

# Bichromatic laser emission from dipyrromethene dyes incorporated into solid polymeric media

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Bichromatic laser emission from dipyrromethene-based solid-state dye lasers is reported. The dependence of this dual emission on different factors and its origin and causes are discussed in the light of different models proposed in the literature. Our experimental results indicate that the long-wavelength emission can be explained in terms of reabsorption/reemission effects and inhomogeneous broadening of the  $S_0$ - $S_1$  transition. The short-wavelength emission corresponds to the usual  $S_0$ - $S_1$  transition and dominates at low dye concentration. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743879]

## I. INTRODUCTION

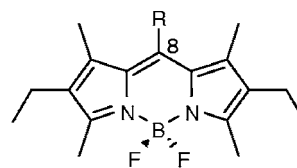
As a result of the continuous effort to produce improved dyes for laser applications, Pavlopoulos and co-workers developed in the late 1980s the dipyrromethene- $\text{BF}_2$  (PM) dyes, also known as boron difluoropyrromethene (BODIPY) dyes. These dyes emit in the green-red region of the electromagnetic spectrum with high fluorescence quantum yields, owing to their low triplet absorption losses at the fluorescence emission wavelengths,<sup>1-10</sup> and have demonstrated efficient laser emission both in liquid<sup>2,7,9,11,12</sup> and solid state,<sup>13-25</sup> although they are sensitive to photoreactions with oxygen, which makes them relatively unstable in air-saturated solutions.<sup>14,26</sup>

Studies carried out on some commercial PM dyes had shown that their photophysical and lasing properties strongly depend on their molecular structure<sup>5,8,27,28</sup> and that adequate substituents in the molecular core can enhance their laser action.<sup>29,30</sup> Thus, we proceeded to synthesize analogs of the PM laser dye commercially known as Pyrromethene 567 (PM567, Fig. 1) to study the effect of changing the methyl group at position 8 of this molecule by other substituents, while maintaining the four methyl groups at the 1, 3, 5, and 7 positions and the ethyl groups at the 2 and 6 positions.<sup>31,32</sup> The substituents were aliphatic and aromatic (Fig. 1): ( $\omega$ -acetoxy)polymethylene (dye PnAc), ( $\omega$ -methacryloyloxy)polymethylene (dye PnMA), *p*-(acetoxy)polymethylene)phenyl (dye PArnAc), and *p*-(methacryloyloxy)polymethylene)phenyl (dyes PArnMA) groups. These

new dyes lased efficiently and with remarkable photostability when properly incorporated into adequate polymeric matrices.<sup>32-34</sup>

In the course of the above studies, we observed that some of the samples with these new dyes exhibited bichromatic laser emission.<sup>34</sup> Bichromatic laser emission from single laser dyes has been previously reported by other authors under certain circumstances. When Rhodamine 640 was dissolved in methanol solutions containing randomly distributed highly scattering titanium dioxide particles, bichromatic laser emission was observed, depending on dye concentration, pump energy, and scattering particle density.<sup>35-39</sup> Coumarin dyes have also been found to emit amplified spontaneous emission (ASE) in the form of two distinct narrow bands in certain solvents, with the apparition of the two ASE bands depending on dye concentration and pump power.<sup>40-43</sup>

In this work, we present results on the bichromatic laser



| dye    | R  | <i>n</i>    |
|--------|--|-------------|
| PM567  | -Me  | —           |
| PnAc   | $-(\text{CH}_2)_n\text{OCOMe}$                                   | 1,3,5,10,15 |
| PnMA   | $-(\text{CH}_2)_n\text{OCOC}(\text{Me})=\text{CH}_2$             | 1,3,5,10,15 |
| PArnAc | $-\text{Ph}-p-(\text{CH}_2)_n\text{OCOMe}$                       | 1,3         |
| PArnMA | $-\text{Ph}-p-(\text{CH}_2)_n\text{OCOC}(\text{Me})=\text{CH}_2$ | 1,3         |

FIG. 1. Molecular structures of the dipyrromethene- $\text{BF}_2$  dye PM567 and the newly synthesized analogs.

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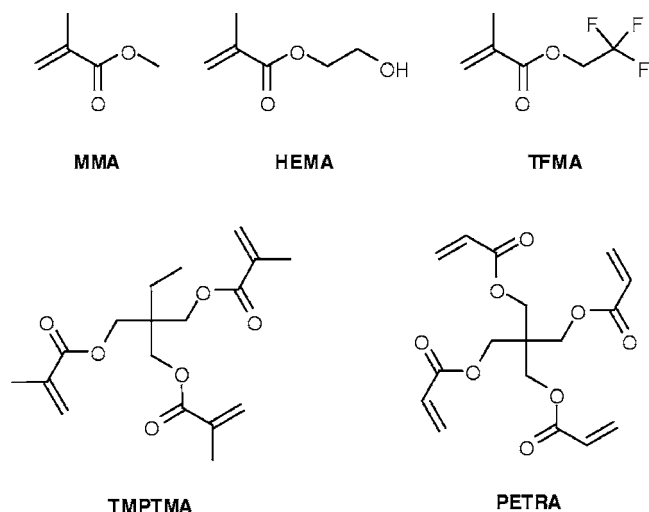


FIG. 2. Molecular structures of monomers: methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2,2,2-trifluoroethyl methacrylate (TFMA), trimethylolpropane trimethacrylate (TMPTMA), and pentaerythritol tetraacrylate (PETRA).

emission from some analogs of the dye PM567 incorporated into solid polymeric matrices. The dependence of this dual emission on different factors is studied, and its origin and causes are discussed.

## II. EXPERIMENT

Details of the synthesis of the new PM dyes have been reported elsewhere.<sup>31,32</sup> Linear and cross-linked copolymers, obtained by copolymerization of methyl methacrylate (MMA) with adequate comonomers, were used as hosts for the lasing dyes. In the linear polymeric formulations, the comonomers were 2-hydroxyethyl methacrylate (HEMA) and 2,2,2-trifluoroethyl methacrylate (TFMA) (Fig. 2). Cross-linking comonomers were trimethylolpropane trimethacrylate (TMPTMA) and pentaerythritol tetraacrylate (PETRA), with three and four polymerizable double bonds per molecule, respectively (Fig. 2).

Model dyes  $PnAc$  and  $PARnAc$  were dissolved in the different matrices, rendering materials  $PnAc/COP(MMA\text{-comonomer})$  and  $PARnAc/COP(MMA\text{-comonomer})$ , where COP is shorthand for copolymer. Monomeric dyes  $PnMA$  and  $PARnMA$  were linked covalently to the polymeric chains, rendering the corresponding terpolymers  $TERP(PnMA\text{-MMA-comonomer})$  and  $TERP(PARnMA\text{-MMA-comonomer})$ , respectively, where TERP is shorthand for terpolymer. The methods of preparation of the polymer dye samples have been described elsewhere.<sup>31</sup>

The laser samples were in cylindrical shape, 10 mm diameter and 10 mm high, and were pumped transversely with 5 mJ, 6 ns, 532 nm pulses from a frequency-doubled  $Q$ -switched Nd:YAG (yttrium aluminum garnet) laser, in a plane-plane oscillation cavity. A detailed account of the laser experimental setup and the detection and analysis apparatus used can be found elsewhere.<sup>34</sup>

Photophysical properties of solid polymeric samples were measured from disk-shaped samples with a thickness

from 0.2 to 1 mm and dye concentrations of  $0.45 \times 10^{-3}$  and  $1.5 \times 10^{-3} M$ . Absorption was registered on a Varian Cary-4E spectrophotometer in transmittance mode, and fluorescence measurements were recorded on a Fluorolog3-22 fluorimeter in the front-face configuration, orientating the sample  $0^\circ$  and  $22.5^\circ$  with respect to the excitation and emission beams, respectively. To elucidate the possible double emission of the studied systems, the fluorescence spectra were registered at three different excitation wavelengths: 470, 490, and 510 nm.

## III. RESULTS

In the characterization of the laser operation of solid-state dye lasers, an important parameter is the lasing stability, i.e., the evolution of the laser emission with the number of pump pulses in the same position of the sample. This parameter is measured as the number of pump pulses needed for the dye laser output to drop by a given percentage with respect to the initial lasing energy. When the spectra of the laser emission are registered as a function of the number of pump pulses, a slight hypsochromic shift in the wavelength of the peak of the laser emission is observed, as a general rule, which is a consequence of the decrease of the concentration of the dye in the irradiated region as a result of the photodegradation of the dye molecules with the increased number of pump pulses.<sup>34</sup>

In our studies on the lasing properties of the modified PM dyes, we noticed routinely the above behavior. However, we recently came to observe<sup>34</sup> an unusual feature in some of the registered spectra: the apparition of two peaks in the laser emission spectral band separated by 10–14 nm. The intensity of the peak more to the blue increases with the number of pump pulses simultaneously to a decrease in the intensity of the peak more to the red.

Trying to characterize this simultaneous dual band laser emission, we proceeded in a previous work<sup>34</sup> to study in some detail the spectral evolution of the laser emission of the monomeric dye P10MA incorporated by covalent bonding into matrices with different amounts of monomers MMA and PETRA, 98:2, 90:10, and 80:20 (Fig. 3). The dye concentration was  $1.50 \times 10^{-3} M$ . In the matrices with the lowest content of PETRA, it is seen that the peak which appears more to the blue showed much lower intensity than the peak at about 563 nm, even after 100 000 pump pulses in the same position of the sample. As the PETRA content in the matrix increases (and, thus, also does the degree of cross-linking in the polymer), the blueshifted peak becomes more conspicuous, and its intensity rises steadily with the content of PETRA and with the number of pump pulses, until eventually becoming higher than the peak at the longer wavelength. In a linear copolymer of P10MA with MMA, with no PETRA, the blueshifted peak only began to appear after 300 000 pump pulses in the same position of the sample.

In Fig. 4 it is shown the evolution of the intensity of the laser output with the number of pump pulses at the emission wavelengths of 563 and 551 nm for the material  $TERP[P10MA\text{-}(MMA\text{-PETRA } 90:10)]$ . It is seen that the emission at 563 nm firstly decays, whereas the emission at

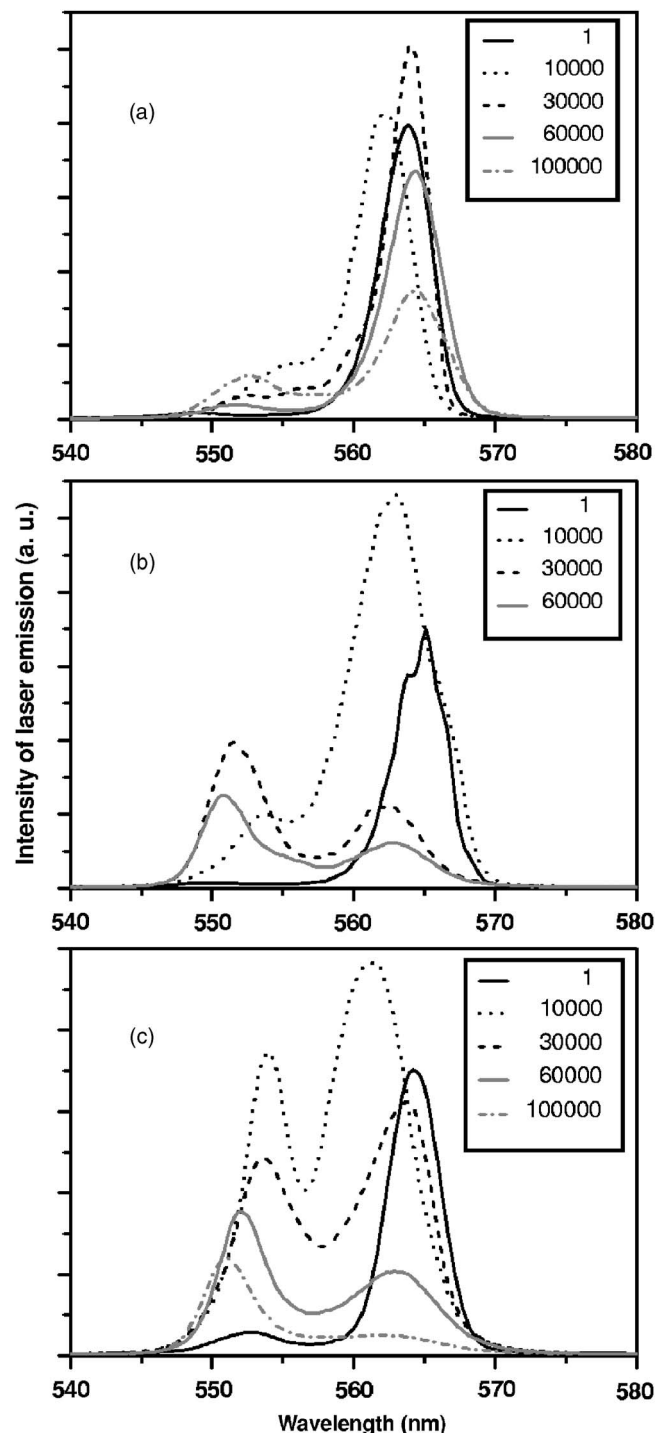


FIG. 3. Spectra of the laser emission of (A) TERP[P10MA-(MMA-PETRA 98:2)], (B) TERP[P10MA-(MMA-PETRA 90:10)], and (C) TERP[P10MA-(MMA-PETRA 80:20)] after the indicated number of pump pulses in the same position of the sample.

551 nm increases in such a way that there seems to be a certain correlation between the evolutions of both emissions. After about 15 000 pump pulses, both emissions maintain approximately the relationship between their intensities, evolving similarly.

In the light of the above results, we ventured some hypothesis (misguided, as we will discuss later on) to explain this unexpected behavior of the modified PM dyes,<sup>34</sup> but it soon became clear to us that in order to gain a better insight

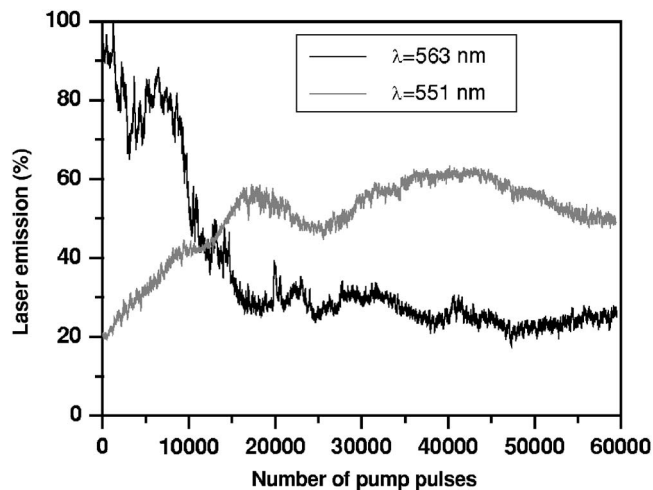


FIG. 4. Evolution of the laser emission with the number of pump pulses for the two laser peaks of the spectrum of the terpolymer TERP[P10MA-(MMA-PETRA 90:10)]. Dye concentration,  $1.50 \times 10^{-3} M$ .

into the origin of the bichromatic emission more detailed studies would be necessary. Thus, we proceeded to perform a systematic study of the dependence of the dual-wavelength laser emission on a number of parameters: dye concentration, dye-matrix interaction (dye dissolved into the polymeric matrix or linked covalently to polymeric chains), matrix structure (degree of cross-linking), aromatic or aliphatic character of the substituent at position 8 of the PM ring, and pump fluence. To this end, we extended our studies to alkyl- and phenyl-substituted model and monomer dyes. The dyes used were P15Ac, P15MA, PAr1Ac, PAr1MA, PAr3Ac, and PAr3MA, all of them with a common PM core, but differing in the substituent at position 8. These dyes were dissolved in, or bonded to, polymers with different free volumes in their structure, as determined by a different degree of cross-linking.

In the following sections we first illustrate the spectral behavior of the laser emission of the selected dyes with examples chosen to show clearly the dependence on the particular parameter considered, well understood that the observed tendencies are common to all the dyes considered in this work. Then, we will discuss and interpret the results obtained by making use of the complementary information provided by absorption and fluorescence photophysical measurements.

### A. Effect of dye concentration

The effect of dye concentration on the laser emission bands is illustrated in Fig. 5, where the spectral evolution of the laser emission with the number of pump pulses for the model dye PAr3Ac, with concentrations of  $0.45 \times 10^{-3}$  and  $1.50 \times 10^{-3} M$ , is shown. At the lower dye concentration, only the emission peaked at  $\sim 550$  nm does appear. When the dye concentration was raised to  $1.50 \times 10^{-3} M$ , the spectrum of the initial emission has also a single peak, albeit at 572 nm. As the sample is repeatedly pumped, a second spectral band appears around 555 nm, close to the position of the spectral single band of the less concentrated samples at  $0.45 \times 10^{-3} M$ .

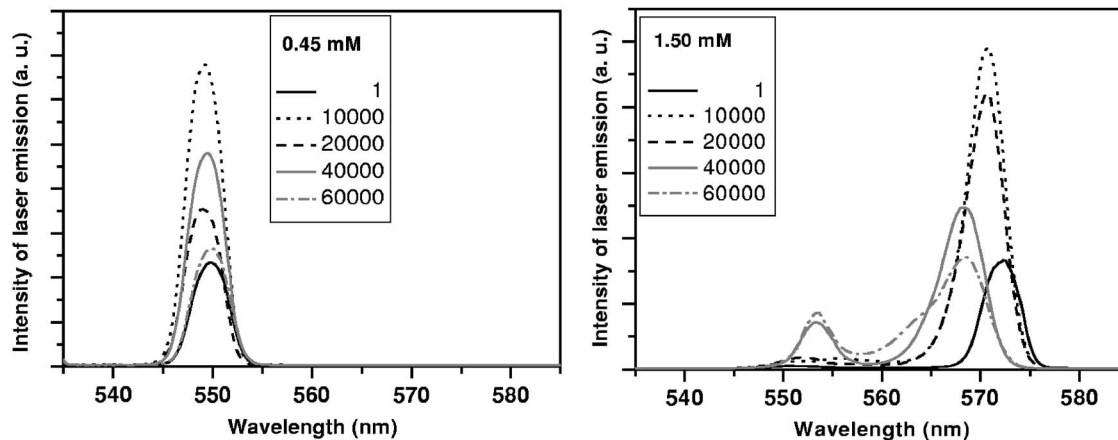


FIG. 5. Spectra of the laser emission of PAR3Ac/COP(MMA-TFMA 7:3) at two different dye concentrations ( $0.45 \times 10^{-3}$  and  $1.50 \times 10^{-3} M$ ) after the indicated number of pump pulses in the same position of the sample.

### B. Effect of dye-matrix interaction

The spectral composition of the laser emission and its evolution with the number of pump pulses also depend on the dyes being dissolved in the polymeric matrix or being bonded covalently to the polymeric chains. A particularly clear example of these differences in behavior is shown in Fig. 6, where the spectral evolution with the number of pump pulses of the 8-aryl dye PAR1Ac dissolved in the copolymer COP(MMA-TFMA 7:3) or with the same chromophore forming the terpolymer TERP[PAR1MA-(MMA-TFMA 7:3)] is depicted. The dye concentration was  $0.80 \times 10^{-3} M$ .

It is seen in Fig. 6 that for the model dye PAR1Ac, there is a single-peaked spectral emission at 554 nm. The spectral position of this emission does not change with the number of pump pulses. In the copolymer with the monomer dye PAR1MA, where the dye is bonded covalently to the polymeric chains, the initial laser emission exhibits a single peak at 571 nm, a redshift of 17 nm with respect to the model dye with the same dye concentration in a matrix with the same polymer composition. The spectrum of the bonded dye changes with the number of pump pulses, and after 20 000 pump pulses a dual emission is well established, with peak maxima at 570 and 560 nm. After 60 000 pump pulses the spectrum has evolved to a single peak at about 557 nm, close to the position of the single-peaked emission of the model dye.

### C. Effect of matrix structure

To assess the possible influence of the matrix structure on the spectral evolution of the bichromatic emission, the lasing behavior of a given dye incorporated into matrices with increasing degree of cross-linking (i.e., with decreasing free volume) was studied. Matrices containing monomers TFMA, TMPTMA, and PETRA, with one, three, and four polymerizable double bonds, respectively, were used. Figure 7 shows the evolution with the number of pump pulses of the spectrum of the monomer dye P15MA, with an aliphatic substituent, in matrices with increased degree of cross-linking.

It is seen in Fig. 7(a) that the sample with the linear polymeric formulation (MMA-TFMA 7:3) exhibits a single emission at a wavelength close to 565 nm under irradiation

with up to 40 000 pump pulses. The expected hypsochromic shift due to the decrease in dye concentration resulting from dye degradation is observed. When the cross-linking monomer TMPTMA, with three polymerizable double bonds, is present in the matrix in proportion MMA-TMPTMA 95:5, the spectrum of the laser emission begins to show a second

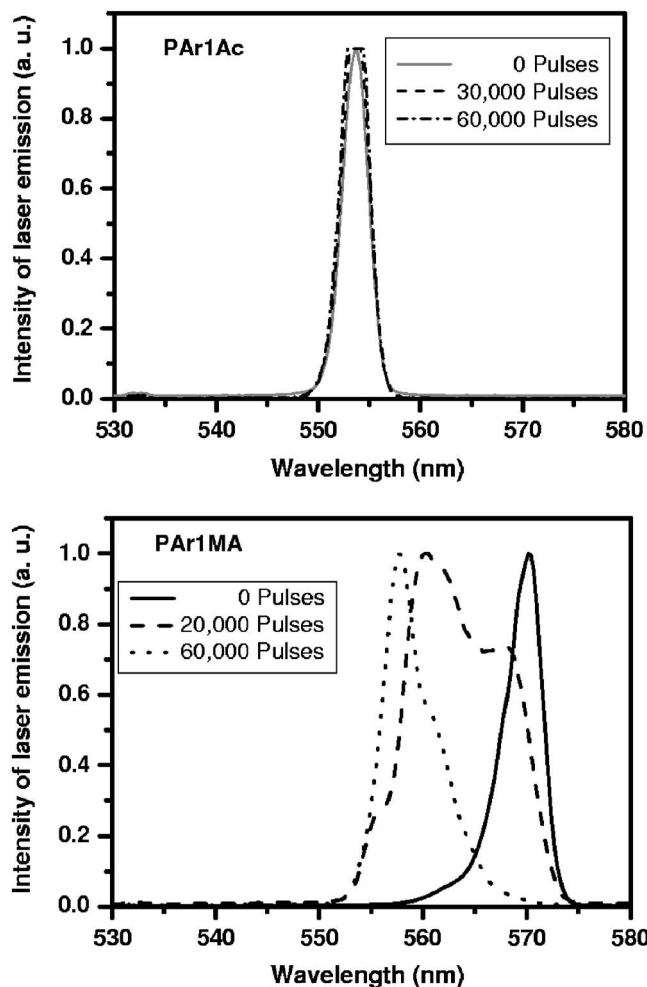


FIG. 6. Normalized spectra of the laser emission after the indicated number of pump pulses in the same position of the sample of materials PAR1Ac/COP(MMA-TFMA 7:3) and TERP[PAR1MA-(MMA-TFMA 7:3)]. Dye concentration,  $0.80 \times 10^{-3} M$ .

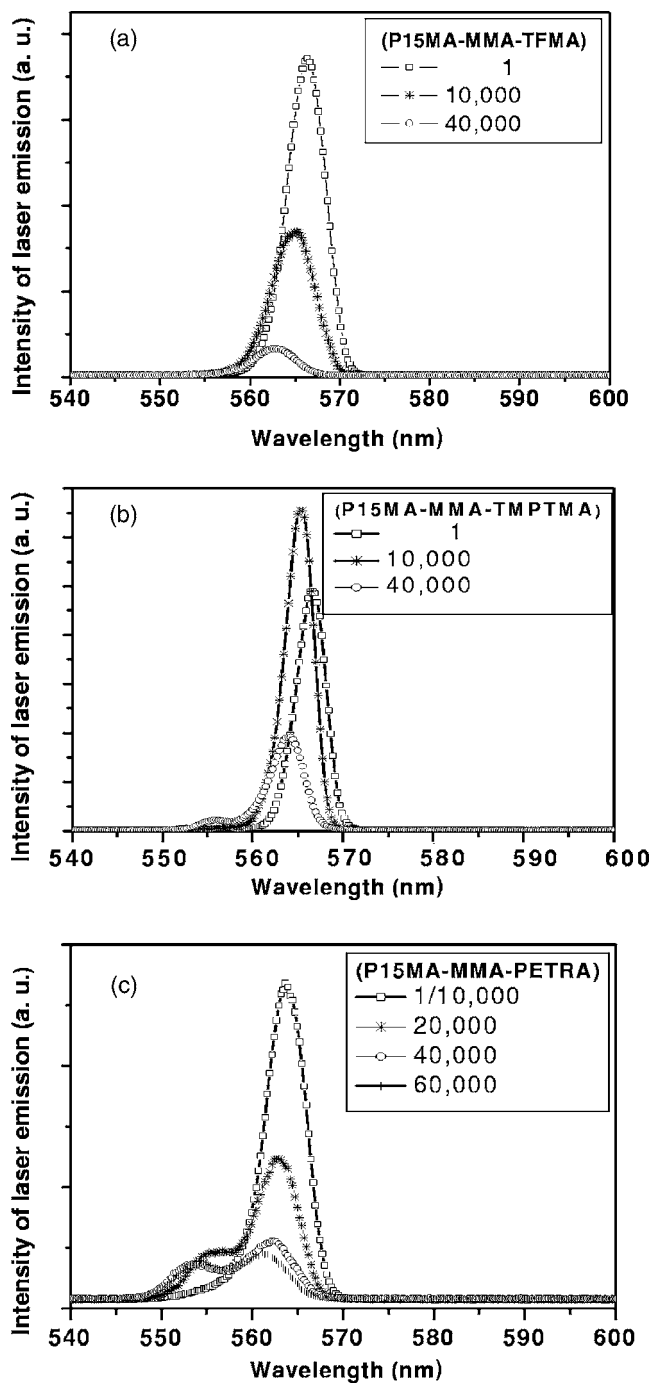


FIG. 7. Spectra of the laser emission of the terpolymers (A) TERP[P15MA-(MMA-TFMA) 7:3], (B) TERP[P15MA-(MMA-TMPTMA) 95:5], and (C) TERP[P15MA-(MMA-PETRA) 95:5] after the indicated number of pump pulses in the same position of the sample. Dye concentration,  $1.50 \times 10^{-3} M$ .

peak at  $\sim 556$  nm after 40 000 pump pulses [Fig. 7(b)]. When the degree of cross-linking is increased, by using the monomer PETRA in the matrix in proportion MMA-PETRA 95:5, the second peak appears neatly after 20 000 pump pulses. After 60 000 pump pulses in the same position of the sample, the two peaks have almost the same intensity [Fig. 7(c)].

#### D. Effect of pump fluence

Another influential factor in the observed bichromatic emission is pump fluence. It was found that the relationship

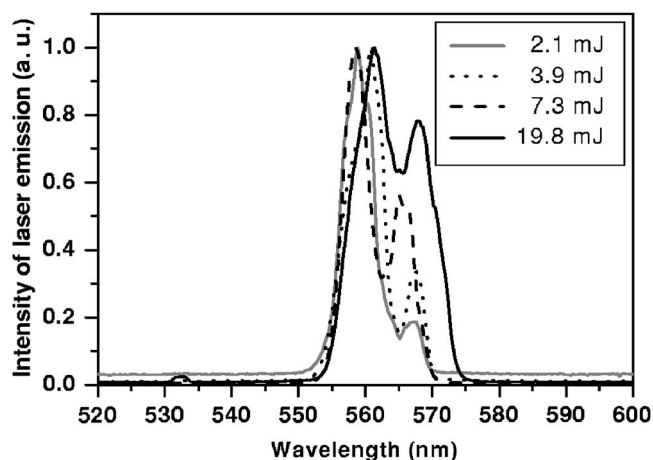


FIG. 8. Spectra of the laser emission at different pump fluences for the material PAr3Ac/COP(MMA-HEMA 7:3). Dye concentration,  $1.50 \times 10^{-3} M$ . In the experimental conditions used, 1 mJ of pump energy corresponds to about  $30 \text{ mJ/cm}^2$  pump fluence. Thus, the fluences in the figure were approximately 63, 117, 319, and  $594 \text{ mJ/cm}^2$ .

between the intensities of the two peaks varies with pump fluence, with the long-wavelength becoming more important as pump fluence increases. To illustrate clearly this effect, a matrix composition was chosen where the two spectral peaks were already present in the initial laser emission at low pump fluence. Model dye PAr3Ac dissolved in COP(MMA-HEMA 7:3) fulfills this condition. Figure 8 shows the spectra of the laser emission of this material at different pump fluences.

#### IV. DISCUSSION

Based just on the results obtained with dye P10MA and summarized in Fig. 3, we speculated in a previous work<sup>34</sup> that the long-wavelength emission was the usual emission from dye P10MA, whereas the short-wavelength emission originated from another emitting dye formed by a scission reaction at position 8, which produced the separation of the alkyl radical group and the entrance of a hydrogen radical from the medium, giving rise to the PM567 analog containing the same substituents at positions 1–3 and 5–7, but without substituent at position 8, which we denoted 8-H-PM. We had found that the dye 8-H-PM did appear as a by-product (albeit in traces) in the last step of the synthesis of the analog of PM567, and that a solid polymeric material formed with this synthetic 8-H-PM dye incorporated into PMMA gave rise to laser emission centered at 554 nm, i.e., in the same spectral region where the short-wavelength peak appears in the dual-wavelength laser emission from P10MA samples.

The results obtained in the present work allow us to conclude that although the formation of 8-H-PM is possible as a photodegradation product of the studied dyes, this is neither the only nor the most significant mechanism responsible for the observed bichromatic emission. We base this affirmation on two experimental facts: (1) the dependence of the bichromatic emission with dye concentration reveals that, at low concentrations, only short-wavelength band is observed (Fig. 6), which means that in the hypothesis of this band originating from the degradation product 8-H-PM, it must be assumed that there is no laser emission from the

initial dye in the matrix; (2) when the pump fluence is increased, the long-wavelength emission increases (Fig. 8), even as the photodegradation processes became more important with higher pump fluence, which should result in an *increase* of the short-wavelength emission, if the formation of dye 8-H-PM was the total and unique responsible for that emission.

As indicated in the Introduction, there are a number of reports on the simultaneous emission of two peaks of laser radiation in liquid solutions of dyes under certain specific conditions. Thus, Sha *et al.*<sup>36,37</sup> and Vaveliuk *et al.*<sup>39</sup> observed bichromatic emission dependent on dye concentration and pump energy in solutions of Rhodamine 640 (Rh640) in methanol with TiO<sub>2</sub> dispersing nanoparticles. In these conditions, a single laser peak (at about 617 nm) was emitted at low dye concentrations ( $\sim 10^{-4}M$ ), whereas at dye concentrations of about  $10^{-2}M$  two peaks appeared simultaneously in the laser emission, at 620 and 650 nm. With dual-wavelength emission established, the ratio between the intensities of the long-wavelength and short-wavelength emission peaks was found to increase with pump fluence.<sup>36–39</sup> The bichromatic emission also depended on the concentration of the dispersing TiO<sub>2</sub> particles, with the long-wavelength peak dominating for a lower density of scattering particles and the short-wavelength peak dominating for a higher density of scattering particles.<sup>36,37</sup>

In their attempt to explain the double laser emission observed in the solutions of Rh640 in highly scattering media, Sha *et al.* proposed three different models and discussed them in the following terms on the basis of their experimental evidence:<sup>37</sup>

- (1) The short-wavelength emission at 620 nm originates in the singlet manifold and the long-wavelength emission at 650 nm originates in the triplet manifold. Nevertheless, this model does not explain why the emission at 650 nm was the first to appear at high dye concentration.
- (2) A photoisomer is formed in the dye solution which is responsible for the long-wavelength emission. This model does not explain why only the short-wavelength mode lases at low dye concentration and high pump energies, because under these conditions photoisomer formation is also possible.
- (3) Aggregates are formed in the dye solution at high concentration, as indicated by the absorption spectrum. This assumption explained most of the observed dye behavior, and the authors proposed that single molecules were responsible for the short-wavelength emission, and an aggregate complex was responsible for the long-wavelength emission.

Further evidence for mechanism (3) operating in the laser emission of Rh640 in scattering media was provided by Vaveliuk *et al.*, who assigned the bichromatic emission to simultaneous laser emission from single and aggregate molecules which coexist in the ground state.<sup>39</sup> These authors registered absorption and emission spectra from single and aggregate molecules in highly concentrated dye solutions. They observed partial overlapping between the aggregate absorption cross section and the single molecule emission cross

section, which makes it possible the transfer of energy from the excited monomer to the ground state dimer. Increasing pump energy increases the population of excited monomers and, thus, the intensity of the dimer emission because of the increased energy transfer.

In our case, the results obtained as a function of the dye concentration (Sec. III A), illustrated in Fig. 5, rule out models (1) and (2) for the same reasons discussed above. On the other hand, our photophysical measurements rule out the presence of aggregates at least up to the highest dye concentrations used herein. Figure 9 shows normalized absorption and fluorescence spectra at different excitation wavelengths of dye PAr3Ac in the same matrix and at the same concentrations than those used to obtain the lasing results presented in Fig. 5. The shape of the absorption spectrum at the highest dye concentration used in this work ( $1.5 \times 10^{-3}M$ ) in thin disks (0.2 mm) is quite similar to those obtained in more diluted systems, which would indicate that there is no aggregation of the dye. The small broadening observed in Fig. 9(a) in the main absorption band in the  $0.45 \times 10^{-3}M$ , 1 mm thick sample could be due to the saturation in the maximum (where the absorbance is higher than 2.5, which means that less than 0.3% of the incident photons are transmitted through the sample). In the fluorescence spectra [Figs. 9(b)–9(d)], the sample with the highest thickness and dye concentration exhibits a shoulder or band at lower energies with respect to the position of the maximum emission. Nevertheless, a reduction in either dye concentration or disk thickness resulted in a clear reduction of the intensity of that shoulder.

The fact that the fluorescence spectrum depends on the thickness of the sample is an indication of reabsorption/reemission phenomena.<sup>44,45</sup> These effects become more important as the thickness of the sample increases and produce a decrease in the fluorescence intensity at the shorter wavelengths (those overlapping with the absorption spectrum), which leads to an apparent increase of the fluorescence intensity at longer wavelengths in normalized spectra (shift and/or new band to the red). Thus, this phenomenon does not imply emission from two different species but rather the emission of only one species, the fluorescence spectrum of which depends on external factors (dye concentration and pathlength). Thus, for low thickness of concentrated dye samples (i.e., 0.2 mm in  $1.5 \times 10^{-3}M$ ), the fluorescence spectrum does not change with the excitation wavelength [Figs. 9(b)–9(d), solid lines], but increasing the thickness of the sample to 1 mm leads to excitation-wavelength-dependent fluorescence bands [Figs. 9(b)–9(d), dashed lines].

On the other hand, the fluorescence spectrum of the  $1.5 \times 10^{-3}M$  samples with 1 mm thickness does change with the excitation wavelength [Figs. 9(b)–9(d)] that could be an argument in favor of the presence of a second species, formed at high dye concentrations, which would emit fluorescence with relative intensity depending on the excitation wavelength. Nevertheless, when the thickness of the samples with dye concentration of  $1.5 \times 10^{-3}M$  is reduced to 0.2 mm, the fluorescence spectrum does not change with the excitation wavelength.

Reabsorption/reemission effects lead to an apparent new

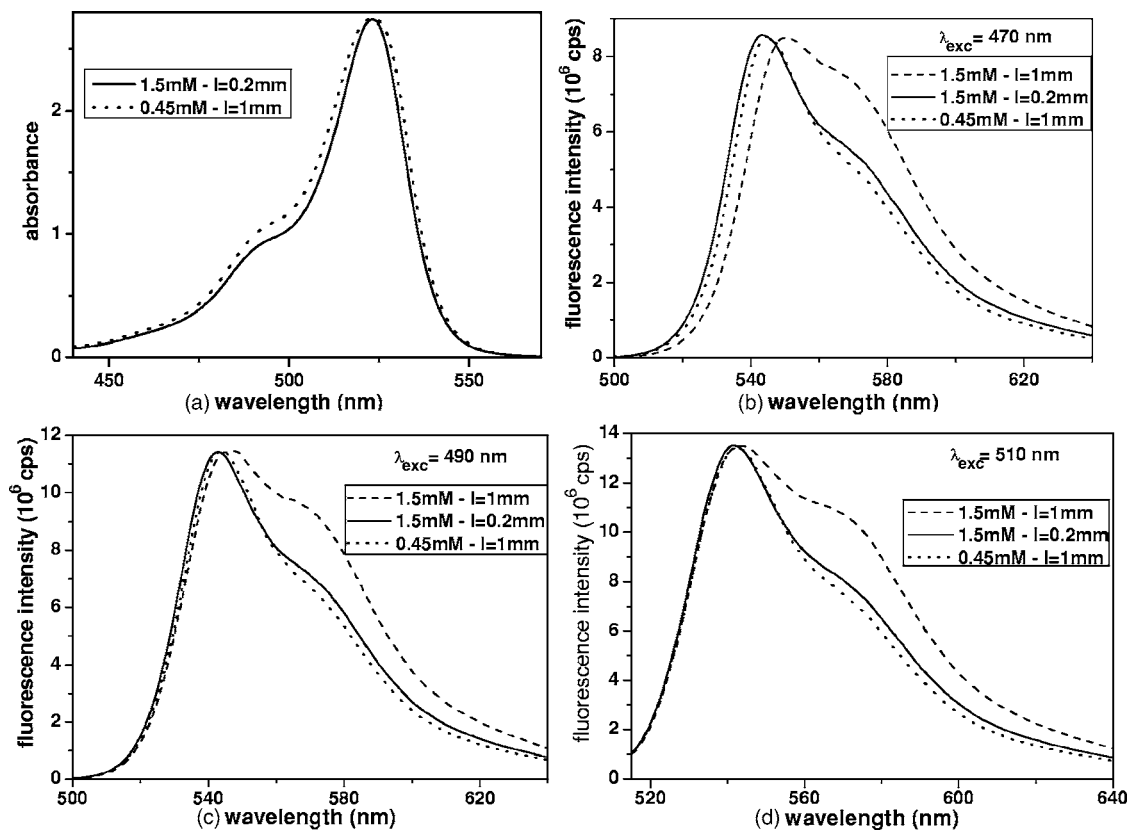


FIG. 9. Normalized absorption and fluorescence spectra at three different excitation wavelengths of PAR3Ac/COP(MMA-TFMA 7:3). Sample concentration and thickness ( $l$ ) of sample as indicated in the figure. The fluorescence intensity is given in counts/s.

fluorescent band at 565 nm, which is actually a strong contribution of the vibronic shoulder (0-1 band). In the sample with lower concentration, the emission of the 0-0 band is dominant and, as a result, laser emission at the shorter wavelength of 550 nm is observed (Fig. 5, left). When the dye concentration is raised to  $1.5 \times 10^{-3} M$ , reabsorption effects increase the losses at the short emission wavelengths, where there is the greatest overlapping with the absorption spectrum, and gain at the 0-1 band dominates the laser transition, resulting in lasing at 572 nm. As the sample is repeatedly pumped, the dye is photodegraded and the effective dye concentration in the pumped volume decreases, reabsorption decreases, and laser emission at the second, shorter wavelength appears (Fig. 5, right).

When samples incorporating the monomeric dye PAR1MA, with concentration of  $0.8 \times 10^{-3} M$  (halfway between those considered in the above discussion with PAR3Ac), were tested, differences of laser behavior that depend on the way the dye was incorporated into the matrix did appear (Fig. 6). When the model unbounded dye exhibited only short-wavelength emission, the same concentration of the corresponding monomeric dye bounded to the polymeric chains initially exhibited only long-wavelength emission, with short-wavelength emission appearing only after irradiation with a number of pump pulses. This behavior can be understood taking into account that when the dye molecules are linked covalently to the polymeric matrix, gradients of concentration of the dye in the sample could appear. Thus, regions of higher local concentration are spread out, and

long-wavelength emission dominates initially, according to the mechanism discussed above. After some thousands of pump pulses, dye degradation lowers the dye concentration at the point of excitation and short-wavelength emission appears.

Another piece of evidence for the origin of the long-wavelength band is provided by the behavior of the laser emission in samples with high dye concentration, where a given dye is incorporated into different matrices. In Fig. 7 are presented spectra of different terpolymers incorporating the monomer dye P15MA. It was found that the rate of degradation of the dye in these materials increased with the rigidity of the polymer matrix, so that the dye was much more stable in the matrix with the linear polymeric formulation MMA-TFMA than in the cross-linked matrices. Accordingly, the long-wavelength emission dominates in the linear matrices [Fig. 7(a)], as it is characteristic for high dye concentration. In the cross-linked matrices, the dye concentration decreased faster with the number of pump pulses, and thus short-wavelength emission appears which becomes more important as the degree of cross-linking increases: in the MMA-TMPMA 95:5 matrix, the short-wavelength emission is observed after 40 000 pump pulses [Fig. 7(b)], whereas in the more cross-linked MMA-PETRA 95:5 matrix, it is well developed after 20 000 pump pulses [Fig. 7(c)].

On the other hand, the behavior followed by our compounds under increasing pump fluence (Fig. 8) can be understood in terms of inhomogeneous broadening of the absorption spectrum due to an effective vibrational temperature.

Under high intensity excitation, the vibrational temperature increases and the spectrum becomes inhomogeneously broadened, with the vibrational levels of the ground state being populated via the  $S_1$  manifold after powerful excitation.<sup>46</sup> The mechanism involves excited-state absorption. In short,<sup>46</sup> as the pump intensity increases,  $S_1$ - $S_2$  transitions are excited by the same pump pulse. Relaxation from  $S_2$  to the vibrational manifold of  $S_1$  occurs very quickly, in the subpicosecond time scale, and then vibrational population is transferred to the vibrational manifold of the ground state due to stimulated emission. As a consequence, during the nanosecond pulse a steady-state distribution of vibrational population in the ground state is created, which in turn produces inhomogeneous broadening due to coupling with vibronic levels of the  $S_1$  manifold.<sup>46</sup> Thus, as the pump energy increases, also does the contribution to the laser emission of the vibronic shoulder at lower energies, and the long-wavelength emission increases.

Bichromatic ASE depending on dye concentration, pump fluence, and the nature of the solvent was also observed by Sastikumar and Masilamani<sup>41,42</sup> and Masilamani and Aldwayyan<sup>43</sup> in liquid solutions of coumarin and quinolone dyes. These authors argued that this bichromatic emission originates from a new molecular species, called *superexciplex*, formed under laser excitation due to the interactions between excited dye molecules and solvent molecules. Its formation, which needs two excited molecules, requires a high concentration of excited molecules, obtainable only under laser excitation and not under lamp excitation. In our case, the results obtained as a function of the dye concentration and pump fluence would be consistent with the superexciplex hypothesis, but results such as those shown in Fig. 7(a), where there is only long-wavelength emission, contradict that hypothesis: for it to hold, it would be necessary to accept that in conditions such as those illustrated in Fig. 7(a), there is *only* laser emission from the superexciplex, which means that the formation of the superexciplex should be as fast and efficient as to suppress the laser emission from the single dye molecules.

## V. CONCLUSION

In summary, the reported photophysical and laser results indicate that the bichromatic laser emission observed in the modified PM dyes incorporated into polymeric matrices can be explained in terms of reabsorption/reemission effects and inhomogeneous broadening of the  $S_0$ - $S_1$  transition. The short-wavelength emission corresponds to the usual homogeneous  $S_0$ - $S_1$  transition and dominates at low dye concentration. The long-wavelength emission appears when reabsorption/reemission and inhomogeneous broadening dominates, and gain at the vibrational shoulder competes advantageously with that of the short-wavelength mode.

In all the previously reported studies, bichromatic laser and ASE emissions were observed in liquid solutions of dyes both in neat dye solutions and in dye solutions containing scatterers.

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