Optical Properties of Rhodamine B Dye Doped in Transparent Polymers for Sensor Application

R. M. Ahmed¹,∗ and M. Saif²

¹Physics Department, Faculty of Science, Zagazig University, Zagazig 44519, Egypt
²Chemistry Department, Faculty of Education, Ain Shams University, Roxy 11711, Cairo, Egypt

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In the present study, the casting method has been utilized for preparing different concentrations of Rhodamine B (Rh-B) doped in different transparent polymers. The spectral characteristics of the prepared samples are studied by absorption and fluorescence spectroscopy. The optical absorption measurements have been carried out in the wavelength region from 325 nm to 800 nm, and the fluorescence spectra has been investigated at different excitation wavelengths at room temperature. Besides, the effects of the concentration of the Rh-B dye and heat treatment temperature on the optical properties of the samples have been studied. Moreover, the effect of the thickness on the absorption and fluorescence has been included in the study. Based on the change of the absorption for Rh-B dye incorporation into different transparent polymer hosts, heat sensor testing has been investigated via recording the temperature changes in which the sample is alternately heated up to 70 °C and then cooled to room temperature in repeated cycles.

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I. INTRODUCTION

A great deal of interest has been concerned with the incorporation of organic dyes into solid matrices, owing to useful applications such as light concentrators in solar cells, optical waveguides, laser materials, sensors, and nonlinear optical materials [1].

Although both inorganic glasses and polymeric materials have been successfully used as host matrices for dyes, polymers offer a number of advantages both from the technical and economical point of view, which include high optical homogeneity, better chemical compatibility with organic dyes, and control over the medium polarity and viscosity in a way similar to conventional solvents [2, 3].

Moreover, polymers have become profitable for sensor technologies, because of their low cost materials and their fabrication techniques being quite simple. In the past few decades significant interest has been shown in polymer-based sensing materials, which exhibit a change of their absorption and/or fluorescence characteristics in response to an external stimulus. Some examples of these stimuli include heat, deformation, chemicals, light, and others, which make the sensors useful for a wide range of technologies [4].

∗Electronic address: rania8_7@hotmail.com, rmkhalil@zu.edu.eg
Polymer films containing luminescent dyes are widely used in sensors. To maximize the effectiveness of the sensor, one often chooses polymer-dye combinations in which the dye dissolves in the solvent of the polymer [5].

An important member in the family of poly (acrylic esters) is poly (methyl methacrylate) (PMMA). Although PMMA has a poor heat resistance [6], it has been widely used in many fields, because of its outstanding chemical stability, transparent optical property, and excellent biocompatibility. It can incorporate dye molecules to become colorful and functional. Indeed, incorporating dyes into polymer supported matrices, such as PMMA, could keep them far away from the disturbance of external environments, which remarkably influences the spectral properties of dyes [7].

Besides, Polyvinylacetate (PVAc) is known to be one of the most important commercial polymers as a result of its low cost and the high performance of the products, combined with the wide range of its properties. It has enormous technical and economic importance, even though its degradation at high temperature is still an intensively studied problem by many scientists [8].

Herein, we have been concerned with studying the optical properties including the absorbance, fluorescence, quantum yield of fluorescence, Stokes shift, and the energy yield of fluorescence for the samples of Rh-B dye doped in different transparent polymer hosts as PMMA, PVAc, and their blends. The effects of the concentration of the doped dye as well as the change in the thickness of the samples have been studied. Moreover, the change of temperature has been tested based on the change of the absorption of the prepared samples.

II. EXPERIMENTAL METHOD

II-1. MATERIALS

PMMA (poly methyl methacrylate) obtained from (BDH England) and PVAc (poly vinyl acetate) obtained from (Sigma-Aldrich) were reported to have molecular weights of 145,000 and 167,000 $g\cdot mol^{-1}$, respectively. Moreover, Rhodamine – B (Rh-B) obtained from Merck, was used in this study without further purification. In addition, chloroform with a purity of 99.8% (HPLC) was used as a common solvent for PMMA, PVAc, and Rh-B.

II-2. PREPARATION OF THE SAMPLES

Films with thickness ($45 \pm 10$) $\mu m$ were prepared by using the solution-cast technique. PMMA, PVAc, and $Rh-B$ had been dissolved in chloroform separately. Different concentrations of $Rh-B$ ($5 \times 10^{-5}$, $5 \times 10^{-4}$, and $1 \times 10^{-3}$ mol%) were added to the two homopolymers and also their blend (PVAc/PMMA 50/50). Afterwards, the solutions were stirred followed by heating at 55 $^\circ$C for 10 minutes in an oven. Then the solutions were poured into glass Petri dishes and left for 2 hours at 45 $^\circ$C. Finally the films of the samples were removed and then cut as desired. It was observed that, only for the concentration of $Rh-B$ ($5 \times 10^{-5}$ mol %) doped in PVAc, the film was colorless, which may be attributed to the existence of $Rh-B$ in lactone form [9].
II-3. CHARACTERIZATION

A UV-visible spectrophotometer (UV-1601PC Shimadzu) connected with a TCC controller (TCC-240A) was used for the measurements of UV/Vis absorption spectra, and its variation with temperature for the prepared samples. In addition, the emission spectra were recorded with a L55 Perkin-Elmer spectrophotometer equipped with a 150 W pulse-xenon lamp as the excitation source.

III. RESULTS AND DISCUSSION

![Absorption spectra of different concentrations of Rh-B doped samples](image)

**Fig. 1**: Absorption spectra of different concentrations of Rh-B doped (a) PMMA, (b) (PMMA/PVAc 50/50), and (c) PVAc [Inset: absorption peak value versus dye content at $\approx 557 \pm 1$ nm (1st peak), at $\approx 521 \pm 2$ nm (2nd peak), and at $\approx 354 \pm 2$ nm (3rd peak)].

Fig. 1 shows the absorption spectra at room temperature for PMMA, PVAc, and their blend (PMMA/PVAc 50/50) doped with different concentrations of Rh-B measured in a range of wavelengths from 325 to 800 nm. It could be seen that there is an absorption
band at \((557 \pm 1)\) nm, which originates from the \(\pi - \pi^*\) transitions from the binding \textit{HOMO} (highest occupied molecular orbital) to the anti-binding \textit{LUMO} (lowest unoccupied molecular orbital) along the longest dimension of the conjugated system. However, the shoulder around \((521 \pm 2)\) nm is usually ascribed to the dimmer. The bands below 450 nm represent the transitions to the mesomeric limit structures with shorter conjugation units and originate from \(n - \pi^*\) transitions from the \textit{NHOMO} (next highest occupied molecular orbital) to the \textit{LUMO} [10].

Moreover, as shown in the inset, the absorption peak values increased with increasing \textit{Rh-B} content, due to the increase of the number of the absorbing species according to Beer’s law [11, 12]. Also, it can be seen that the absorption peak values for \textit{Rh-B} dye doped in PMMA were greater than that doped in \((\text{PMMA/PVAc 50/50})\), which were also greater than that doped in PVAc, for the same concentrations of the doped dye.

![Fluorescence spectra](image)

**FIG. 2:** Fluorescence spectra of a concentration of \textit{Rh-B} \((1 \times 10^{-3})\) doped in (a) PMMA, (b) \((\text{PMMA/PVAc 50/50})\), and (c) PVAc at different excitation wavelengths.

Fig. 2 illustrates that the fluorescence spectra of \textit{Rh-B} concentration \((1 \times 10^{-3} \text{ mol}%)\) doped in PMMA, \((\text{PMMA/PVAc 50/50})\), and PVAc excited at different wavelengths is
centered at (596.5 and 627.9) nm, (595.0) nm, and (587.9) nm, respectively, for any excited wavelength. In fact, fluorescence occurs when a molecule absorbs photons from the UV-visible light spectrum, causing a transition to a high-energy electronic state and subsequently emits photons as it returns to its initial state. Some energy within the molecule is lost through heat or vibrations, so that the emitted energy is less than the exciting energy; i.e., the emission wavelength is always longer than the excitation wavelength [13].

FIG. 3: Fluorescence spectra for different concentrations of Rh-B doped in (a) PMMA, (b) (PMMA/PVAc 50/50), and (c) PVAc at \( \lambda_{\text{excitation}} = 470 \) nm

The fluorescence spectra of different concentrations of Rh-B doped in different transparent polymer hosts are shown in Fig. 3. It is known that the fluorescence of a molecule depends on its structure and environment, such as the interaction with the solvent and other dissolved compounds in the matrix, the temperature, and the concentration of the fluorescing species. Herein, the fluorescence intensity increased linearly with increasing Rh-B concentration. Hence, no concentration quenching effect was observed in the studied Rh-B concentration range as the dye–dye interaction is negligible [14].

On the other hand, by increasing the concentration of Rh-B doped in PMMA,
<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (mol%)</th>
<th>Absorption Spectra</th>
<th>Fluorescence Spectra</th>
<th>FWHM (nm)</th>
<th>∆λ (nm)</th>
<th>Φf %</th>
<th>Ef %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>5 × 10⁻⁵</td>
<td>558.6</td>
<td>1148.0</td>
<td>577.5</td>
<td>48.5</td>
<td>18.9</td>
<td>3.22</td>
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<td></td>
<td>5 × 10⁻⁴</td>
<td>557.4</td>
<td>1153.2</td>
<td>586.4</td>
<td>52.8</td>
<td>29.0</td>
<td>5.45</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻³</td>
<td>557.2</td>
<td>1356.4</td>
<td>596.5</td>
<td>623.8</td>
<td>66.8</td>
<td>39.3</td>
</tr>
<tr>
<td>PMMA/PVAc 50/50</td>
<td>5 × 10⁻⁵</td>
<td>558.3</td>
<td>1125.4</td>
<td>577.1</td>
<td>38.2</td>
<td>18.8</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁴</td>
<td>558.0</td>
<td>1151.6</td>
<td>587.0</td>
<td>59.3</td>
<td>29.0</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻³</td>
<td>558.4</td>
<td>1219.4</td>
<td>595.0</td>
<td>617.9</td>
<td>61.5</td>
<td>36.6</td>
</tr>
<tr>
<td>PVAc</td>
<td>5 × 10⁻⁵</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁴</td>
<td>558.9</td>
<td>1145.6</td>
<td>584.3</td>
<td>49.9</td>
<td>25.4</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻³</td>
<td>558.1</td>
<td>1152.0</td>
<td>587.9</td>
<td>58.0</td>
<td>29.8</td>
<td>6.50</td>
</tr>
</tbody>
</table>

(PMMA/PVAc 50/50), and PVAc a red shift in wavelength from 577.5 to 596.5, from 577.1 to 595.0, and from 584.3 to 587.9 nm, was observed from the lowest to the highest concentration, respectively, as seen in Table I. This is mainly due to ground state absorption. Furthermore, the observed peak and shoulder for the highest concentration of Rh-B doped in PMMA and its blend, respectively, at long wavelengths could be attributed to the existence of intermolecular interactions in the ground state in the PMMA films and also in its blend [15].

One of the most important characteristics of the dye doped in solid matrix is the Stokes shift ∆λ, that indicates the difference in the dipole moments between the ground state $S_0$ and the first excited state $S_1$ of the dye molecules [16, 17]. Furthermore, it is a measure of self-absorption of the emitted light; it was calculated from [18]

$$\Delta \lambda = \lambda_f - \lambda_a. \quad (1)$$

Where $\lambda_f$ and $\lambda_a$ are the wavelengths at the fluorescence and absorbance maxima, respectively.

In addition, the ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield, $\phi_f$, which was calculated for the as prepared samples relative to BASF-241 dye doped in PMMA as a reference ($\phi_{ref} \approx 99\%$), according to the following equation [19]:

$$\phi_f = \phi_{ref}(P_{ref}/P)(n/n_{ref})(a/a_{ref}). \quad (2)$$
Where $\phi_{\text{ref}}$ is the fluorescence quantum yield of a reference, $P$ is the absorbance at the excitation wavelength, $n$ is the index of refraction and $a$ is the area under the fluorescence curve. Moreover, the energy yield of the fluorescence $E_{\text{fluo}}$ which could be used instead of $\phi_f$ [17], was estimated for the samples from the equation [20]:

$$E_{\text{fluo}} = \frac{\phi_f \lambda_a}{\lambda_f}.$$  

(3)

The spectral parameters such as the absorption bandwidth ($\Delta \nu_{1/2}$), full width at half maximum ($FWHM$), $\lambda_a$, $\lambda_f$, $\Delta \lambda$, $E_{\text{fluo}}$, and $\phi_f$ were calculated and are listed in Table I. It can be clearly seen from Table I that the absorption bandwidth became broader by increasing the concentration of the doped dye. This may be due to the inhomogeneous distribution of the dye molecules in the polymer matrix. The distribution of dye molecules surrounded by host media having subtly different chemical and dielectric character causes this inhomogeneous broadening [21].

![Absorbance and fluorescence intensity at a concentration of Rh-B (5 x 10^{-5}) doped in (PMMA/PVAc 50/50) for different thicknesses.](image)

FIG. 4: Absorbance and fluorescence intensity at a concentration of Rh-B ($5 \times 10^{-5}$) doped in (PMMA/PVAc 50/50) for different thicknesses.

Moreover, it could be observed that the fluorescence bandwidth of the Rh-B dye doped in the different polymer matrix became broader by increasing its concentration. In general, one can say that the spectral characteristics of the lasing dye in the polymer depend on the intermolecular interaction between the dye molecule and the macromolecules [16].

In addition, the values of the Stokes shift were increased by increasing the doped dye in the different polymer matrixes, which indicates a low self absorption of the emitted radiation by the dye molecules, and that could affect directly the fluorescence quantum yield and consequently the energy yield of the fluorescence. Furthermore, from Table I,
FIG. 5: Variation of absorption peak values with different heating temperature (∆) and also with the exposure time of heating at 70°C (●) for different concentrations of Rh-B doped in (a) PMMA, (b) (PMMA/PVAc 50/50), and (c) PVAc.

it could be estimated that the values of the fluorescence quantum yield and the energy yield of the fluorescence for different concentrations of Rh-B dye doped in PMMA were high in comparison with the corresponding concentrations in the other samples. Moreover, doping Rh-B dye in the blend (PMMA/PVAc 50/50) could enhance its properties more than doping it in PVAc only.

On the other hand, various thickness (37.5, 72.5, and 190) µm of the concentration of Rh-B (5 × 10^{-5} mol %) doped in (PMMA/PVAc 50/50) have been prepared for showing the effect of the film thickness on the optical parameters of the sample, as seen in Fig. 4. It was observed that the absorption and fluorescence peak values have increased by increasing the thickness of the sample. The higher absorbance of the thicker samples is due to the
increased scattering losses in this sample [22, 23].

The temperature dependence of the absorption for the studied samples in the temperature range from 28 to 70 °C is shown in Fig. 5. It can be seen that the absorption peak values are decreased by increasing the value of the exposed temperature, which illustrates clearly that Rh-B dye has a strong temperature dependence, in agreement with the literature [24]. Also, Fig. 5 shows that there was a decrease in the absorption peak values from increasing the exposure time of heating at 70 °C for all samples except for the lowest concentration of dye (5 × 10^{-5} mol %) doped in PMMA and (PMMA/PVAc 50/50), which had a totally opposite behavior compared to the all other samples, indicating a partial recovery of the thermal damage as a consequence of a thermally activated process [25]. In addition, it is well known that at temperatures lower than the glass transition point of PMMA (≈ 100 °C [26]), its molecular chains begin to move. Hence it is possible to think that these movements can facilitate changes of the dye position in the host material [27].

![Graph showing sensitivity of heating for a concentration of Rh-B](image)

**FIG. 6:** Sensitivity of heating for a concentration of Rh-B (1 × 10^{-3}) doped in (a) PMMA, (b) (PMMA/PVAc 50/50), and (c) PVAc.

As an application for our study, the samples of a concentration of Rh-B dye (1 × 10^{-3} mol %) doped in PMMA, (PMMA/PVAc 50/50), and PVAc, have been chosen to be tested as sensing materials for heat. The samples were heated up to 70 °C, in order to investigate the thermal effect on the their absorption, and then gradually cooled to the room temperature, 28 °C, after an annealing of 8 minutes at the maximum temperature, 70 °C, as seen in Fig. 6.

A common way to express the previous study is using the sensitivity, which is defined as the ratio between the change in the absorbance at the time of heating (A) and the initial
absorbance \((A_0)\) [28]:

\[
S = \frac{A - A_o}{A_o} \times 100\%.
\] (4)

It was observed that after cooling the samples to room temperature the absorption did not return to its initial value, indicating that the dye absorbance suffers from thermal degradation in the range of temperature from 28–70 °C. In other words, it could be seen that a partial recovery of the thermal bleaching was clearly regarded after cooling to room temperature and a decrease in the maximum recovery with successive cycles was obviously observed, in agreement with the literature [25]. From the above results, it may possibly be said that all the tested samples have a characteristic behavior upon their exposure to heat. Besides, it can be deduced from Fig. 6 that the highest sensitivity for heat was achieved by doping Rh-B dye in PVAc.

IV. CONCLUSION

The absorption peaks values as well as the fluorescence intensity were increased by increasing the concentration of Rh-B dye doped in the different transparent polymer hosts and also the thickness of the samples. Moreover, the spectral characteristics, including the absorption bandwidth \((\Delta \nu_{1/2})\), full width at half maximum \((FWHM)\), Stokes shift \((\Delta \lambda)\), fluorescence quantum yield \((\phi_f)\), and the energy yield of fluorescence \((E_{flu})\), were obviously depending on the dye content. On the other hand, doping the dye in a blend of PMMA and PVAc enhanced the optical properties of PVAc. In addition, the lowest concentration of Rh-B dye doped in PMMA and its blend with PVAc showed an opposite behavior after heating, in comparison to the other samples in which the absorption peak values were increased by increasing the exposure time of heating; that indicates a partial recovery of the thermal damage. Also, doping the dye in PVAc displayed the highest sensitivity for heating as an application for a heat sensor. On the other hand, doping the blend of PMMA/PVAc with the Rh-B dye showed an improvement of the sensitivity to heat more than that of PMMA.

References