Measurement of Thermal Diffusivity, Optical Transmission and Optical Absorption Peaks of Laser Dyes R6G Doped in Poly (Methylmethacrylate) Using Photoacoustic Technique and Fibre Optics Spectrophotometer

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ABSTRAK

Dengan menggunakan teknik spektroskopi fotoakustik (PA), pengukuran peresapan terma Rhodamine 6G (R6G) didop dalam matriks pepejal poli(metilmetalkrilat) (PMMA) pada pelbagai kepekatan dilaporkan. Nilai peresapan terma didapati bertambah dengan kepekatan 'dye' disebabkan pertambahan penyerapan optik molekul 'dye' dalam matriks polimer. Spektrofotometer serabut optik, uv-sinar nampak juga digunakan untuk mengukur spektrum optik sampel. Hasil kajian menunjukkan bahawa transmisi penggal dalam kawasan merah (500-600) nm berganjak kepada jarak gelombang yang lebih tinggi bila kepekatan 'dye' bertambah. Transmisi maksimum (83%) didapati berlaku pada sampel PMMA yang didopkan dengan kepekatan 'dye' R6G yang paling rendah, iaitu 3.1×10^{-4} mol/l.

ABSTRACT

Using the photoacoustic (PA) spectroscopic technique, we report the thermal diffusivity measurement of the Rhodamine 6G (R6G) doped at different concentrations in solid matrix poly(methylmethacrylate) (PMMA). The value of the thermal diffusivity was found increasing with dye concentration due to the increase of optical absorption of dye molecules in the polymer matrices. A uv-visible fibre optics spectrophotometer was also used to measure the optical spectrum of the samples. The result shows that the transmission cut off in a red region (500-600) nm shifted to the higher wavelength when the dye concentration increased. The maximum transmission (83%) was observed for the PMMA sample doped with the lowest concentration of dye, i.e. 3.1×10^{-4} mol/l of R6G.

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INTRODUCTION

Organic dyes have been used for many years in both lasers and optically pumped amplifiers. A solid-state dye laser offers attractive qualities such as high quantum efficiency, a large choice of pump source, and a broad emission bandwidth. They are of continuing interest because of their capacity, with different dyes, to cover the spectrum from the ultraviolet to the infrared (Amaud *et al.* 1996; Mark and King 1995).

Solid-state dye lasers were first demonstrated as early as 1967 and have recently reached the commercial market. Numerous research works have been done for dyes doped in several different solid matrices including polymers, solgel, ormosil and xerogel glasses. Efficient solid-state dye lasers were recently obtained using polymeric matrices. One of the main concerns in recent research for particular laser dyes and solid hosts is to provide a high laser damage threshold and a long lifetime against photodegradation. The photostability of some organic laser dyes improves when molecules are trapped into solid matrices (William *et al.* 1995; Cazeca *et al.* 1997). Poly (methyl methacrylate) (PMMA) is a well-known polymeric matrix that is the most commonly used for solid-state dye lasers. It has a good optical transparency and a lower laser damage threshold. Rhodamine 6G (R6G) is the most widely employed laser dye in recent years. R6G is a xanthene derivative with an optical absorption peak in ethanol at 530 nm and a fluorescence peak at 556 nm. It has a high fluorescence quantum yield ($\approx 95\%$), a low intersystem crossing rate and low exited-state absorption. These properties make it a highly efficient dye for both pulsed and continuous-wave laser actions (Mark *et al.* 1995).

Thermal diffusivity is a unique property for each material and the diffusion of heat in the material is an important transport property that has a major concern for the manufacturing technology. In this paper, we report the thermal diffusivity measurement using the photoacoustic technique for poly(methyl methacrylate)(PMMA) doped with Rhodamine 6G (R6G) at different concentration levels. We also investigated the optical transmittance and absorbance spectrum of the sample using a uv-visible fibre optics spectrophotometer.

MATERIALS AND METHODS

The PA technique is reported to be a versatile tool for optical and thermal characterization of a variety of solid 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 (Rosencwaig and Gersho 1976), for a thermally thick sample, the complex amplitude of the pressure variation inside the 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_0 and T_0 are the ambient pressure and temperature, respectively. I_0 is the incident light intensity and l' is the length of the gas column inside the cavity; 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 (Nibu *et al.* 1999).

The absorption characteristic of materials under normal circumstances can be represented by the equation:

$$A = \log_{10}\left(\frac{I_0}{I}\right) \tag{2}$$

where I_0 is the intensity of the incident radiation and I is the intensity of the radiation transmitted through the sample. The quantity $\log_{10}(I_0/I)$, which is measured directly by the uv-visible spectrophotometers, is called the absorbance (A) or the optical absorption. Transmission (T) is a measurement of how much light is transmitted through a sample. Common applications include the measurement of transmission and absorption of light through the optical filters, optical coatings, and other optical elements such as lenses and fibers (Norman and Mckellar 1980).

PMMA and R6G (BDH Chemicals) were used as received. Two grams of PMMA were dissolved in 25 ml of chloroform. Solutions of five different R6G dye concentrations (3.1×10^{-4} mol/l, 6.3×10^{-4} mol/l, 1.9×10^{-3} mol/l, 3.1×10^{-3} mol/l and 6.3×10^{-3} mol/l) were prepared. Each solution was vigorously stirred to afford a viscous mixture that was then poured into a petry dish and kept in the dark at room temperature for the solvent to be evaporated. After 24 h, the completely solid samples were cut into pellet-shape pieces, 10 mm in diameter and (0.47-0.50) mm in thickness for further measurements.

The experimental set up used for the present study is shown in *Fig. 1*. The diode laser (B & W TEK) 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). The PA signal was then processed using a lock-in amplifier (SR530). The photostability of the samples was first investigated at fixed chopping frequency (i.e. 15 Hz) for 5
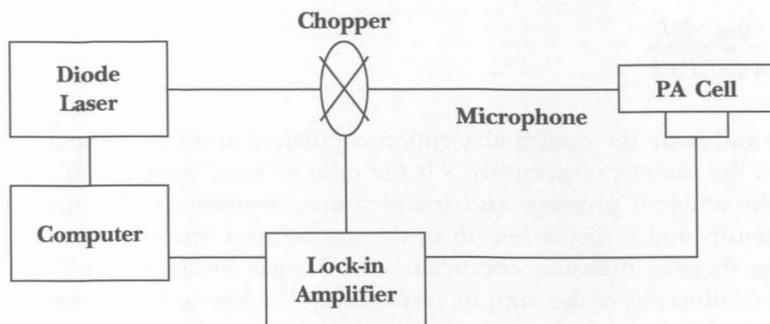
Chopper

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┌──────────┐        ╲ ╱                        ┌──────────┐
│  Diode   │─────────╳──────────────────────────│ PA Cell  │
│  Laser   │        ╱ ╲          Microphone     └────┬─────┘
└────┬─────┘                                         │
     │                                               │
┌────┴─────┐         ┌──────────────┐                │
│ Computer │─────────│   Lock-in    │────────────────┘
└──────────┘         │  Amplifier   │
                     └──────────────┘
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Fig. 1. Schematic diagram of the experimental set-up

different laser powers; 300 mW, 290 mW, 280 mW, 270 mW and 260 mW. After laser irradiation for 1 h, the photoacoustic signal for each PMMA sample was measured for the chopping frequency in the range of (10-150) Hz.

A uv-visible spectrophotometer is a device for measuring spectra; it enables quantitative measurement of light intensities to be made at different wavelengths. In the present study, a uv-visible fibre optics spectrophotometer (OCEAN Optics, S2000) was used to measure the transmission and absorbance spectra of each sample at different dye concentrations. It consists of a uv-visible light source, optical fibre and diode arrays detector, which was interfaced to a personal computer. The acquired data is then displayed and analysed by using the OOIBase software provided by the system.

RESULTS AND DISCUSSION

First, we measured the PA signals as a function of time for five samples with different dye concentrations at a fixed chopping frequency (i.e. 15 Hz). We also measured the variation of PA signals with time for each sample with five different beam powers. The PA signal observed does not significantly change with the increasing time. This indicates that the R6G-doped PMMA samples are stable and do not show any noticeable photodegradation after being exposed to laser irradiation. Thus the value of the PA signal is purely due to the contribution of the R6G-doped PMMA matrix. Therefore this observation confirmed that R6G is a potential candidate for relatively stable laser action in the host used. These properties make it a highly photostable and efficient dye laser medium for both pulsed and continuous-wave laser actions (Mark *et al.* 1995).

A plot of ln (PA Signal) as a function of ln $(f)^{1/2}$ for each sample is shown in *Fig. 2*. The detected photoacoustic signal for the doped sample exhibits $f^{-0.88}$, $f^{-0.93}$, $f^{-0.97}$, $f^{-1.01}$ and $f^{-1.07}$ modulation frequency dependence on increasing dye concentration. This confirmed that the samples used in this study were thermally thick samples.

Since our samples are thermally thick (470 - 500) μm, the thermal diffusivity of each PMMA sample was obtained by fitting the experimental data to the
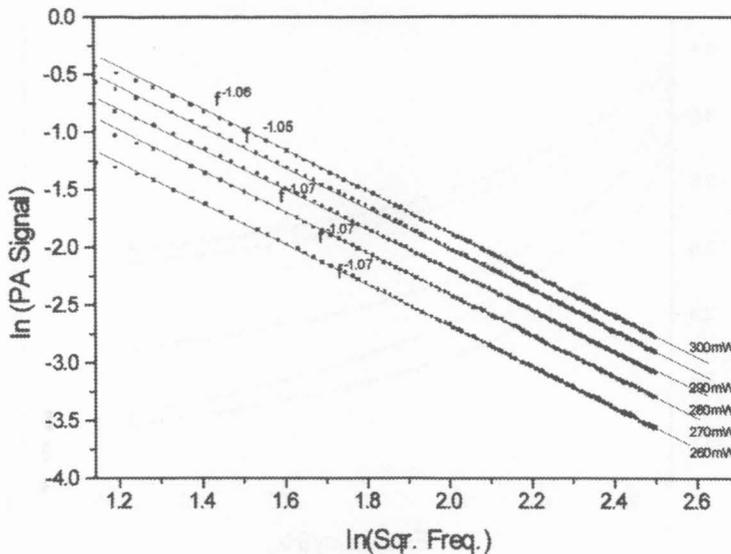
Fig. 2.   Plot of ln (PA Signal) as a function of ln (f)$^{1/2}$ at different laser power for sample at dye concentration 6.3x10^3 mol/l

phase-frequency dependent relation given by Silva *et al.* (1998). This relationship was only considered for thermally thick samples, which is applied to the present condition, i.e.

$$\Phi = \Phi_o + \arctan \{ \, L_s \, [(\, \pi \, / \, \alpha_s) \, f]^{1/2} - 1\}^{-1} \qquad (3)$$

where Φ_o is the initial phase, α_s is the thermal diffusivity, L_s is the sample thickness and f is the chopping frequency. *Fig. 3* shows the phase signal as a function of chopping frequency for different concentrations of R6G doped PMMA samples. The thermal diffusivity values obtained for these samples at different dye concentrations are 1.48×10^{-3} cm^2/s, 1.58×10^{-3} cm^2/s, 1.83×10^{-3} cm^2/s 2.05×10^{-3} cm^2/s and 2.17×10^{-3} cm^2/s, respectively. A plot of the thermal diffusivity as a function of dye concentration is shown in *Fig. 4*. The thermal diffusivity appears to increase with increasing dye concentration in PMMA samples. The plot can be described by an empirical relationship as:

$$\alpha = (1.38 \times 10^{-3}) + 0.298C - 27.34C^2 \qquad (4)$$

where C is the dye concentration in mol/l. The thermal diffusivity value for an undoped PMMA sample could be estimated by extrapolating the curve to C = 0, and the value obtained for the undoped PMMA samples was ~1.38×10^{-3} cm^2/s. This is about 17% higher than the value calculated from the value of k, ρ and C_p of pure PMMA (Costela *et al.* 1995).
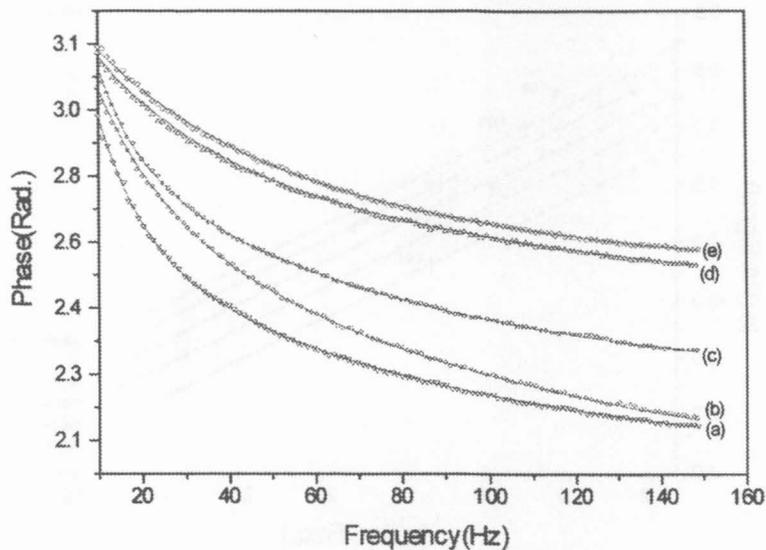
Fig. 3. Phase signal versus chopping frequency for R6G doped PMMA samples at different dye concentrations: (a) 3.1×10^4 mol/l; (b) 6.3×10^4 mol/l; (c) 1.9×10^3 mol/l (d) 3.1×10^3 mol/l (e) 6.3×10^3 mol/l. The solid curves represent the fitting of the experimental data to Eq.(3)

Fig. 4. Thermal diffusivity versus the concentration of dye R6G doped in PMMA samples
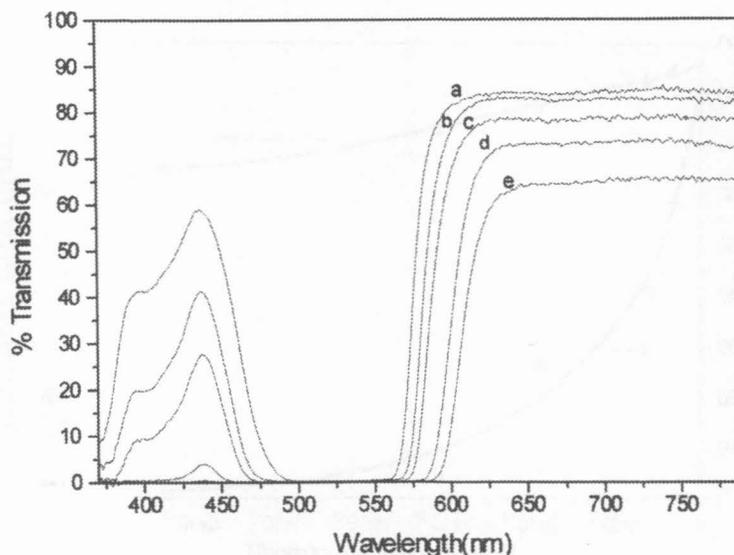
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*Fig. 5. The transmission spectra of the R6G doped PMMA samples
at different concentrations: (a) 3.1x10⁴ mol/l; (b) 6.3x10⁴ mol/l;
(c)1.9x10³ mol/l   (d)   3.1x10³ mol/l   (e) 6.3x10³ mol/l*

Fig. 5 shows the measured transmittance spectra of the samples at different dye concentrations. For $\lambda > 650$ nm, the measured optical transmissions were 83%, 82%, 77%, 73% and 65%, i.e. they decrease with increasing dye concentration. The cut-off transmission occurred in the range of (500-550) nm and became broader when the concentration of dye increases. This material could be a good filter for laser beams, particularly for Ar^+ ion laser with the output of 514 nm. The transmission peak seems to occur at wavelength 438 nm. This peak height decreased with increasing dye concentration as shown in *Fig. 6*. *Fig.* 6 also shows that for $\lambda > 650$ nm, the decreasing of transmission is linear with the dye concentration. The absorbance spectra for R6G–doped PMMA samples at different dye concentrations are shown in *Fig.* 7. The plateau at the top of curves at dye concentrations 3.1×10^{-3} mol/l and 6.3×10^{-3} mol/l is due to the saturation of the spectrophotometer signal, resulting from the higher concentration of dye doped in the samples (Cazeca *et al.* 1997). Obviously, the observed maximum absorbance for R6G-doped in PMMA samples occurred at the wavelength centered around 526 nm.

CONCLUSION

The results presented in this paper lead to two main conclusions. First, the photoacoustic technique is efficient in measuring the thermal diffusivity of polymer samples. Thus it has been used for measuring thermal diffusivity of
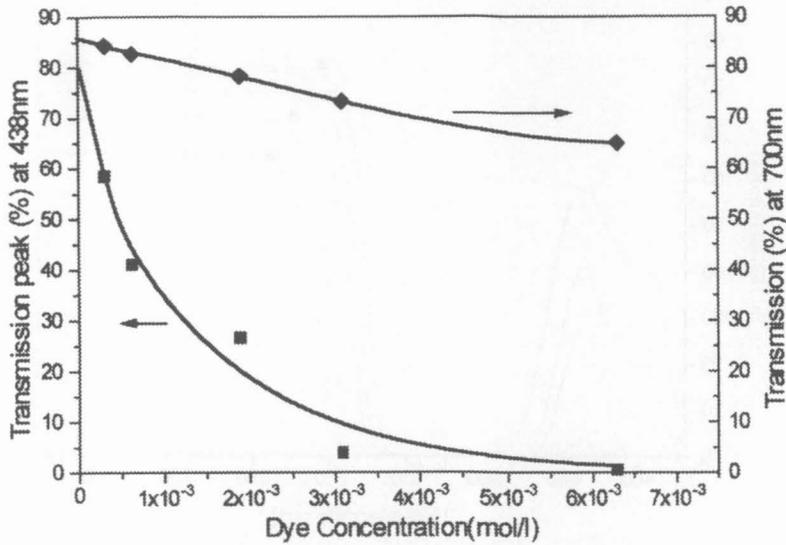
Fig. 6. Optical transmission of PMMA samples doped with
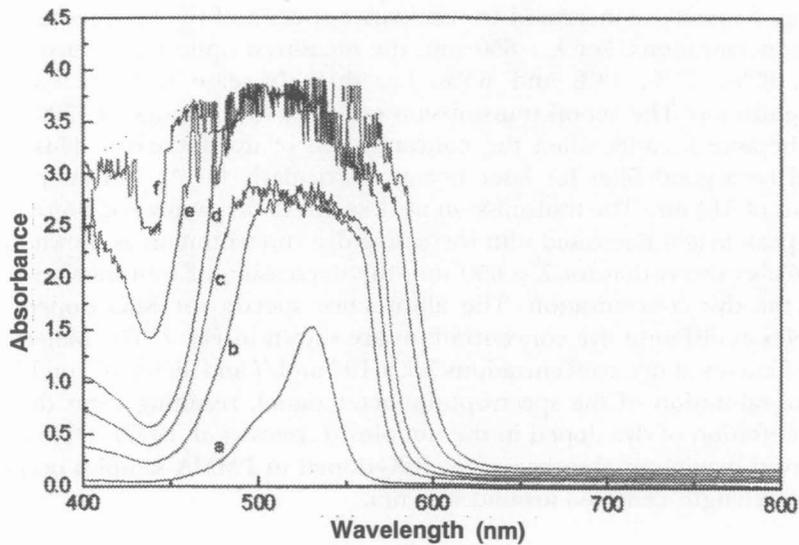different concentration of R6G

Fig. 7 Absorbance spectra of the R6G doped PMMA sample at different dye concentrations:
(a) pure R6G in ethanol (b) 3.1×10^4 mol/l ; (c) 6.3×10^4 mol/l;
(d) 1.9×10^3 mol/l ; (e) 3.1×10^3 mol/l; (f) 6.3×10^3 mol/l

R6G in solid matrix PMMA. We also observed that the thermal diffusivity values of R6G doped in solid matrix PMMA increased with increasing dye concentration and this was due to the increase of optical absorption of the polymer matrices.

In the spectrophotometer measurement, the result shows that the transmission cut-off in a red region (500-600) nm shifted to the higher wavelength when the dye concentration increased. The optical transmission for $\lambda > 650$ nm decreased linearly with the increasing of dye concentration. The maximum value of optical transmission (i.e. 83%) was recorded for PMMA sample doped with the lowest concentration of dye, i.e. 3.1×10^{-4} mol/l.

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