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Photophysical characteristics of coumarin 485 dye doped poly(methyl methacrylate) modified with various additives

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The influence of medium on the photophysical properties of a fluorinated coumarin (coumarin 485, C485) is studied in detail. The absorption and fluorescence characteristics of coumarin 485 dye doped poly(methyl methacrylate) modified with various additives (1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile and ethanol) are studied and the results are compared with the respective liquid mixtures. The fluorescence lifetime, fluorescence quantum yield, radiative and the non-radiative decay constants of C485 in polymer and corresponding monomer compositions are obtained. The gain characteristics of C485 in various modified poly(methyl methacrylate) (MPMMA) matrices are studied at various nitrogen laser powers in a transverse pumping configuration and the results are compared with the gain characteristics in the corresponding liquid mixtures. It is found that the gain of C485 in MPMMA increases with the increase in the dielectric constant of the medium while in the liquid medium, the reverse effect is observed. It is also found that the gain coefficient of C485 in a solid matrix shows 90% reduction when compared to the liquid medium. The photobleaching effect of this dye is also studied for a fixed nitrogen laser power and it is found that the photobleaching effect decreases with the increase in the dielectric constant of the medium. A significant improvement in the photostability was achieved from coumarin 485 doped PMMA modified with ethanol. The number of pumping pulses needed for 80% reduction of the initial output is 13 600 pulses for the input power of 10 kW and the repetition rate of 2 Hz.

1 Introduction

Dye lasers are the most versatile and one of the most successful laser sources known today due to their significant contribution to basic physics, chemistry, biology and additional fields. Such versatility emerges from the large choice of molecular dye species available coupled with the wide variety of excitation sources. The need to use large volumes of organic solvents has limited the use of these lasers in some technical applications. As a result, solid matrices containing laser dyes have been developed in the recent years with the aim of developing practical solid state dye lasers. The high gain and broad visible tunability of liquid-dye lasers are retained in solid host media with the advantage of clean and inexpensive active elements that are readily exchanged to access different spectral regions with different dyes. The very first report on a solid state dye laser demonstrates the stimulated emission from Rhodamine 6G (R6G) in poly(methyl methacrylate) under a 2nd harmonic Nd laser.[1] Subsequently, the laser action from R6G and Rhodamine B (RB) in PMMA was also demonstrated, the latter by Peterson *et al.*[2] Initially, the results obtained were not very encouraging, with low lasing efficiency and fast photodegradation of the dye. A reasonably long-lived laser based on Rhodamine 6G doped PMMA was demonstrated by Wang and Gampel who obtained a conversion efficiency of 47% when pumped by the second harmonic of a Q-switched Nd–YAG laser in a near longitudinal pumping configuration.[3] The highest gain of 50 ± 5 cm^{-1} from the CF$_3$-coumarin dye doped PMMA film under nitrogen laser excitation with the stability of few hundred shots was reported by Itoh *et al.*[4] However, solid state dye lasers have not been widely used because of the low resistance to laser damage of the host materials, the low photobleaching resistance of the dyes and the relatively low laser-conversion efficiency. Photobleaching and laser damage to host materials have been studied by various authors and the conversion efficiency and resistance to dye photobleaching were increased by introducing suitable low molecular weight additives[5,6] or by modifying the rigidity of the polymeric material through controlled crosslinking with a bifunctional monomer.[7]

Since then a number of solid host materials have been developed and in most cases the laser dyes have been dispersed in the solid host. The host material may be silica gel, xerogel or polymers.[8–10] Rahn and King studied the laser performance of four dyes in four solid state hosts such as sol–gel, polycom, ormosil and PMMA.[11] One of the important advantages of transparent polymers compared with inorganic glasses and crystals is that they exhibit superior optical homogeneity, which is extremely important in fabricating conventional optical elements for various laser applications.[12–14] The most frequently used polymeric material is poly(methyl methacrylate) (PMMA) because of its better optical transparency and its superior resistance to laser damage.[15]

A review of the literature showed that most of the work has been done with Rhodamine 6G, which emits in the yellow and red region of the spectrum. Applications in technologically important fields, such as optical data storage and underwater communications would require the development of efficient and photostable lasers also in the blue–green spectral region. There has been little work done on blue–green emitting dye doped polymer lasers. Costela *et al.* studied the laser performance of coumarin 540 A (C540 A) dissolved in a copolymer of 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) 1 : 1 v/v and in pure poly(methyl methacrylate) homopolymer (PMMA) under nitrogen laser (1.2 mJ pulses at 337 nm) excitation. They obtained a

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maximum energy conversion efficiency of 11% and lifetimes of only 2000 pulses at 2 Hz-repetition rate from C540 A incorporated in PMMA by slow rate polymerization.[16]

Further improvements in solid state dye lasers require greater understanding of the photophysical properties of the dye molecules, when these molecules are embedded in polymeric matrices. In this paper, we have studied the photophysical properties [fluorescence quantum yield (ϕ_f), fluorescence lifetime (τ_f), radiative (k_r) and non-radiative decay (k_{nr}) constants] of C485 in both the polymer and the corresponding monomer compositions in detail. Since laser performance is sensitive to small changes in gain and loss due to the molecular environment of the laser dye as well as the physical properties of the host materials, we studied the spectral and gain characteristics of coumarin 485 doped in PMMA and PMMA modified with different low molecular weight additives and the results are compared with the respective monomer compositions. No detailed report is available on the gain characteristics of coumarin dyes in an MPMMA matrix except for a few from our group.[17,18] Gain is an intrinsic parameter of the medium, independent of the spectral response of the detector, and is one of the most useful parameters for intercomparison of different laser media, which enables one to choose the appropriate medium to meet the laser design specifications. We have also studied the photobleaching effect of C485 in PMMA modified with various additives for a fixed nitrogen laser power.

For our investigation, we chose a fluorinated coumarin dye (C485) as the active species and an MPMMA matrix as the host material. C485 is photochemically stable when compared to other coumarins and it exhibits very good emission in the green region. The main factor determining the performance of solid state dye laser is the choice of laser dye.[19] It was reported that an MPMMA matrix is the best host material for coumarin dyes when compared to other polymer hosts.[16]

2 Experimental details

2.1 Materials

The laser dye, coumarin 485 (7-dimethylamino-4-trifluoromethylcoumarin) used in this study was purchased from Exciton Inc., USA and the molecular structure is shown in the Fig 1. The thin layer chromatography (TLC) test was used to confirm the absence of impurities. The organic solvents (1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile and ethanol) used were HPLC grade purchased from Merck (India) Ltd. and used as received.

The monomer MMA (methyl methacrylate) (Lancaster) was purified by washing with 10% aqueous sodium hydroxide to remove the inhibitor, followed by washing with distilled water and drying over calcium chloride, and was stored in a cool, dark place.

2.2 Synthesis of dye doped polymer (DDP) rods

The laser dye coumarin 485 was dissolved in the mixture of freshly purified MMA with various organic solvents (1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile and ethanol) in the ratio of 4 : 1 v/v. Then 3 g l^{-1} of azoisobutyronitrile as initiator were added and the resultant solution was put into a polymerization tube in which thermal radical polymerization was carried out under a nitrogen atmosphere. The polymerization was performed in the dark at 35 °C for the first two days, at 40 °C for the next two days and at 45 °C for the last two days. The rods were cast into a rectangular shape of 2 cm length and 9 mm thickness. The DDP rods fabricated were obtained in polished form and only the ends were polished by conventional grinding and polishing. Thermogravimetric analysis of the synthesized polymer sample showed the absence of residual monomer.

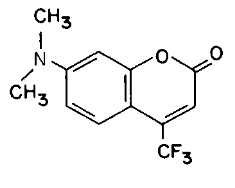

Fig. 1 Molecular structure of coumarin 485.

2.3 Methods

The absorption spectra of C485 in liquid and solid matrices were recorded using an Elico SL 159 spectrophotometer and the fluorescence spectra were recorded using Fluoro MAX 2 spectrofluorometer. The dye concentration used was 0.05 mM for absorption and fluorescence spectra in both liquid and solid media.

Fluorescence lifetime measurements were carried out by the picosecond time-correlated single photon counting technique using a Ti–sapphire laser (TSUNAMI SPECTRA PHYSICS, USA) operating with an intensity maximum at 375 nm. The fluorescence was detected using a two state microchannel plate photomultiplier (MCP-PMT R3809U). The fluorescence decay measured was further analysed using an IBH software library, which includes an iterative shift of the fitted function as part of the χ^2 goodness-of-fit criterion.

The fluorescence quantum yields of these derivatives were calculated using the expression,

$$\phi_f = (A_{sam}/A_{ref}) \times (a_{ref}/a_{sam}) \times (n_{sam}/n_{ref})^2 \times \phi_f^1 \tag{1}$$

where A_{sam} and A_{ref} are the areas under the corrected fluorescence spectrum, a_{sam} and a_{ref} are the absorbances at the exciting wavelength (366 nm), n_{sam} and n_{ref} are the refractive indices of the respective solvent and reference, respectively. The absorbance value at 366 nm is adjusted to 0.05. Quinine sulfate in 0.05 M sulfuric acid was used as the reference for quantum yield determination. ϕ_f^1 is the quantum yield of quinine sulfate (0.546).[20]

A single pass gain measurement using the ASE (amplified spontaneous emission) method proposed by Shank *et al.*[21] was used for studying the gain of dye doped polymer (DDP) rods and liquid solutions pumped by the nitrogen laser. A home-built nitrogen laser of wavelength 337.1 nm, peak power 100 kW and pulse width 10 ns was used as the pumping source. The DDP rod is pumped in the transverse configuration and the rod is kept in a tilted position to avoid optical feedback due to reflections from the ends of the DDP rod. The rod is pumped with a focussed line image of nitrogen laser radiation, produced by a cylindrical lens of focal length 4 cm. The length of the pumped region of the DDP rod can be varied from 0 to 2 cm by using a beam block mounted on a micrometer. The pumped region of the DDP rod has a uniform intensity of pumping. Care was taken to ensure that there was no unpumped region of the sample at the monitoring end of the DDP rod, thus preventing re-absorption of the emitted light. The wavelength corresponding to maximum intensity is measured using constant deviation spectrometer. The intensity at the maximum wavelength of the ASE band is measured using a monochromator (CEL 3134)–photomultiplier (RCA 931 A)–oscilloscope (OS 320, 20 MHz) combination. The gain is calculated using eqn. (2),

$$\frac{I_1(\lambda)}{I_2(\lambda)} = \frac{\exp\{G(\lambda)l_1\} - 1}{\exp\{G(\lambda)l_2\} - 1} \tag{2}$$

where $G(\lambda)$ is the gain at the maximum wavelength. $I_1(\lambda)$ and $I_2(\lambda)$ are the ASE intensities for active lengths l_1 and l_2, respectively.

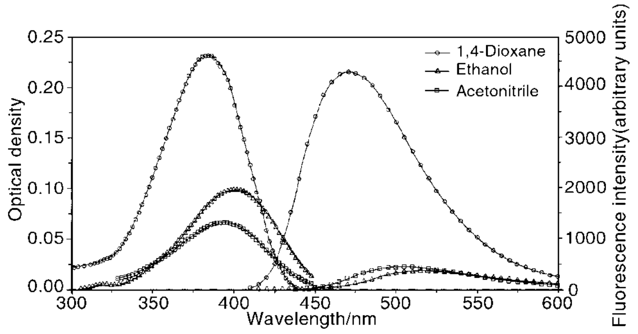

Fig. 2 Absorption and fluorescence spectra of coumarin 485 in various solvents.

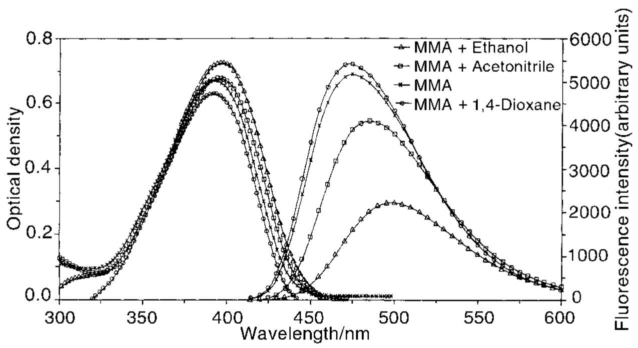

Fig. 3 Absorption and fluorescence spectra of coumarin 485 in various monomer compositions.

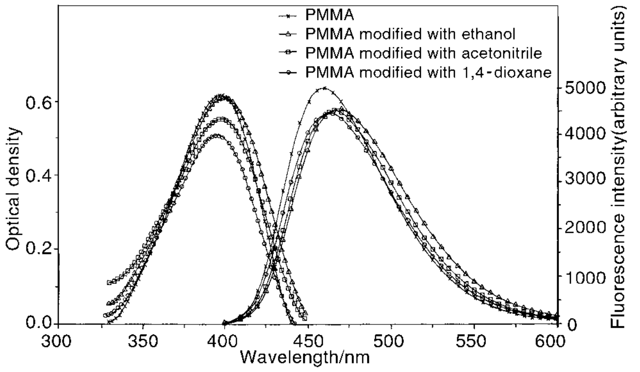

Fig. 4 Absorption and fluorescence spectra of coumarin 485 in various MPMMA matrices.

3 Results and discussion

3.1 Spectral results

The absorption and fluorescence spectra of C485 in various solvents (1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile and ethanol) in the mixture of MMA with each of these solvents in the ratio of 4 : 1 v/v and in modified PMMA (using 1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile, ethanol) are shown in Figs. 2–4. The absorption and fluorescence maxima, molecular absorption coefficients (ε in l mol^{-1} cm^{-1}), oscillator strength (f), absorption bandwidth, fluorescence bandwidth and Stokes shift of C485 in liquid and solid environments are listed in Table 1. The absorption and fluorescence spectra show a red shift with the increase in solvent polarity. This indicates that the excited state of the dye molecule C485 is more polar than the ground state due to intermolecular charge transfer (ICT). On intermolecular charge transfer, there is always the possibility that a molecule gets either distorted in its own plane or twisted out-of plane. The size of the Stokes shift is almost a signature of the charge transfer nature of the transition and provides a measure of the twisting of the molecule in the excited state. The value of the Stokes shift of C485 increases with the increase in polarity of the solvent. The large value of the Stokes shift for C485 in ethanol and acetonitrile indicates its pronounced twisting on excitation.[22] The distortion could also make the molecule less fluorescent and it is actually observed in the present case that the fluorescence intensity of C485 is less in acetonitrile and

Table 1 Spectral characteristics of coumarin 485 in liquid and solid media

		Absorption spectra				Fluorescence spectra		
Serial No	Medium	Peak wavelength/nm	$10^{-4}\,\varepsilon$/l mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$/cm^{-1}	Oscillator strength f/l mol^{-1} cm^{-2}	Peak wavelength/nm	FWHM/nm	Stokes shift/cm^{-1}
1.	Methyl methacrylate (MMA)	392	1.34	5261	0.304	475	78.06	4457
2.	Poly(methyl methacrylate) (PMMA)	396.4	1.37	4706	0.278	459	70.20	3466
3.	1,4-Dioxane	386	4.62	4957	0.987	470	80.69	4630
4.	MMA + 1,4-dioxane	391	1.26	5019	0.270	472	79.10	4389
5.	PMMA modified with 1,4-dioxane	395	1.19	4835	0.248	463	74.70	3718
6.	Chloroform	393	2.46	5322	0.560	470	76.06	4104
7.	MMA + chloroform	394	1.46	5233	0.330	479	79.61	4504
8.	PMMA modified with chloroform	398	1.69	5014	0.365	461	71.90	3434
9.	*n*-Butyl acetate	394	2.38	5054	0.518	481	81.29	4590
10.	MMA + *n*-butyl acetate	392	1.25	5143	0.280	475	78.42	4457
11.	PMMA modified with *n*-butyl acetate	396	1.41	4714	0.286	460	73.52	3513
12.	Acetonitrile	396	1.32	5381	0.306	504	78.20	
13.	MMA + acetonitrile	393	1.36	5268	0.308	486	79.19	4740
14.	PMMA modified with acetonitrile	399	1.30	5226	0.293	465	74.15	3552
15.	Ethanol	404	1.96	5059	0.427	516	74.59	5373
16.	MMA + ethanol	397	1.45	5275	0.330	499	80.76	5148
17.	PMMA modified with ethanol	400	1.43	5138	0.317	468	78.36	3632

Table 2 Fluorescence quantum yield, lifetime, radiative and non-radiative decay constants for C485

Serial No.	Medium	ϕ_f	τ_f	$10^7 k_r/\mathrm{s}^{-1}$	$10^7 k_{nr}/\mathrm{s}^{-1}$
1.	Methyl methacrylate (MMA)	1.036	4.831	21.40	—
2.	Poly(methyl methacrylate) (PMMA)	0.860	4.770	18.02	2.930
3.	1,4-Dioxane	0.953	4.930	19.33	0.953
4.	MMA + 1,4-dioxane	0.956	4.903	19.49	0.897
5.	PMMA modified with 1,4-dioxane	0.650	4.820	13.48	7.260
6.	Chloroform	1. 051	4.884	21.52	—
7.	MMA + chloroform	0.970	4.875	19.89	0.615
8.	PMMA modified with chloroform	0.780	4.850	16.08	4.54
9.	*n*-Butyl acetate	0.847	4.869	17.39	3.142
10.	MMA + *n*-butyl acetate	1.066	4.797	22.22	—
11.	PMMA modified with *n*-butyl acetate	0.970	4.940	19.64	0.607
12.	Acetonitrile	0.270	1.96	13.77	37.24
13.	MMA + acetonitrile	0.780	4.270	18.27	5.15
14.	PMMA with acetonitrile	0.950	4.990	19.04	1.00
15.	Ethanol	0.190	1.887	10.07	42.92
16.	MMA + ethanol	0.370	2.670	13.85	23.59
17.	PMMA modified with ethanol	0.670	4.970	13.48	6.640

ethanol than in other moderately polar solvents This intensity is further increased in the mixture of MMA with these solvents. This is due to the decrease in polarity of the medium, which reduces the possibility of twisting the molecule out-of-plane. We observed that there is no change in the spectral profile of C485 in the solid matrix. The peak wavelengths of absorption and fluorescence spectra show a blue shift when compared to those in the liquid medium. This is due to the decrease in the relative permittivity of the medium in the solid matrix. The spectral characteristics of the lasing dyes in the polymer depend on the intermolecular interaction between the dye molecule and macromolecules. The intermolecular interaction may crucially affect the laser characteristics of the dye molecules; these characteristics are determined by the degree of overlap of dye absorption and fluorescence bands.[23] The full width at half maximum of both the absorption and fluorescence spectra of C485 in a solid matrix is slightly narrower than that in the respective liquid mixture. The Stokes shift of C485 in a solid matrix is less than that in the liquid medium.

3.2 Measurement of fluorescence quantum yield

We calculated the fluorescence quantum yield of C485 in various solvents (1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile and ethanol) in the mixture of MMA with each of these solvents in the ratio of 4 : 1 and in PMMA modified with (1,4-dioxane, chloroform, *n*-butyl acetate, acetonitrile, ethanol) and the values are listed in Table 2. We found that the value of quantum yield of C485 in ethanol and acetonitrile is very much less compared to that in the other solvents studied and this value is slightly increased in the mixture of MMA with these solvents in the ratio of 4 : 1. The presence of the strong electron acceptor CF_3 group in the 4 position of C485 leads to a sharper decrease in the quantum yield with the increase in charge transfer into the pyrone part of the system and the weakening of the bond between the substituent at the 7 position and the polar solvent.[24] The observed fluorescence quantum yield values of C485 in the present investigation coincide with the literature values.[25]

3.3 Fluorescence lifetime, radiative and non-radiative rate constants

The fluorescence lifetime, radiative and non-radiative rate constants of C485 in liquid and solid environments are listed in Table 2. The fluorescence decay profiles of C485 in liquid and solid matrices are shown in Figs. 5–7. The fluorescence decay of C485 exhibits single exponential decay in all the matrices except for in ethanol, in which it exhibits biexponential decay and the percentage of the second component is very small. The fitting parameters of C485 in ethanol are $\tau_1 = 1.88$ ns (96.7), $\tau_2 = 4.4$ ns (3.3), $\chi^2 = 1.02$. The second component ($\tau_2 = 4.4$ ns) is due to the H-bonding effect between C485 and ethanol. The fluorescence lifetime value obtained in the present investigation matches the reported values.[26]

The radiative and non-radiative rate constants are calculated using the expression, $k_r = \phi_f/\tau_f$ and $k_{nr} = (1-\phi_f)/\tau_f$. In the liquid medium, the fluorescence lifetime of C485 decreases dramati-

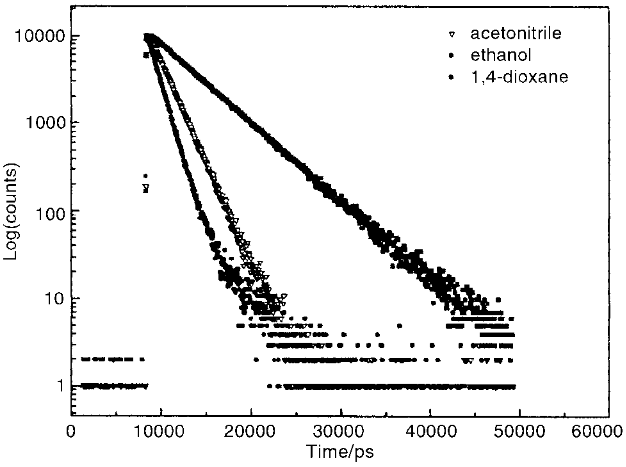

Fig. 5 Fluorescence decay profile of C485 in various solvents.

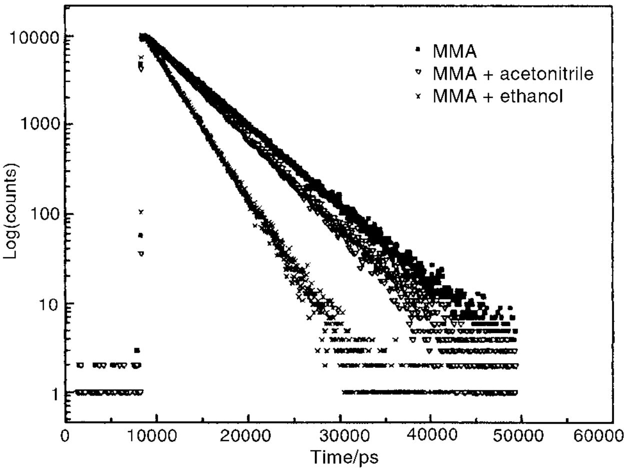

Fig. 6 Fluorescence decay profile of C485 in various monomer compositions.

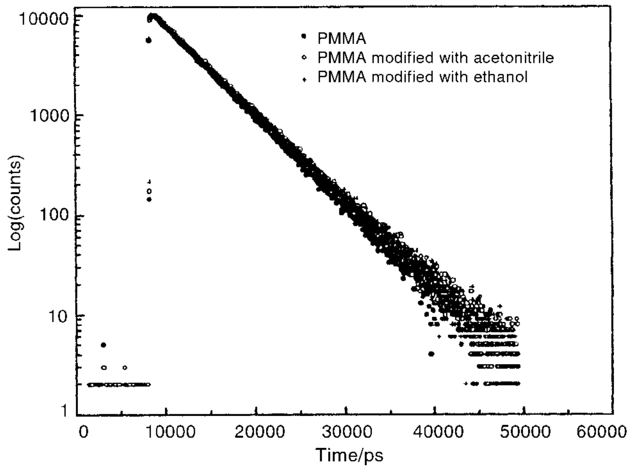

Fig. 7 Fluorescence decay profile of C485 in solid media.

cally as the solvent polarity increases, but it is essentially unaffected in the solid medium. We observed that the fluorescence lifetime of C485 increases with the increase in the relative permittivity of the MPMMA matrix.

3.4 Amplified spontaneous emission spectra

The dye doped polymer rods were pumped by a nitrogen laser, radiating at 337.1 nm with a pulse duration of 10 ns and a repetition rate of 1 Hz. The nitrogen laser output was focussed by a cylindrical quartz lens of focal length 4 cm on to the rod. This produced a line-shaped image of uniform intensity and the amplified spontaneous emission (ASE) was obtained at right angles to the pump laser beam. The peak wavelength of the ASE spectra was measured by using a constant deviation spectrometer that was calibrated using a mercury lamp. The measured peak wavelengths of the ASE spectra of C485 are listed in Table 3.

3.5 Gain studies

The experimental set-up to measure the gain of C485 dye in liquid and solid media is described in Section 2.3. We synthesized DDP rods with different concentrations. The rod with 20 mM concentration exhibits very good laser action and this rod was used for the gain and photobleaching studies. In the liquid medium, the concentration of 5 mM itself exhibits very good laser action. The gain coefficient varies linearly with

Table 3 Gain characteristics of coumarin 485 in liquid and solid media

Sl. No.	Medium	ASE/nm	10^{19} Gain/cm^2 molecule^{-1} kW^{-1})
1.	Methyl methacrylate (MMA)	492	2.05
2.	Poly(methyl methacrylate) (PMMA)	479	0.215
3.	1,4-Dioxane	475	2.39
4.	MMA+1,4-dioxane	490	2.36
5.	PMMA modified with 1,4-dioxane	483	0.213
6.	Chloroform	481	2.33
7.	MMA+chloroform	493	2.58
8.	PMMA modified with chloroform	484	0.227
9.	*n*-Butyl acetate	488	1.653
10.	MMA+*n*-butyl acetate	493	2.58
11.	PMMA modified with *n*-butyl acetate	483	0.195
12.	Acetonitrile	515	1.24
13.	MMA+acetonitrile	501	1.835
14.	PMMA modified with acetonitrile	488	0.236
15.	Ethanol	—	—
16.	MMA+ethanol	516	1.465
17.	PMMA modified with ethanol	487	0.273

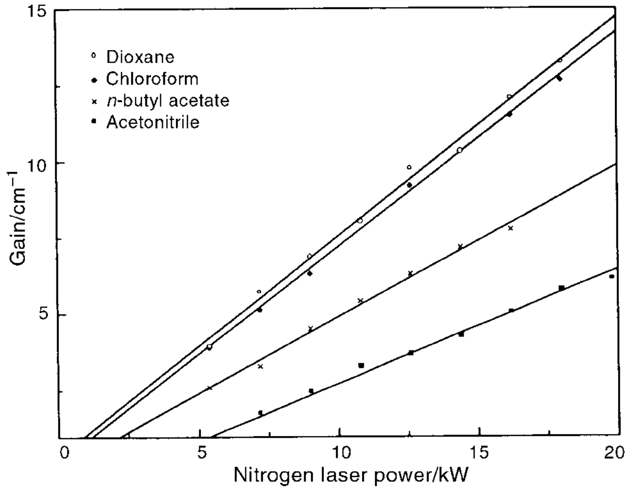

Fig. 8 Variation of gain with nitrogen laser power for coumarin 485 in various solvents.

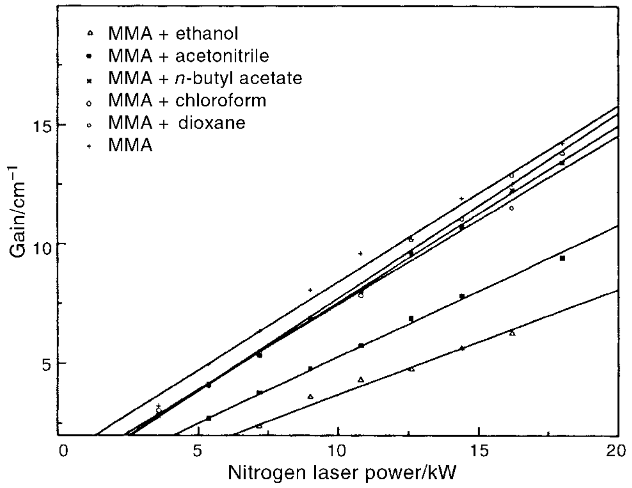

Fig. 9 Variation of gain with nitrogen laser power for C485 in mixtures of solvents.

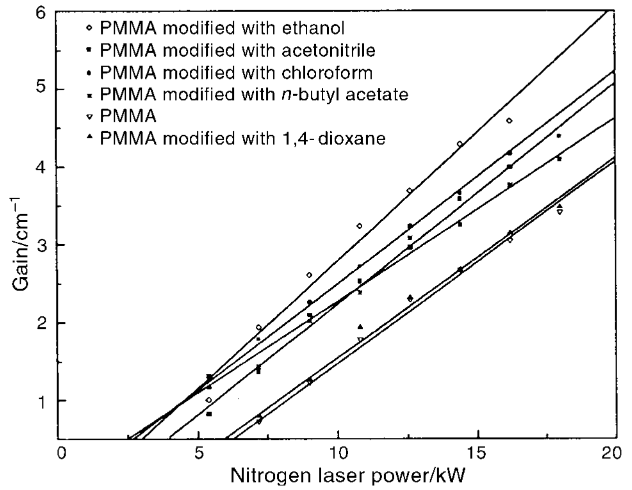

Fig. 10 Variation of gain with nitrogen laser power for C485 in solid media.

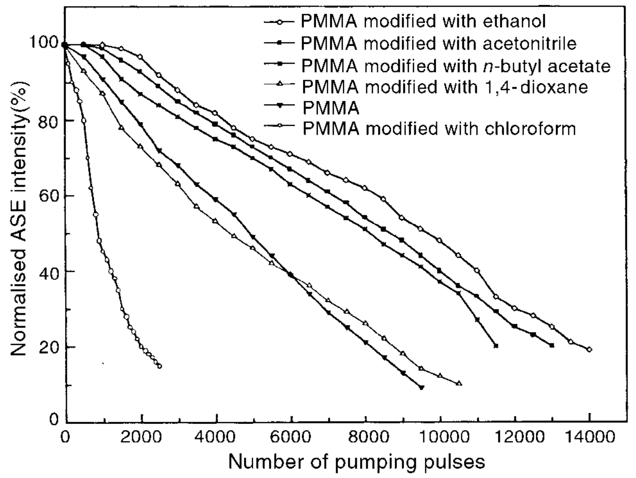

Fig. 11 Variation of ASE intensity with the number of pumping pulses.

the pump power in all cases and Figs. 8–10 show the variation of gain per unit length with the nitrogen laser power in kW. The values of the gain coefficient ($cm^2\ kW^{-1}\ molecule^{-1}$) of C485 in the liquid, the monomer and in PMMA modified with various additives are listed in Table 3. The gain coefficient of C485 in the solid medium is less than that in the liquid. The main reason for this decrease in gain coefficient of C485 in a solid matrix is the dye re-absorption and inhomogeneity produced at higher concentration. For a 20 mM concentration of C485 in MPMMA, the separation of the molecules may be enough for them to interact with each other to form aggregates. The decrease in the gain coefficient of C485 in the solid medium may be due to the decrease in relative permittivity of the medium.[27] Polymerization causes a decrease in the relative permittivity ($\varepsilon_{MMA}=4$, $\varepsilon_{PMMA}=2.9$) and this results in a shift of equilibrium between dye monomer molecules and their aggregates towards the latter.[6] The chemical structure and physical properties of the polymer may crucially affect the laser characteristics of the dye molecules in the polymer matrix.[23]

3.6 Photobleaching studies

The dye photobleaching effect of the DDP rod under nitrogen laser excitation was studied by focusing the beam on the DDP rod with a quartz cylindrical lens. The repetition rate of the nitrogen laser was kept at 2 Hz and the power of the nitrogen laser was kept at 10 kW. The length of the excited region was 2 cm and the rod was fixed rigidly. The ASE output was continuously monitored with the monochromator–PMT–CRO set-up. The variations in ASE intensity with a number of pumping pulses are shown in Fig. 11. We observed that the photobleaching effect decreases with the increase in the relative permittivity of the medium. This confirms that increasing the polymer's plasticity by adding different low molecular weight dopants reduces the brittle fracture limit of PMMA, which improves the material's damage resistance. The photobleaching efficiency of the dye in the polymer matrix depends on the dye solubility in the matrix and the chemical interaction of the dye molecule with the macromolecules. The observed dependence of resistance to dye photobleaching in polymers on the presence of additives of low molecular weight is due to the cross-relaxation between the vibrational levels of the polymer macromolecules and those of the impregnated additive compounds.[6] The structure and molecular characteristics of the plasticizer caused microdamage of the PMMA. The introduction of various plasticizers into the PMMA retarded the process of nucleation of the scattering centers that initiate laser damage.[28]

4 Conclusion

The absorption and fluorescence characteristics of C485 in liquid and solid environments have been studied in detail. It was found that there is no change in the spectral profile of C485 in a solid matrix at low concentration. This conservation of spectral profiles indicates a lack of dye aggregation in the solid phase at the concentration of 0.05 mM. The gain characteristics of C485 in the solid medium show 90% reduction when compared to those in the liquid. The main reasons for this decrease in gain coefficient of C485 in a solid matrix are the dye re-absorption and inhomogeneity produced at higher concentration. In the solid medium, only the use of a concentration of 20 mM produces laser action, whereas in the liquid medium, a concentration of 5 mM causes very good laser action. The quantum yield and gain studies confirm that the fluorine-substituted coumarin molecules get distorted in the highly polar environment and this can be reduced by modifying the medium with less polar solvents. However, in the solid medium, the fluorescence quantum yield and gain increase with the increase in the relative permittivity of the MPMMA matrix. The photobleaching studies on C485 show that the photobleaching effect decreases with the increase in the relative permittivity of the medium. We achieved significant improvements in the photostability of 13 600 pulses for 80% reduction in the initial output from coumarin 485 doped PMMA modified with ethanol.

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