



Gain studies of Rhodamine 6G dye doped polymer laser

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Received 21 May 1998; received in revised form 8 February 1999; accepted 26 February 1999

Abstract

Solid state dye doped polymer is an attractive alternative to the conventional liquid dye solution. In this paper, the laser characteristics of Rhodamine 6G (Rh6G) doped polymethyl methacrylate (PMMA) rods, modified with ethyl alcohol (EtOH), are examined by nitrogen laser, and second harmonic Nd : YAG laser excitations in a transverse pumping configuration and the variation of small signal gain of the dye in solid medium for different pump powers are studied. The photobleaching of dye doped polymer rod is also studied. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Dye lasers; Optical polymers; Solid dye lasers

1. Introduction

The use of solid matrix for dye lasers gets rid of many of the common problems associated with static or flowing liquid systems like evaporation, flow fluctuation stagnant films, solvent or dye poisoning and even explosion. Simple organic polymer hosts or plastics used as host material for dye lasers provide an alternative to the conventional liquid dye lasers. One of the important advantages of transparent polymers compared with traditional optical materials (inorganic glasses and crystals) is that it is possible to introduce organic dyes that play the role of active components into polymers, which appreciably changes the characteristics of the polymer matrix [1–3]. Different organic polymers can be used as solid host material and the most frequently used polymeric material is polymethyl methacrylate (PMMA) because of its best optical transparency and resistance to laser damage. The low solubility of the majority of the conventional laser dyes in PMMA causes some limitations. Good solubility of dyes are achieved by introducing modifying additives which also enhances laser damage resistance [4]. Ethyl alcohol is chosen as an additive because it combines good solubility for xanthene dyes and enhancement of host laser damage resistance. Dymau et al. [4] studied the lasing efficiency, photodestruction and photobleaching of Rh6G doped polymer rods under second harmonic Nd : YAG laser (longitudinal) excitation. Since gain is an intrinsic parameter of the medium independent of the

spectral response of the detectors, measuring gain is one of the most useful parameters for intercomparison of different laser media. No work on gain studies in solid environment has so far been reported. In this paper small signal gain of Rh6G in solid matrix, in liquid matrix under nitrogen laser excitation (337.1 nm) and in solid matrix under Nd : YAG (532 nm) laser excitation are studied. The photobleaching of Rh6G dye doped polymer rods under nitrogen laser excitation and second harmonic of Nd : YAG laser excitation are studied.

2. Experimental procedure

2.1. Synthesis of dye doped polymer rods

The monomer used for synthesis of dye doped polymer is methyl methacrylate (MMA) whose structure is shown in Fig. 1(a). The dye chosen is laser grade Rhodamine 6G (Rh6G) supplied by Exciton, whose structure is shown in Fig. 1(b). 6 mM concentration of Rh6G in ethanol and in a mixture of MMA and EtOH are prepared and absorption and emission spectra of these solutions are recorded by using Hitachi U2000 spectrophotometer and Hitachi F2000 spectrofluorometer, respectively. These spectra are shown in Fig. 2. The peak wavelength of absorption and emission spectra are tabulated in Table 1.

The dye doped polymer rods are synthesized by thermal polymerisation method. The initial MMA compositions is cleared of foreign inclusions. MMA and EtOH are taken in the ratio 4 : 1 (v/v) and 6 mM concentration of Rh6G in this

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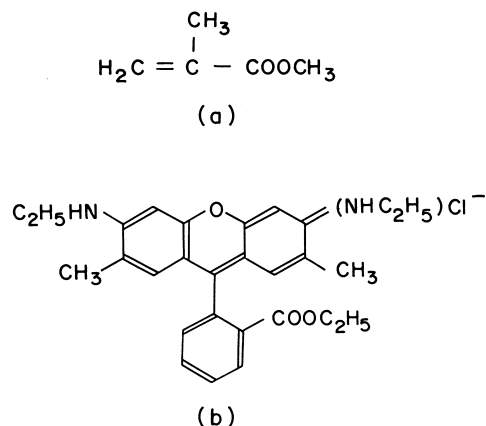


Fig. 1. (a) Structure of methyl methacrylate. (b) Structure of Rh6G.

mixture is prepared. 1 gm of benzoyl peroxide per 100 ml of the solution is used as an initiator for polymerization. The solution is taken in polymerising tubes and kept in nitrogen atmosphere. Thermal polymerization is carried out in a thermostat controlled water bath (solid state laboratory bath). The temperature of the water bath is maintained at 50°C and the polymerization occurred in 24 hours. Polymer rods of length 2 cm and diameter 1.5 cm; length 3.5 cm and diameter 1.5 cm are obtained. The rods are polished to the optical quality required, and these are shown in Fig. 3. The absorption and fluorescence spectra for solids are obtained as explained by Costala [3,10].

2.2. Dye doped polymer laser (DDPL)

The dye doped polymer (DDP) rods, thus fabricated is pumped by nitrogen laser, built by us, radiating at 337.1 nm

Table 1
Spectral characteristics of Rh6G

Solvent	Peak wavelengths of			
	Absorption (nm)	Fluorescence (nm)	ASE (nm)	Gain (cm ⁻¹ kW ⁻¹)
EtOH	532	570	580	1.66
MMA	535	553	Not lasing	–
MMA and EtOH	531	570	580	0.7
PMMA	526	566	Not lasing	–
PMMA + EtOH	514	586	585	0.28

and operated at a repetition rate of 1 pulse per second with pulse duration of 10 ns using transverse pumping configuration. The nitrogen laser output is focused by a cylindrical quartz lens of focal length 5 cm onto the rod. This produces a line shaped image of uniform intensity and the dye laser output is obtained at right angles to the pump laser beam. The peak wavelength of laser emission is measured by using a spectrograph and is found to be 585 nm, and tabulated in Table 1. The amplified spontaneous emission (ASE) spectra is recorded on a photographic film and is shown in Fig. 4(a). Hg is shown for reference in Fig. 4(b).

2.3. Gain studies

A single pass gain measurement using the ASE method proposed by Shank et al. [5] is used to calculate the small signal gain of dye Rh6G in polymer medium. The experimental set-up to measure gain for dye in liquid medium has been described previously [6]. The same method is adopted here. The dye doped polymer rod is placed on the platform of dye stand and kept in a slanting position to avoid optical

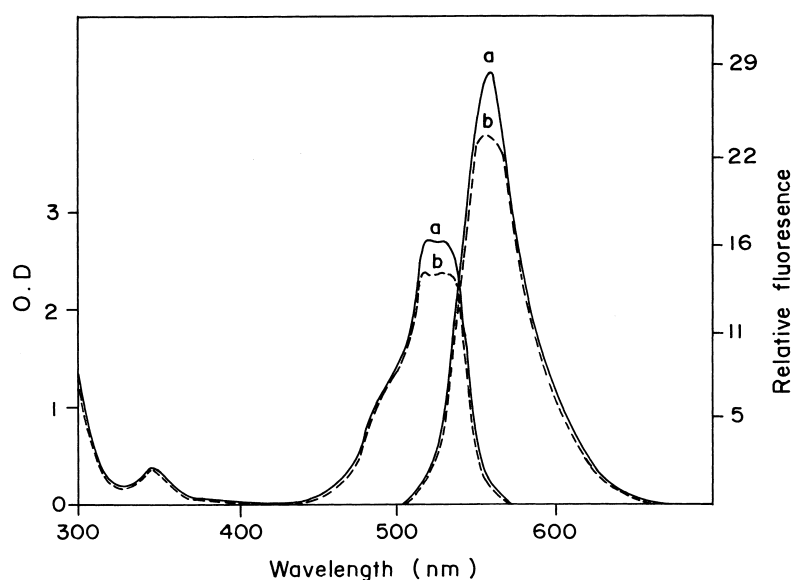


Fig. 2. (a) Absorption and fluorescence spectra of Rh6G in EtOH. (b) Absorption and fluorescence spectra of Rh6G in a mixture of MMA and EtOH solution.

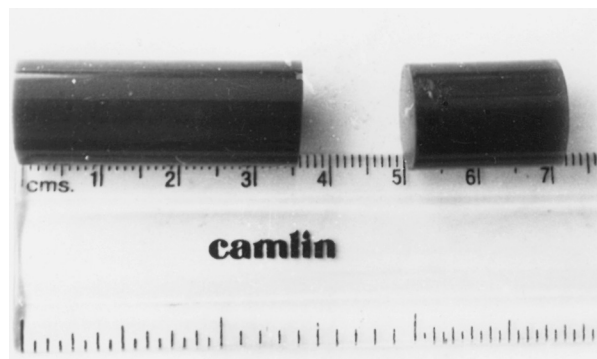


Fig. 3. Photograph of rhodamine 6G doped poly methyl methacrylate rods.

feedback. The DDP rod is pumped with a focused line image of the laser radiation, which is produced by a cylindrical lens of focal length 5 cm. The length of the pumped region of the DDP rod is varied from 0 to 20 mm by using a beam block mounted on a micrometer. The pumped region of the DDP rod had a uniform intensity of pumping. Care is taken to see that there is no unpumped region of the DDP rod at the monitored end of the DDP rod, thus preventing the reabsorption of the emitted light. To determine the gain at any wavelength, the amplified spontaneous emission intensities $I_1(\lambda)$ and $I_2(\lambda)$ for active lengths l_1 cm and l_2 cm, respectively of the pumped region of the DDP rods are measured using monochromator (CEL 3134), photomultiplier (RCA 931A) and oscilloscope (ECIL-05-768A) set up. The active lengths of DDP rods are kept at 10 and 20 mm and always ensuring that the gain is unsaturated. The gain is computed using the equation

$$\frac{I_1(\lambda)}{I_2(\lambda)} = \frac{[\exp(G(\lambda)l_1) - 1]}{[\exp(G(\lambda)l_2) - 1]} \quad (1)$$

A graph is drawn between nitrogen laser intensity and gain per unit length $G(\lambda)$ and is shown in Fig. 5(a). The

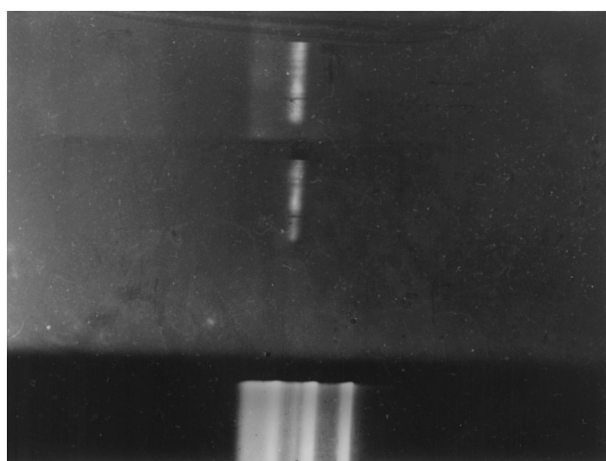


Fig. 4. Spectroscopic recording of (a) ASE of Rh6G polymer rods under nitrogen laser excitation. (b) Hg spectra.

gain varies linearly with pump intensity. The gain per unit length of Rh6G dye doped polymer excited by nitrogen laser is $0.28 \text{ (cm)}^{-1} \text{ (KW)}^{-1}$. The gain data is tabulated in Table 1.

In order to compare the gain of dye Rh6G in solid matrix with that of Rh6G in liquid solution (under nitrogen laser excitation), the gain experiment is repeated for Rh6G in liquid medium. 6 mM concentration of Rh6G in EtOH and the same concentration of Rh6G in a mixture of MMA and EtOH (4 : 1) are prepared. The peak wavelength of ASE emission of Rh6G in these solutions under nitrogen laser excitations are measured and tabulated in Table 1. Gain measurements are repeated for liquid medium. The active lengths of the liquid dye medium are kept at 5 and 10 mm. The gain is computed using the Eq. (1). The variation of gain of Rh6G in EtOH with that of nitrogen laser power is shown in Fig. 5(c). The gain per unit length per kW power of Rh6G in EtOH is $1.66 \text{ (cm)}^{-1} \text{ (kW)}^{-1}$. The variation of gain of Rh6G in MMA and EtOH mixture with nitrogen laser power is shown in Fig. 5(b). The gain per unit length per kW power of Rh6G is $0.7 \text{ (cm)}^{-1} \text{ (KW)}^{-1}$. The results show that gain of Rh6G in EtOH is higher than that in a mixture of MMA and EtOH and the gain of Rh6G in solid matrix (PMMA) is much lesser than that of Rh6G in liquid medium (MMA + EtOH). This may be due to the presence of MMA. In liquid solution the molecules are homogeneously mixed, but in solid matrix it is inhomogeneously mixed and the chemical structure and physical properties of polymer matrices have effect on the position of absorption and emission peak of a dye [7]. The spectral characteristics of the lasing dyes in polymer depend not only on intramolecular interaction in individual dye molecules but also on intermolecular interaction in dye molecules and macro molecules. The intermolecular interaction may crucially affect the laser characteristics of the dye molecules, these characteristics are determined by degree of overlap of dyes absorption and fluorescence bands. Polymerization causes a decrease in the dielectric constant ($\epsilon_{\text{MMA}} = 4$, $\epsilon_{\text{PMMA}} = 2.9$) and this results in a shift of equilibrium between dye monomer molecules and their aggregates towards the latter [8]. The decrease in dielectric constant of the medium causes the decrease of gain [9]. Hence the gain of dye molecule in solid PMMA is lesser than that in liquid medium. The dielectric constant of MMA + EtOH is lesser than that of EtOH. Hence the gain of Rh6G in the mixture of MMA and EtOH is lesser than that in EtOH.

The gain measurement is repeated by exciting the DDP rod by second harmonic output of Nd : YAG laser (Continuum model No. 10 surlite, $\lambda = 532 \text{ nm}$, energy 200 mJ, pulse width 7ns). The active lengths of the rod used are kept at 10 and 20 mm, always ensuring that the gain is unsaturated. The gain is computed using Eq. (1). The variation of gain with Nd : YAG laser intensity is shown in Fig. 6. The gain varies linearly with input power and saturated for higher powers. The calculated gain per unit length for the unsaturated region is found to be $5 \text{ (cm)}^{-1} \text{ (MW)}^{-1}$. The small

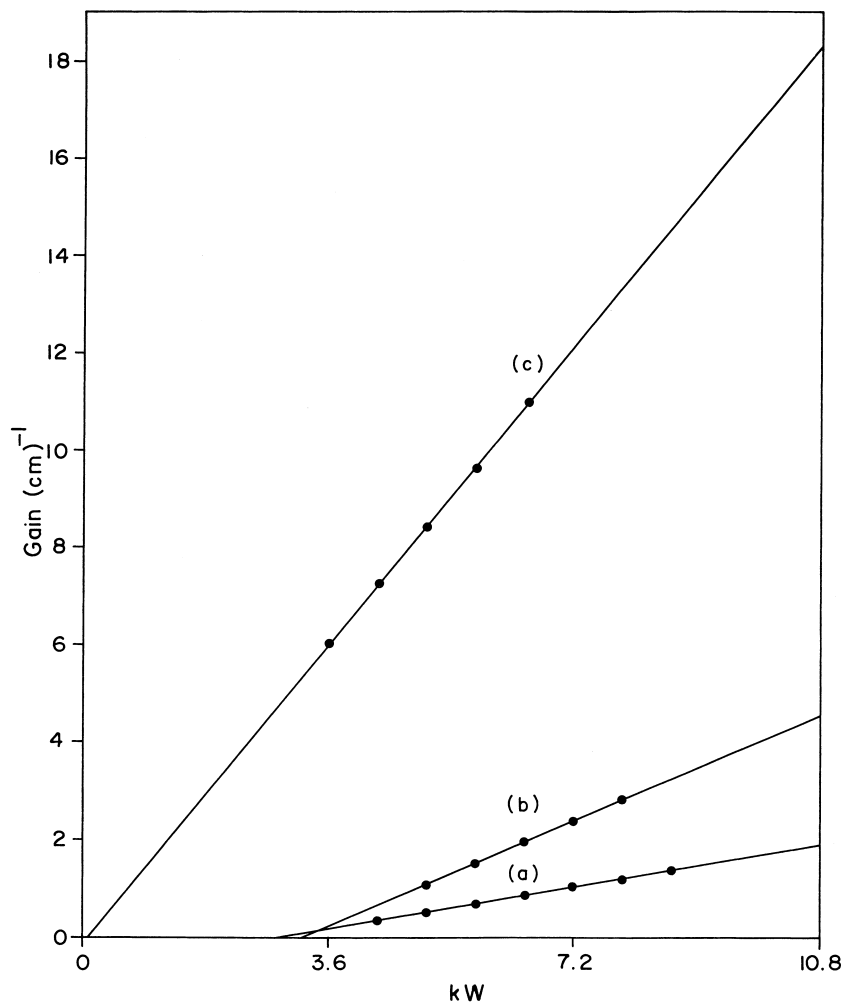


Fig. 5. Under nitrogen laser excitation (a) variation of gain of Rh6G polymer rod (b) variation of gain of Rh6G in MMA and EtOH solution. (c) Variation of gain of Rh6G in EtOH.

signal gain of Rh6G in PMMA under 2nd harmonic Nd : YAG laser excitation is lower than that under nitrogen laser excitation.

2.4. Dye photobleaching

In order to study the photobleaching effect of the dye the nitrogen laser beam is focused by a quartz cylindrical lens of 5 cm focal length, on the DDP rod, which is rigidly fixed. The repetition rate of nitrogen laser is kept at 1 Hz and the power is kept constant. The radiation intensity is kept at $5 \times 10^5 \text{ W cm}^{-2}$. The length of the excited region is 2 cm. The ASE output of DDP rod traverses a distance of 1 m before being apertured by a pin hole on the outside of the monochromator (CEL 3134) and detected with a photomultiplier tube (RCA 931A). The time integrated signal from the photomultiplier is fed to one of the channel of the cathode ray oscilloscope (ECIL-05-768A). The amplitude of dye laser output (ASE intensity) displayed on Channel 1 is noted down when Channel 2 indicates the required nitrogen laser

pump power. The output intensity of the laser is measured continuously with number of excitation pulses. The variation of ASE intensity with number of pump pulses are shown in Fig. 7(a). The output intensity decreases by 20% of its initial value after 1500 pulses the same decreases by 50% after 5000 pulses, and decreases by 80% after 7800 pulses. The same experiment is repeated by exciting the rigidly fixed DDP rod with second harmonic Q-switched Nd : YAG laser (532 nm). The repetition rate is kept at 1 Hz. The radiation intensity is kept at $2 \times 10^8 \text{ W cm}^{-2}$. The output power of the dye doped polymer rod for constant Nd : YAG power is continuously measured. The output intensity of dye doped polymer laser decreases by 20% of its initial value after 375 pump pulses and by 50% of its initial value after 1140 pump pulses. The variation of output power with number of pump pulses are shown in Fig. 7(b). The DDP rod is exposed to 2nd harmonic output of mode locked Nd : YAG laser (Continuum energy 11 mJ, pulse width 35 ps). The repetition rate is kept at 1 Hz. The radiation intensity is kept at $3 \times 10^9 \text{ W cm}^{-2}$. The dye laser output

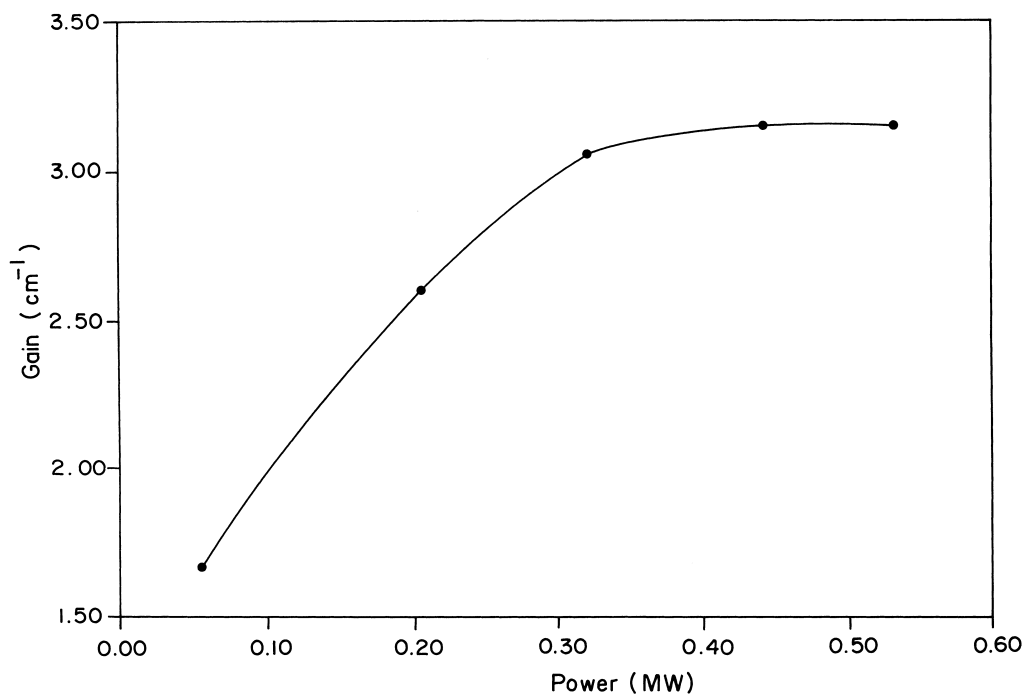


Fig. 6. Variation of gain of Rh6G polymer rod with 2nd harmonic Nd : YAG laser excitation.

intensity decreases by 100% after 10 pump pulses. The main cause of degradation of dyes in polymeric matrices is the thermal destruction of the dye due to poor heat dissipation in the polymer host [10]. It was established that the photobleaching rate is linearly dependent on radiation intensity J and that at relatively low radiation intensity ($J < 10^6 \text{ W/cm}^2$) the dye destruction occurs from first excited state (singlet or triplet) electron state. At higher intensities ($J > 10^7 \text{ W/cm}^2$)

saturation of $S_0 S_1$ transition (S_0 is the ground state and S_1 is the excited singlet level) is enhanced, and the dye molecule are excited into higher singlet S_n states. As a result dye photobleaching occurs from S_n states. Also two photon excitation of the dye molecules can give rise to electron energy transfer from dye molecule to the macro molecules with a subsequent vibrational relaxation of the first excited state [4].

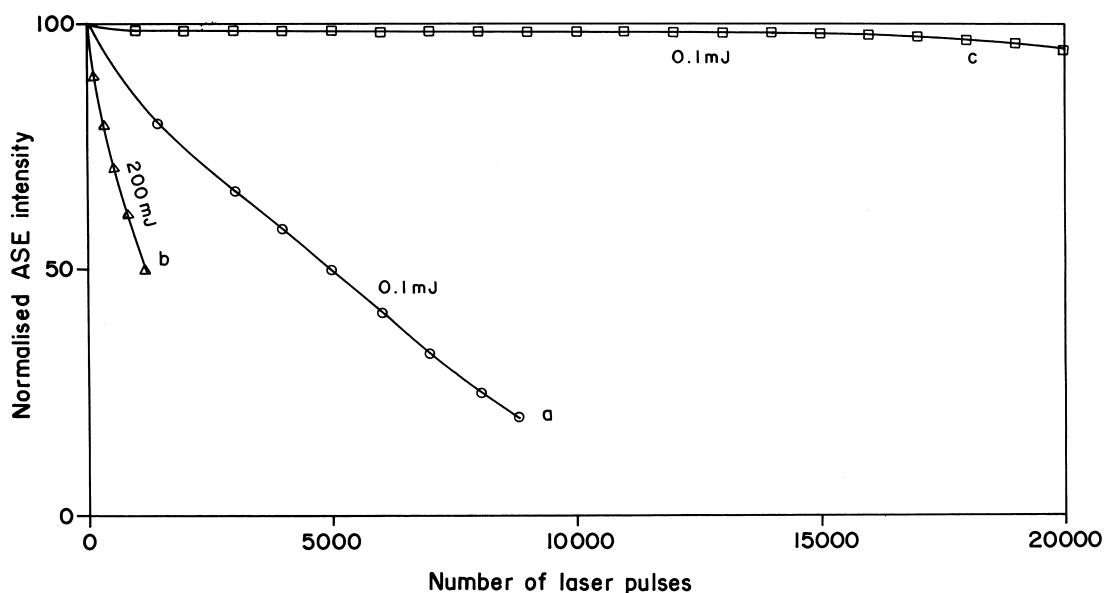


Fig. 7. Photobleaching of Rh6G polymer rod (a) In a fixed position under nitrogen laser excitation. (b) In a fixed position under Q-switched 2nd harmonic Nd : YAG laser excitation. (c) Rotating about its cylindrical axis with 20 rpm under nitrogen laser excitation.

Rh6G dye doped polymer exhibits less bleaching rate when exposed to nitrogen laser excitation (10 ns, 0.1 mJ, 337 nm). The bleaching rate is higher when exposed to 2nd harmonic of Q switched Nd : YAG (200 mJ, 7 ns). The bleaching rate is very fast when exposed to 2nd harmonic mode locked Nd : YAG laser (11 mJ, 35 ps). This indicates that the photobleaching depends on the power and the pulse width of the excited laser source.

The DDP rod is uniformly rotated (20 rpm) about its cylindrical axis and excited by nitrogen laser and the output intensity is monitored continuously. The variation of output intensity with number of pumping pulses are shown in Fig. 7(c). The dye doped polymer laser intensity decreases to 5% of its initial value after 20,000 pulses. The bleaching rate is very slow when compared to the rod which is kept in a fixed position Fig. 7(b). This indicates that if the exposed region is continuously changed photobleaching rate can be very much minimised.

3. Conclusions

Rh6G dye doped polymethyl methacrylate polymer rods are synthesised and laser characteristics are studied. The results obtained help us to choose the composition and method of synthesising dye doped polymer materials for laser excitation. The variation of laser gain of Rh6G in solid matrix under nitrogen laser (337.1 nm) excitation and second harmonic Nd : YAG laser (532 nm) excitation are studied and is intercompared with that in liquid medium. The photobleaching of the polymer rods under nitrogen laser excitation, Q-switched 2nd harmonic Nd : YAG laser (532 nm, 7 ns, 200 mJ), mode locked 2nd harmonic Nd : YAG laser (532 nm, 35 ps, 11 mJ) are also studied. It is observed that Rh6G dye doped polymer exhibited less

photobleaching rate when exposed to nitrogen laser excitation. It is suggested that for low bleaching rate low power nitrogen laser may be a suitable pumping source. If the rod keeps rotating while pumping, the laser damage is less.

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