Photostability of novel copolymers functionalized with laser dyes based on modified rhodamine 6G and 1,8-naphthalimide

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Abstract

Modified rhodamine 6G molecules (Rh-Al or Rh-Aln) with polymerizable double bonds had been copolymerized with 1,8-naphthalimide derivatives. In copolymers PRNAM, naphthalimide moieties are connected to rhodamine moieties at nitrogen atom of rhodamine moiety, and in copolymers PRNM naphthalimide moieties are connected to rhodamine moieties at ester group of rhodamine moiety. We report on their photostability in liquid solution and in solid film. The photodegradation kinetics of novel copolymers functionalized with laser dyes based on modified rhodamine 6G and 1,8-naphthalimide has been studied by UV–VIS absorption spectroscopy. The results show that the rates of the photofading reactions of these novel copolymers follow quasi-first-order. The photostability of the copolymers functionalized with laser dyes in solid films is better than that in solutions. The different type of the copolymer shows the different photostability.

Keywords: Photostability; Rhodamine 6G; Laser dyes; Copolymers

1. Introduction

Although until recently liquid-solution dye lasers were the main system used to achieve coherent tunable radiation in the visible region, solid-state dye lasers are attracting attention as alternatives to liquid-phase dye lasers with obvious technical advantages such as compactness, manageability, non-toxicity, no solvent evaporation, non-flammability, suppression or minimization of flow fluctuation, etc. The development of a tunable solid-state laser has been the subject of extensive research during the past decade. More and more work has been done using sol–gel materials [1–12] or polymers [13–23] as solid matrices for laser dyes. Work with polymers has indicated that polymer materials offer a number of advantages compared with the available sol–gel matrices, which include higher optical homogenates [24], better chemical compatibility with organic dyes and inexpensive fabrication techniques, although they suffer from relatively low laser-damage threshold. Recently modified polymer matrices have resulted in significant improvements in the resistance of these materials to damage caused by laser radiation [14,19,25]. However, up to now these polymer-based lasers have suffered from several disadvantages, mainly low laser-damage resistance of the plastic host and thermal and photobleaching of the dye. The lack of photostability has been the major factor that has limited their commercial use.

Rhodamine 6G, as one of the most frequently employed dye laser materials, has attracted a great deal of attention. We have reported significant increases in photostability in solid-state dye lasers based on modified rhodamine 6G dyes with two covalently boned identical 1,8-naphthalimide groups dissolved in a copolymer of 2-hydroxyethyl methacrylate (HEMA) and MMA in a 1:1 (v/v) ratio [22]. 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. The fluorescence lifetimes of these new compounds had been investigated by single-photon counting technique [27]. 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 [28], which has been 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 these trichromophoric rhodamines was the main reason for good photostability of these compounds. NA moieties act as a triplet acceptor relative to Rh moieties.

Since the naphthalimide moiety can act as a good energy pumping antenna and an internal photostabilizer for rhodamine molecules, we synthesized novel modified rhodamine copolymer materials with naphthalimide antenna [27]. These new modified rhodamine 6G molecules were copolymerized with 1,8-naphthalimide derivatives and/or MMA resulting in several copolymer products shown in Fig. 1. Previous work on the modified rhodamine copolymers made by Costela et al. [17,21] demonstrated that the polymeric chain would provide additional channels for the elimination of the absorbed energy along the polymer backbone. It can be expected that the photostability of the copolymer products synthesized in this work would be significantly improved due to the elimination of excess energy through the polymer backbone but also the presence of naphthalimide antenna acting as internal photostabilizer. In this paper the stability of rhodamine 6G derivatives covalently bound to polymeric chains both in solution and in film are determined. Magnificent increases in photostability have been obtained for some of these materials, possible mechanism and processes responsible for the behavior of these materials are discussed.

2. Experimental

Rhodamine 6G [26] (chloride salt, SIGMA Co.) was used as received. Novel copolymers functionalized with laser dyes PRNM, PRM and PRNAM based on modified rhodamine 6G and 1,8-naphthalimide were synthesized and characterized as described in Ref. [27].

![Diagram of molecular structures of copolymer products PRNM, PRM and PRNAM.](image-url)
For comparison, based on the composition of PRNM-5 we prepared the mixture model systems mPRhNA, which comprised rhodamine 6G and N-(2-hydroxyethyl)-naphtalimide and PMMA, and mPRh which comprised rhodamine 6G and PMMA. Then we studied the photo-stability of their solution in chloroform and their thin films. We also studied the photo-stability of rhodamine 6G and the mixture of rhodamine 6G and N-(2-hydroxyethyl)-naphtalimide (molar ratio 2.05:1, denoted by RhNA) in chloroform solution. The dye concentration was chosen so that the absorption (A) of all samples (including chloroform solution in 1 cm quartz cell and solid film) at about 530 nm was \( \approx 1 \).

All photochemical reaction experiments were carried out at room temperature. The dye degradation experiments were carried out using a photochemical reaction apparatus (British Applied Photophys. Limited) with a high-pressure mercury lamp (200 W) as the light source. The distance between the lamp and the sample was 200 mm. Absorption spectra were recorded on an UV–VIS spectrophotometer (Shimadzu UV-260), unless otherwise noted, in chloroform solutions.

Liquid solutions, in chloroform, of rhodamine 6G and the novel copolymers PRNM, PRM and PRNAM were also prepared. The photophysical properties in the liquid solvents were determined for a dilute dye concentration. Spectral measurements were performed in the same sealed 1-cm-pathway quartz cell. The solid samples were studied in thin film, which was obtained by dissolving the novel copolymer in chloroform to obtain a homogeneous solution, and then casting the solution on the surface of a quartz plate at an appropriate adjusted speed. The films were allowed to dry slowly at room temperature in the dark for 24 h. The films thus obtained were optically transparent in the visible region.

The photochemical reaction of these novel copolymers functionalized with laser dyes based on modified rhodamine 6G and 1,8-naphtalimide, as shown in Fig. 2. There is a linear relationship between the concentration of dye [Dye] and the absorbency (A) at the maximum wavelength. Therefore, the absorbency values (A) were used directly as the function with the changes of irradiation times (t).

The experimental results of the corresponding model systems rhodamine 6G, mPRh, mPRhNA and RhNA in chloroform solution are shown in Fig. 2. There is a linear relationship between \( \ln(A_0/A_i) \) and the irradiation time, which means that the photochemical reaction of rhodamine 6G, mPRh, mPRhNA and RhNA is of quasi-first-order kinetics decay. For the same solvent, the photo-stability of rhodamine 6G solution was greatly improved by adding PMMA but slightly improved by adding \( N \)-((2-hydroxyethyl)-naphtalimide, as shown in Fig. 2 and Table 2.

The experimental results of the novel copolymers PRM in chloroform solution are shown in Fig. 3. There is a linear relationship between \( \ln(A_0/A_i) \) and the irradiation time, which means that the photochemical reaction of PRM is of quasi-first-order kinetics decay. The rate constant of photochemical reaction of PRM-2 is the smallest among the copolymers PRM, whereas the rate constants of photochemical reaction of PRM-1, PRM-3 and PRM-3.
and PRM-4 are similar, as shown in Table 2. The photostability of the copolymers PRM in solution is better than that of rhodamine 6G in the same solvent, and nearly equivalent to that of \( m \text{PRh} \) except for PRM-2. Our experimental results shown in Table 2 suggest that only for some chromophore content, the covalent linkage of the dye to the polymeric chain would provide additional channels for the elimination of the absorbed energy along the polymer backbone. This indicates that from the point of view of the dye photostability there is an optimum chromophore content.

For the novel copolymers PRNM-3–PRNM-7 in chloroform, there is a linear relationship between \( \ln(A_0/A_t) \) and the irradiation time. That is to say, the photochemical reaction of PRNM-3–PRNM-7 is of quasi-first-order kinetics decay also. The rate constants of photochemical reaction of the copolymers in chloroform are shown in Table 3. For the novel copolymers PRNM-1 and PRNM-2, the absorbency \( (A) \) initially grew rapidly until to the maximum (the ratio \( A_{\text{max}}/A_0 \) was 2.23 and 1.53 respectively) and then dropped with irradiation time \( (t) \) increased, as shown in Fig. 4. This is a strange and interesting phenomenon and difficult to be explained. To compare the photostability of PRNM-1 and PRNM-2 with the others, we took their maximum as the start of photodegradation, and then plotting \( \ln[Dye_0/Dye]_t \) vs. irradiation time \( (t-t_{\text{max}}) \), we also could obtain a straight line (shown in Table 3). In the chloroform solution, the rate constant of photochemical reaction of the copolymers PRNM ranged from 0.0361 to 0.0957 h\(^{-1}\) and the difference between them was small. From Table 1, it is observed that the rhodamine chromophore contents and the ratio of N-AE/Rh-Al are quite different in PRNM series. So our experimental result suggest the rhodamine chromophore contents in PRNM series have little effect on their photochemical reaction.

The absorbency \( (A) \) of copolymers PRNAM-1–PRNAM-5 initially grew rapidly until to the maximum but then dropped with irradiation time \( (t) \) increased (see Fig. 5) and their ratio \( A_{\text{max}}/A_0 \) were listed in Table 4. The plot of \( \ln[Dye_0/Dye]_t \) vs. irradiation time \( (t-t_{\text{max}}) \) is a straight line for the copolymers PRNAM, their rate constants of photochemical reaction are tabulated in Table 4. For the same solvent, the photostability of PRNAM-4 is the highest among the copolymers PRNAM, and the others are similar, as shown in Table 4.

3.2. The photostability of novel copolymers functionalized with laser dyes in thin films

There is a linear relationship between \( \ln(A_0/A_t) \) and the irradiation time for the copolymers PRM and PRNM and for the mixture system: \( m \text{PRh} \) and \( m \text{PRhNA} \) in film. So, the photochemical reaction of copolymers PRM and PRNM in film is of quasi-first-order kinetics.
decay. Their experimental results are listed in Tables 5 and 6 respectively. The rate constants of photochemical reaction of PRM-1–PRM-4 in film, which are almost identical, are smaller than that of mPRh and mPRhNA, as shown in Table 5. Our investigation provides evidence that the covalent linkage of the dye to the polymeric chain would provide several new dissipative channels not available in the PMMA solution for the elimination of the absorbed energy along the polymer backbone to increase the photostability of the copolymers [17,23,31].

The rate constants of photochemical reaction of novel copolymers PRNM-1–PRNM-7 are tabulated in Table 6. For the thin films, there is nearly no difference among the photostability of PRNM-1–PRNM-7. The experimental results of copolymers PRNAM-1–PRNAM-5 in film were shown in Figs. 6 and 7. Like the absorbency of the copolymers PRNAM in solution, their absorbency in film first went up, and then declined with irradiation time ($t$) increased as shown in Fig. 6. Similarly, there is a linear relationship between ln $A_{0}/A_t$ and the irradiation time ($t - t_{\text{max}}$), which means that the photochemical reaction of PRNAM-1–PRNAM-5 in film is of quasi-first-order kinetics decay also. The rate constants of photochemical reaction of PRNAM-1–PRNAM-5 in film are tabulated in Table 7.

It is well known that the covalent binding of a chromophore to a polymer chain restricts its mobility.

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Rh-Al group (%/w/w)</th>
<th>N-AE group (%/w/w)</th>
<th>N-AE/Rh-Al (mol/mol)</th>
<th>$M_w$</th>
<th>$T_g$ ($^\circ$C)</th>
<th>Relative fluorescence integration ratio $\phi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRNM-1</td>
<td>0.02</td>
<td>1.35</td>
<td>100:17:1</td>
<td>32056</td>
<td>0.690</td>
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<tr>
<td>PRNM-2</td>
<td>0.045</td>
<td>2.51</td>
<td>88:47:1</td>
<td>26546</td>
<td>0.583</td>
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<tr>
<td>PRNM-3</td>
<td>0.19</td>
<td>5.45</td>
<td>46:67:1</td>
<td>40995</td>
<td>1.136</td>
<td></td>
</tr>
<tr>
<td>PRNM-4</td>
<td>0.15</td>
<td>2.65</td>
<td>28:24:1</td>
<td>92676</td>
<td>122.68</td>
<td>1.092</td>
</tr>
<tr>
<td>PRNM-5</td>
<td>0.41</td>
<td>4.96</td>
<td>19:2:1</td>
<td>16779</td>
<td>2.762</td>
<td></td>
</tr>
<tr>
<td>PRNM-6</td>
<td>1.21</td>
<td>26.5</td>
<td>35:1</td>
<td>19166</td>
<td>2.683</td>
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</tr>
<tr>
<td>PRNM-7</td>
<td>0.69</td>
<td>4.32</td>
<td>10:1</td>
<td>19860</td>
<td>114.42</td>
<td>3.163</td>
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<tr>
<td>PRM-1</td>
<td>0.24</td>
<td></td>
<td></td>
<td>16185</td>
<td>82.66</td>
<td>0.863</td>
</tr>
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<td>PRM-2</td>
<td>0.342</td>
<td></td>
<td></td>
<td>12968</td>
<td>0.594</td>
<td></td>
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<tr>
<td>PRM-3</td>
<td>0.494</td>
<td></td>
<td></td>
<td>31488</td>
<td>0.532</td>
<td></td>
</tr>
<tr>
<td>PRM-4</td>
<td>0.909</td>
<td></td>
<td></td>
<td>16085</td>
<td>105.28</td>
<td>0.981</td>
</tr>
<tr>
<td>PRNAM-1</td>
<td>0.47</td>
<td>2.20</td>
<td>7:49:1</td>
<td>68287</td>
<td>1.371</td>
<td></td>
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<tr>
<td>PRNAM-2</td>
<td>0.62</td>
<td>2.67</td>
<td>6:89:1</td>
<td>92676</td>
<td>1.177</td>
<td></td>
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<tr>
<td>PRNAM-3</td>
<td>0.81</td>
<td>2.21</td>
<td>4.37:1</td>
<td>51194</td>
<td>90.95</td>
<td>1.160</td>
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<tr>
<td>PRNAM-4</td>
<td>2.68</td>
<td>6.13</td>
<td>3.66:1</td>
<td>41052</td>
<td>1.696</td>
<td></td>
</tr>
<tr>
<td>PRNAM-5</td>
<td>4.24</td>
<td>5.43</td>
<td>2.05:1</td>
<td>38450</td>
<td>97.9</td>
<td>1.484</td>
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</table>

The fluorescence emission integration $\phi$ of Rh-Al moiety in PRNM or PRM or PRNAM relative to that of Rh-Al monomer (integrated from 450 to 630 nm) excited at 335 nm. All experiments were performed in CHCl$_3$ at room temperature.

**Fig. 5.** The photostability of copolymers of PRNAM-1 (●), PRNAM-2 (□), PRNAM-3 (▲), PRNAM-4 (●) and PRNAM-5 (△) at $t_{\text{max}}$ in chloroform.

**Fig. 6.** The photostability of copolymers of PRNAM-1 (●), PRNAM-2 (■), PRNAM-3 (△), PRNAM-4 (×) and PRNAM-5 (+) at $t_{\text{max}}$ in film.
Therefore, in the copolymers there should be a decrease in the rates of bimolecular reactions leading to photochemical degradation. This, together with the ameliorated dissipation of the excess energy, facilitated by the additional channels provided by the covalent linkage of the dye to the polymeric chains, helps to explain the photostability of PRM is better than that of \( m \)PRh and \( m \)PRhNA.

The difference of the photostability between PRM and PRNM (or PRNAM) is due to NA groups presented in PRNM (or PRNAM) which could lead to an electronic transfer process from rhodamine to naphthalimide chromophores, followed by the emission of transferred energy from the NA molecules, avoiding the appearance of heat in the medium [22].

In general, the photostability of laser dyes in solid films is inferior to that in solution, because of poor thermal dissipation of solid films. As seen in Tables 2–7, the photostability of the novel copolymers functionalized with laser dyes based on modified rhodamine 6G and 1,8-naphthalimide in solid films is far superior to that in chloroform solutions. Since oxygen is a good electron acceptor and abundant in nature, the reaction of dyes in the excited state with dissolved oxygen is usually involved in the primary process of chemical reaction of dyes. Singlet oxygen (\( ^1O_2 \)) [32] and superoxide anion (\( O^-_2 \)) [33], which are all formed in photosensitization of dyes, are known to be the main factors causing the photofading of dyes in solutions. For the equilibrium oxygen concentration in polymers which is about \( 10^{-3} \) mol/l [14] is similar to, and even slightly less than, the concentration of \( O_2 \) in the air-saturated solu-

![Fig. 7. The rate of photodegradation of PRAM-1 (●), PRNM-2 (■), PRAM-3 (▲), PRAM-4 (×) and PRAM-5 (+) at \( \lambda_{\text{max}} \) in film.](image)

**Table 2**
The rate constants \( k \) of photochemical reaction of compounds at \( \lambda_{\text{max}} \)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Rh 6G</th>
<th>( m )PRh</th>
<th>( m )PRhNA</th>
<th>RhNA</th>
<th>PRM-1</th>
<th>PRM-2</th>
<th>PRM-3</th>
<th>PRM-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>534.2</td>
<td>533.8</td>
<td>534.0</td>
<td>533.8</td>
<td>519.2</td>
<td>524.0</td>
<td>528.0</td>
<td>532.0</td>
</tr>
<tr>
<td>( k ) (h(^{-1}))</td>
<td>0.2311</td>
<td>0.1194</td>
<td>0.112</td>
<td>0.151</td>
<td>0.1023</td>
<td>0.0331</td>
<td>0.1196</td>
<td>0.1701</td>
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</tbody>
</table>

**Table 3**
The rate constants \( k \) of photochemical reaction of copolymers PRNM at \( \lambda_{\text{max}} \)

<table>
<thead>
<tr>
<th>Dye</th>
<th>PRNM-1</th>
<th>PRNM-2</th>
<th>PRNM-3</th>
<th>PRNM-4</th>
<th>PRNM-5</th>
<th>PRNM-6</th>
<th>PRNM-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>525.0</td>
<td>533.6</td>
<td>526.3</td>
<td>525.4</td>
<td>532.2</td>
<td>529.0</td>
<td>528.0</td>
</tr>
<tr>
<td>( k ) (h(^{-1}))</td>
<td>0.0361</td>
<td>0.0439</td>
<td>0.0573</td>
<td>0.0465</td>
<td>0.0957</td>
<td>0.0541</td>
<td>0.0681</td>
</tr>
</tbody>
</table>

**Table 4**
The rate constants \( k \) of photochemical reaction and \( A_{\text{max}}/A_0 \) of copolymers PRNAM at \( \lambda_{\text{max}} \)

<table>
<thead>
<tr>
<th>Dye</th>
<th>PRNAM-1</th>
<th>PRNAM-2</th>
<th>PRNAM-3</th>
<th>PRNAM-4</th>
<th>PRNAM-5</th>
<th>PRNAM-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>516.4</td>
<td>515.4</td>
<td>526.0</td>
<td>518.8</td>
<td>527.2</td>
<td></td>
</tr>
<tr>
<td>( k ) (h(^{-1}))</td>
<td>0.0201</td>
<td>0.0201</td>
<td>0.0313</td>
<td>0.0098</td>
<td>0.0209</td>
<td></td>
</tr>
<tr>
<td>( A_{\text{max}}/A_0 )</td>
<td>1.54</td>
<td>1.52</td>
<td>1.48</td>
<td>1.20</td>
<td>3.57</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5**
The rate constants \( k \) of photochemical reaction of copolymers PRM at \( \lambda_{\text{max}} \)

<table>
<thead>
<tr>
<th>Dye</th>
<th>( m )PRh</th>
<th>PRM-1</th>
<th>PRM-2</th>
<th>PRM-3</th>
<th>PRM-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>532.2</td>
<td>522.6</td>
<td>527.2</td>
<td>531.8</td>
<td>534.4</td>
</tr>
<tr>
<td>( k ) (h(^{-1}))</td>
<td>0.075</td>
<td>0.0452</td>
<td>0.0343</td>
<td>0.0354</td>
<td>0.0575</td>
</tr>
</tbody>
</table>
tion [30], so singlet oxygen (O$_2$) and superoxide anion (O$_2^-$) were not the fatal factors causing the photodegradation of the novel copolymers in film. In the solid film, the polymeric main chains arrange themselves parallel, regularly and tightly. In that way, two relatively isolated chromophores on the different molecule may approach so close that triplet excitation energy can be transferred from rhodamine moieties to naphthalimide moieties. This process would result in the increasing of the photostability of the novel copolymers in the film. The micro-Brownian motion of molecule is reduced in films, so the probability of reaction between chromophores and singlet oxygen or superoxide anion in films is lowered, which also promote their stability. In addition, the covalent linkage of the dye to the polymeric chain would provide new dissipative channels for the elimination of the absorbed energy, and the naphthalimide moiety can act as acceptors of excess energy. All these can significantly increase the photostability of the copolymer PRNM.

Several workers have revealed intramolecular singlet energy transfer from antennas to rhodamine [22, 27,28,34–36]. As seen in Table 1, the ratio of fluorescence emission integration of rhodamine moieties in PRNM–PRNM-7 is higher than that for PRNAM. The naphthalimide moiety can act as acceptors of excess energy to significantly increase the photostability of the copolymer PRNAM.

We have studied such intramolecular interactions in related dyes, in which naphthalimide was connected with rhodamine system (Fig. 8). For bichromophoric rhodamine dye TR-1 (Fig. 8), there is an effective intramolecular singlet energy transfer from the naphthalimide moiety to the rhodamine moiety, so its ratio of fluorescence emission integration of rhodamine moiety is 1.24 [28]. We also found the ratio of fluorescence emission integration of rhodamine moiety for TR-1 to be 1.165 [37]. In TCR-2, two naphthalimide moieties are connected to a rhodamine at nitrogen atom of rhodamine moiety respectively separated by methylene groups. When a naphthalimide moiety connected to a rhodamine at ester group of rhodamine moiety separated by methylene groups, such as TR-1, can enhance the fluorescence quantum yield of the dye by a factor of 1.24. It can thus be considered that the more effective channel for intramolecular singlet energy transfer from the antenna to the lasing chromophore is that antenna chromophores are linked to the rhodamine at ester group of rhodamine. In copolymers PRNM (Fig. 1), naphthalimide moieties are connected to rhodamine moieties at nitrogen atom of rhodamine moiety respectively separated by methylene groups. When a naphthalimide moiety connected to a rhodamine at ester group of rhodamine moiety separated by methylene groups, such as TR-1, can enhance the fluorescence quantum yield of the dye by a factor of 1.24.

The rate constants $k$ of photochemical reaction of copolymers PRNM at $\lambda_{\text{max}}$ was calculated (Table 6). The rate constants $k$ of photochemical reaction $A_{\text{max}}/A_0$ of copolymers PRNAM at $\lambda_{\text{max}}$ was also calculated (Table 7).

### Table 6

<table>
<thead>
<tr>
<th>Dye</th>
<th>mPrhNA</th>
<th>PRNM-1</th>
<th>PRNM-2</th>
<th>PRNM-3</th>
<th>PRNM-4</th>
<th>PRNM-5</th>
<th>PRNM-6</th>
<th>PRNM-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>532.0</td>
<td>524.6</td>
<td>534.4</td>
<td>527.4</td>
<td>527.8</td>
<td>533.2</td>
<td>532.0</td>
<td>530.8</td>
</tr>
<tr>
<td>$k$ (h$^{-1}$)</td>
<td>0.084</td>
<td>0.0291</td>
<td>0.0283</td>
<td>0.0258</td>
<td>0.0236</td>
<td>0.0378</td>
<td>0.0315</td>
<td>0.046</td>
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### Table 7

<table>
<thead>
<tr>
<th>Dye</th>
<th>PRNAM-1</th>
<th>PRNAM-2</th>
<th>PRNAM-3</th>
<th>PRNAM-4</th>
<th>PRNAM-5</th>
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<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>521.4</td>
<td>520.0</td>
<td>529.0</td>
<td>521.2</td>
<td>531.0</td>
</tr>
<tr>
<td>$k$ (h$^{-1}$)</td>
<td>0.0072</td>
<td>0.008</td>
<td>0.0123</td>
<td>0.0016</td>
<td>0.0066</td>
</tr>
<tr>
<td>$A_{\text{max}}/A_0$</td>
<td>1.28</td>
<td>1.23</td>
<td>1.15</td>
<td>1.06</td>
<td>1.21</td>
</tr>
</tbody>
</table>
When the antenna is connected to a rhodamine at nitrogen atom of rhodamine moiety separated by methylene groups, the intramolecular CT transfer or triplet energy transfer from rhodamine moiety to the antenna moiety is more effective [22,34]. Therefore, much higher photostability of PRNAM series could be expected due that the naphthalimide moiety acts as an more effective excess energy acceptor in this structure.

As seen in Table 1, the data of average molecular weights indicate that the mechanical properties of these copolymers are available. The glass transition temperatures of the copolymers are far higher than that of Rh6G/PMMA \( T_g = 70 \, ^\circ C \) [29] which means that the thermal stability of the copolymer products in this work are raised when compared with that of Rh6G/PMMA solid solution, whereas the photostability of PRNAM when the ratio of N-AE/Rh-Al (mol/Mol) is between 2.05:1 and 7.49:1 is far superior to that of PRNM when the ratio is between 10:1 and 100:1. So we can conclude that the structure and ratio in PRNAM are favorable for laser dyes with high photostability and high thermal stability.

As the above results show, in the search for more stable and efficient solid-state laser dyes, a mechanism of energy transfer follows by fluorescence emission in a suitable combination of dyes can be an efficient way of internal stabilization, by radiative dissipation of the absorbed pump energy which is not converted into laser emission. The purpose of this research was to gain a deeper insight into the mechanism of photodegradation of chromophores in the polymers. The results presented here show that there is a significant improvement in the photostability of the organic chromophores in novel modified rhodamine copolymers with naphthalimide moieties. Although further research is needed, the experiments reported here show a possible way towards developing a practical solid-polymer laser dye.

4. Conclusion

We have synthesized novel copolymers functionalized with laser dyes based on modified rhodamine 6G and 1,8-naphthalimide. The rate of the photofading reactions of the novel copolymers follow quasi-first-order. Intramolecular energy transfer from antenna to rhodamine is very efficient, and energy transfer in the copolymer PRNAM series is the most efficient among these novel copolymers. The photostability of the copolymers in solid films is better than that in solutions. In solid film, there may be intermolecular energy transfer, which lead to higher photostability of the copolymers in film. Furthermore the photostability of PRNAM is far superior to that of PRNM and PRM, so PRNAM are favorable for laser dyes with high photostability and thermal stability.

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