JOURNAL OF
Materials
CHEMISTRY

Synthesis and spectral properties of novel laser copolymers based on modified rhodamine 6G and 1,8-naphthalimide

He Tian,*[a] Yuanjun He[a] and Chen-Pin Chang[b]

[a]Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, China. E-mail: hetian@ecust.edu.cn; Fax: +86-21-64248311
[b]Department of Chemistry, Fu Jen Catholic University, Shin Chuang, Taipei, China

Received 10th January 2000, Accepted 12th May 2000
Published on the Web 7th August 2000

The excellent photostability of the trichromophoric rhodamine dyes (TCR-1 and TCR-2) containing two 1,8-naphthalimides as antennas had been observed for the solid lasing operation using the dyes in methacrylate. Further understanding of the stabilization mechanism operating in these compounds would require a study of photophysical properties. The fluorescence lifetimes of TCR-1 and TCR-2 have been measured by the single-photon counting technique and the intramolecular singlet energy transfer from the naphthalimide moiety (NA) to the rhodamine moiety (Rh) has been observed. In order to obtain laser dye polymer materials with a high laser-radiation-damage threshold, modified rhodamine 6G molecules (Rh-Al or Rh-Aln) with polymerizable double bonds have been copolymerized with 1,8-naphthalimide derivatives. The absorption spectra of these new copolymers indicate there is little or no interaction between the two NA and the Rh moieties in their ground state, however, the fluorescent spectra indicate that energy transfer from the NA group to the Rh-Al or Rh-Aln group in the copolymers does occur. In comparison, energy transfer was not observed in an equal molar mixture of monomers corresponding to the copolymers, which demonstrated that intramolecular energy transfer in the copolymer synthesized in this study occurred mainly along the polymeric chain.

Introduction

Until recently liquid dye lasers were the main system used to achieve tunable lasers in the visible region. Nevertheless, solid-state dye lasers are attracting attention as alternatives to conventional liquid-solution dye lasers because of their technical and economical advantages such as compactness, manageability, non-toxicity, non-flammability, no solvent evaporation, easy miniaturization and easy design of integrated optical systems, *etc.* The first observation of stimulated emission from rhodamine 6G in poly(methyl methacrylate) (PMMA) was described as early as 1967 by Soffer and McFarland,[1] while Peterson and Snavely reported lasing experiments based on rhodamine B and rhodamine 6G in the same polymer one year later.[2] Since then more and more work has been done using silica gels[3–15] or polymers[16–26] as solid matrices for laser dyes. Work with polymers has indicated that polymer materials seem to show higher optical homogenates,[27] better chemical compatibility with organic dyes and inexpensive fabrication techniques, although they suffer from relatively low laser-damage threshold. However, modified polymer matrices have resulted in significant improvements in the resistance of these materials to damage caused by laser radiation.[17,22,28]

We have reported[25] significant increases in photostability in solid-state dye lasers based on modified rhodamine 6G dyes with two covalently bonded identical 1,8-naphthalimide groups (TCR-1 and TCR-2, Fig 1) dissolved in a copolymer of 2-hydroxyethyl methacrylate (HEMA) and MMA in a 1 : 1 (v/v) rate. It was suggested that the presence of the 1,8-naphthalimide molecules as acceptors of the excess energy is effective in stabilizing the rhodamine 6G laser dye. Further understanding of the stabilization mechanism operating in these compounds (TCR-1 and TCR-2) would require a study of photophysical properties. Therefore, the fluorescence lifetimes of these new compounds TCR-1 and TCR-2 has been investigated by single-photon counting technique in this paper. The fluorescence spectra of these dyes showed that an efficient intramolecular singlet energy transfer from the naphthalimide moiety (NA) to the rhodamine moiety (Rh) exists,[29] which should be confirmed by means of fluorescence lifetime data. It can be considered that the intramolecular charge transfer or/and energy transfer between NA and Rh in TCR-1 and TCR-2 would be the main reason for good photostability of these compounds. NA may be acting as a triplet acceptor relative to Rh.

Since the naphthalimide moiety can act as a good energy pumping antenna and an internal photostabilizer for rhodamine molecules, we decided to synthesize novel modified rhodamine copolymers with naphthalimide moieties, and thus obtain laser dye polymer materials with a high laser-radiation-damage threshold. The laser dye monomers, modified rhodamine 6G molecules (Rh-Al or Rh-Aln) with polymerizable

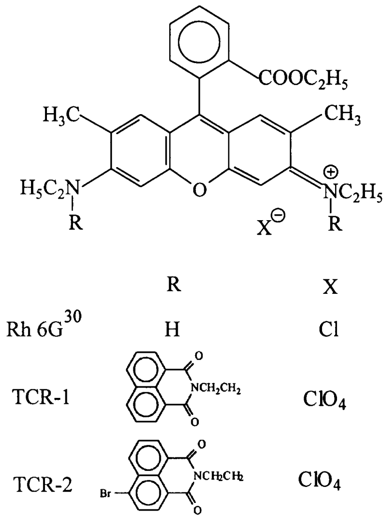
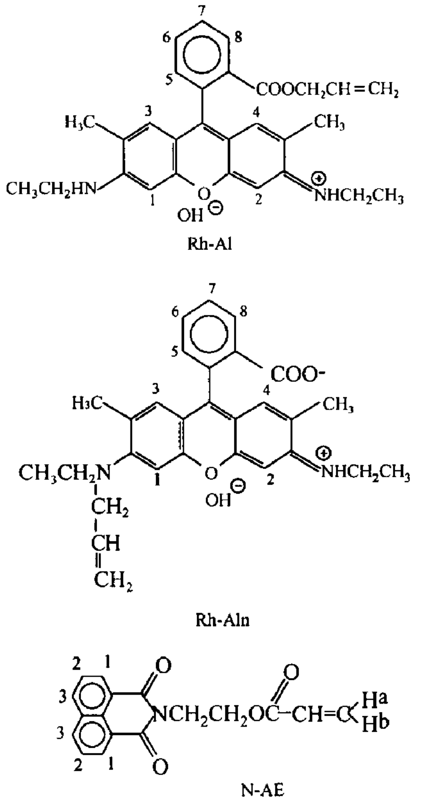


Fig. 1 Molecular structures of trichromophoric rhodamine dyes.

DOI: 10.1039/b000141o

J. Mater. Chem., 2000, **10**, 2049–2055


Rh-Al

Rh-Aln

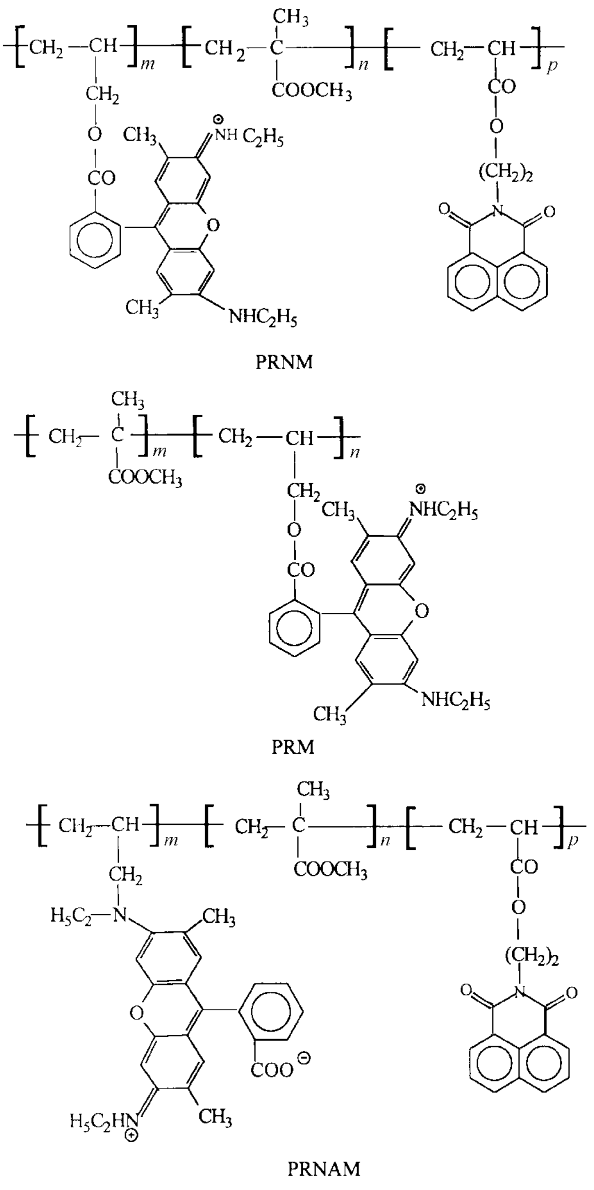
N-AE

Fig. 2 Molecular structures of laser dye monomers.

double bonds, were synthesized and their chemical structures are shown in Fig. 2. These new modified rhodamine 6G molecules (Rh-Al or Rh-Aln) were copolymerized with 1,8-naphthalimide derivatives and/or MMA resulting in several copolymeric products shown in Fig. 3. The absorption spectra and fluorescent properties of these copolymers have been investigated. Previous work on the modified rhodamine copolymers made by Costela *et al.*[20,24] demonstrated that the polymeric chain would provide additional channels for the elimination of the absorbed energy along the polymer backbone. This will increase the photostability and lasing efficiencies of laser materials similar to those found for the parent dye in liquid solution. For the copolymeric products synthesized in this paper, the photostability and lasing efficiencies of these laser materials were significantly improved due to the elimination of excess energy through the polymer backbone and also the presence of naphthalimide antennas acting as internal photostabilizer.

Experimental

Fluorescence lifetimes of compounds were measured by the single-photon counting technique (Edinburgh FL 900) with a hydrogen-filled flash lamp or a nitrogen lamp as the excitation source. Data were analyzed using a nonlinear least-squares fitting program with deconvolution method. The temporal resolution after deconvolution of the exciting pulse is ~200 ps. UV-VIS absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer and fluorescence spectra were determined with a Hitachi-850 fluorescent spectrometer. ^{1}H-NMR spectra were recorded on a Bruker AM 500 spectrometer with tetramethylsilane as internal reference. Mass spectra were carried out on a HP5989 mass spectrometer. The average molecular weight of copolymer was obtained with a Waters 410 GPC. All solvents were commercial (analytical grade) or purified with standard procedures.


PRNM

PRM

PRNAM

Fig. 3 Molecular structures of copolymeric products PRNM, PRM and PRNAM.

Laser dye monomer preparations

The synthesis procedure for *N*-[(2-acryloyl)ethoxy]-1,8-naphthalimide (N-AE) was as follows: *N*-(2-hydroxyethyl)-1,8-naphthalimide (1.2 mmol) was dissolved in dry tetrahydrofuran (THF, 50 mL), then acryloyl chloride (0.5 mL) and triethylamine (0.5 mL) were added slowly to the solution. The mixture was stirred for 8 h at room temperature. The precipitate was filtered off and washed with THF, and the filtrate was vacuum concentrated, then cooled and recrystallized in the refrigerator. The final light yellow crystals were obtained and dried under vacuum. Yield 80%, mp 106–108 °C.

^{1}H NMR(CDCl$_3$): δ 4.53(t, 2H, CH$_2$-N), 4.57(t, 2H, CH$_2$-O-CO), 5.81(d, 1H, H^a), 6.08(m, 1H, -CH=CH$_2$), 6.38(d, 1H, H^b), 7.78(t, 2H, 2×H^2, J=8.0 Hz, 7.47 Hz), 8.24(d, 2×H^3, J=8.27 Hz), 8.62(d, 2H, 2×H^1, J=7.21 Hz). MS(EI) *m/z*: 295(32.95%) [M$^+$]. Elemental analysis for $C_{17}H_{13}NO_4$: calcd/found: C:69.15/69.07, H:4.40/4.49, N: 4.75/4.69, O: 21.70/21.64%.

The modified rhodamine 6G dye monomers (Rh-Al and Rh-Aln) were obtained as follows.[24] A mixture of rhodamine 19 (10 mmol, obtained from rhodamine 6G by hydrolization and acidification), allyl chloride (5 mL), anhydrous sodium carbonate (50 mmol), hydroquinone (trace), and dimethylformamide

Table 1 The fluorescence lifetime data of trichromophoric rhodamine dyes in different solvents

Solvent	Tetrahydrofuran (THF) τ_1/ns; τ_2/ns	Ethyl acetate (EA) τ_1/ns; τ_2/ns	Ethanol (EtOH) τ_1/ns; τ_2/ns
TCR-1	1.37(79.5%), 4.63(20.5%)	1.49(72.8%)	1.12(69.9%), 4.65(30.1%)
	Ex = 330 nm,[a] Em = 400 nm[a]	Ex = 330 nm, Em = 400 nm	Ex = 330 nm, Em = 400 nm
	3.43	3.58	3.68
	Ex = 330 nm, Em = 600 nm	Ex = 330 nm, Em = 600 nm	Ex = 330 nm, Em = 600 nm
TCR-2	0.89(66.0%), 5.23(34.0%)		0.74
	Ex = 340 nm, Em = 400 nm		Ex = 340 nm, Em = 400 nm
	3.10		3.87
	Ex = 340 nm, Em = 600 nm		Ex = 340 nm, Em = 600 nm

[a]Note: Ex is the excitation wavelength, Em is the detected wavelength for fluorescence lifetimes.

(DMF, 100 mL) was heated at 50 °C in the dark, with stirring, under an argon atmosphere, for 30 h. Vacuum evaporation of the solvent yielded a mixture, from which Rh-Al and Rh-Aln were separated by flash column chromatography (silica gel, chloroform–ethanol 85 : 15 (v/v) as eluant). The first component separated from the column was Rh-Aln and the second was Rh-Al. The resulting dry solids were used without further purification.

Rh-Al: Yield 35%, mp 239–241 °C.

^{1}H NMR(CDCl$_3$): δ 1.41(t, 6H, 2 × CH$_3$-CH$_2$, J = 6.93 Hz), 2.30(s, 6H, 2 × CH$_3$-Ar), 3.55(m, 4H, 2 × CH$_2$-CH$_3$), 4.50(d, 2H, O-CH$_2$-CH=, J = 5.87 Hz), 5.15(m, 2H, CH$_2$=CH), 5.65(m, 1H, CH=CH$_2$), 6.60(s, 2H, H^3/H^4), 6.73(s, 2H, H^1/H^2), 7.32(d, 1H, H^5, J = 7.47 Hz), 7.58(br, 2H, 2 × NH), 7.77(t, 1H, H^7, J = 7.60 Hz), 7.83(t, 1H, H^6, J = 7.47 Hz, 1.07 Hz), 8.34(d, 1H, H^8, J = 7.74 Hz).

Rh-Aln: Yield 15%, mp > 300 °C.

^{1}H NMR (CDCl$_3$): δ1.05(t, J = 7.10 Hz, 3H, CH$_3$-CH$_2$-), 1.35(t, J = 7.33 Hz, 3H, CH$_3$-CH$_2$-), 1.95(s, 3H, CH$_3$-Ar), 2.16(s, 3H, CH$_3$-Ar), 3.16(m, 2H,-CH$_2$-CH$_3$), 3.28(m, 2H, -CH$_2$-CH$_3$), 3.62(d, J = 5.72 Hz, 2H, -CH$_2$-CH=CH$_2$), 5.15(d, 1H, H-CH=CH-), 5.25(d, 1H, H-CH=CH-), 5.84(m, 1H, -CH=CH$_2$), 6.44(s, 2H, H^3/H^4), 6.56(s, 1H), 6.89(s, 1H), 7.18(d, J = 7.33 Hz, 1H, H^5), 7.64(m, 2H, H^6/H^7), 8.09(d, 1H, H^8).

Preparation of copolymeric products PRNM, PRM and PRNAM

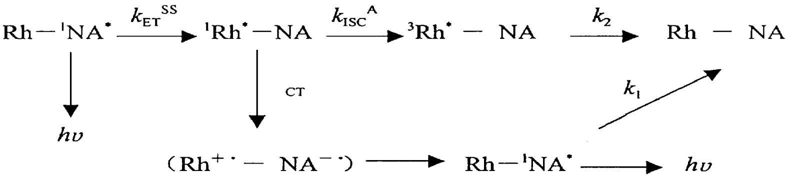
The modified rhodamine 6G dye monomer (Rh-Al or Rh-Aln), N-AE (0.21 mmol) and freshly purified MMA (1 mL) were dissolved in chloroform (5 mL), and then 2,2′-azobis(isobutyronitrile) (AIBN, 50 mg) was added as a free radical initiator, and the mixture was stirred and sufficiently degassed by argon gas for 4 h, and the system was sealed. Polymerization was performed in the dark at 60 °C over a period of three days and then at 80 °C for about one day. After cooling, purification was carried out by three cycles of dissolving in chloroform (3 mL) with subsequent precipitation by dropping into vigorously stirred ethanol. The precipitates were filtered off and dried in vacuum to give PRNM copolymeric products. Copolymeric product PRM resulting from Rh-Al and MMA was obtained in a similar way. PRNM-1 and PRNM-2 were obtained by adding Rh-Al 0.21 mmol and 0.62 mmol into the mixture, respectively; PRNAM-1 and PRNAM-2 by adding Rh-Aln 0.21 mmol and 0.32 mmol respectively, and PRM-1 and PRM-2 by adding Rh-Al 0.11 mmol and 0.53 mmol respectively. In the preparation processes, the contents of N-AE and MMA were confirmed.

Average chromophore contents of NA and Rh in PRNM, PRM and PRNAM were determined by spectroscopy of chloroform solutions of purified samples of the copolymers, using as references the maximum-absorption coefficient of the corresponding Rh-Al, Rh-Aln and N-AE in the same solvent. Average molecular weights of these copolymers were obtained with a Waters GPC. DSC determined the glass transition temperatures, T_g.

Results and discussion

The fluorescence lifetime data of trichromophoric rhodamine dyes TCR-1 and TCR-2 in different solvents are listed in Table 1. The fluorescence lifetimes data detected at 400 nm were considered as resulting mainly from the antenna naphthalimide group (NA) in TCR-1 and TCR-2. The lifetimes determined at 600 nm were considered as resulting from the rhodamine group (excited at 330 or 340 nm), because the fluorescence emission spectral region of NA is between 380–450 nm. The fluorescence lifetimes detected at 400 nm for TCR-1 and TCR-2 decay according to two exponential kinetic processes. This phenomenon is very similar to the results for other multi-chromophoric rhodamines (*e.g.* PPO-rhodamine, where PPO = 2,5-diphenyloxazole).[31] This indicates that some interactions between NA and Rh in these trichromophoric rhodamine systems exist. A previous study[29] demonstrated that singlet energy transfer from the naphthalimide group to the rhodamine group occurred in TCR-1 and TCR-2 (excited in UV region). The fluorescence of the antenna (NA) was obviously quenched owing to the fast intramolecular singlet–singlet energy transfer (Intra-SSET) from NA to Rh. The main weighting fluorescence lifetimes (τ_1), which are in fact the characteristics of the naphthalimide moiety, were shortened by Intra-SSET comparing with that of naphthalimide (4.0–4.2 ns).[32]

It can be suggested that charge transfer from the rhodamine group to the naphthalimide group could take place in the systems, especially in TCR-2 whose naphthalimide group has a bromine (Br) group 4-substituent. For TCR-1, the antenna group is a non-substituted 1,8-naphthalimide acceptor, whose reduction potential energy is −1.23 eV.[32a,33b] For TCR-2, the acceptor is 4-bromo-1,8-naphthalimide, whose reduction potential energy is about −1.0 eV. These acceptors NA make a negative value of free energy and make the intramolecular charge transfer between NA and Rh thermodynamically feasible. Therefore, when excited in the UV region, some



Scheme 1

Table 2 Fluorescence integration (between 530–650 nm) ratio of the trichromophoric rhodamine dyes relative to that of rhodamine 6G in EtOH excited at 529 nm

$\frac{\text{TCR-1}}{\text{Rh6G}}$	0.98	$\frac{\text{TCR-2}}{\text{Rh6G}}$	0.69

possible excited state processes in these trichromophoric systems would take place as shown in Scheme 1, where k_{ET}^{SS} is the rate constant for intramolecular singlet energy transfer between NA and Rh.

The intramolecular SSET process was confirmed by the phenomenon that the fluorescence emission of NA was obviously quenched;[29] k_1, k_2 and k_{ISC}^{A} are the rate constants for the non-radiation processes. In order to prove the intramolecular charge transfer (CT) between NA and Rh, the fluorescence emission of TCR-1 and TCR-2 were determined by excitation at 529 nm (the maximum wavelength of rhodamine 6G) and the results are shown in Table 2. As seen in Table 2, the fluorescence emission of the rhodamine group in trichromophoric rhodamine dyes was quenched, especially in TCR-2. This fluorescence quenching of the Rh moiety by the heavy-atom effect of NA moieties in TCR-2 provides evidence for the intramolecular charge transfer from Rh to NA.[33a] Therefore, the above mechanism processes are reasonable. There are two emission processes for Rh-^{1}NA* ($h\nu$), which result in the two exponential fluorescence decay lifetimes (detected at 400 nm) shown in Table 1. From Table 1, it is also found that the fluorescence lifetimes of naphthalimide group and rhodamine group depend on the solvent polarity.

The photostabilization observed in the solid samples of TCR-1 and TCR-2 could be related to an energy transfer or charge transfer from rhodamine to naphthalimide chromophore, followed by the radiative emission from NA moiety, avoiding heat production in the medium. Previous experiments had already elucidated the possible paths from Rh to NA, based on the fact that the fluorescence emission in the blue spectral region (320–430 nm, peak at 360 nm) was observed when TCR-1 and TCR-2 was excited with a laser of 534 nm.[25] The fluorescence lifetime data are also in agreement with the mechanism processes proposed above.

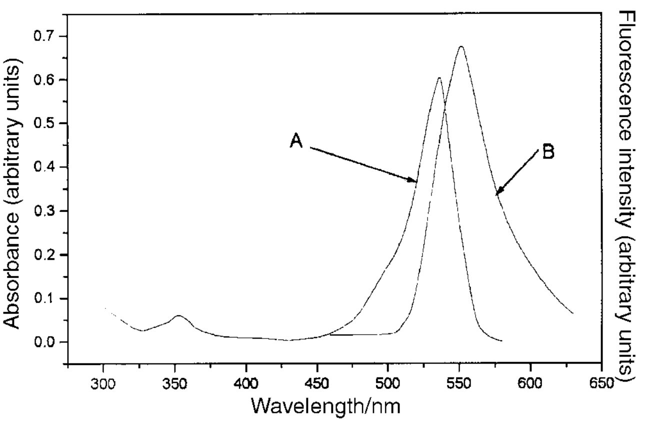


Fig. 4 The absorption (A) and fluorescence spectra (B, excited at 347 nm) of Rh-Al in CHCl$_3$.

When the function of the naphthalimide moiety was confirmed as a good energy pumping antenna and an internal photostabilizer for rhodamine molecules, novel modified rhodamine copolymers with naphthalimide moieties were synthesized. Thus new laser dye polymer materials with a high laser-radiation-damage threshold were obtained based on the consideration of economical advantages such as compactness, manageability, non-toxicity, non-flammability and no solvent evaporation, easy miniaturization and easy design of integrated optical system. We expected that the photostability and lasing efficiencies of the copolymeric products synthesized would be significantly improved due to not only the elimination of excess energy through the polymer backbone but also the presence of naphthalimide antennas acting as internal photostabilizers. At first, the dye monomers, modified rhodamine 6G molecules (Rh-Al or Rh-Aln) with polymerizable double bonds, were synthesized (Fig. 2). Subsequently, these new modified rhodamine 6G molecules (Rh-Al or Rh-Aln) were copolymerized with 1,8-naphthalimide derivatives and/or MMA resulting in several copolymeric products as shown in Fig. 3. The average chromophore content, average molecular weight and glass transition temperatures of the copolymers are listed in Table 3.

As seen in Table 3, Rh-Al and Rh-Aln can enter into copolymer formation, but in lower proportion than N-AE and MMA. It is highly probable that steric hindrance of the rhodamine group and self-resisting polymerization of rhoda-

Table 3 The average chromophore contents, the weight-average molecular weight (*M*w) and the glass transition temperatures (T_g /°C) of the copolymers

	Rh-Al group (%w/w)	Rh-Aln group (%w/w)	N-AE group (%w/w)	*M*w	Polydispersity index (*D*)	T_g/°C
PRNM-1	0.41		4.96	16779	1.58	122.68
PRNM-2	0.69		4.32	19860	1.52	114.42
PRM-1	0.34			12968	1.51	82.66
PRM-2	0.91			16085	1.47	105.28
PRNAM-1		2.68	5.13	41052	1.57	90.95
PRNAM-2		4.24	5.43	38450	1.88	97.9

Table 4 The absorption (λ_{max}^{ab}/nm) and fluorescence maximum wavelengths (λ_{max}^{fl}/nm)^a of monomers and copolymers in CHCl$_3$

	Rh-Al	Rh-Aln	N-AE	PRNM-1	PRNM-2	mPRNM-1^a	mPRNM-^{a}2	PRM-1	PRM-2	PRNAM-1	PRNAM-2
λ_{max}^{ab}	532	514	332	334 528	335 525	334 529	335 530	347 521	529	334 517	334 523
λ_{max}^{fl}	533	536	381	381 549	380 547	380 548	380 547	437 545	549	380 545	380 543

$^a\lambda_{max}^{fl}$ values were obtained at the excitation of their maximum absorption wavelength in the ultraviolet region for relevant materials. The mPRNM-1 and mPRNM-2 are the equal molar mixture model systems containing Rh-Al, N-AE and PMMA corresponding to PRNM-1 and PRNM-2, respectively.

Table 5 The fluorescence emission integration of N-AE moiety (∫ P(N-AE)) in PRNM or mPRNM or PRNAM relative to that of N-AE monomer (integrated from 350 to 450 nm) ∫ P(N-AE)/∫ (N-AE) and the fluorescence emission integration of Rh-Al moiety (∫ P(Rh-Al)) in PRNM or mPRNM or PRM relative to that of Rh-Al monomer (integrated from 450 to 630 nm) ∫ P(Rh-Al)/∫ (Rh-Al) excited at λ ex. All experiments were performed in $CHCl_3$ at room temperature

	λ ex/nm	∫ P(N-AE)/∫ (N-AE)	∫ P(Rh-Al)/∫ (Rh-Al)
PRNM-1/N-AE	334	0.897	
PRNM-2/N-AE	335	0.844	
mPRNM-1/N-AE	334	0.772	
mPRNM-2/N-AE	335	0.950	
PRNM-1/Rh-Al	334		2.762
PRNM-2/Rh-Al	335		3.163
mPRNM-1/Rh-Al	334		0.828
mPRNM-2/Rh-Al	335		0.875
PRM-1/Rh-Al	337		1.974
PRM-2/Rh-Al	337		1.933
PRNAM-1/N-AE	334	0.834	
PRNAM-2/N-AE	334	0.767	
PRNAM-1/Rh-Aln	334		1.696
PRNAM-2/Rh-Aln	334		1.484

mine monomers prevent chain growth. The average molecular weights indicate that the mechanical properties of these copolymers are available. The glass transition temperatures of the PRNM series are higher than that of PMMA ($T_g = 105$ °C), which means that the thermal stabilities of the copolymeric product PRNM systems synthesized in this paper are raised.[34] However, the lower T_gs of PRM and PRNAM series imply that the thermal stability of the PRM and PRNAM systems are not increased.

The absorption and fluorescence properties of Rh-Al, Rh-Aln, N-AE, PRNM, PRM, PRNAM and the corresponding equal molar mixture system (mPRNM) examined in chloroform solutions are listed in Table 4 and shown in Fig. 4–8. Comparison with the absorption spectra of the corresponding monomers indicates that the absorption spectra of the new copolymeric products in solution is the exact sum of that of the constituent chromophores. This indicates that there is little or no interaction between chromophores in their ground state for the copolymers, so that their individual characteristics should be maintained in the copolymers.

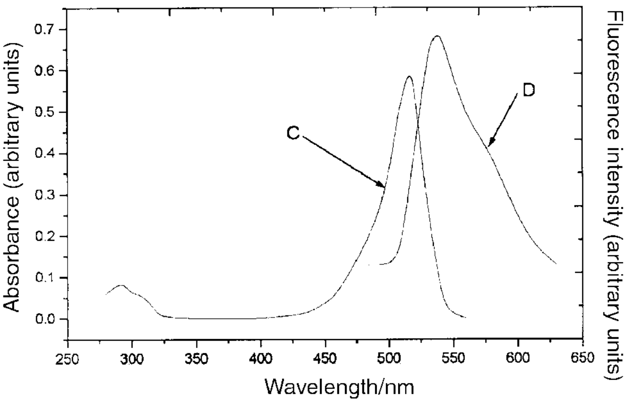


Fig. 5 The absorption (C) and fluorescence spectra (D, excited at 300 nm) of Rh-Aln in $CHCl_3$

The ratio of fluorescence emission integration between the N-AE moiety in PRNM or PRNAM and N-AE monomer (integrated from 350 to 450 nm) and those between the Rh-Al moiety in PRNM or PRM and Rh-Al monomer (integrated from 450 to 630 nm) are tabulated in Table 5. As seen in Fig. 6 and Table 5, the fluorescence emission integration of Rh-Al moiety in PRNM is improved greatly. At the same time, the fluorescence of N-AE moiety in PRNM is partly quenched. The results mean there is an effective intramolecular singlet energy transfer from the N-AE moiety to the Rh-Al moiety in PRNM due to the larger overlap between the absorption of the Rh-Al moiety and emission of the N-AE moiety in copolymers. The obvious increase of fluorescence emission integration of Rh-Al moiety in PRNM is advantageous to improvement of lasing efficiency of the copolymer.[21,29] In comparison the energy transfer has not been observed in the equal molar mixture system corresponding to copolymers. This demonstrated that the singlet energy transfer occurred mainly along the polymeric chain in the copolymers. On the other hand, this result has also confirmed that Rh-Al monomer had indeed been copolymerized with N-AE and MMA in spite of its lower proportion. From Table 5, it is also observed that the ratio of fluorescence emission integration ∫ P(Rh-Al)/∫ (Rh-Al) of PRNM is much greater than that of PRM. This indicated that the naphthalimide moiety in copolymer PRNM greatly increases the

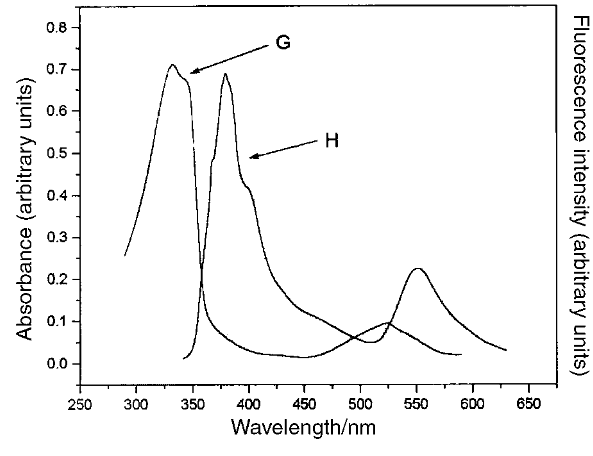


Fig. 6 The absorption (G) and fluorescence spectra (H, excited at 334 nm) of PRNM-1 in $CHCl_3$

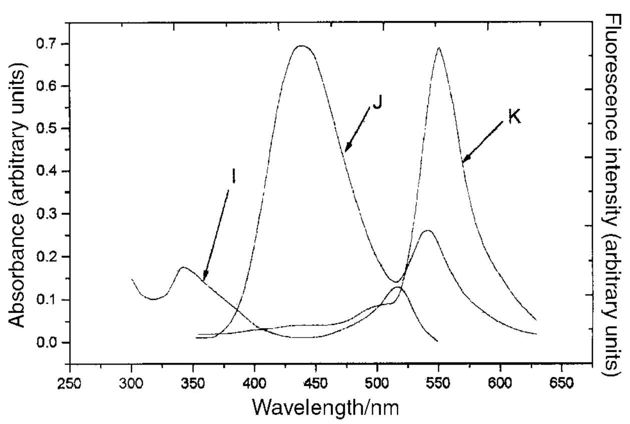


Fig. 7 The absorption (I) and fluorescence spectra (J, excited at 337 nm) of PRM- 1 in $CHCl_3$ and fluorescence spectra of PRM-2 (K, excited at 337 nm).

fluorescence of PRNM because of obvious intramolecular energy transfer from naphthalimide moiety to Rh-Al moiety in PRNM. Thus, the naphthalimide moiety which acts as acceptors of excess energy can significantly increase the efficiency and photostability of the copolymer materials.[25] Meanwhile, copolymer chains would also significantly increase the efficiency and photostability of the copolymer materials.[24] When copolymeric products PRM-1, PRM-2, PRNAM-1 and PRNAM-2 were excited in the ultraviolet region, intramolecular energy transfers were found in these materials (Table 5 and Fig. 7 and 8). It is interesting that a new maximum emission peak (at 437 nm) exists in the copolymer product PRM-1 (Fig. 7). This phenomenon may be caused by the formation of an excimer.

As seen in Table 5, the ratio of the fluorescence emission integration between the rhodamine moiety in PRNM and corresponding rhodamine monomer has increased greatly as compared with that in PRNAM, which may be caused by the different copolymerization position of the rhodamine moiety in copolymers. The intramolecular energy transfer from the N-AE moiety to rhodamine moiety in PRNM seems to be more effective than that in PRNAM.

It is well known that the covalent binding of a chromophore to a polymer chain restricts its mobility.[35] Therefore, in the copolymers there should be a decrease in the rates of bimolecular reactions leading to photochemical degradation, as well as a hindering of the internal micro-motion of the excited fluorophore avoiding non-fluorescent deactivation of its excitation energy by means of rapid internal rotation or conformational changes.[34–37]

As previous research[25] showed in the search for more stable and efficient solid-state dye lasers, a suitable design of dye combination, in which there is energy transfers or charge transfer between chromophores, can be an efficient means of stabilization. The internal processes can dissipate the pump energy, which is not directly converted into laser emission.

In this study, the fluorescence lifetimes of trichromophoric rhodamine dyes have been measured and the existence of intramolecular energy transfer and charge transfer in these dyes demonstrated. It was demonstrated that the existence of a naphthalimide moiety in trichromophoric rhodamine dyes is advantageous to the higher fluorescence quantum yield and the stability. In order to obtain laser dye polymer materials with a high laser-radiation-damage threshold, modified rhodamine 6G molecules (Rh-Al or Rh-Aln) with polymerizable double bonds have been copolymerized with 1,8-naphthalimide derivatives. The absorption spectra of these new copolymers indicate there is little or no interaction between NA and Rh moieties in their ground state, however, the fluorescent spectra indicate that energy transfer from NA group to Rh-Al or Rh-Aln group in the copolymers occurs. In comparison, energy transfer has not been observed in the equal molar mixture system corresponding to copolymers, which demonstrated that intramolecular energy transfer in the copolymers synthesized in this study occurred mainly along the polymeric chain. It is expected that lasing efficiency and thermal stability and photostability of these copolymers should increase greatly.

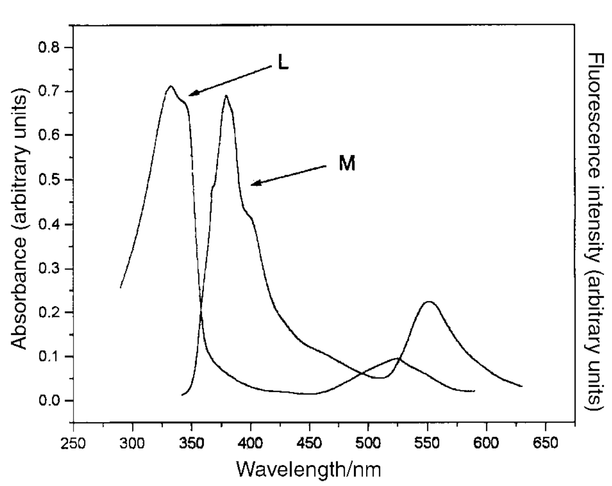


Fig. 8 The absorption (L) and fluorescence spectra (M, excited at 334 nm) of PRNAM-1 in $CHCl_3$

Acknowledgements

This work was financially supported by NSFC/ China (Project No. 29836150 and 29625611).

References

1 B. H. Soffer and B. B. McFarland, *Appl. Phys. Lett.*, 1967, **10**, 266.
2 O. G. Peterson and B. B. Snavely, *Appl. Phys. Lett.*, 1968, **12**, 238.
3 T. Fujii, A. Ishii and M. Anpo, *J. Photochem. Photobiol. A*, 1990, **54**, 231.
4 E. T. Knobbe, B. Dunn, P. D. Fuqua and F. Nishida, *Appl. Opt.*, 1990, **29**, 2729.
5 J. C. Altman, R. E. Stone, B. Dunn and F. Nishida, *IEEE Photonics Technol. Lett.*, 1991, **3**, 189.
6 T. Fujii, Y. Murata and M. Matsui, *Res. Chem. Intermed.*, 1992, **18**, 87.
7 D. Lo, J. E. Parris and J. L. Lawless, *Appl. Phys. B: Lasers Opt.*, 1993, **56**, 385.
8 U. Narang, F. V. Bright and P. N. Prasad, *Appl. Spectrosc.*, 1993, **47**, 229.
9 K. S. Lam, D. Lo and K. H. Wong, *Appl. Opt.*, 1995, **34**, 3380.
10 M. Canva, P. Georges, J. F. Perelgritz, A. Brum and J. P. Boilot, *Appl. Opt.*, 1995, **34**, 428.
11 C. F. Zhao, R. Gvishi, U. Narang, G. Ruland and P. N. Prasad, *J. Phys. Chem.*, 1996, **100**, 4526.
12 G. Ruland, R. Gvishi and G. Ruland, *J. Am. Chem. Soc.*, 1996, **118**, 2985.
13 T. Suratwala, Z. Gardlund, K. Davidson, D. R. Uhlman, S. Bonilla and N. Peyghambarian, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 953 and 973.
14 L. Hu and Z. Jiang, *Opt. Commun.*, 1998, **148**, 275.
15 T. Suratwala, Z. Gardlund, K. Davidson, D. R. Uhlman, J. Watson and N. Peyghambarian, *Chem. Mater.*, 1998, **10**, 190.
16 A. U. Acuna, F. Amat-Guerri, A. Costela, A. Douhal, J. M. Figuera, F. Florido and R. Sastre, *Chem. Phys. Lett.*, 1991, **187**, 98.
17 K. M. Dyumaev, A. A. Manenkov, A. P. Maslyukov, G. A. Matyushin, V. S. Nechitailo and A. M. Prokhorov, *J. Opt. Soc. Am. B*, 1992, **9**, 143.
18 M. Bondar, O. Przhonska and Y. Tikhonov, *J. Phys. Chem.*, 1992, **96**, 10831.
19 F. Amat-Guerri, A. Costela, J. M. Figuera, F. Florido and R. Sastre, *Chem. Phys. Lett.*, 1993, **209**, 352.
20 M. L. Ferrer, A. U. Acuna, F. Amat-Guerri, A. Costela, J. M. Figuera, F. Florido and R. Sastre, *Appl. Opt.*, 1994, **33**, 2266.
21 R. Sastre and A. Costela, *Adv. Mater.*, 1995, **2**, 198.

22 A. Costela, F. Florido, I. Garcia-Moreno, R. Duchowicz, F. Amat-Guerri, J. M. Figuera and R. Sastre, *Appl. Phys. B: Lasers Opt.*, 1995, **60**, 383.

23 F. Amat-Guerri, A. Costela, J. M. Figuera, F. Florido, I. Garcia-Moreno and R. Sastre, *Opt. Commun.*, 1995, **114**, 442.

24 A. Costela, I. Garcia-Moreno, J. M. Figuera, F. Amat-Guerri, R. Mallavia, M. D. Santa-Maria and R. Sastre, *J. Appl. Phys.*, 1996, **80**, 3167.

25 A. Costela, I. Garcia-Moreno, H. Tian, J. Su, K. Chen, F. Amat-Guerri, M. Carrascoso, J. Barroso and R. Sastre, *Chem. Phys. Lett.*, 1997, **277**, 392.

26 F. L. Arbeloa, T. L. Arbeloa, I. L. Arbeloa, A. Costela, I. Garcia-Moreno, J. M. Figuera, F. Amat-Guerri and R. Sastre, *Appl. Phys. B: Lasers Opt.*, 1997, **64**, 651.

27 F. J. Duarte, *Appl. Opt.*, 1994, **33**, 3857.

28 R. E. Hermes, T. H. Allik, S. Chandra and J. A. Hutchinson, *Appl. Phys. Lett.*, 1993, **63**, 877.

29 (*a*) H. Tian, Y. Tang and K. Chen, *Dyes Pigm.*, 1994, **26**, 159; (*b*) J. Su, H. Tian and K. Chen, *Dyes Pigm.*, 1996, **31**, 69.

30 J. N. Kauffman, *Appl. Opt.*, 1980, **19**, 3431; the structure shown as Rh 6G is really Rhodamine 5GDN Extra, here we call it simply still Rh 6G.

31 J. Arden, G. Deltau, V. Huth and K. H. Drexhage, *J. Lumin.*, 1991, **48**(49), 352.

32 (*a*) M. S. Alexiou, V. Tychopoulos, S. Ghorbanian, J. H. P. Tyman, R. G. Brown and P. I. Brittain, *J. Chem. Soc., Perkin Trans. 2*, 1990, 837; (*b*) H. Tian, W. Ni, J. Su and K. Chen, *J. Photochem. Photobiol. A*, 1997, **109**, 213.

33 (*a*) H. Tian, *J. Photochem. Photobiol. A*, 1995, **91**, 125; (*b*) H. Tian, T. Xu, Y. Zhao and K. Chen, *J. Chem. Soc., Perkin Trans. 2*, 1999, 545.

34 F. Higuchi and J. Muto, *Phys. Lett.*, 1981, **81A**, 95; F. Higuchi and J. Muto, *Phys. Lett.*, 1981, **86A**, 51.

35 K. Horie and I. Mita, *Adv. Polym. Sci.*, 1989, **89**, 77.

36 L. Bokobza, *Prog. Polym. Sci.*, 1990, **15**, 337.

37 H. Itagaki, K. Horie and I. Mita, *Prog. Polym. Sci.*, 1990, **15**, 361.