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Synthesis of Solid State Dye Laser Materials by Gamma Irradiation Polymerization

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ABSTRACT. Solid state dye laser (SSDL) monomers of rhodamine B dissolved in ethylene glyeol and added in a 2-hydroxyethyl-methaerylate methyl-methacrylate (volume mixture 1:1) copolymerized by gamma irradiation polymerization method (GIM) using Cobalt 60 and compared with couventional thermal polymerizatiou uethod (CTM) using oven. The fluorescence spectra, lasing, refractive index, and color difference are ineasured and discussed.

Key Words: *Solid State Dye Laser, rhodamine B, P(MMA-HEMA) copolymer, Fluorescence analysis, gamma irradiation, polymerization.*

1. Introduction

Dye lasers have attractive properties due to their broad spectral range tuning and high quantum efficiency. They are simpler to produce and cheaper in comparison with other laser sources. Two types of dye-doped active laser medium are mainly used, namely liquid and solid-state. The second type has some operational advantages relative to the first.

At present, research on solid-state dye lasers is a very active field. Organic dyes are doped in organic, inorganic glasses or in composite organic–inorganic materials. The processability, photo-stability and thermostability of the solid-state dye laser materials are sought to be improved continuously. Solid-state dye lasers have been developed as an attractive alternative to conventional liquid dye lasers, due to its low cost fabrication techniques, compactness, lack of toxicity or flammability, suppression of flow fluctuations, and the suppression of evaporation of solvent.

Several solid-host materials such as poly(methyl meth-acrylate) (PMMA), polystyrene, polyethyl-acrylate and polybutadiene[1-2] *etc.*, have been embedded with dyes to obtain laser emission.

However, low laser-damage resistance, low photobleaching threshold of dyes and relatively low laser efficiency has suppressed the usage of this class of lasers.

Therefore, the higher laser-damage resistance dye-doped host materials have been developed such as: modified polymers[3-4] (modified-PMMA), co-polymers[5] (poly(2-hydroxyethyl methacrylate) (PHEMA)), sol-gel[6-7] (tetra-methoxysilane (TMOS), tetraetboxysilane (TEOS)).

Most of the research in dye-doped polymers was done with Rhodamine[6,8,9], which emits in the yellow to red regions of the spectrum. Very little research has been carried out on blue and UV emitting solid-state dye lasers[10]. However, in the future, the blue and UV lasers might be required in some important fields, such as medical, tele-communications, optical data storage,

In this work, Fluorescence Spectra and lasing output from two prepared solid state dye laser samples of rhodamine B dissolved in Ethylene glycol (conc. 5×10^{-5} M) and mixed with 2-hydroxyethyl-methacrylate and methyl-methacrylate copolymer (volume mixture 1:1) polymerized by conventional thermal method (CTM) and gamma irradiation method (GIM) are measured and compared.

2. Experimental

The structure formulae of the additive ethylene glycol, Rhodamine B and copolymer poly(2-hydroxyethyl-methacrylate methyl-methacrylate) are depicted in fig. 1.

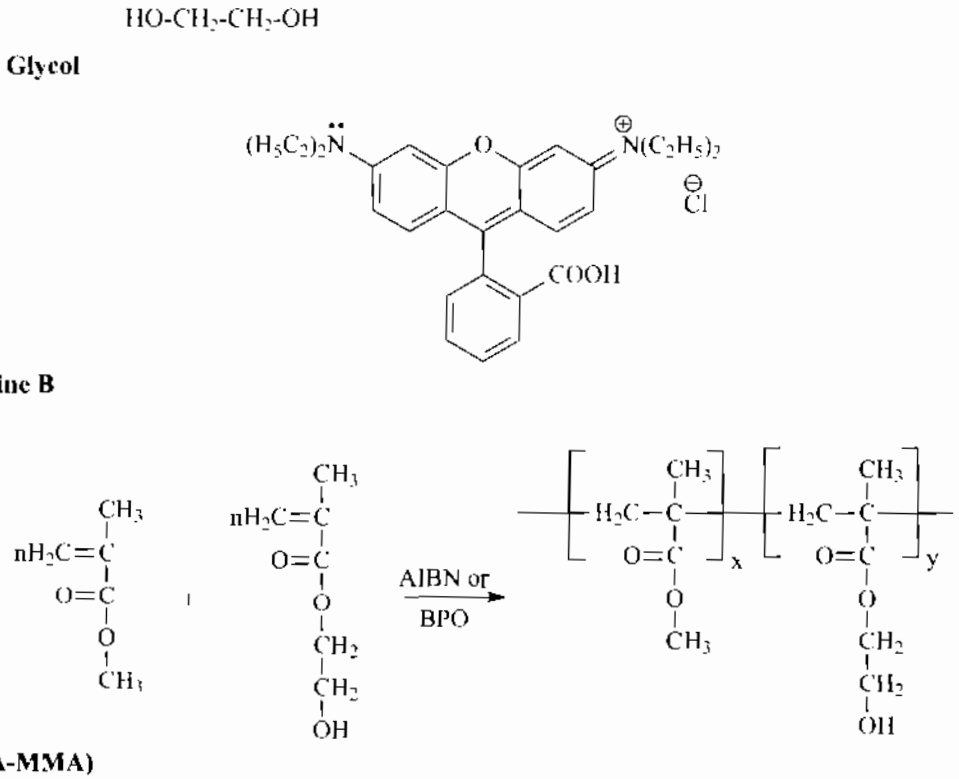

Fig.1. Structural formulae of Ethylene Glycol, Rhodamine B, and P(HEMA-MMA).

2.1 *Sample preparation*

The samples were prepared and copolymerized using two methods of polymerization, *conventional thermal method* (CTM) polymerization using oven and *γ-irradiation method* (GIM) polymerization using Cobalt 60.

The rhodamine B dye was dissolved in Ethylene glycol (EG) and left in ultrasonic water bath for two hours. The dye used was highly pure (>99%) as the impuities lead to a

decrease in lasing efficiency. The dye concentration was 5×10^{-5} M. This mixture then added to HEMA-MMA monomer mixtures (volume 1:1) for copolymerization. Larger dye concentration leads to aggregation of dye molecules to form dimmers thereby reducing the photostability of the host. 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 .The dye dissolution was carried out in asonicator.

Two samples were prepared. For the first sample, polymerization was brought about by conventional thermal method (CTM) using initiators 2, 2-azo bis isobutyronitrile (conc. 0.015 g/l). Polymerization process was carried out in cylindrical polypropylene mould where kept in oven under controlled temperature conditions for several days (40° for 5 days and 50° for 3 days) and cooled gradually for 6 hours to avoid thermal stress/strain. For the second sample, polymerization was brought abont by γ-irradiation method (GIM) without using initiator. In this case, polymerization process was carried out in cylindrical glass mould where kept in cobalt 60 under 8 kGy γ-irradiation condition. Two polymerized sample rods were formed with diameters of 12 mm and 20 mm length and optical quality surface was obtained by conventional grinding and polishing.

2.2 *Fluorescence spectra and lasing measurement*

The experimental setup for fluorescence and lasing measurements is shown in figure 2.

The excitation was performed using frequency-doubled Q-switched Nd:YAG laser model *LQ 129A* made by SolarLS, Belarus. It is capable of giving 10nm pulses of energy more than 170 *mJ*. The pump energy was rendered into a line image by a quartz cylindrical lens (f = 150 *mm*) and used to transversely excite the solid state dye laser samples.

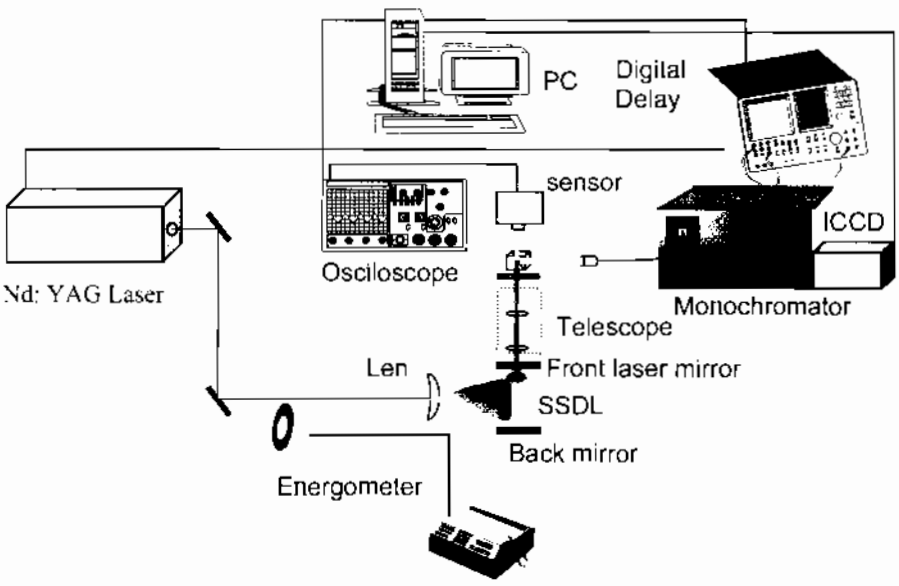

Fig. 2. Schematic diagram of solid state dye laser experimental setup.

The fluorescence and lasing generated out of the cavity was collected by fiber optics into monochromator/ICCD camera and sensor, respectively, and analyzed (10 μJ and 6mJ only were used to excite the samples to generate fluorescence and lasing, respeetively).

3. Results and Discussion

The GIM polymerization method used for copolymerizing HEMA-MMA/EG-RB sample has the following advantages:

1- The polymerization time was reduced from 8 days in the case of conventional thermal method (CTM) to less than 2 hours in the case of gamma irradiation method (GIM).
2- No initiator was used in the case of gamma irradiation method.
3- The cross link was enhanced due to the formation of free radieals by irradiation.

In the case of GIM method, several samples was tested to see the effect of polymerization process (from 1 kGy to 64 kGy dosages) using *cobalt 60* system. The complete polymerization occurred at around 8 kGy dosage. No sign of complete polymerization was recognized at less than 4 kGy dosage. The color of the dye inside the copolymer matrixes of the GIM samples was affected when dosage irradiation increased above 8 kGy. From the results of color measurement using color-meter device (CIE L* a* b* -system), it was clear there was not much difference between the colors of CTM sample and GIM- at 8 kGy, as shown in Table 1. The small differences between the two samples can be recognized from the refractive index difference, where n=1.5055±0.0002 and n=1.5033±0.0002 were measured for CTM and GIM samples, respectively, using Abbe refractometer.

Table .1 Color measurements of conventional thermal method (CTM) and γ-irradiation method (GIM) samples measured by color-meter device (CIE L* a* b* - system).

Color type	Color Scale	CTM sample	GIM sample
Lightness	From 0 (dark) to 100 (light)	49.76	47.31
Red-to-green	+90 (red) to – 90 (green)	-20.27	-17.68
Yellow-to-Blue	+90 (yellow) to -90 (blue)	16.09	13.30

Fluorescence spectra of P(MMA-HEMA)/EG-RB samples eopolymerized by GIM and CTM methods measured using 532 nm output wavelength from Nd:YAG laser is shown in fig. 3. The fluoreseence spectra for P(MMA-HEMA)/EG-RB sample copolymerized by GIM method reveals double increase in the intensity compared with P(MMA-HEMA) /EG-RB sample copolymerized by CTM method.

The fluorescence life times for SSDL P(HEMA-MMA)/EG-RB samples of concentration 5×10^{-5} M was determined. The incoherent fluorescence upconversion techniqne was used as in *ref.* [11]. The corresponding fluorescence lifetime for both SSDL samples P(HEMA-MMA)/EG-RB copolymerized by CTM and GIM methods were $\tau_F \approx 4.8$ ns and $\tau_F \approx 5$ ns, respectively. The spectra covers nearly the same range of wavelengths.

There are a red –shifted in GIM spectra by several nanometer.

Lasing speetra of P(MMA-HEMA)/EG-RB samples copolymerized by GIM and CTM methods measured using 532 nm output wavelength from Nd:YAG laser is shown in fig. 4. The lasing spectra for P(MMA-HEMA)/EG-RB sample copolymerized by GIM method reveals an increase in the intensity and red shifted by ≈ 3 nm compared with P(MMA-HEMA) /EG-RB sample copolymerized by CTM method.

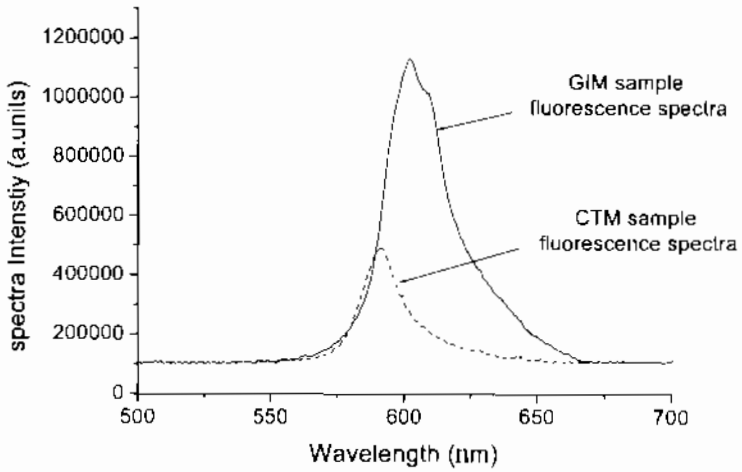

Fig. 3. Fluorescence spectra from samples prepared by γ-irradiation polymerization method (GIM) and conventional thermal polymerization method (CTM).

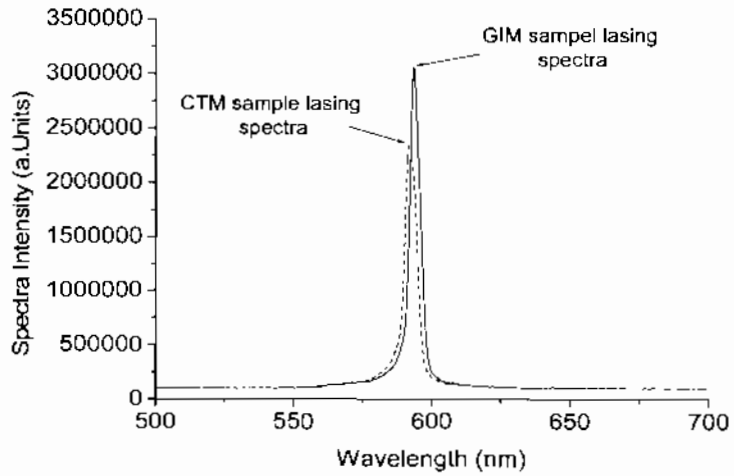

Fig. 4. Lasing spectra from samples prepared by γ-irradiation polymerization method (GIM) and conventional thermal polymerization method (CTM).

Conclusion

We have fabricated and synthesized solid state dye laser materials by γ-irradiation polymerization method without adding initiator. The consumed time in fabrication and synthesis bas been reduced by 90% by this method. We have shown that fluorescence and lasing intensities of GIM samples were higher than CTM samples synthesized by conventional thermal method using oven. The complete polymerization for GIM 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[12].

References

[1] **Soffer B.H.** and **McFarland B.B.**, *Appl. Phys. Lett.* **10(10)**, (1967), 266.

[2] **Peterson O.G.** and **Snavely B.B.**, *Appl. Phys. Lett.* **12(7)**, (1968), 238.

[3] **Gromov D.A., Dyumaev K.M., Manenkov A.A, Maslyukov A.P., Matyushin G.A., Nechitailo V.S.** and **Prokhorov A.M.**, *J. Opt. Soc. Am. B* **2(7)**, (1985), 1028.

[4] Dyumaev K.M., Manenkov A.A., Maslyukov A.P., Matyushin G.A., Nechitailo V.S. **and Prokhorov A.M.**, *J. Opt. Soc. Am. B* **9(1)**, (1992), 143.

[5] **Amat-Guerri F., Costela A., Figuera J.M., Florido F.** and **Sastre R.**, *Chem. Phys. Lett.* **209**, (1993), 352.

[6] **Costela A., Florido F., Garcia-Moreno I., Duchowicz R., Amat-Guerri F., Figuera J.M.** and **Sastre R.**, *Appl. Phys.* **B60**, (1995), 383.

[7] **Arnaud Dubois,** Micbeal Canva, Alain Brun, Frédéric Chaput and Jean-Pierre Boilot., *Appl. Opt.* **35(18)**, (1996), 3193.

[8] **Knobbe E.T., Dunn B., Fuqua P.D.** and **Nishida F.**, *Appl. Opt.* **29**, (1990), 2729.

[9] **Reisfeld R., Brusilovsky D., Eyal M., Mirron E., Burstein Z.** and **Ivri J.**, *Chem. Phys. Lett.* **160**, (1989), 43.

[10] **Duarte F.J., Taylor T.S., Costela A., Garcia-Moreno I.** and **Sastre R.**, *Appl. Opt.* **37** (1998), p. 18.

[11] **Al-ghamdi, A.A.** and **Bain A.J.**, *The International Symposium on Optical Science, Engineering, and Instrumentation.* SPIE's 43rd Annual Meeting, pp. 267-277, 19-24 July 1998.

[12] **Zhang Wei'an, Shen Xiaofeng, Li Yu,** and **Fang Yue'e,** *Radiation physics and chemistry*, **67** pp. 651-656, 2003.

تصنيع مواد ليزر صبغات الأجسام الصلبة بواسطة البلمرة بأشعة جاما

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المستخلص. تم استخدام طريقة البلمرة بواسطة أشعة جاما في تصنيع مواد ليزر صبغات الأجسام الصلبة نوع رودامينB المذابة في إثيلين الجلايكول المضافة في ثنائي هيدروكسي إيثيل ميثا أكريليت وميثايل ميثا أكريليت حيث تم مقارنة هذا التحضير بطرق البلمرة الحرارية المعتادة باستخدام الفرن. كما تم قياس ومناقشة طيف الفلورة والليزر المتولد ومعامل الانكسار واختلاف اللون.