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PHOTOACOUSTIC MEASUREMENT OF THERMAL DIFFUSIVITY OF LASING DYES R6G INCORPORATED IN POLY(METHYL METHACRYLATE)(PMMA) AND COPOLYMER OF METHYL METHACRYLATE(MMA) WITH 2-HYDROXYETHYL METHACRYLATE[P(MMA:HEMA)]

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ABSTRACT

The application of photoacoustic technique was demonstrated for measuring the thermal diffusivity of R6G doped in solid matrix poly(methylmethacrylate) *(PMMA) and copolymer of* methyl methacrylate*(MMA)* with 2-hydroxyethyl methacrylate*(HEMA) [P(MMA:HEMA)]. The thermal diffusivity value obtained for R6G-doped PMMA is higher than the copolymer of R6G-doped [P(MMA:HEMA)]. The optical spectra of the samples were measured by using a fibre optics spectrophotometer. The result shows that the R6G-doped [P(MMA:HEMA)] offers a good optical transmission and improved surface quality when compared to R6G-doped PMMA.*

Keyword*: Photoacoustic, thermal diffusivity, PMMA, P(MMA:HEMA)*

INTRODUCTION

Visible–wavelength tunable lasers have been used in spectroscopy, underwater sensing, medicine, and other fields. In the last decade there has been a renewed interest in the use of solid matrices containing lasing dyes to build practical tunable solid-state dye lasers as an attractive alternative to conventional liquid solution dye lasers. The broad visible tunability of solid-state dye lasers is readily exchanged to access different spectral regions with different lasing dyes (1,2).

Lasing has been reported for dyes doped in several different host materials including polymers, solgel, ormosil and xerogel glasses. The use of a synthetic polymer hosts for lasing dyes present a number of advantages such as compactness, manageability and lack of flammability. They also provide an inexpensive fabrication technique, which would facilitate miniaturization and the design of intergrated optical system (1,3).

One of the main concerns in recent research has been the search for particular lasing dyes and solid hosts that provide a high laser damage threshold and a long lifetime against photodegradation (1). Many promising new hosts have been investigated for laser performance, but often little is known of their thermal properties. In this paper we present photoacoustic measurement of thermal diffusivity of *poly (methylmethacrylate)*(PMMA) and copolymers of *methyl methacrylate* (MMA) with *2-hydroxyethyl methacrylate* (HEMA) [P(MMA:HEMA)] doped with the lasing dyes Rhodamine 6G (R6G).

PMMA is the most frequently used polymeric matrix for solid-state dye lasers. This matrix shows a good optical transparency in the visible spectra range and considering its laser damage resistance, it rank first among the polymers that could be employed as host materials in high power lasers (3). P(MMA:HEMA)] copolymers have recently been considered to be used as a solid-state dye laser-host. However, no detailed studies have been done of the thermal properties of these polymers. William *et al.* (1999) have reported that R6G doped P(MMA:HEMA)] copolymer shown to retain the excellent visible transparency of PMMA. In

comparison with other polymeric matrices, P(MMA:HEMA) also offers an improved surface quality and more uniform dye distribution. The particular advantages of these P(MMA:HEMA) copolymers are their compatibility with polar dyes and their high laser damage threshold. This is because when the PMMA matrix is modified by copolymerizing MMA with HEMA, the rigidity of the matrix increases, protecting the dye from bleaching by the polymer cage effect (4).

The PA technique is reported to be a versatile tool for optical and thermal characterization of a variety of samples. The PA technique makes use of the detection of acoustic waves generated by a modulated optical irradiation when it interacts with a sample kept inside a closed cavity. According to Rosencwaig-Gersho theory (5), for a thermally thick sample, the complex amplitude of the pressure variation inside the photoacoustic cavity is given by

$$Q= \frac{-i\beta\mu^2\gamma P_0 I_0}{4\sqrt{2}T_0 l'a'k} \tag{1}$$

where β and μ are the optical absorption coefficient and the thermal diffusion length of the sample, respectively. γ is the ratio of heat capacities of air; P_o and T_o are the ambient pressure and temperature, respectively; I_o is the incident light intensity and l' is the length of the gas column inside the cavity. The a' and k are the thermal diffusion coefficient of the gas inside the cavity and the thermal conductivity of the sample, respectively. We have selected the chopping frequency and the sample thickness in such a way that the sample under investigation is thermally thick in all the experiments. From the above equation, it is clear that under identical experimental conditions, the PA Signal amplitude is directly proportional to the optical absorption coefficient of the sample (6).

MATERIALS AND METHOD

PMMA, HEMA and R6G supplied by BDH (England) were used as received. In the present work, two different R6G-doped polymer samples were prepared, such as R6G doped PMMA polymer and R6G doped P(MMA:HEMA) copolymer. For R6G doped PMMA polymer samples, the amount of 2 g of PMMA were dissolved in 25 ml of chloroform. A dye solution with the concentration of 6.3×10^{-4} moll^{-1} was prepared. The mixture was vigorously stirred to afford a viscous solution that was then poured into a pettry dish and left in a dark room at room temperature for 24 hours. After 24 hours the solid samples were cut into pieces to the desired size and thickness.

In preparation the R6G doped P(MMA:HEMA)] copolymer sample, the R6G dye was first dissolved in a mixture of MMA and HEMA. The P(MMA:HEMA) copolymer was prepared in proportions 1:1 and the concentration of R6G in the solution was 6.3×10^{-4} moll^{-1}. The mixture was poured into a pettry disc and then kept in an oven maintained at 50°C for one week for thermal polymerization. The completely polymerized samples were cut into pieces to the desired size and thickness for further experiments.

Fig.1 shows the experimental set up used in the present study. The diode laser (B & W TEK INC) beam, which after being mechanically chopped by an optical chopper (SR540) was focused onto the sample kept inside a non-resonant PA cell. The photoacoustic signal generated in the closed cavity was detected using a sensitive microphone (Cirkit product, UK). The PA Signal was then processed using a lock-in amplifier (SR530). The photostability of the samples were first investigated at fixed chopping frequency 15Hz with 5 different laser powers (i.e 300mW, 290mW, 280mW, 270mW and 260mW). After laser irradiation for one hour, the photoacoustic signal for each PMMA sample was measured for the chopping frequency in the range of (10-150) Hz. The transmission and absorption spectra of each sample at different dye concentration were then measured by an uv-visible fibre optics spectrophotometer (OCEAN Optics).
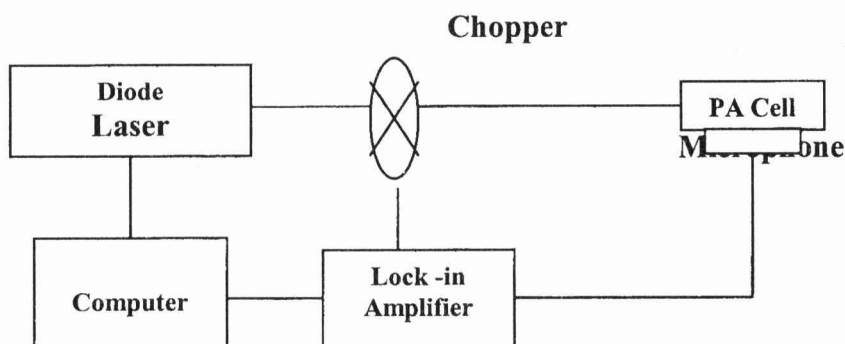
Chopper

Fig. 1. Schematic diagram of the experimental set-up.

RESULTS AND DISCUSSION

We first study the effect of laser power on photostability of the dye molecules at fixed chopping frequency 15Hz with five different laser powers 300mW, 290mW, 280mW, 270mW and 260mW. A plot of PA signal as a function of time with 290mW laser power for R6G doped PMMA and R6G doped P(MMA:HEMA)] is shown in Fig.2. The plot shows that there is no significant decrease in the PA signal with the increasing of time for both R6G-doped samples. This indicates that the dye molecules impregnated in both R6G-doped matrices remain photostable and do not show any noticeable photodegradation after laser irradiation. The value of the PA Signal is purely due to the contribution of the R6G-doped solid matrix. Mark *et al.* 1995 has shown that R6G is efficient and relatively stable laser action in both hosts used. These properties make it a highly photostable and efficient dye for both pulsed and continuous-wave laser actions.

After laser irradiation for one hour, the photoacoustic signals for both samples were measured as a function of chopping frequency in the range of (10-150) Hz. A plot of ln (PA Signal) as a function of ln $(f)^{1/2}$ is shown in Fig. 3. The detected photoacoustic signal at different laser power for both R6G-doped PMMA and R6G-doped P(MMA:HEMA) samples (300mW, 290mW, 280mW, 270mW and 260mW) varies as $\sim f^{-0.94}$ modulation frequency dependence. Thus the sample under investigation was thermally thick for all the frequency used due to the $\mu_s < l_s$.

Fig. 4 shows the PA signal phase as a function of the modulation frequency for both R6G-doped PMMA and R6G-doped P(MMA:HEMA) samples. From this figure, the thermal diffusivity of both samples was obtained from the fitting of the phase dependence on modulation frequency of a thermally thick sample. In this case the thermoacoustic phase contribution given by Silva *et al.* 1998 (7), can be simplified as

$$\Phi = \Phi_0 + \arctan \{ l_s [(\pi / \alpha_s) f]^{1/2} -1 \}^{-1} \qquad (2)$$

where Φ_0 is the initial phase, α_s is the thermal diffusivity, l_s is the sample thickness and f is the chopping frequency. The thermal diffusivity value obtained for R6G-doped PMMA samples is higher compared to R6G-doped P(MMA:HEMA) samples. The thermal diffusivity values for R6G-doped PMMA and R6G-doped P(MMA:HEMA) samples are 1.58×10^{-3} cm^2/s and 1.26×10^{-3} cm^2/s, respectively. The literature value of thermal diffusivity of pure PMMA is 1.50×10^{-3} cm^2/s (3).

The measured optical transmittance spectra of the R6G-doped PMMA sample is shown along with the R6G-doped P(MMA:HEMA) sample in Fig.5. From this figure, we observe that both of the PMMA and P(MMA:HEMA) samples show a good optical transmission from ~624nm to 800nm, but the transmission spectra of P(MMA:HEMA) sample (88%) is slightly higher than PMMA sample (82%). Furthermore, in comparison with PMMA sample, P(MMA:HEMA) sample shows a more stable and smooth transmission

curve from ~624nm to 800nm. This indicates that the P(MMA:HEMA) sample offers an improved surface quality and can be prepared to the same good optical quality as PMMA sample (1).

From Fig. 5, the peak of transmission for both of the samples occurs at wavelength 438nm. However, it is observed that the peak of transmission for PMMA sample is higher compared with P(MMA:HEMA) sample. The peak of transmission for PMMA sample and P(MMA:HEMA) sample show transmission of 40% and 24%, respectively. However, both of the samples have the same higher wavelength cutoff at ~565nm.

Fig.6 shows the plot of the optical absorption spectra for both of the PMMA and P(MMA:HEMA) samples. The leveling slope at the top of curves (a) and (b), are due to the saturation of the spectrophotometer. This is happen because of higher concentration of dye doped in these samples This observation agrees well with the one reported by Cazesca *et al.* 1997 (8), where the absorption maximum occurred in a range of 480nm to 570nm with the saturation absorption signals.

CONCLUSION

In this paper, we have measured the thermal diffusivity value for both R6G-doped PMMA and R6G-doped P(MMA:HEMA) by using the Phatoacoustic technique. The thermal diffusivity values for R6G-doped PMMA and R6G-doped P(MMA:HEMA) samples are 1.58×10^{-3} cm^2/s and 1.26×10^{-3} cm^2/s, respectively. This indicates that the thermal diffusivity value obtained for R6G-doped PMMA is higher than R6G-doped P(MMA:HEMA). Both of the R6G-doped PMMA and R6G-doped P(MMA:HEMA) samples show a good optical transmission from ~624nm to 800nm. The transmission spectra of a good surface quality of R6G-doped P(MMA:HEMA) (88%) is slightly higher than R6G-doped PMMA (82%).

ACKNOWLEDGMENT

REFERENCES

(8)   Cazesca, J., X.L. Jiang, J. Kumar, S.K. Tripathy. 1997. Epoxy matrix for solid-state dye laser applications. *App. Opt.* **36.** 4965-4968.

(4)   Costela, A., J.M. Figuera, F.Florido, I.Garcia-Moreno, R.Sastre. 1995. Thermal effects in optical phase conjugation in rhodamine 6G-doped copolymers of 2-hydroxyethyl methacrylate and methyl methacrylate. *Opt. Commun.* **119:** 265-274.

(3)   Guerri, F. A., A. Costela, J.M. Figuera and F. Florido, I. Garcia-Moreno and R. Sastre. 1995. Laser action from a rhodamine 640-doped copolymer of 2-hydroxyethyl methacrylate and methyl methacrylate. *Opt. Commun.* **114:** 442-446.

(2)   Mark, D. and T.A. King D.1995. Comparison of laser performance of dye molecules in sol-gel, polycom, ormosil, and poly(methylcrylate) host media. *App. Opt.* **34** 3193-3199.

(6)   Nibu, A. G., B. Aneeshkumar, P. Radhakrishnan and C.P.G. Vallabhan. 1999. Photoacoustic study on photobleaching of Rh6G doped in poly (methyl methacrylate). *J. Phys. D: Appl. Phys.* **32:** 1196-1200

(5)   Rosencwaig, A. and A. Gersho. 1976. Theory of the photoacoustic effect with solid. *J. Appl.* **47**: 64-69.

(7)   Silva, T.S., A.S. Alves, I. Pepe, H. Tsuzuki and O.Nakamura, M.M.F. d'Aguiar Neto, A. Ferreira da Silva, N. Veissid and C.Y. An. 1998. Thermal diffusivity of lead iodide. *J. Appl. Phys.* **83**: 6193-6195

(1)   William, J.W., S.M. Giffin, L.T. McKinnie, J.C. Sharpe, A.D. Woolhouse, T.G. Haskell and G.J. Smith. 1999. Thermal and optical properties of polymer hosts for solid-state dye lasers. *App. Opt.* **38**: 2504-2509
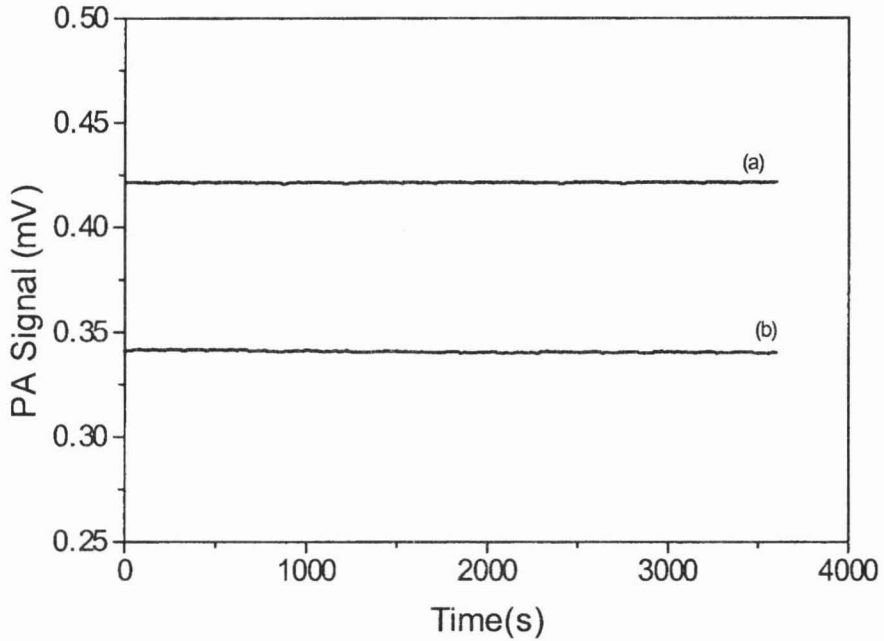
Fig.2 Plot of PA Signal as a function of time at laser power 290mW
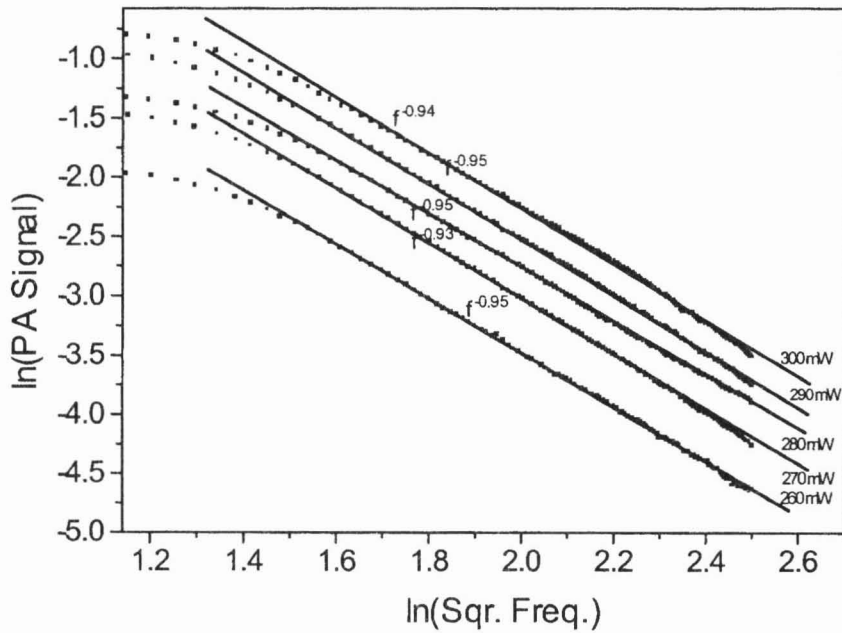for (a) R6G-doped PMMA and (b) R6G-doped P(MMA:HEMA) samples.

Fig.3. Plot of ln (PA Signal) as a function of ln $(f)^{1/2}$ at different laser
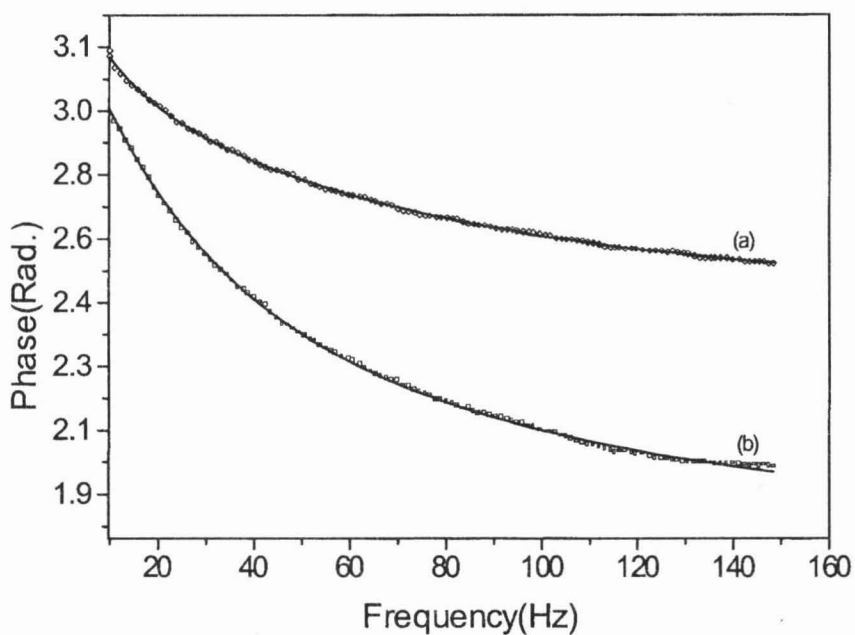power for R6G-doped P(MMA:HEMA) samples.

Fig. 4. Phase signal versus chopping frequency for (a) R6G-doped PMMA and (b) R6G-doped P(MMA:HEMA) samples. The solid curves represent the fit to the experimental data by Eq.(2).
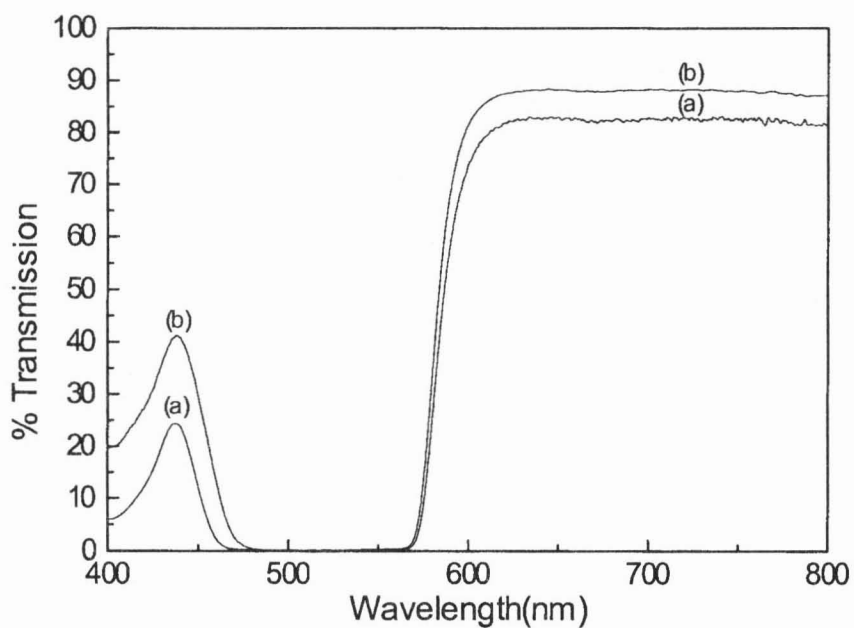

Fig.5.Transmission spectra of the (a) R6G-doped PMMA and (b) R6G-doped P(MMA:HEMA) samples.
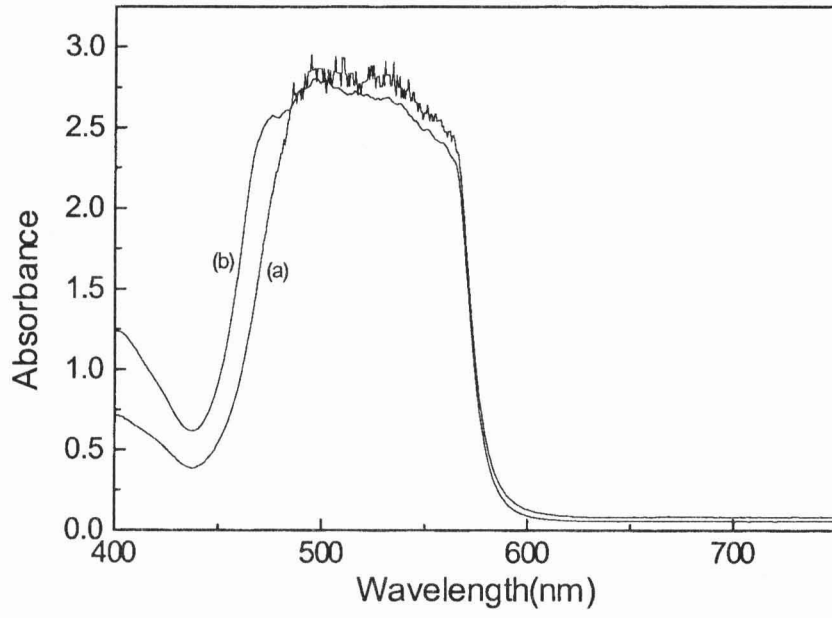
Fig. 6. Absorbance spectra of (a) R6G-doped PMMA and (b) R6G-doped P(MMA:HEMA) samples.