution			NO	Liquid	1.43450
Solid	p(MMA+HEMA)	Ethylene Glycol	Dye added	CTPM	1.52
Solid				GIPM	1.528

Figure 3. Absorption spectra of the rhodamine-B laser medium at a concentration of 5×10^{-5} mol/dm^3, in the three host materials listed in Table I.

Table II shows the decadic molar absorption coefficient at the absorption peak ε_{max} and the absorption cross section σ_{abs} at 632 nm as calculated for the samples using Equation (1), which is given by:

Table II: Absorption properties for the investigated samples. $\lambda_{abs,MAX}$ **:** Peak Wavelength**;** ε_{MAX} **:** Maximum Absorption Coefficient; σ_{em} : Absorption Cross Section; c: Concentration.

Dye Cons. (in Molar)	Polymerization Method	$\lambda_{abs,MAX}$ (nm)	$\varepsilon_{MAX} \left(mol^{-1}dm^3cm^{-1}\right)$	σ_{abs} (cm^2) at λ_{max} x 10^{-16}
RhB at c= $(5X10^{-5})$	CTPM	554	$3.7X10^3$	0.14
	GIPM	559	$17X10^3$	0.7

$$\sigma = \frac{2.3 \times 10^3 \varepsilon}{N_A} \qquad (1)$$

Where

$$\varepsilon = \frac{A}{c \cdot R}$$

It can be seen that the absorption coefficient for p(MMA:HEMA/EG) laser sample prepared by GIPM is considerably larger than that prepared by CTPM. The same observation is seen for the absorption cross section due to the red-shift of the rhodamine-B absorption peak in the p(MMA:HEMA/EG) laser sample prepared by GIPM.
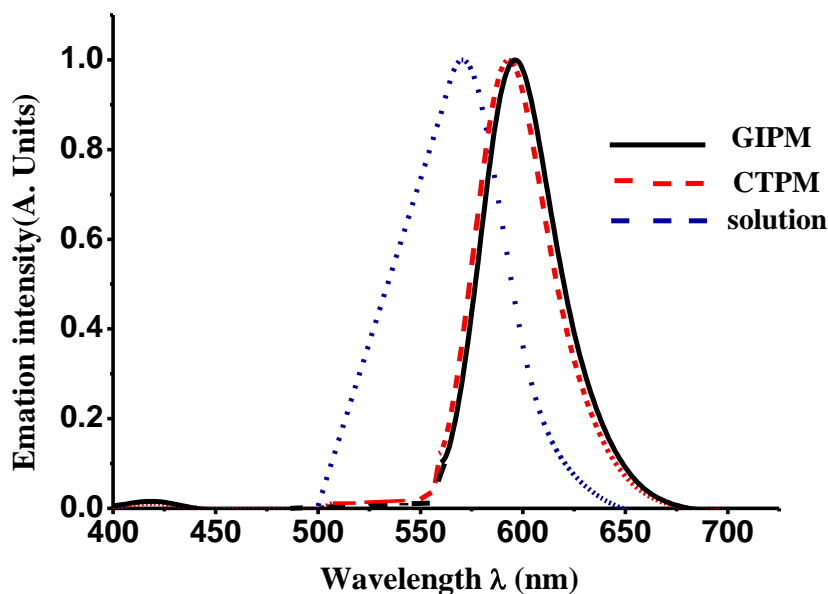
3.2. Emission spectra

Figure 4. Emission spectra of rhodamine-B laser medium at a concentration of $5x10^{-5}$mol/ dm^3, in the three host materials listed in Table I.

The fluorescence of the two p(MMA:HEMA/EG) laser samples prepared by CTPM and GIPM (2-mm disk) are collected at an angle of 45° with the incident laser beam (532 nm) using a spectrofluorometer.

Figure 4 shows a 3-nm difference in the emission spectra peak for p(MMA:HEMA/EG) laser media samples prepared by CTPM and GIPM. This might be due to the change in the refractive index or the polarity, or both[17]. However, the emission spectra peak for Sol(MMA:HEMA/EG) seems to deviate slightly (23–25 nm) from that of the other two samples for the same reason concerning the refractive index. From the emission spectra, we performed the following important measurements for the p(MMA:HEMA/EG) laser media samples prepared by CTPM and GIPM.

3.3. Fluorescence quantum yield Q_f:

Table III shows the fluorescence quantum yield Q_f at the indicated concentration in the dye-doped polymer medium p(MMA:HEMA/EG) prepared by CTPM and GIPM, which was determined from the following relation:

$$\text{(2)}$$

The fluorescence quantum yield has a higher value for Rhodamine-B in the sample prepared by GIPM than CTPM.

Table III: Emission properties for the investigated samples. $\lambda_{em,MAX}$: Peak Wavelength; ϕ_f : Fluorescence quantum yield; τ_f : Fluorescence life time; σ_{em} : Emission Cross Section; c: Concentration

Dye Cons. (in Molar)	Polymerization Method	$\lambda_{em,MAX}$ (nm)	ϕ_f	τ_f (ns)	σ_{em} (cm^2) at λ_{max} x 10^{-16}
RhB at c= (5X10^{-5})	CTPM	593	0.76	3	4.3
	GIPM	596	0.88	7.3	2.03

3.4. Fluorescence life time τ_f

The fifth column of Table III shows the fluorescence life time at the indicated concentration in the dye-doped polymer medium P(MMA:HEMA/EG) prepared by CTPM and GIPM, which was calculated from Equation (3) represented by the following relation:

$$(3)$$

This equation shows that the square of the refractive index is inversely proportional to the fluorescence life time. In general, the life time is shorter in solid media than in liquid media. Table III shows that the life time of P(MMA:HEMA/EG) prepared by GIPM is larger than that of the sample prepared by CTPM. The fluorescence life time obtained for the latter is similar to that recorded by a related study[17], which gave a life time of 3.5 ns in the sol-gel and at a pumping wavelength 530 nm.

3.5. Emission cross sections

Table III also shows the emission cross section prepared by the two methods, which were calculated using the following relation:

$$(4)$$

This relation shows that the emission cross section is inversely proportional to the square of the refractive index. Table III clearly indicates that the emission cross section decreases for the laser sample prepared by GIPM when compared to laser sample prepared by CTPM. Previous studies[20,21] have shown that the emission cross section is reduced as the refractive index increases.

Table IV shows Stoke's spectral displacement for the investigated samples, and indicates that the displacement is less in p(MMA:HEMA/EG) as prepared by the two methods compared with that recorded for Sol(MMA:HEMA/EG). It was also observed that the Stoke's spectral displacement is smaller for solid media than liquid media, as reported in previous studies[16,13], which is attributed to the reduction of the dielectric constant after polymerization.

Table IV: Stoke's spectral displacement for the indicated media

Hosts	Polymerization Method	RhB
SOL(MMA:HEMA/EG)	Solution	22 nm
P(MMA:HEMA/EG)	CTPM	16 nm
P(MMA:HEMA/EG)	GIPM	15 nm

3.6. Laser efficiency

The output laser pulses produced from p(MMA:HEMA/EG) laser mediums of concentration 1×10^{-3} M and concentration 5×10^{-5} M prepared by CTPM and GIPM methods as a function of pumped energy were measured. The pumping energy against output pulses from p(MMA:HEMA/EG) medium

of concentration $1x10^{-3}$ M and concentration $5x10^{-5}$ M prepared by CTPM and GIPM methods is shown in figures 5 and 6, respectively.
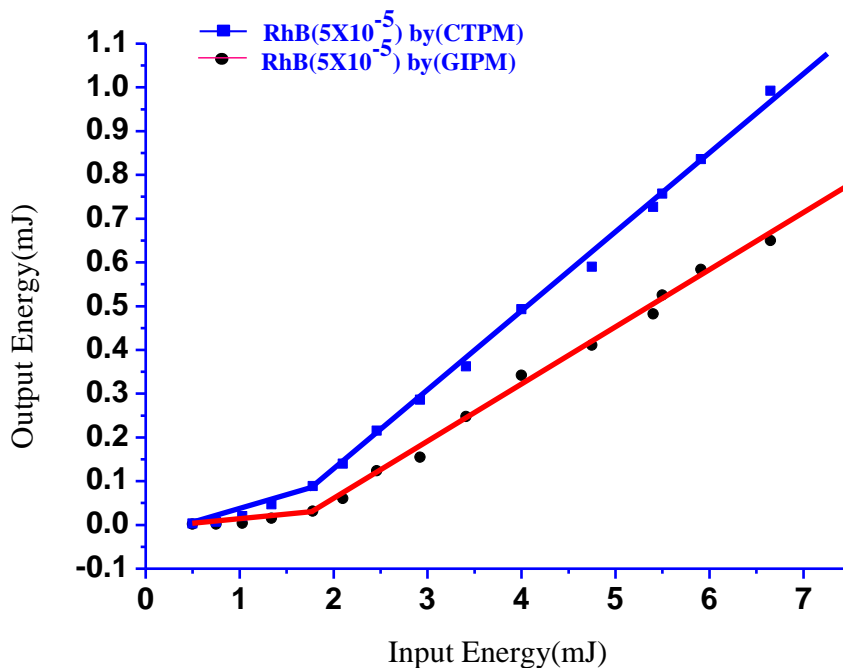

Figure 5. Efficiency measurements of P(MMA:HEMA/EG) at concentration $1x10^{-3}$ M prepared by CTPM and GIPM methods.
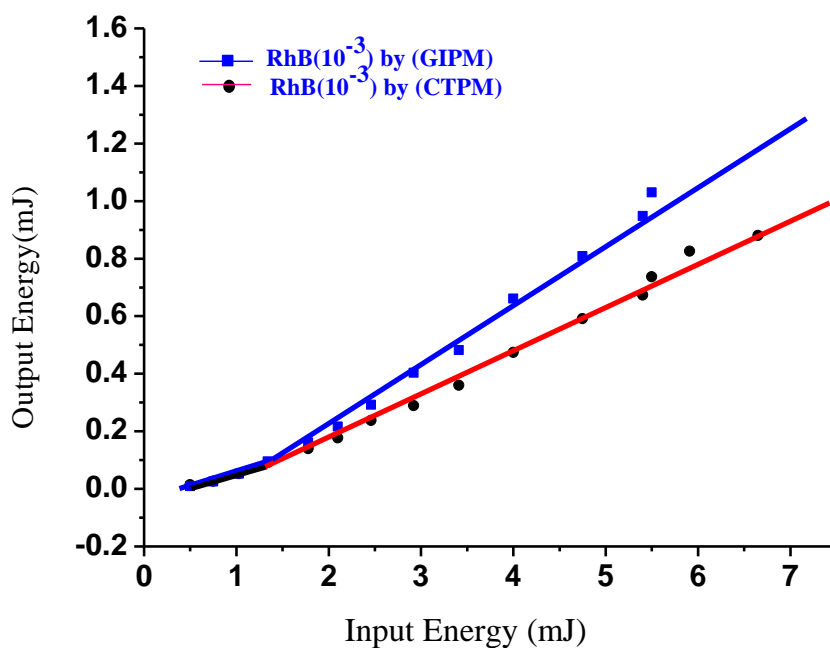

Figure 6. Efficiency measurements of P(MMA:HEMA/EG) at concentration $5x10^{-5}$ M prepared by CTPM and GIPM methods

For all samples, without exception, an increase in the laser output from p(MMA:HEMA/EG) laser mediums emerging with increasing pump energy, which caused by the increase in the number of excited molecules accompanied by an increase in the number of photons emitted. The laser efficiency is determined by dividing output laser pulses from p(MMA:HEMA/EG) on the input pump energy. As shown in figures 5 and 6, p(MMA:HEMA/EG) laser medium of concentration $1x10^{-3}$ M prepared by γ−irradiation polymerization method (GIPM) provides high efficiency with value around 45.6% , determined efficiency values of other p(MMA:HEMA/EG) mediums listed in table V.

Table V: Optical properties values for CTPM and GIPM methods

p(MMA:HEMA/EG) Concentration (Molar)	Preparation Method	Laser Efficiency (%)
$(1X10^{-3})$	CTPM	14.9
	GIPM	22.5
$(5X10^{-5})$	CTPM	11.4
	GIPM	16.5

3.7. Structure Limitation

The dense and compact nature of the formed p(MMA:HEMA/EG) laser medium prepared by GIPM has contributed in the increase of laser intensity (produced by Rhodamine-B molecules) was due to:

1-   The trapping of Rhodamine-B within the high cross-linked polymer formed by the effect of gamma radiation at specific experimental conditions mentioned in the sample preparation section.

2-   The immobilization of Rhodamine-B due to presence of H-Bonds between Carboxylic groups present at Rhodamine-B, and Hydroxyl group within polymeric chain.

So, the presence of trapped and immobilized Rohdamine-B within polymer matrix will hinder and reduce the thermal transitions (Rhodamine-B molecular rotation, re-orientation, collisions, and Vibration-rotation interactions) due to non-mobility effect produced by polymeric matrix. The consumption of thermal energy will be manifested by the high intensity emission spectrum or output fluorescence (Electronic Transitions) and then the synthesized Rhodaime-B material expected to provide high laser output.

The use of gamma radiation (GIPM) to synthesize Rhodamine-B is favorable over conventional thermal polymerization method using Ovens (prior art synthetic methods) because it guarantees a fast or short synthetic method and a non-contamination synthetic process (purity of the procedure). It produces a high laser damage resistance materials, which might attributed also to the high dense polymeric network structure formed as a result of effect of gamma radiation on MMA and HEMA monomers. The investigated Rhodamine-B material has shown that the intensity of output laser is three times the power of the laser intensity gained by conventional method using Ovens (CTPM). It has wavelength at 622 nm, and its frequency doubling (λ= 311 nm) could be useful for the treatment of

Vitiligo (skin-color change in Dermatology application) disease.

4. CONCLUSION

Dye-Doped Polymer samples were fabricated and synthesized successfully using γ-ray radiation without adding initiator. This new laser polymerization method, called the Gamma Irradiation Polymerization Method (GIPM), was used to measure photo-physical properties and compare them with those of Dye-Doped Polymer laser samples prepared by the Conventional Thermal Polymerization Method (CTPM) using an oven. The measured and calculated photo-physical properties of Dye-Doped Polymer samples prepared by GIPM clearly showed optimum results. The measured absorption and emission spectra of the Dye-Doped Polymer samples of rhodamine-B prepared by GIPM showed red-shifted spectra in comparison with CTPM samples. The calculated photo-physical values (absorption molar coefficients, absorption cross sections, fluorescence quantum yields, and fluorescence life times) for the rhodamine-B samples prepared by GIPM showed higher values when compared with samples prepared by CTPM, whereas emission cross sections showed lower values.

The consumed time in fabrication and synthesis has been reduced 90% by GIPM method. The complete polymerization for GIPM sample was at 8kGy. As a future work, the dispersion degree, intercalation spacing and thermal stabilities of these samples will be studied with X-ray diffraction, high-resolution transmission electron microscopy and thermal gravimetric analysis, respectively.

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