Laser performance of pyrromethene 567 dye in solid polymeric matrices with different cross-linking degrees

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We report on the laser action of pyrromethene 567 (PM567) incorporated into copolymers of methyl methacrylate (MMA) with different methacrylic and acrylic cross-linking monomers: ethyleneglycol dimethacrylate, trimethylolpropane trimethacrylate, tetraethyleneglycol diacrylate, pentaerythritol triacrylate, and pentaerythritol tetraacrylate (PETRA). The vol/vol proportion of the different co-monomers in each copolymer formulation was systematically varied, and the effect of each composition on the lasing properties of PM567 was evaluated. The laser samples were transversely pumped at 534 nm with 5.5 mJ/pulse from a frequency doubled *Q*-switched Nd:KGW laser. Lasing efficiencies of up 26% and good stability with a drop of the initial laser output of 30% after 100 000 pump pulses at 5 Hz in P(MMA:PETRA 95:5) were demonstrated. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1398598]

I. INTRODUCTION

The use of solid matrices doped with organic dye molecules as an alternative to conventional liquid-solution dye lasers has been extensively studied.[1] The large volumes required, flammability, solvent evaporation, flow fluctuation, and toxicity are some of the disadvantages of liquid-solution dye lasers that would be ameliorated by the use of a solid host for the dye molecules. Therefore, solid-state dye lasers could potentially find many applications in various fields including medicine, remote sensing, and spectroscopy. Relevant features of solid-state dye lasers are a low energy-per-pulse threshold, a compact and maintenance free system, and a low cost gain medium. Synthetic polymer hosts have advantages as compared with other matrices because polymers exhibit good compatibility with organic dyes, high optical homogeneity, and control over medium polarity and viscoelasticity in a way similar to conventional solvents[2] allowing miniaturization and low-cost integrated optical system designs. The main drawback of these materials when they were initially compared with silica gels was their lower thermal resistance. However, the development of new modified polymers with much improved laser-radiation-damage threshold[3,4] has alleviated this problem, and stabilities in polymeric materials incorporating rhodamine dyes comparable or even higher than those obtained with silica gels when used under the same conditions have been demonstrated.[5] The above properties, combined with the adaptability of polymers to inexpensive fabrication techniques and the easiness with which relevant properties of these materials, such as free volume, chemical composition, molecular weight, microstructure and viscoelasticity, can be modified in a controlled way,[6,7] make polymers very attractive materials to be used as hosts in solid-state dye lasers.

One of the main problems encountered upon the use of these solid matrices is the thermal and/or photodegradation of the dye, tentatively explained in terms of the poor heat dissipation in the matrix.[5,6] In a similar way, Popov recently analyzed[8] the dye photodestruction mechanism in a solid-state polymeric dye laser and concluded that the increased mobility of the excited dye molecules as a result of the heating process involved in the optical excitation is an important factor in the dye degradation kinetics. Attempts to reduce the photodegradation rate of dye doped polymeric matrices include the systematic variation of the polymeric matrix composition and the covalent binding of the dye to the polymeric chain, both actions aimed at increasing the heat dissipation rate.[1] In this way, we carried out the synthesis of new dye molecules based on molecular modifications of rhodamine 6G (Rh6G) that facilitate when copolymerized with adequate monomers the dissipation, along the polymer backbone, of the absorbed energy that is not converted into light emission.[5] The photostability reached with the new terpolymer with 7:3 molar proportion of the monomers 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) increases by a factor 2.6 the useful lifetime of the solid solutions of Rh6G in the HEMA:MMA copolymers.[6] It is well known from laser efficiency measurements that the extent of sample degradation changes widely with the matrix composition. Pursuing this idea, we have also studied the effect of the microscopic rigidity of the polymeric matrix on laser operation, which was increased by cross-linking of the polymer chains.[9] With Rh6G as the active molecule, a significant increase of laser efficiency and durability was obtained in polymeric matrices of HEMA cross-linked with 10% ethyleneglycol dimethacrylate (EGDMA).

However, further progress in photostability would be necessary before an operational solid-state dye laser was

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(PM-567)

CH₂=C–COO–CH₂–CH₂–OOC–C=CH₂   **EGDMA**

(Figure: TMPTMA structure)   **TMPTMA**

CH₂=CH–COO⟮CH₂–CH₂–O⟯₄OC–CH=CH₂   **TEGDA**

(Figure: PETA structure)   **PETA**
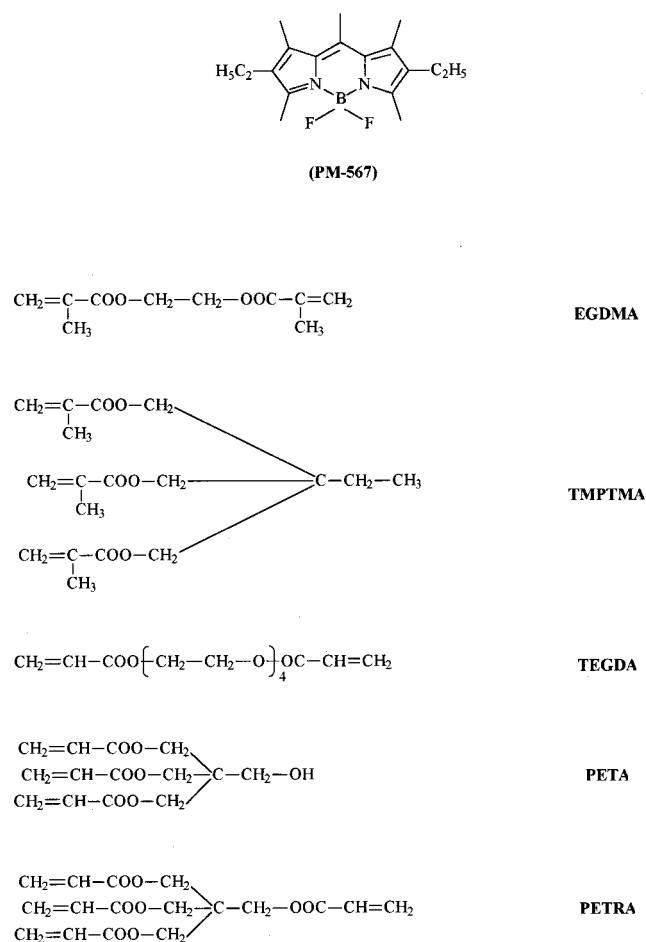
(Figure: PETRA structure)   **PETRA**

FIG. 1. Molecular structure of PM567 dye and the cross-linking monomers selected in this work: methacylic (EGDMA, TMPTMA) and acrylic (TEGDA, PETA, and PETRA).

competitive with liquid dye lasers. To this aim, in this article we study the effect on the lasing properties of pyrromethene dyes of increasing the rigidity of the polymeric host matrix by controlled cross-linking of the polymeric chains with bi-, tri , and tetrafunctional monomers. The pyrromethene family of dyes, developed by Boyer and co-workers, promised enhanced laser efficiency and photostability[10–15] because they exhibit high quantum fluorescence yields owing to their low triplet absorption losses at the fluorescence emission wavelengths.[16,17] In particular, a pyrromethene-BF₂ complex known as pyrromethene 567 (PM567), the molecular structure of which is shown in Fig. 1, exhibits excellent laser efficiency in both liquid and solid solutions[4,18–29] and good photostability in polymer[4,23,24,28–30] host materials. In this work, the PM567 dye was incorporated into a variety of copolymers of MMA with different molar proportions of methacrylic and acrylic cross-linking monomers such as EGDMA, trimethylolpropane trimethacrylate (TMPTMA), tetraethyleneglycol diacrylate (TEGDA), pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETRA) (see Fig. 1 for dye and monomer structures). MMA is mono functionalized (one double bond), while EGDMA and TEGDA are double functionalized (two double bonds), TMPTMA and PETA are triple functionalized (three double

bounds), and, finally, PETRA is quadrupole functionalized (four double bonds). The copolymerization of MMA with these monomers leads to a three-dimensional network. MMA was chosen as the pivotal component in the formulations developed because the excellent optical transparency and relatively high laser-damage resistance of poly(methylmethacrylate) (PMMA) makes this material an obliged reference in any strategy directed to improve lasing performance in polymeric solid-state dye lasers. The vol/vol proportion of both monomers in each copolymer formulation was systematically varied, and the effect of each composition on the lasing properties of PM567 was evaluated.

II. EXPERIMENT

A. Methods

The solid laser samples were cast in a cylindrical shape, forming rods of 10 mm diameter and 10 mm length. A cut was made parallel to the axis of the cylinder in order to obtain a lateral flat surface of 4×10 mm. This surface was prepared for lasing experiments by conventional grinding and polishing. The ends of the laser rods were polished by hand to obtain reasonably flat surfaces. No attempt to produce laser grade flat surfaces was made. The dye concentration was in all cases 1.5×10^{-3} M, so that the optical density of the samples at the 534 nm pump wavelength was about 18, for 1 cm optical path.

The air-equilibrated polymer rods were transversely pumped at 534 nm with 5.5 mJ, 6 ns full width at half maximum (FWHM) pulses from a frequency double Q switched Nd:KGW laser (Monocrom STR-2+) at repetition rate up to 10 Hz. The exciting pulses were directed towards the lateral flat surface of the sample with a combination of spherical ($f=50$ cm) and two cylindrical quartz lenses. The first one, with $f=-15$ cm, widened the spherical cross section of the pump beam to illuminate the complete 1 cm length of the dye sample; then, the second lens, with $f=15$ cm and perpendicularly arranged, focused the pump pulses onto the input surface of the solid sample to form a line of 0.3×10 mm, so that the pump fluence was 180 mJ/cm². The oscillator cavity consisted of a 90% reflectivity flat aluminum mirror and the end face of the solid sample as the output coupler, with a cavity length of 2 cm. The cavity was not optimized and did not have tuning elements to select the wavelength.

The dye and pump laser pulses were characterized with the following instruments: GenTec ED-100A and ED-200 pyroelectric energy meters, ITL TF1850 fast risetime photodiode, Tektronix 2430 digital-storage oscilloscope, CM110 monochromator (CVI Laser Corporation), and EMI 9783B photomultiplier. In the photodegradation studies, dye and pump laser signals were sampled with boxcars (Stanford Research Model 250). All the integrated signals were digitized and processes using a PC computer *via* a Computerboard DASH-8 Interface.[31] The estimated error of the energy measurements was 10%.

Absorption and fluorescence spectra of the solid samples were registered from thin disks cut out from the same samples used in the lasing experiments and measured, re-

J. Appl. Phys., Vol. 90, No. 7, 1 October 2001

Costela *et al.* 3161

spectively, on a Shimadzu UV-265 FS spectrometer and on a Perkin-Elmer LS-50B luminescence spectrometer.

B. Materials

1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-difluoro-borate (Pyrromethene 567, laser grade from Exciton) was used as received. The purity of the dye was found to be >99%, as determined by spectroscopic and chromatographic methods. The dye was dissolved in the different polymeric matrices following the methods described below.

Methyl methacrylate (Merck) was washed three times with 10% vol aqueous sodium hydroxide to remove the inhibitor and then twice with distilled water. The monomer, dried over anhydrous $MgSO_4$, was then distilled under reduced pressure before use. Ethyleneglycol dimethacrylate (EGDMA), supplied by Merck, tetraethyleneglycol diacrylate (TEGDA), pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETRA), supplied by Aldrich, and trimethylolpropane trimethacrylate (TMPTMA), supplied by Solrac, were all used as received.

Preparation of polymer dye samples

Freshly purified monomers were used to prepare the samples. The adequate amount of PM567 dye was dissolved in mixtures with different volume/volume proportions of MMA and the corresponding cross-linker monomer, and the resulting mixtures were placed in an ultrasonic bath until complete dissolution of the dye. After further addition of 0.015 g/liter of 2,2'-azobis(isobutyronitrile) (AIBN), used as free radical initiator, the mixture was again sonicated. AIBN is the thermal polymerization initiator of choice, since it leaves UV-transparent end groups on the copolymer. The resulting solutions were filtered into appropriate cylindrical polypropylene molds using a 0.45 μm pore size filter followed by a 0.2 μm pore size filter (Whatman Lab., polytetrafluoroethylene disposable filters). After careful deaeration by bubbling dry argon for 10 min, the molds were sealed. An inert atmosphere avoids the well-known oxygen inhibition of radical polymerization. Polymerization was performed in the dark at 40 °C over a period of two days and then at 45 °C for about one day. The temperature was then raised to 60 °C and increased slowly up to 80 °C over a period of several days, in order to decompose residual AIBN. Finally, the temperature was reduced in steps of 5 °C per day until room temperature was reached, and only then were the samples unmolded. This procedure was essential in order to reduce the buildup of stresses in the polymer samples due to thermal shock.

III. RESULTS AND DISCUSSION

Broadband laser emission with beam divergence of 5 mrad and pulse duration of 5 ns FWHM was obtained from all the materials under study. Laser emission maxima were in the range 560–570 nm, depending on the composition of the polymer matrix, with oscillation bandwidths of 4–7 nm, much narrower than the fluorescence spectral widths. The particular values of both parameters for each of the compositions tried are listed in Table I. The absorption and fluorescence spectra as well as the spectral profiles of the stimulated

TABLE I. Laser parameters[a] of PM567 dissolved in MMA cross-linked with different monomers[b] added in various proportions vol/vol. Dye concentration: 1.5×10^{-3} M. Nd:KGW pump energy: 5.5 mJ/pulse.

Material	λ_{max} (nm)	$\Delta\lambda$ (nm)	Eff (%)
PMMA	567	7	12
P(MMA:EGDMA 95:5)	566	5	10
P(MMA:EGDMA 90:10)	566	4	9
P(MMA:EGDMA 80:20)	564	7	8
P(MMA:TMPTMA 99:1)	563	5	21
P(MMA:TMPTMA 98:2)	563	5	23
P(MMA:TMPTMA 95:5)	564	5	19
P(MMA:TMPTMA 90:10)	565	4	14
P(MMA:TMPTMA 80:20)	561	5	10
P(MMA:TEGDA 95:5)	565	6	14
P(MMA:TEGDA 90:10)	570	6	19
P(MMA:TEGDA 80:20)	566	6	3
P(MMA:PETA 95:5)	568	5	21
P(MMA:PETA 90:10)	570	5	26
P(MMA:PETA 80:20)	569	5	24
P(MMA:PETRA 99:1)	559	5	11
P(MMA:PETRA 98:2)	562	6	13
P(MMA:PETRA 95:5)	564	6	18
P(MMA:PETRA 90:10)	563	5	25
P(MMA:PETRA 80:20)	563	4	22

[a]λ_{max}: peak of the laser emission; $\Delta\lambda_{max}$: FWHM of the laser emission; Eff: energy conversion efficiency.
[b]MMA:methyl methacrylate; EGDMA; ethyleneglycol dymetacrylate; TMPTMA: trimethylolpropane trimethacrylate; TEGDA: tetraethyleneglycol diacrylate; PETA: pentacrythritol triacrylate and PETRA: pentaerythritol tetraacylate.

emission registered for PM567 are very similar for all of the materials studied in this work, with small shifts in the position of the maximum of the laser emission which are correlated with shifts in the fluorescence spectrum. The minimum pump energy producing laser emission was of the order of 50 μJ.

The lasing efficiencies of PM567 in the different polymeric formulations under study, defined as the ratio between the energy of the dye laser output and the energy of the pump laser incident on the sample surface, are tabulated in the third column of Table I. For comparison, the laser parameters of PM567 doped in PMMA homopolymer pumped under identical experimental conditions are also included in Table I. In addition, and to put these numbers in proper perspective, measurements were made of the lasing efficiency of a static solution of PM567 in ethyl acetate, solvent that mimic the MMA monomer present in the solid formulations tested in this work. For this liquid solution, a lasing efficiency of 33% was reached under the same experimental conditions as the solid samples (same optical density as that of the solid sample and using the end face of the 1 cm optical path dye cell as the output coupler). Two notes of caution are needed when analyzing the efficiency obtained in liquid and solid solutions. In the first place, the reflectivity of the output coupler in the oscillator cavity has not been optimized for laser operation in any case. Our main concern in this work is not so much to optimize the laser output as to study the photostability and relative efficiency of operation in different polymeric materials under otherwise identical conditions. Second, as indicated in the experimental section, the finishing of

the surface of the solid samples relevant to laser operation was not laser grade. Thus, improvements in lasing efficiency are to be expected in these samples with enhanced optical quality of their surface. Although our materials exhibit good optical homogeneity, it is unlikely that the sole effect of the poor polishing of the samples surfaces could explain the important differences in efficiency between solid and liquid solutions. A more important source of distortions could be the thermal lensing effect experienced at the solid-state gain media under our hard excitation regime.[32]

From the data reported in Table I it is clear that both the proportion and the nature of the cross-linking monomer play an important role in the effectiveness of laser operation. With the exception of the monomer EGDMA, the increase of the rigidity of the polymeric matrix by cross-linking improves the lasing efficiency with respect to that exhibited by the PM567 embedded in the linear PMMA. This laser parameter first increases monotonically with the amount of the cross-linking monomer present in the matrix reaching, for a certain molar proportion of each monomer, an optimum value: 23% for P(MMA:TMPTMA 98:2); 19% for P(MMA:TEGDA 90:10); 26% for P(MMA:PETA 90:10), and 25% for P(MMA:PETRA 90:10). These improvements can be attributed to the decrease of the polymer free volume that induces a significant reduction of the rotational and vibrational molecular freedom.[7] As a result, nonradiative decay of excited dye molecules is prevented leading to a significant increase of the emission quantum yield of the dye. For a certain concentration of the cross-linking monomer, the free volume available within the polymeric matrix will be completely occupied by the dye. Increasing the concentration beyond this point will result in the dye molecules being partially excluded from the shrinking free volume, and formation of dimers and higher aggregates, with their deleterious effect on laser operation, will be forced. In order to lend support to this tentative conclusion, a more detailed study of free volume holes and their distribution inside the matrix is currently in progress.

Taking into account the lasing efficiency, it seems that the addition of acrylic monomers to PMMA results in a matrix for PM567 dye better than those based on methacrylic ones. Furthermore, to optimize the laser action, these latter monomers have to be added in much lower molar proportion (5% and 2% for EGDMA and TMPTMA, respectively) than the acrylic ones (10% for TEGDA, PETA and PETRA), which could be related to a slower increase of the glass transition temperature of the matrices based in acrylic monomers. Notwithstanding, the behavior that both series of monomers induces is similar in that improvements in lasing efficiency are reached as the number of double bonds of each monomer increases. In fact, the presence of three (TMPTMA and PETA) and four (PETRA) double bonds in the same carbon atom leads to an overgrown network polymer, which results in the best laser performance of PM567 dye.

Some of the laser efficiency values reached in this work improve our previous results obtained when PM567 was dissolved in MMA with different lineal comonomers, with the exception of the results obtained when the dye was embedded into P(MMA:TFMA 7:3), in which case an efficiency of
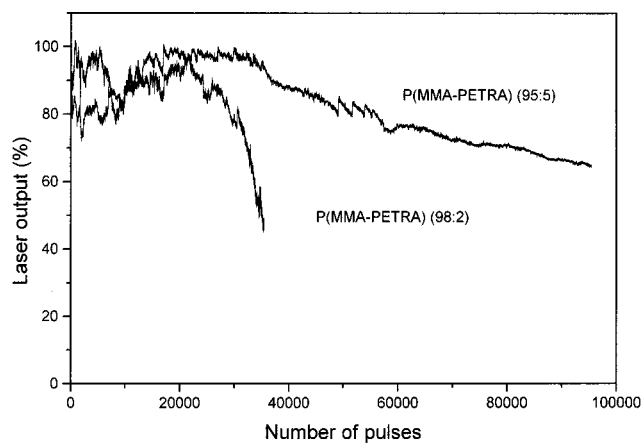

FIG. 2. Normalized laser output as a function of the number of pump pulses for PM567 dissolved in P(MMA:PETRA 98:2) and P(MMA:PETRA 95:5). Dye concentration: 1.5×10^{-3} M. Pump energy and repetition rate: 5.5 mJ/pulse and 5 Hz, respectively.

30% was obtained, under identical experimental conditions.[29] Laser emission from PM567, incorporated into different polymeric materials, has also been investigated by other authors. Jones *et al.*[33] reported a lasing efficiency of ≈24% for PM567 dispersed in a copolymer of MMA and lauryl methacrylate (LMA) pumped the sample with 100 mJ in microsecond pulses at 490 nm. Rahn and King[20] obtained efficiencies of ≈7.5% with PM567 incorporated into a nitrogen-saturated matrix of modified PMMA (PMMA with low-molecular weight additives, such as ethanol), and of ≈4.5% when the matrix was air saturated. On the other hand, by incorporating PM567 in a named but not described "modified acrylic plastic" matrix of unknown composition, Hermes *et al.*[18] reported slope efficiencies as high as 77% with pump energies of up to 150 mJ at 532 nm. Allik *et al.*[4] obtained slope efficiencies of 50% when the PM567 dye was dissolved in a so-called high temperature plastic matrix and pumped at 532 nm with energies of up to 50 mJ. Ahmad, Rahn, and King[34] reported a slope efficiency of 65% for the PM567 dissolved in PMMA with pump fluences up to 1.9 J/cm^2. Modification of this polymer with a triplet quencher (perylene) yielded energy conversion efficiencies up to 71%. It should be noticed that in all the referred cases pumping was longitudinal and the reflectivity of the output coupler optimized.

The evolution of the laser output as a function of the number of pump pulses in the same position of the sample was studied for the different materials at a repetition rate of 1, 5, and 10 Hz. In Fig. 2 the evolution of the laser output of PM567 dye with the number of pump pulses is shown graphically for the matrices based on MMA with 2% and 5% of PETRA as cross-linker monomer. In Table II are listed the intensities of the laser output after n pump pulses referred to the initial intensity of the laser emission $[I_n(\%) = (I_n/I_0) \times 100$, where I_0 is the initial intensity]. When the samples were pumped at 1 Hz repetition rate, the number of pump pulses registered was 5000 and 10 000. In the experiments carried out at 5 and 10 Hz, the data tabulated correspond to 10 000 pulses and to a number of up to 100 000 pump

TABLE II. Influence of the pumping repetition rate on the useful lifetime[a] of PM567 dissolved in MMA with different cross-linked monomers added in different vol/vol molar proportions. Dye concentration: 1.5×10^{-3} M. Nd:KGW pump energy: 5.5 mJ/pulse.

Material	1 Hz		5 Hz		10 Hz	
	$I_{5000}(\%)$	$I_{10\,000}(\%)$	$I_{10\,000}(\%)$	$I_n(\%)$[b]	$I_{10\,000}(\%)$	$I_n(\%)$[b]
PMMA	85	70	50	5 (15 000)	1	
P(MMA:EGDMA 95:5)	90	90	47	15 (18 000)	26	11 (17 000)
P(MMA:EGDMA 90:10)	60	45				
P(MMA:EGDMA 80:20)	45	25				
P(MMA:TMPTMA 99:1)			80	35 (50 000)	40	40 (50 000)
P(MMA:TMPTMA 98:2)					90	20 (30 000)
P(MMA:TMPTMA 95:5)			20	40 (18 000)	50	20 (28 000)
P(MMA:TMPTMA 90:10)					40	10 (30 000)
P(MMA:TMPTMA 80:20)					10	2 (17 000)
P(MMA:TEGDA 95:5)	65	50				
P(MMA:TEGDA 90:10)	100	100				
P(MMA:TEGDA 80:20)	60	45				
P(MMA:PETA 95:5)	100	100	84	65 (28 000)	50	20 (25 000)
P(MMA:PETA 90:10)	75	70				
P(MMA:PETA 80:20)	50	35				
P(MMA:PETRA 99:1)			50	20 (20 000)		
P(MMA:PETRA 98:2)			80	60 (35 000)	80	30 (20 000)
P(MMA:PETRA 95:5)			95	70 (100 000)	80	80 (45 000)
P(MMA:PETRA 90:10)					75	18 (28 000)
P(MMA:PETRA 80:20)			20	10 (20 000)	2	

[a]Intensity of the dye laser output after n pump pulses referred to initial intensity I_0; $I_n(\%) = (I_n/I_0) \times 100$.
[b]Intensity of the dye laser output after the number of pulses indicated within parenthesis.

pulses, depending on the material, as is indicated in Table II within parenthesis. For the sake of clarity, the experimental results corresponding to $n = 10\,000$ and 1 Hz repetition rate are also represented in Fig. 3.

Initially, the photostability of PM567 embedded into polymeric matrices of MMA with cross-linked acrylic (TEGDA and PETA) and methacrylic (EGDMA) monomers was analyzed at 1 Hz repetition rate. It was observed that the intensity of the laser output decreases with the number of pump pulses, the rate of this decrease depending on the composition of the polymeric matrix. As seen in previous work with rhodamine dyes,[6] in the majority of these materials there is an apparent relationship between lasing efficiency and photostability: the higher the efficiency, the lower the rate of degradation. For all the selected monomers, there is a degree of cross-linking (5% of EGDMA, 10% of TEGDA, and 5% of PETA) that improves the photostability exhibited by PM567 into the PMMA homopolymer. This effect is specially remarked for the materials P(MMA:TEGDA 90:10) and P(MMA:PETA 95:5), where no sign of degradation is observed after 10 000 pump laser pulses. In order to gain a

better insight into the photostability of these materials, their useful lifetime was determined pumping the samples at 5 and 10 Hz repetition rates. When the pump repetition rate increases, the degradation rate in the studied materials increases significantly. Thus, after 10 000 pump pulses, the emission from the dye doped into P(MMA:EGDMA 95:5) remains 90%, 47%, and 26% of its initial value at pumping repetition rate of 1, 5, and 10 Hz, respectively. Following the same behavior, the laser emission induced in PM567 dissolved in P(MMA:TEGDA 90:10) drops completely after 10 000 and 4 000 pulses, when the pumping repetition rate increases from 5 to 10 Hz. It seems that at high repetition rate, the dissipation channels of the energy released to the medium as heat are not fast enough, and as a result the thermal degradation of the dye is enhanced. These results are in good agreement with our recent study on the effect of the heat load on the stability of polymeric dye lasers. In that study,[35] the capability of each material to dissipate the heat generated in the sample as a consequence of the pump energy excitation was characterized by photothermal deflection spectroscopy. Recent experimental results obtained with this
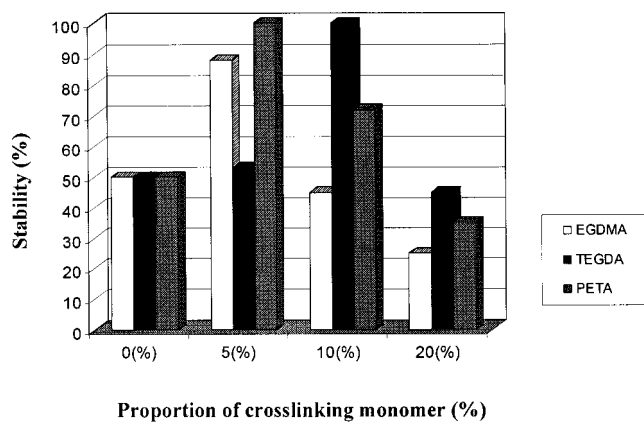
FIG. 3. Dependence with the percentage of the cross-linking monomers EGDMA, TEGDA and PETA added to MMA of the stability of the laser output after 10 000 pump pulses referred to the initial intensity I_0 of the laser emission $[I_n(\%)=(I_n/I_0\times100)]$. Dye concentration: 1.5×10^{-3} M. Pump energy and repetition rate: 5.5 mJ/pulse and 1 Hz, respectively.
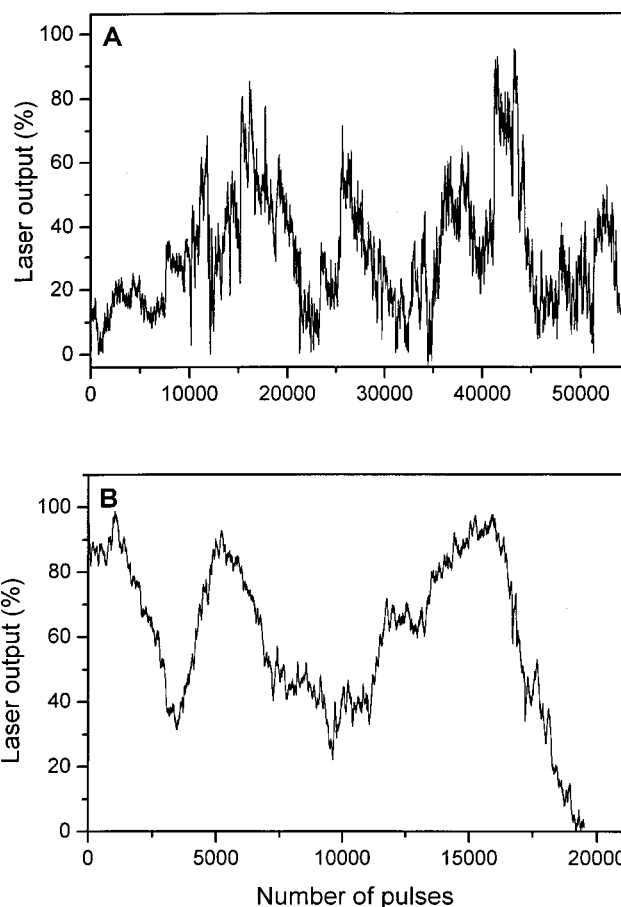

FIG. 4. Irregular behavior with strong oscillations observed in the laser output of PM567 dissolved in (A) P(MMA:TMPTMA 99:1) and (B) P(MMA:TMPTMA 95:5) as a function of the pump pulses at 10 and 5 Hz repetition rate, respectively. Dye concentration: 1.5×10^{-3} M. Nd-KGW pump laser energy: 5.5 mJ/pulse.

technique[36] evidenced that the accumulation of heat into the material increased significantly for pumping repetition rates higher than 1 Hz.

The laser photostability not only improved by optimizing the polymer free volume by cross-linking, but also by increasing the number of polymeric chains cross-linked by each monomer. Thus, the best performance was reached when the dye was embedded into the matrix P(MMA:PETRA 95:5), in which case the laser emission remained at 70% (5 Hz) and 80% (10 Hz) of its value after 100 000 and 45 000 pump pulses, respectively. When dye PM567 was dissolved in P(MMA:PETA 95:5) the laser output dropped by 35% (5 Hz) and 80% (10 Hz) after 28 000 and 25 000 pump pulses, respectively.

As can be seen in Fig. 4, the laser emission of PM567 dissolved in matrices based on methacrylic monomers, especially in TMPTMA, exhibits an irregular behavior, with strong oscillations over several thousand pump pulses resulting in the laser emission going down to near zero, only to near fully recover afterwards. Taking onto account that the glass transition temperature (Tg) increases significantly with the cross-linking degree of the material, inducing changes in the local movements of polymer chains which leads to large changes in a number of physical properties, the oscillations in the laser output could be related to gradient of temperature produced under irradiation conditions in samples where thermal diffusion could be partially hindered. In addition, this irregular behavior could be reflecting the presence of residual free double bonds that remains into the matrices due to the soft thermal conditions selected to carry out the polymerization.

To confirm this hypothesis and in a further attempt to improve the stability of the laser output, some samples were subjected to a postpolymerization thermal treatment in order to reach the total polymerization of the residual double bonds. This thermal treatment consisted basically of a small increase of the temperature, from 80 to 95 °C, during seven days, and then decreasing it from 95 °C to room temperature at a rate of 5 °C/h. As can be seen in Fig. 5, after this treat-ment, the laser output exhibits a more regular behavior, with a drastic reduction of both width and frequency of the oscillations, without decreasing the lasing efficiency. At was expected, this effect is especially noted in the matrix with higher proportion of the cross-linking monomer. In addition, the lasing photostability of PM567 dissolved in the thermally postcured P(MMA:TMPTMA 95:5) significantly improves the previous results obtained with this material since it remains at 88% of the initial laser output after 20 000 pump pulses at 5 Hz. These results are reflecting that the supplemental thermal treatment is inducing the total polymerization of the residual double bonds. In fact, after the postpolymerization treatment just described no residual monomer could be detected, neither by IR absorption spectroscopy of sample films nor by gravimetric monitoring after exhaustive treatment of the samples under high vacuum conditions at 50 °C. However, further increase of the postcure temperature up to 115 °C during two days leads to a partial destruction of dye molecules, reflected in a drastic decrease in both lasing efficiency and photostability. Thus, after this final thermal treatment, the PM567 dye dissolved in P(MMA:TMPTMA 95:5) exhibits an efficiency of only 12%, with a drop of the initial laser output of 80% after 8000 pump pulses at 5 Hz repetition rate. Consequently, the development of solid-state dye
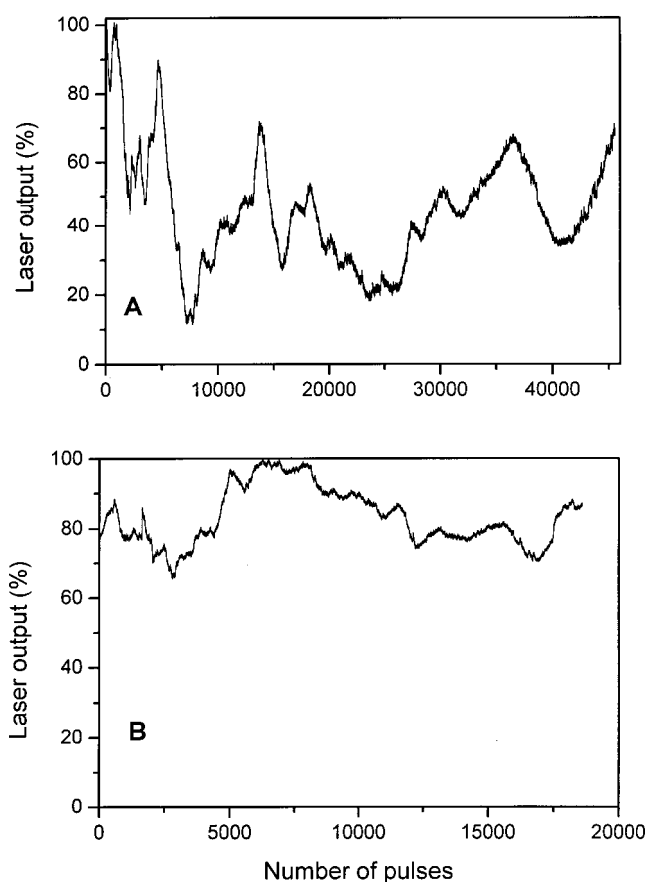
FIG. 5. Influence of the postpolymerization thermal treatment on the laser output of PM567 dissolved in (A) P(MMA:TMPTMA 99:1) and (B) P(MMA:TMPTMA 95:5) as a function of the pump pulses at 10 and 5 Hz repetition rate, respectively. Dye concentration: 1.5×10^{-3} M. Nd-KGW pump laser energy: 5.5 mJ/pulse.

lasers based on cross-linked matrices requires a very careful optimization of the thermal conditions selected to carry out the final polymerization of the material in order to avoid the presence of residual monomer and free double bonds without inducing the thermal degradation of the dye molecules.

The results obtained in this work clearly improve the photostabilities reported for PM567 derivative in our previous work where the laser emission from the dye dissolved in lineal matrices of MMA with different co-monomers remained 20% of the initial value after 10 000 pump pulses at 1 Hz repetition rate.[29] Photostabilities higher than those obtained in the present article have been reported by Allik *et al.*[4] for PM567 doped in an undefined high temperature plastic material, in which case 78% of the initial lasing efficiency was retained after 95 000 pump pulses. In addition, Ahmad, Rahn, nd King[34] reported high photostability for PM567 in pure PMMA with 270 000 pulses emitted before the conversion efficiency fell to half its initial value for a pump fluence of 0.16 J/cm^2. When PMMA was modified with 1,4-diazobicyclo[2,2,2]octane singlet oxygen quencher, the longevity increased to 550 000 pump pulses. In a previous article, Rhan and King[20] had reported a drop on the laser output to 60% of the initial value after 7000 pulses from PM567 in a nitrogen-saturated MPMMA matrix and a drop to 10% of the initial value after 3000 pulses when the matrix

was air saturated. In the studies carried out by Jones *et al.*[33] the laser output of PM567 in P(MMA-LMA) dropped to 10% of the initial value after 1000 shots. In all the above referred cases pumping was longitudinal at 10 Hz repetition rate.

The results presented in this work together with those reported in our previous studies on solid-state dye lasers confirm that the best dye/host combination is specific for each dye molecule and that there is not a universal polymeric matrix to develop efficient and stable solid-state dye lasers: the photophysical and photochemical properties of each dye require a proper adjustment of the polymer structure composition in order to obtain optical, thermal, and mecanodynamical properties of the matrix which optimize its laser action. In addition, the rigidity of the matrix results to be of uppermost importance to optimize the laser performance of a given dye. Work in progress is directed to evaluate the free volume and its distribution inside the polymer systems selected as hosts for organic dyes, as well as its relationship with relevant properties of the dye either dissolved or covalently bonded to the polymer. This information would be of great value in the search for strategies to improve the material's photostability.

ACKNOWLEDGMENT

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