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Study of Photobleaching of Organic Laser Dyes in Solid Materials

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Abstract – A technique is described for easuring the rate of photobleaching of organic laser dye molecules in solid polymer matrices. For solid arrangements of rhodamine 6 G (Rh6 G) in appropriate copolymer details of 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA), lasing efficiencies like those found in ethanolic arrangement and improved photochemical solidness contrasted and those obtained in past polymeric materials were illustrated.

Keywords: Dye, Photobleaching, Solid Materials, Organic Laser

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INTRODUCTION

Due to their critical commitment to science and innovation, color lasers are the most adaptable and one of the best laser sources. Dye lasers are used in spectroscopic investigations and photo chemical experiments. A dye laser can be considered as a special device to convert electromagnetic radiation from one wave length to another wave length which can be tuned (1). In the solid, fluid, or gas stage, the dyes were utilized for lasing. However, the most habitually utilized laser media are fluid arrangements of dyes in proper organic solvents.

Even though organic dye laser have been reported to have wide range of tunability and high optical gain, the liquid dye lasers have some common practical disadvantages, such as, the requirement of large volume of toxic and flammable organic solvents, static or flowing liquid dye solutions and evaporation of the solvent. This restricts the use of dye laser in some technical applications. Since the beginning of color laser improvement, endeavors have been made to tackle the issues presented by color arrangements by integrating color particles into solid lattices. A solid state color laser forestalls harmfulness and combustibility issues and is reduced, adaptable and simple to work and maintain. Soffer and Mcfarland and Peterson and Snavely announced the principal perceptions of animated discharge from solid lattices doped with organic dyes as ahead of schedule as 1967 and 1968, individually.

Apart from their use as active laser media dye doped polymers find many applications in the modern photonic technology (2-5). These potential applications are due to the nonlinear characteristics of dyes in liquid and solid media. Accordingly, in request to distinguish reasonable dyes in polymer media, satisfactory information on the optical properties of color doped polymers and a more noteworthy understanding of the photophysical properties of color atoms in polymer grids is significant. Further studies on the optical non-linear characteristics of solid medium will lead to fabrication of new elements, which have potential applications in optical limiting, bistability and optical storage devices. This study presents a Photobleaching of organic laser dyes in solid materials.

The influence of a medium on the photophysical properties of a fluorinated (coumarin 485) was concentrated in detail by Vijila et al (2001). They saw that the convergence of coumarin 485 in altered PMMA increases with an increase in the dielectric steady of the medium, while the opposite impact increases in the fluid medium. The gain coefficient of coumarin 485 in a solid has additionally been appeared to diminish by 90% contrasted with the fluid medium. They noted the photobleaching effect decreases with the increase in dielectric constant of the medium. This confirms that the fluorine-substituted coumarin molecules get distorted in the highly polar environment and it can be reduced by modifying the medium with less polar solvents (6).

The laser qualities of Coumarin 490-doped polymethyl methacrylate bars altered with EtOH under nitrogen laser and third consonant symphonious laser were concentrated through Somasundaram et al (2000). They reported that gain of the dye in the solid medium is less than that of the liquid medium and also laser damage is less when rotating the rod which excited (7).

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Ramalingam et al (1998) reported the conversion efficiency of the polymer rods under 2 nd harmonic Nd:YAG laser to be 18% and for the liquid R6G solution of the same concentration under same conditions to be 25%. Photobleaching was additionally concentrated by measuring the quantity of pumping beats, after which the yield diminished by 20% of the original worth (8).

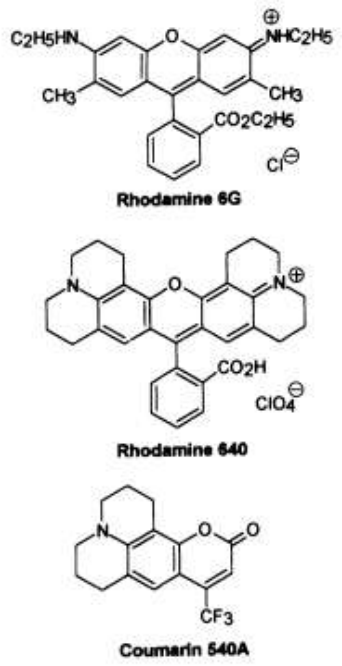
Costela et al (1997) increased the photostability of the dye doped polymer by doping R6G with two covalently bonded 1,8 Naphthalimide groups dissolved in 1:1 MMA:PMMA copolymer. However, the conversion efficiency of dye doped polymer was decreased due to the incorporation of imidazonapthalimide group (9).

Costela et al (1995) obtained the best photostability (≈10,000 pulses) and highest lasing efficiency (~21.5%) when R6G was doped in P(HEMA:MMA)1:1 copolymer. The lasing efficiency similar to that found for R6G in ethanol. Costela et al (1996) obtained lasing efficiency from modified R6G molecules copolymerized with methacrylic monomer and found that lifetime (measured as an 80% efficiency drop) in excess of 20,000 shots with nitrogen laser excitation with a repetition rate of 2Hz (10).

MATERIALS:

Dyes

Most of our work in solid-state dye lasers has been performed with dyes of the Rhodamine and Coumarin families. The Rhodamine dyes are known to give outstanding laser brings about fluid arrangement, with outflow in the yellow-red area of the range, so they are an undeniable best option in any endeavor to build up a solid state color laser. Our most normal decision was the notable Rhodamine 6 G (Rh6 G, Scheme 1) color on the grounds that there were various examinations on this color incorporated into different materials, which would encourage the evaluation of our outcomes contrasted with those recently detailed in the writing. The more unbending Rhodamine 640 atom (Rh640, Scheme 1) was utilized to dissect the impact of the basic inflexibility of the color on laser activity in certain investigations.

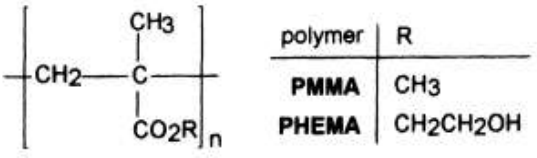


SCHEME 1: Rhodamine 640, Coumarin 540A and Rhodamine 6G Molecular structure

Polymers

We endeavored a substitute anyway related technique in our ongoing examinations, where the material's flexibility was internally increased. This is done through 2-hydroxyethyl methacrylate (HEMA) and copolymerization of methyl methacrylate (MMA) (Scheme 2). Notwithstanding increasing the versatility of the material while maintaining great straightforwardness in the close bright and noticeable otherworldly ranges, the presence of HEMA as comonomer additionally guarantees great solvency of dyes, for example, Rh6 G because of HEMA 's polar character.

Our involvement in laser dyes incorporating polymeric lattices shows that a color polymer material's lasing properties rely generally upon the procedures utilized for its creation. The stringent prerequisites put on laser materials limit these strategies, which make the all around created methods for molding polymeric materials not truly reasonable for ensuring the high optical consistency, absence of internal pressure and immaculateness of the final material needed in this application.



SCHEME 2 Molecular structures of PMMA and PHEMA.

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EXPERIMENTAL SET-UP FOR LASER STUDIES

A schematic diagram of the laser system is shown in Figure 1. A 90% reflectivity fiat aluminum reflect and the end face of the cylindrical example as the yield coupler were shaped by the oscillator depression, with average pit lengths of 4 cm. We used a transversal pump scheme, with the exciting pulses being line-focused onto the lateral flat surface of the sample. Typical pump fluences were 30 mJ/cm2. The airequilibrated polymer rods were usually pumped at 337nm with millijoule pulses of nanosecond duration from a N2 laser. In some experiments the pump was a frequency-doubled Nd:YAG laser (532 nm). The highest pulse repetition rates used were 15 Hz. Absolute pump and dye laser energies were measured with pyroelectric energy meters (not shown in Figure 1). The estimated error in the energy measurements was 10%.

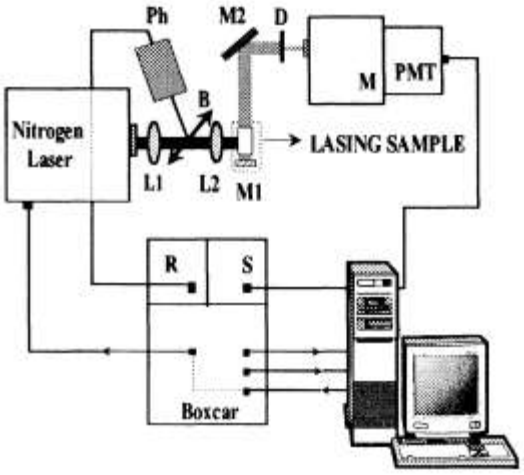

FIGURE 1: Schematic of the exploratory arrangement of the laser framework. B: beam splitter; D: Iris diaphragm; LI: spherical lens; L2: cylindrical lens; M: monochromator; M1 and M2: aluminium flat mirrors; Ph: photodiode; PMT: photomultiplier; R: reference; S: signal.

Modified Rhodamine 6G Copolymerized with Methacrylic Monomers

Since the essential driver of color debasement incorporated into polymeric lattices gave off an impression of being the warm annihilation of the color because of helpless warm scattering in the polymer have, sub-atomic alterations that encourage the dissemination of assimilated energy that isn't changed over into light emanation ought to forestall early corruption. One such modification can be the covalent linkage of the dye to the polymeric chain, that would provide additional channels for the energy elimination along the polymer backbone, with the corresponding increase in the laser's photostability. In addition to the effect of improving the dissipation of energy, the covalent bonding of a chromophore to a polymer chain must restrict its mobility, decreasing the rate of biomolecular reactions leading to photochemical degradation, hindering the internal micromotions of the excited fluorophores, and avoiding non-emissive deactivations via rapid internal rotations or conformational changes.

To apply the above ideas to rhodamines, it was first necessary to modify the Rh6G molecules so that polymerizable double bonds were incorporated in the appropriate positions. Two new monomers containing the Rh6G chromophore and an allyl or a methacryloyl group in the same molecule were synthesized (Rh-A1 and RhBzMA, respectively; Scheme 3) and, subsequently, copolymerized with mixtures of HEMA and MMA (11). The preparation of the polymerized dye laser samples involves mixing a suitable amount of the polymerizable dye monomer with freshly purified HEMA, placing the mixture in an ultrasonic bath until complete dissolution of the dye, and then adding appropriate amounts of pure MMA and free radical initiator, 2,2'-azobis(isobutyronitrile) (AIBN). After filtering and deaeration, polymerizations were performed in the dark at 40C for two days, and then at 45C for about one day. The temperature was then raised to 60C and increased slowly up to 80C over a period of several days, in order to decompose residual AIBN. Finally, the temperature was reduced in steps of 5C per day until room temperature was reached.

A summary of the data obtained with some of the new terpolymers (11) is shown in Table I, where the previous results obtained with Rh6G dissolved in the copolymer P(HEMA:MMA 1:1) are also included for comparison. In Figure 5 the effect of the repetition rate on the laser lifetime is shown graphically for two of the materials.

The lasing properties of the terpolymer with the Rh6 G allyl ester as comonomer are obviously more regrettable than those of the corresponding model color disintegrated in P(HEMA: MMA 1:1) (Tab. I), while the terpolymers containing the P(h6 G as comonomer methacryloyl-subbed maintain the lasing proficiency. Thus, the covalent linkage of the dye to the polymeric chain is producing the expected results only in the case of the terpolymers with the RhBzMA comonomer. Although no single cause is expected to fully explain the behaviour of these rather complicated polymer systems, it seems, in a first approximation, that the distance between the chromophore's functional group and the main polymeric chain (Scheme 3) should play a role in the different behaviour between the two comonomers. The practical gathering of the chromophore is close to the polymeric main chain in the terpolymers with the RhA1 comonomer. This could result in interactions between the excited dye chromophores and the macromolecules, with electronic energy transfer to the polymer main chain and the formation of free radicals (12). These active radicals could in turn interact with the dye groups and stimulate their destruction. The chromophore's pendant gathering is far taken out

from the main polymeric chains in the terpolymers with the methacryloyl-subbed Rh6 Gas comonomer, resulting in no immediate interaction. The predominant impact for this situation is the improved scattering of the overabundance assimilated energy through the extra channels gave by the color's covalent bonding to the polymeric chain and the resulting improvement in photostability.

COUMARIN-DOPED GAIN MEDIA

The dye Coumarin 540A (C540A, Scheme 1) was incorporated into two-different polymeric matrices (13) a 1:1 v/v copolymer of HEMA and MMA, and a pure PMMA homopolymer. AIBN was used as thermal free radical initiator, and polymerizations were performed in the dark at 40C for about 62 hours, and then at 50C for two days. Under these conditions lasing efficiencies of 8% and 9.5% were obtained for C540A/P(HEMA:MMA 1:1) and 540A/PMMA, respectively, with lifetimes of less than 500 shots (Figure 2, curves B and C), for a dye concentration of 3 10-M and transversal pumping at 337 nm with pulses of 1.2 mJ at 2 Hz repetition rate. When the solid solution of C540A in PMMA was prepared by a method involving reduced concentration of initiator and gentle thermal treatment (35C during two days, followed by two days at 40C and a week at 45C), that results in the polymerization taking place at very slow rate, an efficiency of 11% and a lifetime of 2000 pulses (Fig. 7, curve A) were obtained. These outcomes upgrade laser proficiency by factor 2 and photostability by two greatness orders corresponding to the best exhibition dependent on coumarin-doped PMMA materials answered to date.

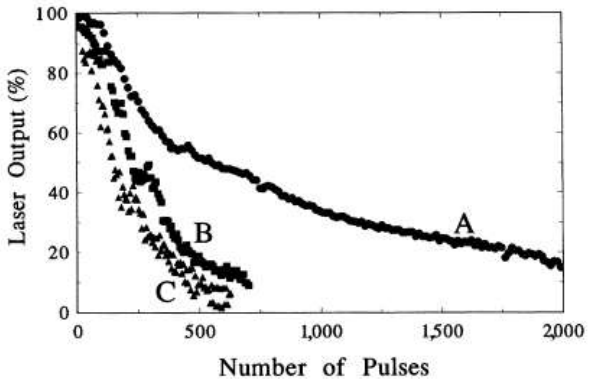

FIGURE 2: Normalized laser yield as a component of the quantity of siphon beats for C540A solid arrangements in: (A) slowly polymerized PMMA; (B) normally polymerized PMMA; (C) P(HEMA:MMA 1:1). N2-1aser pump energy and repetition rate: 1.2mJ/ pulse and 2 Hz, respectively. Dye concentration: 3 10 M.

RHODAMINE-BASED GAIN MEDIA

Due to its high fluorescence quantum yield, low intersystem crossing rate , and low energized state assimilation at both siphon and lasing frequencies, Rhodamine 6 G, most likely the most popular of all laser dyes, has been habitually investigated in solid-state color lasers in an assortment of solid hosts. Albeit past examinations on this atom gave numerous insights into the components of photodegradation and photostability of solid-state frameworks, the laser execution of Rh6 G in solid networks was still a long way based on what was routinely obtained in fluid arrangements toward the beginning of the 1990s. In particular, when incorporated into polymeric materials the laser emission lasted for no longer than a few hundred shots (14, 15).

Rhodamine 6G Dissolved in Polymeric Media

When pumping at 337 nm, broad-band laser emission with peak wavelength around 590 nm was obtained from all the samples studied, with efficiencies depending on the matrix composition, as shown in Figure 2. The highest lasing efficiency'(21.5%) was obtained with the HEMA:MMA 1:1 composition. This efficiency is similar to that obtained in liquid solutions of Rh6G in ethanol under equivalent experimental conditions.

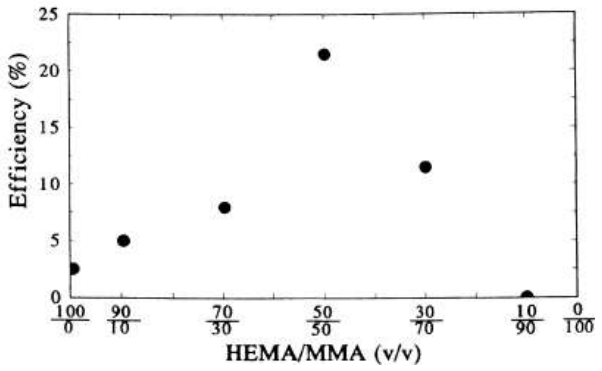

FIGURE 2 Energy conversion efficiency of Rh6G in various copolymers as a function of the HEMA:MMA ratio (vol/vol) in the polymeric matrix. N2-1aser pump energy (337nm): 2.4mJ/pulse. [Rh6G] 1.0 10-3M.

Rhodamine 640 Dissolved in HEMA:MMA Copolymer

Having discovered a material with a decent harmony among inflexibility and adaptability, we at that point continued to study the effect of the basic unbending nature of the color atom on the lasing properties. The laser conduct of Rhodamine 640 (Rh640), a color identified with Rh6 G yet with a more unbending structure (Scheme 1), was dissected for this reason. We contended that the higher inflexibility of Rh640's atomic structure could inhibit non-radiative rot measures, decline the measure of energy that shows up as warmth locally

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and along these lines improve photostability contrasted with Rh6 G's.

Related Studies

For the last years we have been collaborating with other groups to further explore the possibilities of the materials we are developing. In particular, the group of Prof. Guerra (Universidad Complutense, Madrid, Spain) investigated flashlamp-pumping of solid-state dyedoped materials (16), and F. J. Duarte (Eastman Kodak Co., Rochester, NY, USA), in collaboration with J. J. Ehrlich and T. S. Taylor (US Army Missile Command, Redstone Arsenal, AL, USA), built and tested dispersive laser oscillators to be used with the new materials (17).

When a laser rod (14mm diam. and 267mm length) of Rh6G/ P(HEMA:MMA 1" 1), placed in a simple resonator made up of two flat mirrors (total reflector and 30% reflector, respectively), was pumped with a xenon coaxial flash-lamp with UV and blue light filtered out, (18) laser emission with pulses of up to 500 ns duration (FWHM) were obtained. The normal excitation energy was 150J per beat, and the pole was illuminated by more than 30 pumping shots during the estimations, with no perceptible yield corruption watched (19, 20). Rather than other detailed solid-state color materials, the solid-state test accordingly has noteworthy photostability. When samples of Rh6G/P(HEMA:MMA 1" 1) and P[RhBzMA(HEMA:MMA7"3)] in a wedge-type geometry (20mm diam. and trapezoidal cross-section) were placed in a narrow-linewidth multiple-prism grating oscillator (21), laser emission with 4-5% efficiency and linewidth.

CONCLUSION:

Organic dye laser have been reported to have wide range of tunability and high optical gain, the liquid dye lasers have some common practical disadvantages, such as, the requirement of large volume of toxic and flammable organic solvents, static or flowing liquid dye solutions and evaporation of the solvent. This study presents a Photobleaching of organic laser dyes in solid materials. For solid arrangements of rhodamine 6 G (Rh6 G) in reasonable copolymer plans of 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA), lasing efficiencies like those found in ethanolic arrangement and improved photochemical dependability contrasted and those obtained in past polymeric materials were illustrated.

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