

Glycidyl Methacrylate as a New Host Material for Laser Dyes

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ABSTRACT: This article reports on the laser action of pyrromethene 597 and pyrromethene 567 doped in the novel solid polymeric matrix glycidyl methacrylate. Mirrorless lasing was observed when samples with diameters of 10 mm and lengths of 20 mm, with different dyes concentrations, were transversely pumped at 532 nm. The influence of the dye concentration on the laser measurements included the peak wavelengths, output energies, conversion efficiencies, and laser gains. Relatively high lasing effi-

ciencies (up to ~ 60%) were obtained from these new polymeric materials with very good photostability, where a decrease of only 65% in the initial laser output energy was observed after pumping by 60,000 shots of 15 mJ at 10 Hz. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 59–63, 2007

Key words: dyes/pigments; fluorescence; photophysics; radical polymerization; solid-state structure

INTRODUCTION

Dye lasers are very attractive for wide applications in different fields because of the high gain, broad tunability, and high tolerance to the pump parameters of the dyes. Solid-state dye lasers (SSDLs) have been developed as the practical alternative to the conventional liquid dye lasers due to their compactness, low cost of fabrication, ease and safety in handling and operation, and lack of toxicity, flammability, flow fluctuations, and solvent evaporation problems. SSDL-based polymer,^{1–6} sol-gel,^{7,8} xerogel,⁹ glasses,¹⁰ epoxies,¹¹ and other materials^{12,13} that all aim at high-damage thresholds and long-lived performance have been widely reported. Polymeric matrices have some important advantages over other host materials because they are simple to prepare and cheap to produce, and the most frequently used polymeric material is poly(methyl methacrylate) (PMMA). In the search for a new polymeric host for SSDL, glycidyl methacrylate (GMA) monomer appeared to be a good candidate because it contains both acrylic and epoxy groups and, thus, was supposed to combine the advantages of these two groups (i.e., high optical homogeneity, high transparency in the visible region of the electromagnetic spectrum, composition controllability during formation, high resistance to photochemical degradation).

In this article, we report for the first time on GMA as a new promising polymeric host of SSDL. The laser characteristics, including the gain, amplified spontaneously emission, and the photostability of two pyrromethene dye (PM-567 and PM-597) doped GMA were examined under transverse pumping at 532 nm. Optimization of the laser characteristics was performed by the variation of the dye concentration in the polymeric host.

EXPERIMENTAL

Materials

Pyrromethene-benzo-fused pyrromethene (BF₂) complexes were obtained from Exciton, Inc. (Dayton, OH), and were used without further purification. GMA was purchased from Fluka (Japan) and was purified from hydroquinone by vacuum distillation, and 2,2'-azobis (isobutyronitrile) (AIBN), purchased from Acros Organics (NJ), was recrystallized in ethanol before use. The molecular structure of the dyes and monomer molecules selected in this study are shown in Figure 1.

Methods

The solid samples were prepared as follows: 3 g/L of AIBN used as a thermal free-radical initiator was dissolved in the freshly purified GMA monomer, and the mixture was placed in an ultrasonic bath until the complete dissolution of AIBN was obtained. Then, the dye was added to obtain the desired concentration, and the mixtures was again sonicated. Polymerization was performed at 60°C over a period of 7 days.

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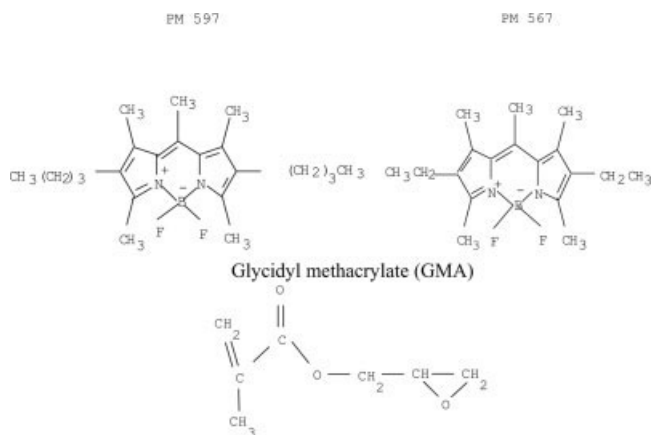


Figure 1 Molecular structure of the pyrromethene dyes (PM-567 and PM-597) and organic monomer GMA.

The temperature was then reduced in steps of 10°C per day until room temperature was reached. Rods 20 mm in length and 10 mm in diameter were ground and polished to the required optical quality. The bulk density of the rods was 1.86 g/cm^3 . We checked the internal optical quality of the undoped polymer rods by passing a He-Ne laser beam of 2 mW and 632.8 nm through the rods, where no dispersion or distortion of the laser beam was observed. The optical transmission (T) and reflection (R) of the undoped polymer (2-mm disk) are presented in Figure 2. Excellent T ($\approx 80\%$) and very low R ($\approx 2\%$) values in the range 450–800 nm were observed. Many rod samples of different concentrations (1×10^{-2} , 8×10^{-3} , 5×10^{-3} , 3×10^{-3} , 1×10^{-4} , 8×10^{-4} , 5×10^{-4} , and 3×10^{-4} mol/L) of PM567 and PM597 dye doped GMA polymer were prepared.

The excitation of 532 nm for the prepared rod samples was provided by a frequency doubled Q-

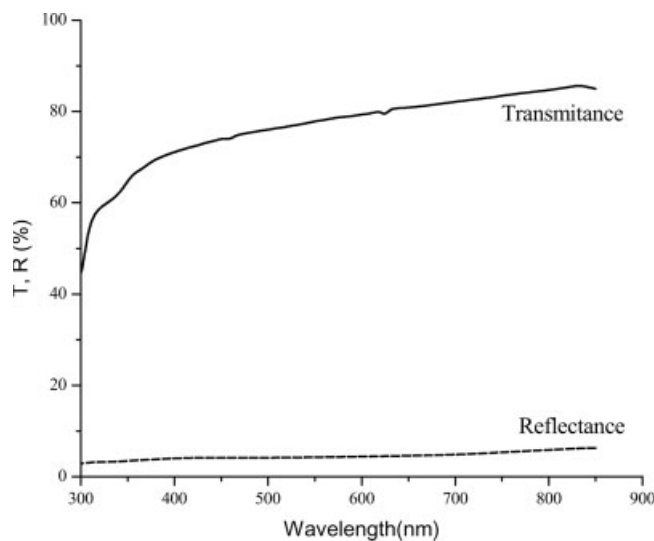


Figure 2 T and R of undoped GMA polymer.

switched Nd-YAG laser (Continuum, SL I-10) emitting 8 ns (full width at half-maximum) at a repetition rate of 10 Hz. The samples were transversely pumped, and a combination of a concave lens ($f = -10$ cm) and a cylindrical lens (focal length (f) = 10 cm) was used to line focus the pump beam on the rod surface.

RESULTS AND DISCUSSION

The spectral profiles of the laser emission, together with the absorption (A) and fluorescence (F) spectra, of the pyrromethene laser dye (PM567 and PM597) doped GMA polymer are shown in Figure 3(a,b). The dye samples were allowed to emit in the superradiant mode without the use of a cavity mirror because optical feedback was provided by R at the polymer air

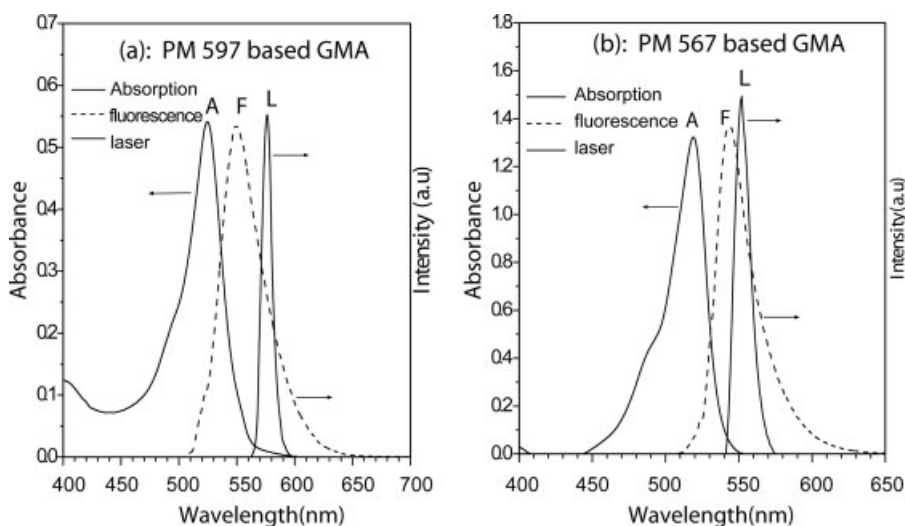


Figure 3 UV-vis A , normalized F ($\lambda_{\text{exc}} = 485$ nm), and laser emission (L ; $\lambda_{\text{exc}} = 532$ nm) spectra for: (a) PM597 and (b) PM567-doped GMA.

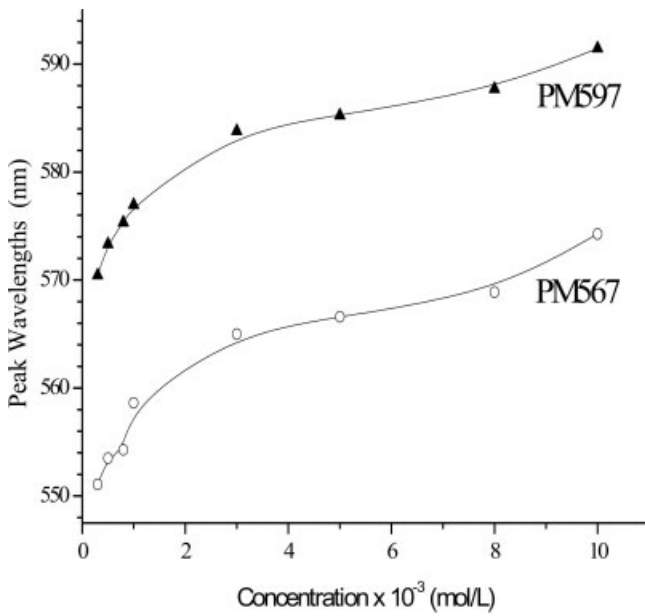


Figure 4 Laser peak wavelength emission as a function of PM dyes concentration.

interface. *A* and *F* spectra were obtained from thin discs with a dye concentration of 5×10^{-5} mol/L and measured on a PerkinElmer spectrophotometer and PerkinElmer LS-50B luminescence spectrometer, respectively.

The effect of the variation of the dye concentration on the position of the peak wavelength of the laser emission is plotted in Figure 4. The samples were transversely pumped by 5 mJ at 532 nm at 10 Hz. Increasing the dye concentration in the polymeric GMA host from 3×10^{-4} to 1×10^{-2} mol/L induced a redshift in the peak wavelengths toward a longer wavelength. The induced shifts ranged from 551 to

574 nm for the PM567 samples and from 570.4 to 591.4 nm for the PM597 samples. Obviously, this redshift was due to the self-absorption effect.

The influence of the dye concentration on the measurements of energy output versus energy input over a range of energies is shown in Figure 5(a,b). Each data point was measured with a Molecron energy meter (J3-09) as the average of five shots (to minimize probable thermo-optical distortion and dye degradation). Laser action was observed for all samples with thresholds of the order of about 1 mJ. The highest output energy obtained from the PM597 samples was at a concentration of 3×10^{-3} mol/L and that from PM567 samples was at 1×10^{-3} mol/L.

To examine the validity of the prepared samples for lasing action, we measured the laser efficiency and laser gain for each polymeric dye rod. The average energy efficiencies extracted from the previous input-output energy measurements are presented in Figure 6. Relatively high percentages of energy conversion ($>40\%$) were observed for all PM597 samples with an optimum efficiency of about 60% yielded from the 3×10^{-3} mol/L concentration. A strong dependence for the laser efficiency on the concentration of PM567 was observed, where a maximum efficiency of 50% was observed at a 1×10^{-3} mol/L concentration.

A single pass gain was measured by the adoption of the amplified spontaneous emission (ASE) method proposed by Shank et al.¹⁴ The ASE gain was defined as the increase in the ratio of the emitted to the incident light intensity per unit length of the pumped material and calculated according to¹⁴

$$G = (2/L) \times \ln(E/E_{L/2} - 1)$$

where L is the length of the irradiated polymeric dye rod and $E_{L/2}$ is the resulting ASE energy from the

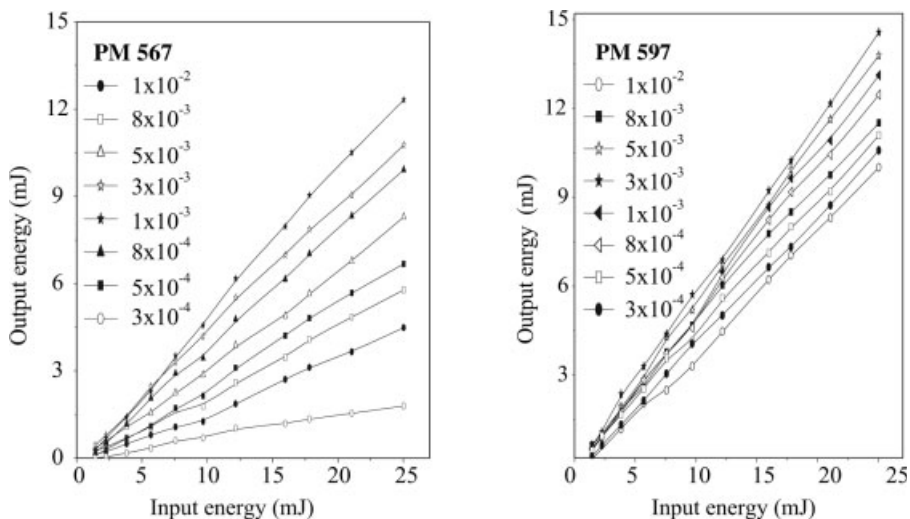


Figure 5 Output energy of (a) PM597 and (b) PM567-doped GMA as a function of pumping energy for different dye concentrations.

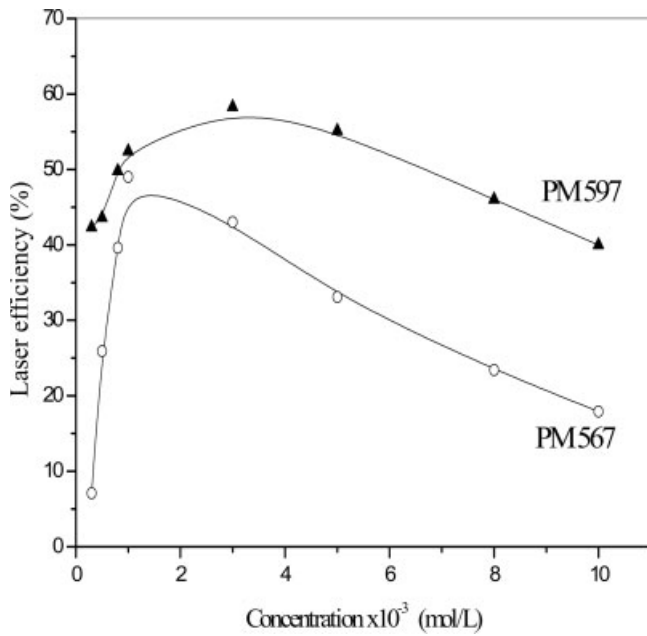


Figure 6 Laser efficiency as a function of concentration for PM597- and PM567-doped GMA.

pumped $L/2$ at the peak wavelength. Figure 7 shows the computed gain for $L = 20$ mm for different concentrations of PM567- and PM597-doped GMA when pumped at 532 nm of 10 mJ at 10 Hz. The gain depended on the dye's concentration where the optimum gain per unit length was 7 cm^{-1} for PM597 samples at concentration of $3 \times 10^{-3} \text{ mol/L}$ and 6.4 cm^{-1} for PM567 samples at $1 \times 10^{-3} \text{ mol/L}$. These were the two concentrations with the highest energy conversions.

Finally, the evolution of the laser output as a function of the number of pump pulses in the same position of the sample is plotted in Figure 8. This study was carried out for the two samples of PM dyes that showed the highest gain and energy conversions. The samples were pumped at 532 nm of 15 mJ at repetition rate of 10 Hz. The time exposure was exactly 100 min. A gradual decrease in the output energy due to the progressive photodegradation and thermodegradation of the dye molecules was observed for both samples. This decrease occurred at a faster rate for the PM567 sample, and after 60,000 shots, the output energy dropped to 50% of its initial value compared

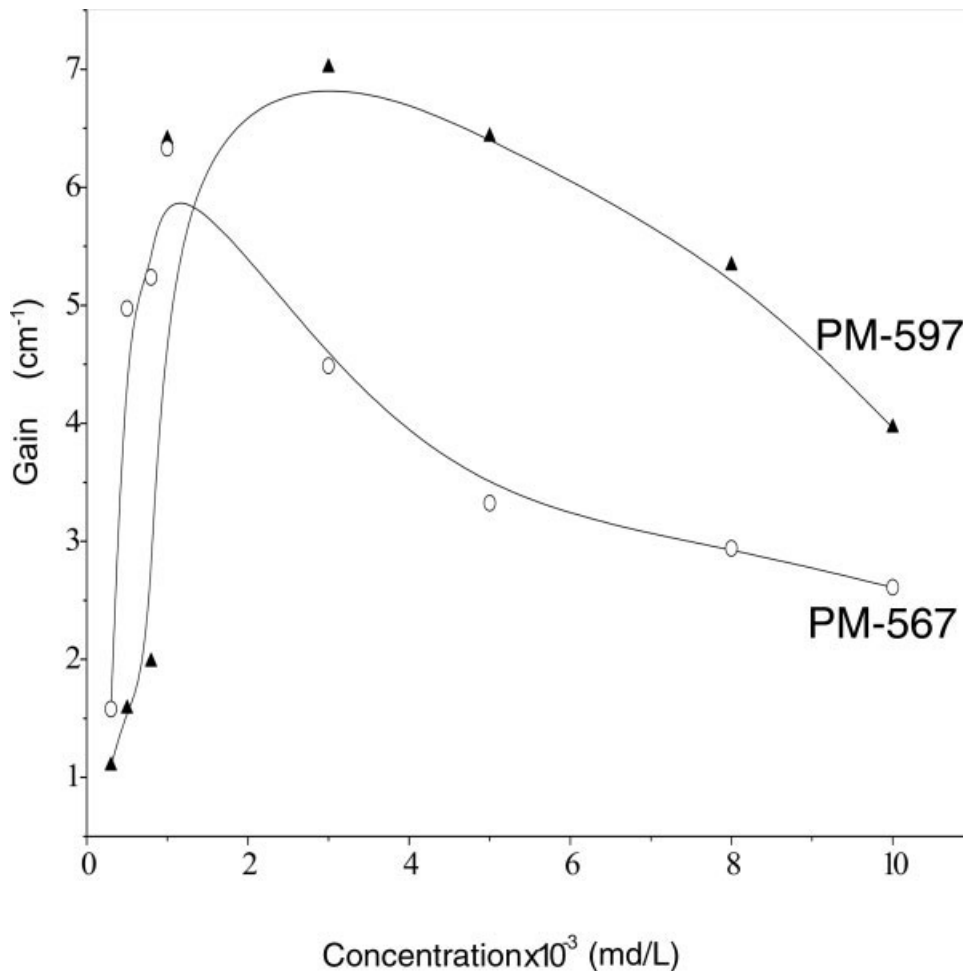


Figure 7 Laser gain as a function PM dye concentration.

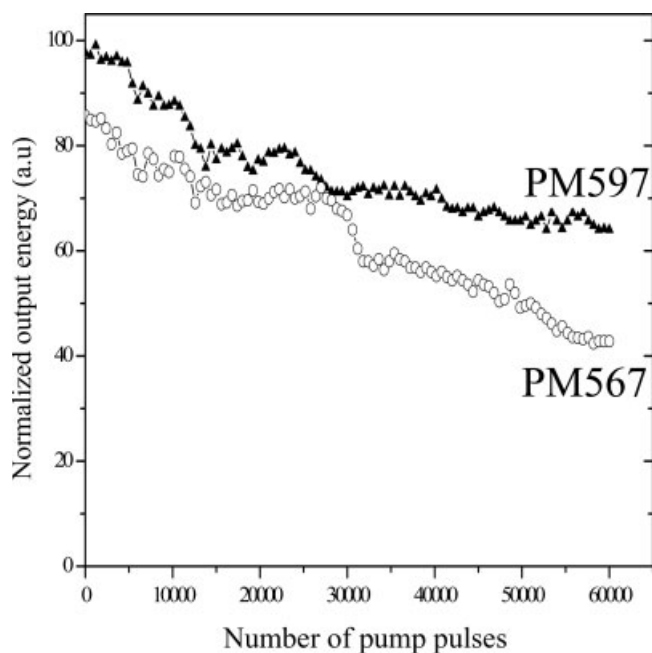


Figure 8 Output energy as a function of the number of pump pulses for PM597- and PM567-doped GMA.

to a drop to only 65% in the case of the PM597 sample. This was attributed to the lower energy conversion obtained for the PM567 sample than for the PM597 sample, where the higher energy deposited in the former sample increased the local temperature; hence, thermodegradation became more active. Longer service life for the samples can be achieved by either a decrease in the pump energy or by pumping a fresh area.

CONCLUSIONS

In this article, we reported an efficient and highly photostable laser operation from PM567 and PM597 dye doped solid polymeric matrix GMA. The detailed laser measurements of output peak wavelengths, output energies, slope efficiencies, and laser gains showed a strong dependence on the PM dyes concentrations. Emission maxima ranged from 551 to 574 nm and from 570.4 to 591.4 nm when 10×20 mm rods of PM567/GMA and PM597/GMA samples, respectively, were transversely pumped at 532 nm. Laser efficiencies for different dye concentrations in the PM597/GMA samples were more than 40% with an optimum value of 60% at a PM597 concentration of 3×10^{-3} mol/L. The corresponding optimum value of laser efficiency for PM567/GMA was 50% at 1×10^{-3} mol/L of PM567. On the other hand, the re-

ported lasing efficiencies of PM597 and PM567 doped on the commonly used polymeric matrix PMMA were only 18%¹⁵ and 12%,¹⁶ respectively. The optimum values of laser gain measurements were 7 and 6.4 cm^{-1} for the PM597/GMA and PM567/GMA samples, respectively. With regard to the photostability measurements, the laser emission of the PM597/GMA and PM567/GMA samples dropped to 65 and 50% of their initial values, respectively, after 60,000 pump shots with a relatively high energy of 15 mJ at a repetition rate of 10 Hz at the same position of each sample. Longer life performance is expected when pumping at lower energies. Correspondingly, the laser emission of PM597/PMMA and PM567/PMMA were reported to drop to 50%¹⁵ and 16%¹⁶ of their initial values after 135,000 and 30,000 pump pulses with much lower energies of 6 and 5.5 mJ, respectively, at a repetition rate 10 Hz. Desired ranges of wavelengths could be achieved by the doping of other laser dyes in the GMA, which appeared to be a very promising polymeric host in comparative with other polymeric hosts.

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