Study of poly(methyl methacrylate) thin films doped with laser dyes

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Abstract

1,1,4,4-tetraphenyl-1,3-butadiene, Coumarin-334 and rhodamine 6G have been used to form single, binary and ternary dye-doped poly(methyl methacrylate) thin films by the dip-coating method. The thickness of the films was controlled by adjusting the polymer concentration. The photophysical properties of the dyes in solution and in film have been investigated by steady-state and time-resolved fluorescence spectroscopy. Excited-state resonance energy transfer between these dyes has been observed leading to a very broad color emission by the ternary system when excited with ultraviolet light. Laser excitation led to radiation enhancement by waveguide gain and to extensive spectral narrowing.

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1. Introduction

Several organic dyes have been widely used as laser sources \cite{1-5} in photoexcited solid-state organic materials. Recently, electroluminescent devices based on organic thin layers have attracted much interest due to their potential application as large-area light-emitting displays \cite{6-10}. Organic dyes are also candidates for making LEDs. However, crystallization and aggregation affect device lifetime, while it takes high vacuum deposition to fabricate the emitting layers. Compared with it, doped polymers have the advantage of excellent and easy film processing, while the polymer matrix can effectively prevent the dye molecules from aggregating and crystallizing. Some groups have successfully fabricated LEDs using inert or active polymers \cite{11-18}. Doping with various dyes can offer a color tuning by exploiting excited-state energy transfer. Thus white electroluminescence has been realized by mixing different dyes in one system \cite{19}. Fabrication of electrically, rather than optically, pumped organic semiconductor lasers (OSLs) is now the ultimate goal of much organic laser research. However, optically pumped thin films of small-weight organic semiconductors are
still an interesting field of investigation. Most recently, Kozlov et al. [20–22] have fabricated optically pumped OSLs with a slab waveguide structure that exhibited very low lasing thresholds. In this paper, single, binary and ternary dye mixtures have been used to dope inert PMMA polymer thin films. The effect of the presence of the polymer and the efficiency of excited-state energy transfer between these dye molecules have been investigated. Broad spectral emission was observed with the ternary dye system, by ultraviolet excitation, while spectral narrowing due to planar waveguide gain can be obtained by laser excitation.

2. Materials and methods

TPB (1,1,4,4-tetraphenyl-1,3-butadiene, Aldrich), Coumarin-334 (Aldrich), rhodamine 6G (chloride salt, Lambda Physik), PMMA (poly(methyl methacrylate), \( M_w = 1.2 \times 10^5 \), Aldrich) and chloroform (Aldrich) were used as received. Films were deposited on clean quartz slides under ambient conditions. First, solutions were made in chloroform by mixing premeasured quantities of the necessary components. After solution preparation, a quartz slide, previously cleaned in sulfuric acid and sodium hydroxide solution by ultrasonication, was dipped in the solution and withdrawn at a speed of 44 mm/min. The obtained film was left to dry in air, then used for spectroscopic measurements.

Absorption measurements were made with a Cary 1E UV-visible spectrophotometer. For fluorescence measurements we used a home-assembled apparatus, consisting of a 150 W xenon lamp and computer driven monochromators and detection system. All parts and software were purchased from Oriel Instruments. Time-resolved fluorescence measurements were made with the photon counting technique using synchrotron radiation in LURE, Orsay, France. The time profile of the excitation pulse was 0.73 ns FWHM. Analysis of the decay profiles was done by iterative least-squares fit performing deconvolution of the data from the excitation pulse. Fluorescence spectra under laser beam excitation were recorded using the third-harmonic (355 nm) of a nanosecond Q-switched Nd : YAG laser. Luminescence was collected with a quartz fiber and analyzed through an OMA III multichannel spectrum analyzer.

3. Results and discussion

It is known that the thickness of a film obtained by dip-coating can be controlled by adjusting the withdrawal speed of the slide and the viscosity of the solution. In the present work, we have used a constant withdrawal speed to obtain the dye-doped PMMA thin films, so the thickness could be controlled by adjusting the polymer concentration (the amount of dye was relatively small, so the effect of the dye molecules could be neglected). The absorbance of TPB-doped PMMA thin films at the absorption maximum (350 nm) increased almost linearly with PMMA concentration, so its value was used to monitor film thickness. In addition, for fixed PMMA concentration, equal to 20 mg/ml, we observed a practically linear relationship between absorbance of TPB in film and its concentration in chloroform. This indicates that the TPB molecules are well dispersed in the PMMA matrix and also well transferred onto the quartz slides with PMMA. Of course, there is a limit above which complete dispersion of the dye cannot be guaranteed. For this reason, high concentrations should be dealt with great care. Fig. 1 shows the fluorescence spectra of TPB-doped PMMA thin films. At the beginning, the luminescence intensity of the films increased with increasing TPB content, then the intensity reached a maximum, at weight ratio of TPB/PMMA equal to \( \frac{190}{150} \). Finally, the intensity went down when the TPB amount was further increased (see inset of Fig. 1). This may be due to the fact that at low TPB concentration, the polymer, working as solid solvent, can effectively prevent dye molecules from aggregating so that the intensity increases with dye concentration. However, at relatively high dye content, the polymer chain cannot effectively disperse the dye. Aggregation of the dye results in luminescence quenching. Nevertheless, compared with solutions, quenching of fluorescence was lower in thin solid films than in solution (Fig. 2), which means that the dye molecules are frozen in polymer matrices and quenching
Fig. 1. Fluorescence spectra of TPB/PMMA films. PMMA concentration in chloroform was 20 mg/ml. TPB/PMMA ratio was (weight percent): (a) 5.0; (b) 7.5; (c) 10; (d) 15; (e) 40; (f) 56; (g) 75. Inset shows the variation of fluorescence intensity at 450 nm with increasing TPB/PMMA ratio.

Fig. 2. Variation of the TPB fluorescence intensity in different chemical environments: (a) in pure chloroform solution; (b) in PMMA thin films. PMMA concentration in chloroform was 20 mg/ml.

by collision is reduced. Table 1 shows the decay times of the TPB molecules in PMMA thin films. TPB decay times could be easily measured in films and they demonstrated a tendency to decrease with increasing TPB concentration. Furthermore, we could not unambiguously measure the decay time in solutions, due to low fluorescence intensities there, i.e. due to quenching, which supports the above conclusions.

Table 1
Decay times (ns) of films and solutions of TPB/PMMA

<table>
<thead>
<tr>
<th>TPB/PMMA (w/w)</th>
<th>Thin film (em. at 450 nm)</th>
<th>Solution (em. at 450 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5/100</td>
<td>3.0</td>
<td>—</td>
</tr>
<tr>
<td>10/100</td>
<td>2.7</td>
<td>—</td>
</tr>
<tr>
<td>40/100</td>
<td>2.6</td>
<td>—</td>
</tr>
<tr>
<td>56/100</td>
<td>2.5</td>
<td>—</td>
</tr>
<tr>
<td>75/100</td>
<td>2.4</td>
<td>—</td>
</tr>
<tr>
<td>1/1</td>
<td>2.2</td>
<td>—</td>
</tr>
</tbody>
</table>

*PMMA in chloroform 20 mg/ml.

Fig. 3. Overlap of the emission spectrum of TPB and the absorption spectrum of Coumarin-334 in PMMA films.

There exists a very large spectral overlap between TPB emission and Coumarin absorption in PMMA films, as seen in Fig. 3, so resonance energy transfer between these two molecules is expected. We have used these two dye molecules to study their interaction in the polymer system. The precursor TPB/PMMA chloroform solution consisted of 2 mg/ml TPB and 20 mg/ml PMMA, where different amounts of Coumarin were added. The films were all obtained at the same withdrawal speed. It has been found that the absorbance of TPB at 350 nm in thin films was almost constant, which means that these films had all the same thickness. The absorbance of Coumarin at 450 nm, as plotted vs. dye concentration, was not too far from...
Table 2
Decay times (ns) of films and solutions of Coumarin/TPB/PMMA

<table>
<thead>
<tr>
<th>Coumarin/TPB (w/w)</th>
<th>Thin film (em. at 500 nm)</th>
<th>Solution (em. at 500 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>7.2</td>
<td>5.8</td>
</tr>
<tr>
<td>0.04</td>
<td>7.2</td>
<td>5.9</td>
</tr>
<tr>
<td>0.05</td>
<td>8.6</td>
<td>5.5</td>
</tr>
<tr>
<td>0.06</td>
<td>8.7</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*PMMA in chloroform 20 mg/ml, TPB 10 mg/ml.

linearity, indicating that all Coumarin molecules were practically transferred into the films. Of course, at high dye concentration, deviation from linearity is indicative of deficient Coumarin transfer.

For the mixtures of TPB with Coumarin in chloroform solutions, emission was observed only from Coumarin. The decay times (Table 2) of these samples also indicated that the emission was exclusively from Coumarin, as concluded from their higher values compared with the values of Table 1. As the solution was excited at the excitation wavelength of TPB (350 nm), it is obvious that successful resonance energy transfer occurred from TPB to Coumarin. Emission spectra of the corresponding films (Fig. 4), showed that most fluorescence comes from energy transfer from TPB to Coumarin. Some fluorescence from TPB itself indicates that microdomains do exist in the film structure that can isolate some TPB molecules from any energy transfer. In Fig. 4 we can see that the intensity of TPB emission in the presence of Coumarin was almost the same for all samples, which means that the interaction between the two dyes rapidly reaches the maximum. On further Coumarin addition, quenching of its emission by self absorption was detected. Under the present conditions, it seems that \( \frac{1}{\tau_0} \) (by weight) of Coumarin over TPB is enough to produce maximum emission of Coumarin fluorescence. A preliminary analysis of the decay kinetics of TPB in the presence of Coumarin was made by using a model of stretched exponentials [23,24]:

\[
I(t) = I_0 \exp\left(-t/\tau_0\right) \times \exp\left[-C_1(t/\tau_0)^f + C_2(t/\tau_0)^{2/f}\right],
\]

where \( C_1 \) and \( C_2 \) are constants and \( 0 < f < 1 \). The constant \( \tau_0 \) corresponds to the decay rate of the donor TPB in the absence of Coumarin. In homogeneous and isotropic distributions of donors and acceptors and when quenching is done by resonance excited-state energy transfer, the value of \( f \) is equal to 0.5 while the second stretched exponential in the above model is equal to zero (i.e. \( C_2 \) is zero). The decay of TPB in the presence of Coumarin was always monitored at 430 nm, i.e at a wavelength where only the emission from TPB is recorded. The decay profile of TPB changed in both shape and intensity indicating an excited-state energy transfer. Analysis of the decay profiles of TPB in the presence of various Coumarin concentrations, in the range 0–0.3 mg/ml, gave \( f = 0.44 \) while \( C_2 \) was in all cases different from zero. The fact that \( f \) was smaller than 0.5 indicates that the distribution of reactants in the film is not homogeneous and isotropic but restricted. Also the fact that \( C_2 \) was different from zero suggests the possibility of energy migration [23]. These preliminary studies are presently being carried on in our laboratory and will be published later.

By taking advantage of the microdomain structure of the polymer thin films, we have tried to
introduce one more dye into the binary system, expecting the emission from a ternary mixture to cover a major part of the visible spectrum, thus aiming to applications in lasers and LEDs. We have used rhodamine 6G as the third dye. Its concentration was kept relatively low in order to avoid any problems of dye aggregation. Rhodamine 6G absorption spectrum contains two peaks, a weak one around 350 nm and the major absorption band at 530 nm. When transferred into a film and excited at 350 nm, the emission was extremely weak compared with the one obtained by excitation at 530 nm. However, when rhodamine was combined with TPB and Coumarin, its decay profile revealed an excited-state resonance energy transfer process, as seen from the curvature of the rising part of the rhodamine decay profile (Fig. 5). So resonance energy transfer should also apply to these molecules. Fig. 6 shows the emission spectra of the ternary-mixture films, excited at 350 nm. From these, we found that when a small amount of rhodamine 6G was added, the emission of Coumarin was not heavily affected by rhodamine, while a small shoulder of rhodamine emission was observed. With increasing amount of rhodamine, the emission of Coumarin could be quenched, apparently, by resonance energy transfer to rhodamine molecules, while higher intensity of rhodamine emission was observed. Furthermore, the emission spectra of these ternary-dye systems covered almost the whole of the visible region when excited with near-UV radiation.

In order to examine the capacity of these thin films for laser applications, we have excited the binary mixture with a pulsed laser beam, using the third harmonic of a Nd : YAG laser (355 nm). An extensive spectral narrowing of the emission spectrum was registered with laser pulses above 2 mJ per pulse. As seen in Fig. 7, the maximum of the narrowed emission occurred at about 490 nm, clearly related with Coumarin emission but excited through TPB. Spectral narrowing was followed by an extensive increase of emission intensity above threshold. Both these phenomena occur when the photon path length becomes greater than the gain length, i.e. the distance necessary for light amplification by a factor equal to the base of natural logarithms [25]. Amplification is, of course, obtained in the present case by confinement within a planar waveguide. Indeed, PMMA index of refraction (1.49) [26] is larger than the index of refraction of the fused silica substrate (i.e. about 1.46) at the observation wavelength. In this respect, glass substrates, with an index higher than 1.5, gave poor results, apparently due to lack of waveguiding and, subsequently, lack of confinement. The most
crucial parameter affecting gain narrowing was found to be the concentration of the donor and acceptor species. Thus too low a concentration did not offer a high enough pumping cross section while too high an acceptor concentration induced concentration quenching. Further studies of the above system are currently being pursued in our laboratory.

4. Conclusions

We have successfully prepared PMMA thin films doped with laser dyes by the dip-coating method. The dyes can be used as probe molecules to monitor the variation of the thin film thickness. PMMA is a good solid solvent for the presently used dyes and can effectively disperse them provided that their concentration is not too high. Otherwise, dye aggregation and quenching of emission is observed. Resonance energy transfer between different dye-molecules was observed in dye-doped polymer thin films and a very broad emission was registered with the ternary system when excited by near-UV radiation. Excitation with laser pulses led to extensive spectral narrowing in the luminescence of the binary system, with TPB being the absorbing and Coumarin-334 the emitting species.

Acknowledgements

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