Solid-state dye lasers based on polymers incorporating covalently bonded modified rhodamine 6G

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(Received 21 July 1995; accepted for publication 24 November 1995)

We report on the lasing action of modified rhodamine 6G dyes copolymerized with methacrylic monomers. The laser samples were transversely pumped with a N₂ laser at 337 nm. Lasing efficiencies similar to those found for rhodamine 6G in ethanol solution have been achieved. Important increases in photostability, with lifetimes in excess of 20 000 shots at 2 Hz, have been obtained. By using a rotating mechanism, a stable output with no sign of degradation after half a million shots has been demonstrated. © 1996 American Institute of Physics.

Solid polymer hosts for lasing dyes are attractive alternatives to liquid-dye lasers, with obvious technical and economical advantages. In the last few years, significant advances have been made towards the development of practical tunable solid-state dye lasers. Most of the recent work has been done using either polymers or silica gels as host media. Work with silica gels has indicated that sol-gel materials seem to show higher photostability than those based on organic polymers, as well as good laser efficiency. Nevertheless, the polymeric materials show a higher optical homogeneity than the available silicate matrices, which is extremely important for narrow-linewidth oscillators. In general, organic dyes show a better solubility, and therefore compatibility, with the polymeric materials, and in addition, these materials are amenable to inexpensive fabrication techniques which would facilitate miniaturization and the free design of integrated optical systems.

The above mentioned advantages suggested to us an approach in which organic polymers were to be used as host media for dye molecules and the laser-related properties of these materials were to be improved on the basis of modifying their characteristics in a controlled way. Very recently, in a study on the lasing properties of solid solutions of rhodamine 6G (Rh6G) in methacrylate copolymers, we presented evidence showing the important role played by the viscoelastic properties of the host material on the laser’s performance. The results obtained represented a significative progress over previous work done with rhodamine dyes. Nevertheless, further progress in photostability is necessary before an operational solid-state dye laser based on rhodamine dyes were competitive with liquid dye lasers. As large local rises in temperature seem to be the main cause of degradation of dyes incorporated into polymeric matrices, molecular modifications facilitating the dissipation of the absorbed energy which is not converted into emission should avoid early degradation. Then, the covalent linkage of the dye to the polymeric chain, which provides additional channels for the elimination of the adsorbed energy along the polymer backbone, should increase the laser’s photostability. To check this idea we copolymerized proton-transfer dyes with methyl methacrylate and significant increases in efficiency and photostability were obtained.

In this letter, we report important increases in photostability, with lasing efficiencies similar to those found for Rh6G in ethanol solution, when a modified Rh6G molecule was copolymerized with methacrylate monomers. Two different monomers containing in the same molecule the Rh6G chromophore and an allyl or a methacryloyl group were synthesized (Rh–Al and Rh–Bz–MA, respectively, see, Fig. 1). These monomers were copolymerized with mixtures of 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA). Details of the synthesis and polymerization processes will be reported elsewhere.

These new terpolymers were cast in a cylindrical shape, forming rods of 10 mm diam and 20 mm length. A cut was made parallel to the axis of the cylinder to obtain a lateral flat surface of 4 x 20 mm. This surface was prepared for lasing experiments by conventional grinding and polishing. The ends of the laser rods were polished until optical-grade fin-

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FIG. 1. Molecular structures of compounds Rh–Al and Rh–Bz–MA.
ish. In all cases the dye concentration was 1.0 \times 10^{-3} \text{ M}.

The polymer rods were transversely pumped by 337-nm pulses obtained from an excimer laser (MPB-AQX 150) filled with the appropriate N\textsubscript{2}/He mixture to work as a N\textsubscript{2} laser (1.7 mJ, \sim 5 ns FWHM, at repetition rates up to 15 Hz). A combination of spherical (\(f = 50 \text{ cm}\)) and cylindrical (\(f = 15 \text{ cm}\)) quartz lenses focused the exciting pulses onto the flat surface of the sample to form a line of \(\sim 0.3 \times 20 \text{ mm}\), so that the pump fluence was \sim 30 mJ/cm\textsuperscript{2}. The oscillator cavity consisted of a \sim 90\% reflectivity flat aluminum mirror and the end face of the cylindrical sample as the output coupler, with a cavity length of 4 cm.

The dye and pump laser pulses were characterized with the following instruments: Gen Tec ED-100A and ED-200 energy meters, ITL TF 1850 fast rise time photodiode, Tektronix 2430 digital oscilloscope, Applied Photophysics M-300 monochromator, and EMI 9763B photomultiplier. In the photodegradation studies dye and pump laser signals were samples with boxcars (Stanford Research System, Model 250). All the integrated signals were digitized and processed by a PC computer through a Computerboard DASH-8 interface.\textsuperscript{9} The estimated error of the energy measurements was 10\%.

A summary of the data obtained is shown in Table I where previous results obtained with solid solutions of Rh6G in a P(HEMA:MMA) copolymer\textsuperscript{7} are also included for comparison. A static solution of Rh6G in ethanol, with the same optical density as the solid sample, and in the same experimental setup (using the end face of the 2 cm optical path dye cell as the output coupler), gave a lasing efficiency of 20\%. Pump threshold energy for laser emission was \sim 0.5 mJ for P[RhAl(HEMA:MMA 1:1)] and \sim 0.6 mJ for P[RhBzMA(HEMA:MMA 1:1)]. Laser-beam divergence was \sim 4 Mrad for P[RhAl(HEMA:MMA 1:1)] and \sim 5 Mrad for P[RhBzMA(HEMA:MMA 1:1)], respectively. When a P[RhBzMA(HEMA:MMA 1:1)] sample with the end faces cut at the Brewster angle was placed in a 6.5 cm long optical cavity, formed by a flat aluminum mirror and an uncoated quartz parallel plate as the output coupler, fully polarized laser output with beam divergence of about 1.5 Mrad was obtained.

In Table I it is seen that the lasing properties of the terpolymer with the allyl ester of Rh6G as comonomer are clearly worse than that of the corresponding model dye dissolved in P(HEMA:MMA 1:1), whereas the terpolymers containing the methacryloyl-substituted Rh6G as comonomer maintain the lasing efficiency at the level of the static liquid solution and improve the photostability with respect to the solid solution. Although no single cause is expected to fully explain the behavior 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 should play a role in the difference in behavior between the two comonomers. In the terpolymers with the RhAl comonomer, the chromophore’s functional group is close to the polymeric main chain, which could result in interactions of the excited dye molecules with the macromolecules. These interactions could give rise to electronic energy transfer from the dye to the polymer main chain, with subsequent radiationless deactivation (vibrational relaxation) of the excited macromolecules and the subsequent formation of free radicals.\textsuperscript{1} These active radicals could interact with the dye molecules and stimulate their destruction. In the terpolymers with the methacryloyl-substituted Rh6G as comonomer, the chromophore’s pendant group is far away from the main polymeric chains, resulting in no direct interaction. In this case, the important effect is the improved dissipation of the excess absorbed energy, facilitated by the additional channels provided by the covalent linkage of the dye to the polymer chain, which results in improved photostability. At low repetition rates (2 Hz), this increase in photostability is particularly noticeable whereas at the 15 Hz repetition rate there is no difference in lifetime between the terpolymer P[RhBzMA(HEMA:MMA 1:1)] and the solid solution of Rh6G in the 1:1 copolymer of HEMA and MMA. It seems that at high repetition rates the extra dissipative channels presented in the terpolymer are not able to dissipate the excess energy fast enough. Then, the material loses its main advantage over the solid solution of Rh6G, and the stability is close in both cases.

Whereas in the experiments performed with Rh6G dissolved in HEMA:MMA copolymers\textsuperscript{7} the best results were obtained with the monomers in the proportion 1:1, in the P[RhBzMA(HEMA:MMA)] terpolymers, the photostability at low repetition rates was greatly increased when the HEMA:MMA proportion was 7:3 (Table I). This is a further indication that there is an optimum copolymer composition for each specific matrix/dye combination.\textsuperscript{7} In Fig. 2 the effect of the repetition rate is shown graphically on the laser lifetime for the P[RhBzMA(HEMA:MMA 7:3)] material.

In order to demonstrate the potential of these materials

<table>
<thead>
<tr>
<th>Material</th>
<th>(\lambda_{\text{max}}(\Delta\lambda))</th>
<th>Eff (%)</th>
<th>Lifetime\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh6G/P(HEMA:MMA 1:1)\textsuperscript{c}</td>
<td>(nm)</td>
<td>593(13)</td>
<td>593(13)</td>
</tr>
<tr>
<td>P[RhAl(HEMA:MMA 1:1)]</td>
<td>589(12)</td>
<td>11</td>
<td>589(12)</td>
</tr>
<tr>
<td>P[RhBzMA(HEMA:MMA 1:1)]</td>
<td>587(11)</td>
<td>18</td>
<td>587(11)</td>
</tr>
<tr>
<td>P[RhBzMA(HEMA:MMA 7:3)]</td>
<td>593(10)</td>
<td>18</td>
<td>593(10)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}\lambda_{\text{max}}: peak of the laser emission; \(\Delta\lambda\): FWHM of the laser emission; Eff: energy conversion efficiency.

\textsuperscript{b}Number of pulses that produce a 80\% drop in the laser output.

\textsuperscript{c}Solid solution of Rh6G in P(HEMA:MMA 1:1). Data from Ref. 7.
as active media in commercial dye lasers, experiments were performed where \( \text{[RhBzMA(HEMA:MMA 7:3)~]} \) laser rods of 20 mm diam and 20 mm length were placed in a rotating system where the sample is scanned in a continuous way, so that the position of the polymer matrix is changed after every pump laser shot.\(^9\) Figure 3 shows the normalized laser output from such a system as a function of the number of laser pulses at a repetition rate of 2 Hz. No sign of degradation in the laser output is seen after 500 000 shots.

Important advances on both efficiency and photostability of polymeric solid-state dye lasers have been reported by Hermes \textit{et al.}\(^3\) using various pyromethene dyes doped in “modified acrylic plastic”. By pumping in a longitudinal configuration with 0.6 J/cm\(^2\) of a frequency doubled Nd:YAG laser at 532 nm they achieved, for one of the dyes in the host polymer system, a useful lifetime (by which the original value of the output energy of the dye laser was reduced by about one third) of greater than 20 000 shots at 3.33 Hz. Our results show that the photostability of the Rh6G chromophore incorporated into adequate polymeric materials compares well with that of the pyromethene dyes, in spite of the pyromethene compounds being intrinsically more photostable than Rh6G.\(^3\) In this regard, it is necessary to take into account that we are pumping the samples at 337 nm in a transversal configuration. A substantial improvement in lifetime is to be expected if the pump wavelength was changed from 337 to 532 nm, as the lower difference in energy between the pump and laser photons at the 532 nm pump wavelength minimizes the energy released to the medium as heat, which should result in a lower thermal degradation of the dye. In fact, in a previous work\(^7\) we have demonstrated that, at a 10 Hz repetition rate, the lifetime of the solid solution of Rh6G in \( \text{P(HEMA:MMA 1:1)} \) increased from 8500 to 45 000 pulses when the pump wavelength was changed from 337 to 532 nm.

This work was supported by Project No. MAT94-0757 of the Spanish CICYT. The materials described in this letter and their utilization in solid-state dye lasers are covered by Spanish Patent 9501419, filed 14 July 1995.


