

# Laser performance of Coumarin 540A dye molecules in polymeric host media with different viscosities: From liquid solution to solid polymer matrix

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Photophysical parameters and lasing properties of Coumarin 540A dye molecules are studied in solutions of increasing viscosity, from liquid solutions in 1,4-dioxane to solid solutions in poly(methyl methacrylate). The fluorescence quantum yield and lasing efficiencies decrease as the viscosity of the solution increases, reflecting the strong influence of the rigidity of the medium on the radiative processes. The photodegradation mechanisms acting on the fluorophores are analyzed by following the dependence of laser induced fluorescence and laser output on the number of pump laser pulses. The fluorescence redistribution after pattern photobleaching technique is used, and Fick's second law is applied to study the diffusion of dye molecules in the highly viscous polymer solutions. The diffusion coefficients of the dye molecules as a function of the increased viscosity of the medium are determined. © 1998 American Institute of Physics. [S0021-8979(98)01702-2]

## I. INTRODUCTION

Liquid solutions of laser dyes are versatile sources of coherent tunable radiation with many applications in different fields.<sup>1</sup> Nevertheless, the need to use large volumes of organic solvents has limited the use of these lasers in some technical applications. As a result, it is not unexpected that in recent years there has been a renewed interest in the use of solid matrices containing laser dyes<sup>2-13</sup> with the aim to develop practical solid-state dye lasers. A solid host for lasing dyes is an attractive alternative to liquid solutions, with obvious advantages, both technical and economic, such as ease of use, the absence of flammable and toxic solutions, and the elimination of the problems caused by flow fluctuations and solvent evaporation.

Although over the years a number of different materials have been used as solid hosts for organic dyes, most of the recent work has been done using either polymers or silica gels as host media. Initially the sol-gel materials seemed to show higher photostability than those based on organic polymers.<sup>3,6</sup> Nevertheless, recent results have demonstrated stabilities in polymeric materials comparable with those obtained with silica gels when used under the same conditions.<sup>13</sup> The polymeric materials exhibit a higher optical homogeneity than the silicate matrices available,<sup>5</sup> which is extremely important for narrow-linewidth oscillators. Other advantages are a much improved compatibility with organic dyes, and adaptability to inexpensive fabrication techniques, which facilitate both miniaturization and the design of integrated optical systems. In addition, the virtually limitless possibilities in structure and chemical composition of polymers confers these materials enough variability to continue to be of interest for many years.

The two main problems found in polymeric solid-state dye lasers are the low laser-damage threshold of the material and the photodegradation of the dye.<sup>10</sup> Recently, we have

carried out a number of studies dealing with these problems.<sup>8-10,13-17</sup> Our approach has been to try to improve the laser-related properties of the dye-doped polymeric materials by using the vast possibilities in polymer synthesis to modify characteristics of the materials in a controlled manner, as well as to design new methods for the incorporation of the active dye molecules in the polymeric matrix.

In a preliminary study, we proceeded to modify the rigidity of the polymeric material by controlled cross linking with a bifunctional monomer,<sup>14</sup> and demonstrated that for a certain degree of cross linking there were significant increases in both lasing efficiency and photostability. The next step was to investigate the effect of varying the viscoelastic properties of the medium on laser performance. This can be achieved by internal modification of the polymer by copolymerization with appropriate monomers. By this method (internal plasticization), we obtained important increases in photostability<sup>8</sup> with lasing efficiencies similar to those found in liquid solution. At this point in the investigation, it was apparent that the main cause of degradation of the dyes incorporated into polymeric matrices was the thermal destruction of the dye due to poor heat dissipation in the polymer host. This being the case, any molecular modification facilitating the dissipation of the absorbed energy not converted into emission should avoid premature degradation. Thus we proceeded to covalently link the dye molecules to the polymeric chains, opening in this way additional channels for the dissipation of energy along the polymer backbone.<sup>13,15,18</sup> To achieve this aim, it was first necessary to synthesize dye molecules incorporating polymerizable double bonds in the appropriate positions, which were then copolymerized with methacrylic monomers. In these new materials, the photostability increased by a factor of more than two with respect to our best previous results.<sup>18</sup>

Most of the work described above was done with dyes of the rhodamine family, mainly with Rhodamine 6G (Rh6G), emitting in the yellow and red regions of the spectrum. Ap-

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lications in technologically important fields, such as optical storage or underwater communications, would require the development of efficient and photostable lasers also in the blue and green spectral regions. There has been little work done on blue-green emitting solid-state dye lasers. Some early studies were reported in the late sixties and the beginning of the seventies,<sup>19–23</sup> but in all cases the laser performance was very poor. Some improvements in lasing properties were reported by Itoh *et al.*,<sup>24</sup> for thin films of Coumarin-doped poly(methyl methacrylate) (PMMA) pumped with a N<sub>2</sub> laser, and by Pacheco *et al.*,<sup>25</sup> for flashlamp-excited Coumarin-doped PMMA rods. In recent years, some detailed studies have appeared on the lasing properties of different dyes emitting in the blue and green,<sup>12,26–31</sup> but in all cases, the dyes were incorporated into sol-gel materials. The only recent studies on polymer-doped blue-green dye lasers have been those reported by our group,<sup>15,32</sup> using proton-transfer dyes dissolved in, or copolymerized with, methacrylic monomers and pumped transversely with pulses from a N<sub>2</sub> laser. Although energy conversion efficiencies of 11%, similar to those obtained in liquid solution, were demonstrated with some of these materials, the laser output decreased by 90% after only one hundred shots. In order to improve the laser photostability in this important spectral region, we have recently initiated a systematic investigation on the lasing properties of polymeric materials incorporating dyes of the Coumarin family and on ways to improve their performance. First, the effects on the laser operation of different polymerization methods, dye concentration, and the composition of the polymeric matrix were evaluated,<sup>17</sup> and conditions were found for which laser efficiencies of 11% and lifetimes of 2000 pulses at a 2 Hz repetition rate were obtained.

Further improvements in photostability require a greater understanding of the degradation mechanisms involved when these fluorophores are embedded in polymeric matrices. To this end, the present work investigates the fluorescence and lasing properties of a number of Coumarin 540A (C540A) solutions with increasing viscosity from liquid solution in 1,4-dioxane to solid solution in PMMA, with solutions of intermediate viscosity obtained by dissolving appropriate amounts of PMMA in 1,4-dioxane. It is well known that for free-rotor dyes the dependence of the fluorescence yield on the viscosity of the solvent essentially reflects the strong influence of rigidity on the nonradiative decay parameters of the molecule.<sup>33</sup> As such, the effect of viscosity on other photophysical processes is not clearly reflected in fluorescence measurements in these molecules. However, in the Coumarin 540 A molecule, the movement of the amine moiety is restricted, which results in a rigid structure where the torsional decay route is inhibited. Consequently, in this case, fluorescence measurements as a function of the medium's viscosity do provide information on the general photophysical behavior of the dye molecules, reflecting the role played by the dynamics of the microenvironment of the dye.

The evolution of the UV-visible absorption spectrum after irradiation and the decrease of the lasing and fluorescence intensity as a function of the number of pump-laser pulses were also studied. The dependence of the lasing parameters

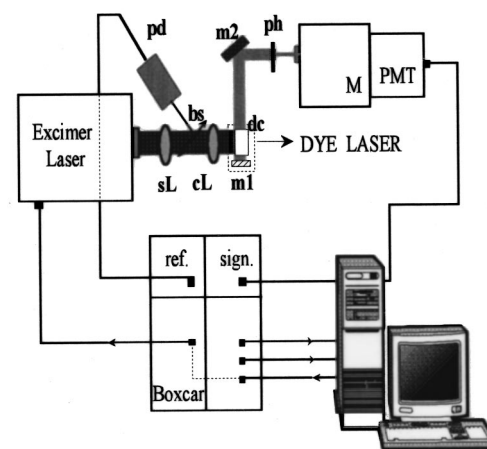


FIG. 1. Schematic of the laser system experimental setup. Pd: photodiode; sL: spherical lens; cL: cylindrical lens; bs: beam splitter; m1,2: aluminium flat mirrors; dc: dye cell/solid sample; ph: pinhole; M: monochromator; PMT: photomultiplier.

on the viscosity of the medium was analyzed, and the rate of recovery of the fluorescence intensity after irradiation was investigated [in an application of the fluorescence redistribution after pattern photobleaching technique, (FRAPP)]<sup>34</sup> in order to obtain information on the mobility of the dye molecules in the different samples, which can be interpreted in terms of the diffusion coefficient.

## II. EXPERIMENT

### A. Laser system and laser induced fluorescence measurements

Polymeric samples were cast in a cylindrical shape, forming rods of 10 mm diam and 10 mm length. A cut was made parallel to the axis of the cylinder in order to obtain a lateral flat surface of  $\sim 6 \times 10$  mm. This surface was prepared for lasing experiments by conventional grinding and polishing. The ends of the rods were polished by hand to obtain reasonably flat surfaces. No attempt to produce laser grade flat surfaces was made. Liquid solutions and samples with different viscosities were contained in a 1-cm-optical path length silica cell carefully sealed with a teflon plug to avoid solvent evaporation during the experiments, thus ensuring a constant sample concentration during the experimental measurements.

A schematic diagram of the laser system is shown in Fig. 1. Laser emission was obtained by pumping the samples transversely at 337 nm with pulses obtained from a commercial excimer laser (MPB-AQX 150) filled with the appropriate N<sub>2</sub>/He mixture to operate as a N<sub>2</sub> laser providing 1.7 mJ,  $\sim 7$  ns full-width at half-maximum (FWHM) pulses, at repetition rates up to 15 Hz. The pump light was focused with a combination of spherical ( $f = 50$  cm) and cylindrical ( $f = 15$  cm) quartz lenses onto the laser cell or onto the lateral flat surface of the solid sample to form a line of  $\sim 0.3 \times 10$  mm, such that the pump fluence was  $\sim 60$  mJ/cm<sup>2</sup>. The oscillator cavity consists of a flat aluminium mirror ( $\approx 90\%$  reflectivity) and the end face of the dye cell or of the cylindrical solid sample as the output coupler, with a cavity length

of 2 cm. The samples were mounted on translation stages which allowed precise vertical and horizontal alignment.

The dye and pump laser pulses were characterized with the following instruments: Gen Tec ED-100A and ED-200 energy meters, an ITL TF 1850 fast risetime photodiode, a Tektronix 7934 storage oscilloscope and a Tektronix 2430 digital oscilloscope, an Applied Photophysics M-300 monochromator, and an EMI 9783B photomultiplier. A fast photodiode (EG&G SGD-100) was used to detect a calibrated fraction of the pump radiation to monitor the stability of the  $N_2$ -laser emission during the experiments. In the photodegradation studies, the dye and pump laser signals were sampled with boxcars (Stanford Research System, Model 250). All the integrated signals were digitized and processed using a PC computer via a Computerboard DASH-8 interface.<sup>9</sup> The estimated error in the energy measurements was 10%.

In order to assure that the volume element of the sample probed in the laser induced fluorescence (LIF) measurements is identical to that irradiated under lasing conditions, the fluorescence was excited with the same pulses from the  $N_2$  laser used for producing laser emission, but this time attenuated by a number of glass windows placed in the optical path so that the laser energy incident on the sample was considerably lower than the pump threshold energy needed to produce laser emission from the dye molecules. The LIF emission was monitored perpendicular to the exciting beam, imaged onto the input slit of the Applied Photophysics M-300 monochromator with a 10-cm-focal length spectroil B spherical lens, and detected with the EMI 9783B photomultiplier.

## B. Materials

Coumarin 540A (2,3,5,6-1H,4H-tetrahydro-8-trifluoromethylquinolizino-[9,9a,1-gh]coumarin) (Lambda-Physik, laser grade) was used as received. The purity of the dye was found to be >99%, as determined by spectroscopic and chromatographic methods. The dye concentration used was  $2 \times 10^{-2}$  M in all experiments. 1,4-dioxane (Merck; Uvasol), used as received, was selected as the solvent since both the C540-A dye and the PMMA polymer demonstrated good solubility, and this solvent is less volatile than other alternative solvents. Studies on the dependence of the lasing properties on sample viscosity were performed by varying the volume/weight (v/w) proportion of solvent/PMMA in the solutions.

Liquid solutions of variable viscosity and constant dye concentration were prepared by dissolving the dye and a determined amount of PMMA in pure 1,4-dioxane by alternative stirring and sonication periods until clear and homogeneous solutions were obtained. The highest concentration of polymer that could be completely dissolved in 1,4-dioxane was 400 g/ℓ. Several attempts were made to obtain solutions with higher polymer concentration. Methods such as direct solution of the polymer or selective evaporation of the solvent from previously obtained more dilute solutions, either by direct room temperature evaporation or by high vacuum lyophilization, were attempted without success. All the solutions with a polymer concentration greater than 400 g/ℓ pre-

sented dye-dye aggregation and inhomogeneities, detected by absorption and fluorescence spectroscopy.

PMMA was obtained by free-radical bulk polymerization of pure MMA under the same experimental conditions described below for solid samples preparation ( $\bar{M}_n = 43\,600$ ;  $\bar{M}_w = 77\,750$ ).

The solid samples were prepared as follows. The dye was dissolved in freshly purified MMA monomer and the resulting mixture was placed in a water-filled ultrasonic bath for periods of up to 10 min until the dye was completely dissolved. Then, 3 g/ℓ of 2,2'-Azo-bis (isobutyronitrile) (AIBN), used as a thermal free-radical initiator, was added and allowed to dissolve in the ultrasonic bath for up to 5 min. The resulting solution was filtered into appropriate cylindrical polypropylene molds using a 0,2  $\mu\text{m}$  pore size filter (Whatman Lab. Div.). After careful deaeration by purging with dry argon, the molds were sealed. Polymerization was performed in the dark at 35 °C over two days, followed by a further two days at 40 °C, and then 50 °C for one week. Under the experimental conditions employed in the preparation of the samples used in the present work, no residual monomer was 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.

Absorption and fluorescence spectra of the solid samples were obtained from thin strips cut from the same samples used in the laser experiments. Because of the high optical density of the dye solutions with different degrees of viscosity, their absorption spectra were recorded by placing a small amount of solution between two quartz plates in order to reduce the optical path. The fluorescence spectra were obtained at room temperature from air-saturated samples placed in the same 1-cm-optical path silica cell used in the laser experiments. Absorption spectra were recorded with a Shimadzu UV-265 FS spectrophotometer. Fluorescence spectra were registered with a Perkin-Elmer LS-50B luminescence spectrometer using a special front to face sample attachment.

Fluorescence quantum yields ( $\phi_f$ ) of C540A in solutions with increased viscosity were estimated from the ratio between the integrated areas under their fluorescence curves and the area corresponding to a solution of C540A in ethyl acetate ( $\phi_f = 0.88$ ), used as a standard.<sup>33</sup> Care was taken to record all curves under identical conditions.

Fluorescence lifetimes of C540A in the different solutions, from liquid to solid, were obtained with a time-correlated single-photon counting spectrometer<sup>35</sup> built using ORTEC583 and 473A discriminators and a 457 time-to-amplitude converter. The samples were excited with a thyratron-gated nanosecond flashlamp (Edinburgh Instr. EI199) filled with nitrogen. The fluorescence emission was passed through a cut-off filter (Schott KV-450) and detected with a Phillips XP2020Q photomultiplier. The kinetic parameters (lifetime and amplitude) of the fluorescence decay were determined using a fitting routine based on the nonlinear least-squares convolution technique.<sup>36</sup>

TABLE I. Viscosity, fluorescence, and laser parameters<sup>a</sup> of the C540A solutions.

Solvent/PMMA (vol/weight)	Viscosity <sup>b</sup> (mPa s)	Fluorescence <sup>c</sup>			Laser emission		
		$\lambda_f$ (nm)	$\phi_f$	$\tau_f$ (ns)	$\lambda_{Lmax}$ (nm)	$\Delta\lambda_L$ (nm)	Eff <sup>f</sup> (%)
10/0	1.18 <sup>c</sup>	501.7	0.30	5.5	504	14	32
9.5/0.5	9.65 <sup>c</sup>	502.8	0.22	6.2	507	14	27
9/1	38.60 <sup>c,d</sup>	503.5	0.22	6.2	508	14	25
8/2	250 <sup>d</sup>	503.5	0.22	6.8	508	10	22
7/3	4000 <sup>d</sup>	511.8	0.21	7.2	510	10	17
6/4	108 000 <sup>d</sup>	522.8	0.15	8.2	514	10	14
0/10	solid matrix	512.0	0.12	8.5	515	8	3

<sup>a</sup> $\lambda_f$ : fluorescence emission maximum;  $\phi_f$ : fluorescence quantum yield;  $\tau_f$ : fluorescence lifetime;  $\lambda_{Lmax}$ : laser emission maximum;  $\Delta\lambda_L$ : FWHM of laser emission; Eff: energy conversion efficiency.

<sup>b</sup>Averaged values of at least five measurements.

<sup>c</sup>Measured by capillary viscosimetry.

<sup>d</sup>Measured by rotational viscosimetry; calibration with water, glycerine, and Brookfield standard fluids.

<sup>e</sup>Excitation at 337 nm.

<sup>f</sup>Pump energy: 1.2 mJ/pulse.

### C. Measurements of the viscosity of the samples

Viscosities of solutions with PMMA concentrations lower than 100 g/ℓ were determined at 25 °C by capillary automatic viscometry (Schott Geräte, model AVS 350). For PMMA concentrations higher than 200 g/ℓ, a rotational viscometer was employed (Brookfield model RVT, with a SSA microadaptor), using as a reference calibrated standard fluids at 25 °C.<sup>37</sup>

## III. RESULTS AND DISCUSSION

A number of C540A solutions with viscosities varying from the liquid to the solid state, were prepared in the following v/w proportions (solvent/PMMA):10/0, 9.5/0.5, 9/1, 8/2, 7/3, 6/4, and 0/10. In all experiments, the dye concentration was  $2 \times 10^{-2}$  M. This concentration had been previously determined as that which induces the highest lasing efficiency and photostability.<sup>17</sup> Increasing or decreasing the dye concentration is detrimental to the laser action. The measured viscosities of the dye solutions are given in Table I. As explained in the experimental section, it was not possible to prepare homogeneous samples for this application with viscosities higher than 108 000 mPa s (solution with a 6/4 v/w solvent/PMMA ratio).

### A. Fluorescence and laser emissions

Broad-band laser emission with pulse durations of  $\approx 4$  ns FWHM was obtained from all the samples studied. The spectral profiles of the stimulated emission together with corrected fluorescence spectra of the different samples are shown in Fig. 2. The laser-emission spectra are much narrower than those of the fluorescence, with bandwidths typical of a laser with many modes running simultaneously, due to the lack of wavelength-selection elements in the cavity. The positions of the maxima of the fluorescence emission as well as the dependence of the laser parameters (peak of the laser emission, oscillation bandwidth, and lasing efficiency) on the viscosity of the samples are presented in Table I. It is observed that both the laser emission and the fluorescence maxima shift towards longer wavelengths when the propor-

tion of PMMA in the sample increases. This can be understood in terms of changes in the polarity of the medium, which increases when the 1,4-dioxane ( $\mu = 0.3$  D) is mixed with PMMA ( $\mu = 1.6$  D).<sup>38</sup> It is well known that the position of the maximum of the fluorescence spectrum is red shifted with increasing solvent polarity.<sup>39</sup> In addition, the lasing oscillation bandwidth seems to decrease when increasing the viscosity of the dye sample. This effect has been previously observed in studies on proton transfer dye lasers. For instance, for solutions of 2-(5'-fluoro-2'-hydroxyphenyl)

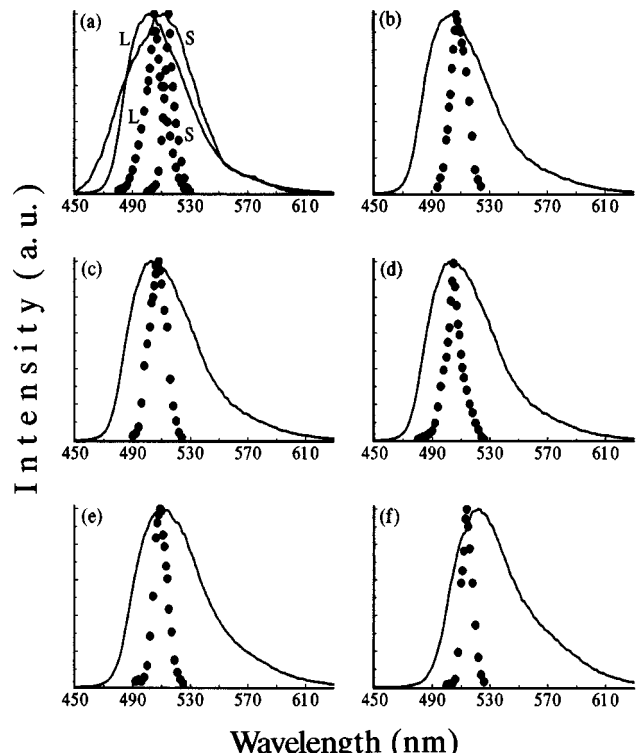


FIG. 2. Normalized fluorescence (solid line) and stimulated emission spectra (dotted line) of C540A solutions with different viscosity: (a) solid matrix (S) and 1.18 (L); (b) 9.65; (c) 38.60; (d) 250; (e) 4000; and (f) 108 000 mPa s.

benzimidazole in 1,4-dioxane the laser emission bandwidth was  $\approx 20$  nm,<sup>40</sup> whereas the bandwidth decreased to  $\approx 12$  nm when the dye was dissolved in PMMA.<sup>15</sup>

Also shown in Table I are the energy-conversion efficiencies of the laser emission (Eff), defined as the ratio of the energy of the dye laser output to the energy of the pump laser incident on the sample surface. Taking into account the dependence of the laser gain on the optical path length of the active medium, the efficiency obtained with the 1-cm-optical path solid sample agrees well with the data reported previously for a 2 cm sample of C540A dissolved in PMMA.<sup>17</sup> When comparing the efficiency of the solid sample with that of the samples contained in silica cells, it should be considered that in the solid sample the laser efficiency is affected by the poor finish of the polished surface, which results in less than optimum coupling between the sample end face and the aluminium back reflector. It is plausible that improving the finish of the samples would result in an increase in efficiency.<sup>15</sup> In the fourth column of Table I, the fluorescence quantum yields of the different C540A solutions containing PMMA are given. When analyzing these values, the high concentration of C540A in the solutions should be taken into account, since the evaluated quantum yields can be affected by secondary processes involving the dye molecules. A close correlation between the changes in Eff and  $\phi_f$  when the viscosity of the medium is increased can be observed.

The laser efficiency clearly decreases when the viscosity of the medium increases (Table I). This dependence cannot be ascribed to quenching processes induced either by PMMA or some impurity associated to the polymer, since the fluorescence lifetime  $\tau_f$  increases with the rigidity of the medium (Table I). Since the viscosity is controlled by the concentration of PMMA in the solution, an increase results in both restrictions in the mobility of the dye molecules and modifications in the polarity of the medium, which increases with the amount of PMMA. To discriminate between these two effects, two solutions with similar viscosity but different polarity were prepared: C540A in 1,4-dioxane and C540A in ethyl acetate, with a dye concentration  $2 \times 10^{-2}$  M. Ethyl acetate was chosen as a solvent because it has a dipole moment ( $\mu = 1.83$  D)<sup>38</sup> close to that of PMMA. Under  $N_2$ -laser irradiation, the lasing efficiency was somewhat higher in the more polar solvent: 35% in C540A/ethyl acetate as compared with 32% in C540A/1,4-dioxane. Thus, the increase in polarity can be ruled out as the cause for the observed decrease in lasing efficiency, and the main contribution to this drop in efficiency with increasing viscosity of the sample seems to be attributed to restrictions in dye mobility. In the case of the solid samples, a possible additional effect caused by triplet state population should be considered, since in solid samples both the concentration and diffusion rate of molecular oxygen are lower than in liquid solutions. In order to investigate this possibility, a solution of C540A in 1,4-dioxane was degassed by the freeze-thaw method pumping down to pressures below  $10^{-4}$  Torr. It was found that the lasing efficiency of the anaerobic solution is the same as that of the same solution saturated with  $O_2$ .

A further effect that could cause an apparent reduction in the lasing efficiency with increasing viscosity of the solution

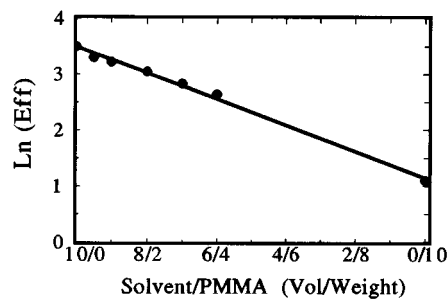


FIG. 3. Logarithm of the laser energy conversion efficiency as a function of the solvent/PMMA vol/weight proportion in the C540A solutions. The straight line corresponds to the best fit of the data points.

is the red-edge absorption of PMMA at 337 nm. Increasing the polymer concentration in the solution increases this absorption, resulting in less pump energy being available for the dye molecules. In order to quantify this effect, the absorption at 337 nm of 1-mm-thick samples with different proportions of 1,4-dioxane PMMA (but with no C540A molecules present in the solution) was determined. The absorbance was found to vary from a value 0 for pure 1,4-dioxane to a value 0.098 for the PMMA solid sample. Normalizing the lasing efficiencies of the different solutions with C540A by the differential absorption of PMMA as the solution viscosity increases, the maximum increase in the values of the efficiencies reported in Table I is around 2%.

When the logarithm of the laser efficiency is represented as a function of the amount of PMMA in the solution, a linear dependence is obtained (Fig. 3). As previously discussed, this relationship can not be explained on the basis of a unique and direct argument. However, an understanding of the effect of increasing the proportion of PMMA in the solutions on the lasing efficiency could be reached by studying how the photophysical parameters of the C540A molecule are affected by the presence of PMMA. The reduction in the fluorescence quantum yield of C540A as the proportion of PMMA in the solution increases is accompanied by a lengthening in the fluorescence lifetime (Table I). These effects are typical of reabsorption and re-emission phenomena and place an upper limit to the lasing capabilities of the system.<sup>41</sup> The effect caused by the presence of PMMA can be resolved in terms of the influence on radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constants of C540A. Using the familiar relationships:<sup>42</sup>

$$k_r = \frac{\Phi_f}{\tau_f}, \quad k_{nr} = k_r \left( \frac{1}{\Phi_f} - 1 \right) \quad (1)$$

and the measured quantum yields and lifetimes (Table I), the values of  $k_r$  and  $k_{nr}$  obtained are shown in Table II. It is apparent from these data that although the values of both parameters,  $k_r$  and  $k_{nr}$ , diminish as the amount of PMMA in the solution increases, the strongest effect is manifested in the radiative decay parameter  $k_r$ , which experiences a four-fold decrease over the range of solvent/PMMA proportions studied.

TABLE II. Rate constants for radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay of the C540A molecule in the different solutions.

Solvent/PMMA (vol/weight)	$k_r \times 10^{-7}$ ( $s^{-1}$ )	$k_{nr} \times 10^{-8}$ ( $s^{-1}$ )
10/0	5.45	1.27
9.5/0.5	3.58	1.25
9/1	3.53	1.26
8/2	3.18	1.15
7/3	2.96	1.09
6/4	1.83	1.04
0/10	1.41	1.03

## B. Dye laser photostability

The laser output intensity was studied as a function of the number of pump pulses at a repetition rate of 10 Hz. It was observed (Fig. 4) that the intensity of the laser output decreases with the number of pump pulses, the rate of this decrease depending on the viscosity of the medium. Maximum stability was obtained with samples with viscosities of up to 250 mPa s (8/2 v/w solvent/PMMA proportion), where no evidence of degradation in the laser output is seen after

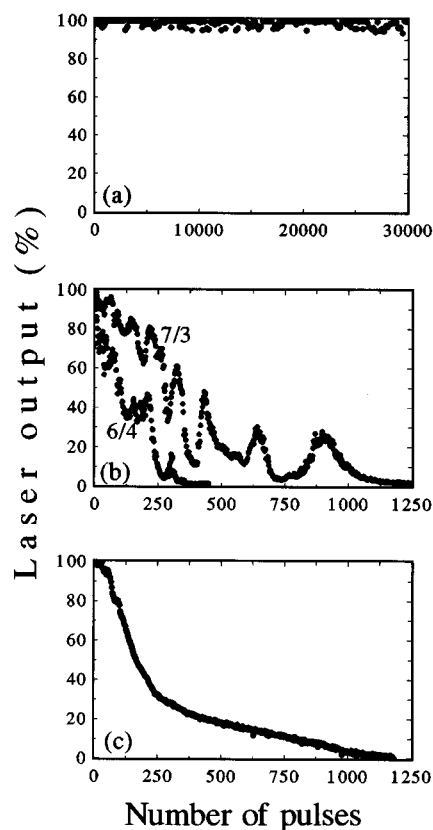


FIG. 4. Normalized laser output as a function of the number of pump pulses for solutions of C540A with different viscosities. (a) solutions with viscosities up to 250 mPa s (8/2 v/w solvent/PMMA proportion); (b) solutions with viscosities of 4000 and 108 000 mPa s (7/3 and 6/4 v/w solvent/PMMA proportions, respectively); and (c) solid sample.  $N_2$ -pump-laser energy and repetition rate: 1.2 mJ/pulse and 10 Hz, respectively. Dye concentration:  $2 \times 10^{-2}$  M. For clarity, in Fig. 4(a) only one of every 100 pulses has been plotted.

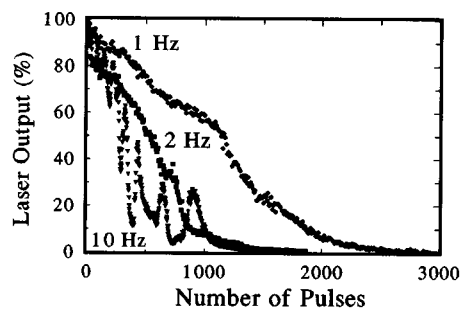


FIG. 5. Normalized laser output as a function of the number of pump pulses for a C540A solution with a 7/3 v/w solvent/PMMA proportion (viscosity: 4000 mPa s) at different pump pulse repetition rates.

30 000 shots [Fig. 4(a)]. Increasing the viscosity of the solution beyond this range leads to a drastic reduction in its apparent stability as well as to an irregular behavior in the laser output with strong oscillations that damp down as the viscosity increases and disappear altogether in the solid samples [Figs. 4(b) and 4(c)]. Special care was taken in the methods of preparation of the samples so as to assure their homogeneity, and rule out inhomogeneities in the active medium as a cause for these oscillations. They could, however, be related to gradients of temperature and dye concentration produced under irradiation conditions in samples where the free diffusion of molecules is partially restricted. The oscillations in the laser output could then reflect the dynamics of the replacement of bleached molecules for some nonirradiated ones in the irradiated volume. Support for this interpretation is provided in Fig. 5, where the laser output is plotted as a function of the number of pulses at different repetition rates for the 7/3 v/w solvent/PMMA C540A solution (viscosity 4000 mPa s). At repetition rates below 2 Hz, there is more time for the diffusion of dye molecules out and into the irradiated region to reach a steady state, and the oscillations disappear. The decrease in the diffusion rate of the dye molecules as the viscosity of the samples increases will be analyzed more thoroughly later on in this article. In the solid sample, the oscillations in the laser output have disappeared completely [Fig. 4(c)], which is probably due to the total confinement of the dye molecules into the glassy polymeric matrix, which restricts their movement.

It is also seen in Fig. 5 that, as observed previously in some solid-state dye lasers,<sup>8</sup> the pump-laser repetition rate affects the degradation rate of the laser output: the higher the repetition rate the faster the degradation. In the present case, the number of pulses needed for an 80% reduction in the laser output in the 7/3 v/w solution decreases from  $\approx 1700$  to  $\approx 350$  pump laser shots when the repetition rate is increased from 1 to 10 Hz. After several hundred shots, the irradiated region presents some damage in the form of bleaching of the dye. This damage, which is irreversible in the solid samples, is temporary in the liquid solutions: even in the case of solutions with viscosity as high as 108 000 mPa s (6/4 v/w solvent/PMMA proportion), the dark, nonemissive line in the pumped region disappears completely after several days at room temperature.

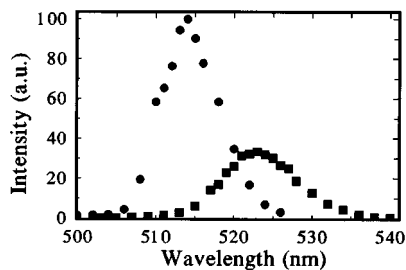


FIG. 6. Laser emission spectra of a C540A solution with a 6/4 volume/weight proportion of solvent/PMMA before (●) and after (■) laser irradiation with 500 000 pump pulses of 337 nm at 10 Hz.

In order to gain a better insight into the degradation mechanisms involved when the fluorophores are embedded in polymeric matrices, a number of photodegradation studies were performed both in solid samples and in the C540A solution with a solvent/PMMA proportion 6/4 v/w. This composition was chosen because the viscosity of the solution is high enough for the bleaching processes to be analogous to those in solid samples, without completely restricting the diffusion of the dye molecules.

First, the 6/4 v/w sample was irradiated with about 500 000 laser shots distributed over the whole volume of the solution at a repetition rate of 10 Hz. It was observed that during irradiation the dye undergoes photoreactions which yield yellow colored products. In Fig. 6, the laser emission spectrum before and after irradiation is plotted. The red shift in the laser emission after irradiation is clearly seen, as well as an important decrease, around 70%, in the lasing efficiency. Additionally, the UV-visible absorption spectrum of the irradiated sample reveals important changes with respect to the nonirradiated solution: the absorption band of C540A at 400 nm decreases dramatically whereas there is an increase in the absorption in the 450–500 nm region. These spectral data are consistent with previous studies on the conventional photolysis of the C540A laser dye which identified a pair of isomeric amides as the photo-oxidation products generated during the irradiation.<sup>43</sup> The above results reveal that the photodegradation of the dye is an irreversible process leading to the generation of products that absorb at the lasing wavelength interfering with stimulated emission. These results are in good agreement with the previously observed degradation in Coumarin solid-state dye lasers,<sup>17</sup> where, although the lower absorption observed in the irradiated solid samples were an indication of photobleaching of the dye molecules, no new features appeared in the spectrum, reflecting the low concentration of the photofragments generated.

Information about the amount of bleached molecules can be obtained by monitoring the decrease in laser induced fluorescence intensity as a function of the number of pump laser pulses. The experiment was carried out as follows. First, the fluorescence of the nonirradiated sample was measured. Then the glass windows placed into the optical path of the pump laser (see experimental section) were removed and the sample was irradiated with the total energy of the N<sub>2</sub> laser (1.2 mJ/pulse) at a repetition rate of 10 Hz. After a given

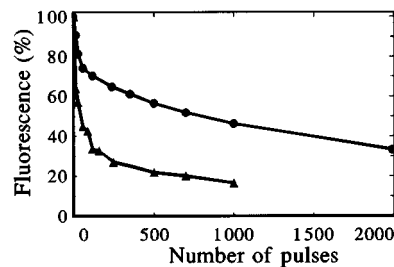


FIG. 7. Normalized laser induced fluorescence emission as a function of the number of pump pulses for solutions of C540A in (●) 6/4 v/w solvent/PMMA and (▲) solid matrix. N<sub>2</sub>-pump-laser energy and repetition rate: 1.2 mJ/pulse and 10 Hz, respectively. The solid lines are just to help the eyes.

number of pump laser pulses, the windows were replaced and the fluorescence emitted by the irradiated sample was measured. The sample is moved to a new position, to avoid accumulative effects, and the operation is repeated with a different number of pump laser shots. The repetition rate of the pump laser was chosen so that the diffusion effects in the time needed to perform each measurement can be neglected for both solid sample and 6/4 v/w solvent/PMMA C540A solutions, assuring that there is no renewal of dye molecules in the irradiated volume during the experiment. The results obtained are plotted in Fig. 7, where it is observed that the degradation is more important in the solid solution than in the less viscous one.

Since the fluorescence emission is a measure of the population of the fluorescent level, a plot of the logarithm of the laser output as a function of the fluorescence intensity after irradiation with different numbers of pump-laser shots should render a straight line. In Fig. 8, such a plot is presented for both the solid and the 6/4 v/w solvent/PMMA solutions. In the experimental dependence, two components

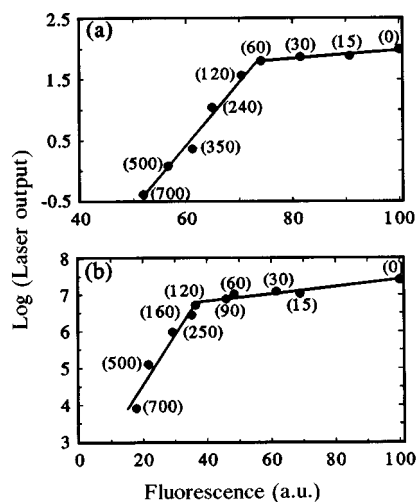


FIG. 8. Logarithm of the laser output as a function of the normalized laser induced fluorescence emission for solutions of C540A in (a) 6/4 v/w solvent/PMMA and (b) solid matrix. Each point corresponds to measurements taken after irradiation of a fresh region of the sample with a given number of pump-laser shots (indicated in parenthesis). The solid lines represent the best linear fits to the experimental points.

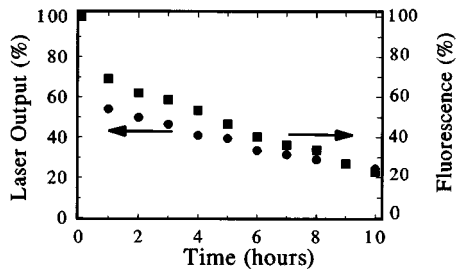


FIG. 9. Normalized laser output (●) and laser induced fluorescence intensity (■) measured 1 h after repeated irradiation of a given volume of the laser sample with 500 full-power pump-laser pulses at 10 Hz. The point at zero time corresponds to emission from the initially nonirradiated sample.

can be observed, indicating the presence of at least two processes detrimental to the laser output. One of these processes involves a photobleaching mechanism which leads to the growing presence of decomposition products that absorb at the laser emission wavelength and that somehow modify the optical properties of the material along the path of the laser beam. The second process could be related to a photothermal mechanism due to large local rises in temperature capable of inducing thermal decomposition of the fluorophores. This is in good agreement with results obtained in our previous studies on different dye/polymer systems<sup>8,14–16</sup> where evidence was presented on the important contribution of photothermal processes to the degradation of the samples. Opening additional channels for the dissipation of the absorbed energy which is not converted into emission, by, for instance, covalently linking the dye molecules to the polymeric chain, should result in an increase of the laser photostability.<sup>13</sup>

### C. Dye diffusion in polymer solutions

In order to gain some insight on the capacity of recovery of the system at high viscosities, an experiment was performed where the 6/4 v/w solvent/PMMA C540A solution was irradiated with 500 full-power pump-laser pulses at a 10 Hz repetition rate, assuring complete disappearance of the dye laser emission. After waiting for one hour, the laser induced fluorescence and laser emissions from the irradiated volume were measured. The procedure was repeated a number of times maintaining the sample in the same position. In this way, the evolution of the recovery of the fluorescence and laser emissions after repeated irradiation of the same volume in 1 h intervals could be followed. In Fig. 9, the results of this experiment over 10 h are plotted, after which the laser sample has been irradiated with a total of 5000 pump pulses distributed in 500 pulse bursts at hourly intervals. The values of the laser output are an average over the first 15 laser shots in each irradiation cycle. It is seen that there is a partial recovery of both fluorescence and laser emissions after the 1 h time intervals. If the logarithm of the laser output at the beginning of each irradiation cycle is represented as a function of the corresponding fluorescence intensity, a linear relationship is obtained, which indicates the renewal of dye molecules in the irradiated volume by a diffusion mechanism.

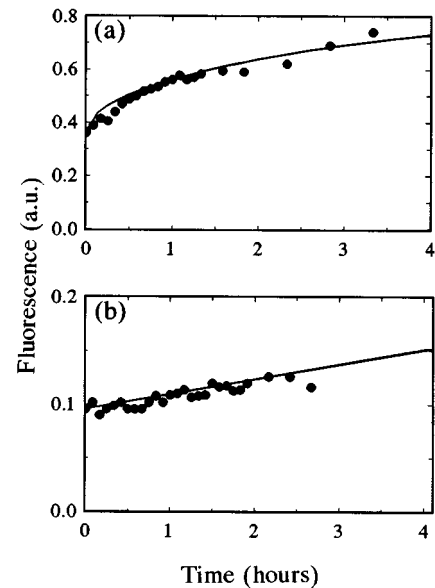


FIG. 10. Laser induced fluorescence emission (●) (normalized to the initial value before irradiation) for short-time experiments (see the text) as a function of the elapsed time after irradiation with 10 000 full-power pump-laser pulses at 10 Hz. (a) solution with 7/3 v/w solvent/PMMA proportion (viscosity: 4000 mPa s); (b) solution with 6/4 v/w solvent/PMMA proportion (viscosity: 108 000 mPa s). The solid lines are theoretical fits to the experimental data by using Eq. (3).

Further information on the mobility of the dye molecules in the different samples, which can be interpreted in terms of the diffusion coefficients, can be obtained from a modification of the above experiment. In this experimental approach, the samples are irradiated with 10 000 full-power pump pulses at a 10 Hz repetition rate, and the recovery of the fluorescence from the irradiated volume is followed at regular time intervals. This is very similar to the FRAPP technique, where a short laser pulse is applied to a small volume element into the sample.<sup>34</sup> Because of the high intensity of the pump light, the dye molecules within the irradiated volume are bleached and fluorescence from that area fades away almost instantaneously. It recovers later as the bleached molecules are gradually replaced by nonbleached dye molecules diffusing from nonirradiated areas into the bleached spot. Then, the rate of recovery of the fluorescence gives information about the mobility in the medium of the dye molecules.

The experiment was performed in the two most viscous solutions (7/3 and 6/4 v/w solvent/PMMA samples with viscosities of 4000 and 108 000 mPa s, respectively). These were chosen because in these samples the degradation processes are more clearly evident. The first experiment, denominated the “long-time experiment,” was carried out over a period of at least 8 h, and the fluorescence emission was probed every hour. In the second one, denominated the “short-time experiment,” the fluorescence was analyzed every 5 min over a period of 3 h. The results obtained are plotted in Figs. 10 and 11, where the fluorescence emission has been normalized to the initial value before irradiation. These results can be used to deduce the diffusion coefficient of the dye molecules in the sample by using a method based



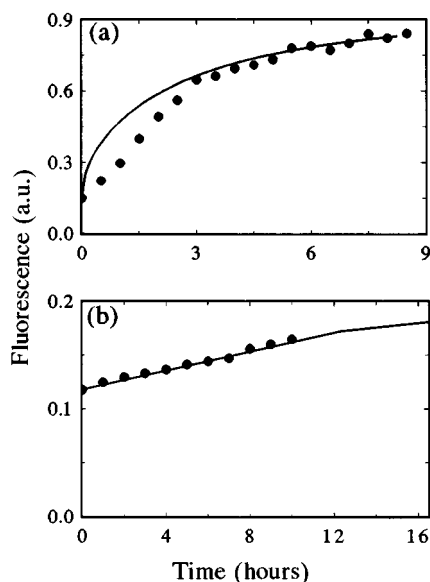


FIG. 11. Laser induced fluorescence emission (●) (normalized to the initial value before irradiation) for long-time experiments (see the text) as a function of the elapsed time after irradiation with 10 000 full-power pump-laser pulses at 10 Hz. (a) solution with 7/3 v/w solvent/PMMA proportion (viscosity: 4000 mPa s); (b) solution with 6/4 v/w solvent/PMMA proportion (viscosity: 108 000 mPa s). The solid lines are theoretical fits to the experimental data by using Eq. (3).

on the direct relationship between fluorescence intensity and concentration of dye molecules.<sup>44</sup> Previous studies have proven that Fick's phenomenological law of diffusion is a reliable macroscopic description of the processes involving diffusion of molecules in polymeric materials.<sup>45</sup> Thus, assuming that the irradiated volume has cylindrical symmetry, the time dependence of the average concentration of dye molecules ( $c$ ) inside that region can be described, using Fick's second law:<sup>46</sup>

$$\frac{dc}{dt} = D \nabla_r^2 c, \quad (2)$$

where  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ) and  $\nabla_r^2$  represents the radial part of the Laplacian operator in cylindrical coordinates.

Equation (2) with the appropriate boundary conditions can be solved analytically. Assuming for the boundary conditions that the nonirradiated volume is very large compared with the dimensions of the irradiated cylinder, the solution of Eq. (2) is:<sup>47</sup>

$$c(t) = 1 - f(\tau) \cdot [1 - c(0)], \quad (3)$$

where

$$f(\tau) = \frac{1}{\tau} \int_0^1 x e^{-x^2/4\tau} \int_0^1 y e^{-y^2/4\tau} I_0\left(\frac{xy}{2\tau}\right) dy dx \quad (4)$$

with  $\tau = tD/a^2$ ,  $a$  = radius of the irradiated cylinder, and  $I_0$  = modified Bessel's function of zero order.

The diffusion coefficient  $D$  can be obtained by fitting Eq. (3) to the experimentally obtained plot of fluorescence recovery. The solid lines in Figs. 10 and 11 are the theoretical fits of Eq. (3) to our experimental data with the values of

TABLE III. Diffusion coefficients of C540A molecules in two different solutions.

Solvent/PMMA (vol/weight)	Viscosity (mPA s)	$D^a$ ( $\text{cm}^2/\text{s}$ )		$D^b$ ( $\text{cm}^2/\text{s}$ )
		long time	short time	
7/3	4000	$7.5 \times 10^{-9}$	$5.0 \times 10^{-9}$	$1.4 \times 10^{-9}$
6/4	108 000	$1.5 \times 10^{-11}$	$4.6 \times 10^{-11}$	$5.2 \times 10^{-11}$

<sup>a</sup>Values obtained from the best fit of Eq. (3) to the experimental fluorescence recovery data.

<sup>b</sup>Estimated from diffusion theory in liquids, Eq. (5).

$D$  listed in Table III. It is seen that the values of the diffusion coefficients predicted by the long- and short-time experiments are in reasonably good agreement.

According to the diffusion theory in liquid solutions, the diffusion coefficient is given by the equation:<sup>48</sup>

$$D = \frac{kT}{6\pi\eta\alpha}, \quad (5)$$

where  $k$  is the Boltzmann's constant,  $T$  is the absolute temperature, and  $\alpha$  is the radius of the particle diffusing in the solvent of viscosity  $\eta$ . Although the special nature of polymeric solutions requires further consideration, Eq. (5) could be used to obtain a rough estimate of the diffusion coefficients in our solutions. Taking a value of 3.9 Å as radius of the C540A molecule, derived from its Van der Waals volume,<sup>49</sup> the values of  $D$  listed in the fifth column of Table III are obtained at room temperature. It is seen that they are of the same order of magnitude as those derived from fitting the experimental fluorescence recovery data, which indicates that it is possible to use the diffusion theory in liquids to obtain reasonable estimates of the diffusion coefficients in polymer viscous solutions.

Equation (5) predicts a drastic reduction in the diffusion coefficients of the C540A molecules as the viscosity of the solution increases, with values of  $D$  ranging from  $4.8 \times 10^{-6} \text{ cm}^2/\text{s}$  for the 1,4-dioxane solution to  $5.2 \times 10^{-11} \text{ cm}^2/\text{s}$  for the 6/4 v/w solvent/PMMA sample. It is generally accepted that, for translational motion of a solute to occur, a space of sufficient size must exist into which the solute molecule can move. Thus, as the polymer proportion increases in the solution, the large C540A molecules, with size comparable to that of the polymer repetition unit, require a cooperative movement of several polymer segments in order to create a large enough space for diffusion to occur, and their diffusion rates are therefore coupled to the polymer relaxation processes which are extremely slow in the glassy state.<sup>50</sup> An increase of the solution viscosity leads to a decrease of the free-volume and, consequently, to a sharp decrease in the calculated diffusion coefficients.

As shown in Fig. 12, there is a linear relationship between the radiative decay constants of C540A and the diffusion coefficients calculated from Eq. (5). This result could be understood in terms of the reduction of free-volume associated to the increase in the polymer concentration, and hence of the viscosity of the medium, which could enhance solute-

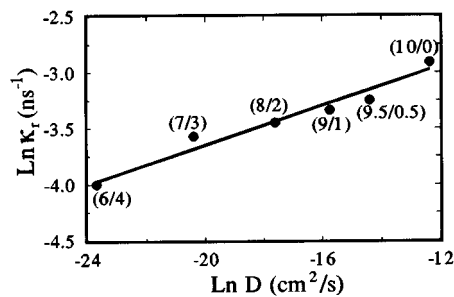


FIG. 12. Radiative decay constants of C540A as a function of the diffusion coefficients predicted by Eq. (5) for solutions of C540A with different viscosities. The volume/weight solvent/PMMA proportion corresponding to each point is indicated in parenthesis. The solid line represents the best linear fit to the experimental points.

solvent molecular interactions which reduce the radiative efficiency. Although this analysis of dye transport as being solely controlled by free-volume is, to a certain extent, a simplification, it could explain why the decrease of both radiative decay rates and lasing efficiencies is strongly linked to the mobility as reflected in the diffusion coefficients.

#### IV. CONCLUSIONS

In the present work, the fluorescence and laser properties of C540A solutions with increasing viscosity, from liquid solution in 1,4-dioxane to solid solution in PMMA, have been investigated. The maxima of both fluorescence and laser emissions are sensitive to the polarity of the media. The fluorescence quantum yield and lasing efficiencies are highly dependent on free-volume of the medium, decreasing as the viscosity of the solution increases. This behavior could be reflecting the strong influence of the rigidity of the medium on the radiative processes, while the nonradiative decay seems to be almost independent of the solution viscosity, probably due to the rigid structure of the Coumarin molecule that inhibits the torsional decay route.

The laser photostability appears to be a function of the elasticity of the medium surrounding the dye molecules. Increasing the viscosity of the solution beyond 250 mPa s leads to a drastic reduction in apparent stability as well as to an irregular behavior in the laser output. The strong oscillations apparent in the laser intensity of the 4000 and 108 000 mPa s solutions as a function of the number of pump pulses could be related to gradients of temperature and dye concentration produced under the irradiation conditions in samples where the free diffusion of molecules is partially restricted. Consequently, this behavior could be reflecting the dynamics of the replacement of bleached molecules for some nonirradiated ones in the irradiated volume.

The study of the dependence of fluorescence intensity and laser output on the number of pump laser pulses provides an insight into the photodegradation mechanisms acting on the fluorophores. The main photodegradation mechanisms of the dye at work have been identified to be photothermal and photobleaching processes, that result in the irreversible and growing presence of decomposition products which absorb at the laser emission wavelength.

The fluorescence redistribution after pattern photobleaching (FRAPP) technique has been used to study the diffusion of dye molecules in the two liquid solutions with the highest viscosities. The diffusion coefficients derived by applying Fick's second law to the experimental fluorescence recovery data corresponding to the 6/4 and 7/3 v/w solvent/PMMA solutions are in good agreement with those determined from the diffusion theory in liquids, revealing the capability of this simple theory to describe the diffusion dynamics in highly viscous polymer solutions.

#### ACKNOWLEDGMENTS

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