I. INTRODUCTION

In recent years, there have been significant advances in the syntheses of a number of new organic dyes that have potential for tunable solid-state laser systems. These dyes are found to possess high quantum fluorescence yield and a reduced triplet–triplet absorption in their fluorescence and laser spectral range.1–3 Owing to numerous advantages, a great deal of effort has been made to synthesize solid-state hosts for these dyes. Polymeric plastics have been a primary choice for the host of the laser dyes, because they can readily form concentrated and uniform solutions with dyes. They are also hydrolytically and thermally stable, and resistant to many solvents such as alcohols and acetone. The high-damage-threshold polymer materials have also played a significant role in the advancement of solid-state dye laser systems. The polymeric plastics have been found to have optical properties suitable for becoming potential laser hosts for the organic dyes. Hermes and co-workers have shown that several of the pyromethene-BF₂ dyes doped in solid-state polymeric hosts exhibited lasing properties with significantly high slope efficiencies.4,5

In this article, we present an in-depth characterization of optical properties of an organic laser dye, C₂₈H₂₀N₂O₂B₂F₄H₂O. The quantum fluorescence yield of this dye is over 90%, which is comparable with those of the majority of conventional laser dyes. Owing to the complex nature of organic dye molecules doped in plastic host, both absorption and scattering must be considered when evaluating laser and optical properties of organic dyes.

Although a single measurement of the total transmission through a sample of known thickness provides an attenuation coefficient based on the Beer’s law of exponential decay, it is impossible to separate the loss due to absorption from the loss due to scattering. Therefore, the absorption coefficient measured by the Cary-14 spectrophotometer will be referred to as the total attenuation coefficient. This problem has been resolved by the one-dimensional, two-flux Kubelka–Munk model6 which has been widely used to determine the absorption and scattering coefficients of turbid media provided the scattering is significantly dominant over the absorption. In the past, researchers have used the diffusion approximation to study turbid media.7–9 Most notably, following the Kubelka–Munk model and diffusion approximation, an excellent experimental method has been described by Van Geert et al. for determining the absorption and scattering coefficients and scattering anisotropy coefficient.1⁰ ¹¹

The Kubelka–Munk coefficients, K and S, can be expressed in terms of the absorption coefficient (μₐ) and the scattering coefficient (μₛ) in the following forms:

\[ K = 2 \mu_a \quad \text{and} \quad S = \frac{1}{2} (1 - g) \mu_a - \frac{1}{4} \mu_a, \quad (1) \]

where \( g \) is the scattering anisotropy coefficient, defined as the average cosine of the scattering angle. These coefficients can be expressed in terms of sample thickness \( t \), diffuse reflectance \( R_d \), and diffuse transmittance \( T_d \) as follows.1²

\[ S = \frac{1}{b t} \ln \left( \frac{1 - R_d (a - b)}{T_d} \right) \quad \text{and} \quad K = S(a - 1), \quad (2) \]

where

\[ a = \left( \frac{1 + R_d^2 - T_d^2}{2 R_d} \right) \quad \text{and} \quad b = \sqrt{a^2 - 1}. \quad (3) \]

The collimated transmittance \( T_c \) can be measured by placing the detector attached to the integrating sphere about 2 m from the sample. In this measurement, a narrow collimated beam is passed through the sample in such a way that any photons that are scattered off the sample are not detected by the detector. The collimated transmittance can be written in terms of the absorption and scattering coefficients following the Beer’s law:

\[ -\ln [T_c] = (\mu_a + \mu_s) t, \quad (4) \]

where \( t \) is the sample thickness and measured in cm. By combining Eqs. (1)–(3), we can solve for the values of \( \mu_a \), \( \mu_s \), and \( g \).
II. MATERIALS AND METHODS

The organic laser dye $C_{28}H_{20}N_2O_2B_2F_4H_2O$ used in this study has been synthesized by Professor Joseph Boyer of the Chemistry Department at the University of New Orleans. The molecular weight of the dye is 531.6. The dye powder has a deep violet color and is soluble in dioxane and water.

A. Solid-state dye material preparation

The dye solution was prepared from a $4 \times 10^{-4}$ M concentration in 2-hydroxyethyl methacrylate (also known as HEMA). A portion of the solution was placed in test tube of 1 cm diameter; 100 mg of benzoyl peroxide, an oxidizing agent, was added. The benzoyl peroxide is used to cure the HEMA, which initiates the free radical polymerization. The prepared solution was heated in a temperature-controlled oven where the temperature was gradually raised to 120 °C in 120 min. The oven temperature of 120 °C was maintained for about 10 min; the oven was then turned off and the sample was left over night for slow cooling. The resulting material was a greenish, solid cylinder. It was then cut into disks and prisms that were then polished for optical measurements.

B. Index of refraction measurement

The index of refraction of the dye doped in solid plastic was measured by the method of minimum deviation using a polished prism that was cut from a solid cylindrical sample. The apex angle was measured to be 37.5°. In this procedure, the solid prism was firmly mounted at the center of an optical goniometer table. By rotating the prism on the optical table, the minimum deviation was observed. Once taking the measurements of the distances between the prism and the projection screen, and also the distance between the location of the incident beam and its location at the minimum angle of deviation, the angle of minimum deviation was determined using simple trigonometry. The values of the apex angle and the angle of minimum deviation were used to determine the index of refraction from

$$\sin \left( \frac{\alpha + \delta_m}{2} \right) = \sin \left( \frac{\alpha}{2} \right),$$

where $\alpha$ is the apex angle of the prism and $\delta_m$ is the angle of minimum deviation. This method was chosen for its simplicity and accuracy. The index of refraction was measured at a number of wavelengths. These values are listed in Table I. The experimental details for measuring index of refraction can be found in Refs. 13 and 14.

These experimental values of $n$ were subsequently least-squares fitted to the 1 pole Sellmeier’s dispersion equation

$$n^2(\lambda) = 1 + \frac{S \lambda^2}{\lambda^2 - \lambda_0^2},$$

where $\lambda$ is the wavelength of the incident light, $S$ and $\lambda_0$, obtained from the least-squares fit of the experimental data to Eq. (6), were then used to recalculate the values of the index of refraction at all wavelengths.

C. Scattering anisotropy coefficient measurement

Using an independent experimental technique, the scattering anisotropy coefficient $g$ of the dye in plastic host can also be obtained from the measurements of scattered light intensities ($I$) at various scattering angles ($\theta$) using a circular goniometer table with a diameter of 20 cm. The sample placed vertically at the center of the goniometer table was only 0.51 cm thick and 1 cm in diameter. Also, the power of incident laser was kept at less than 1 mW throughout the experiment. Based on these experimental parameters, the scattering anisotropy coefficient $g$ can be approximated by the average cosine of the scattering angle according to

$$g = \frac{\Sigma_i \cos \theta_i I_i}{\Sigma_i I_i},$$

where the sums are over all values ($i$) of the scattering angles and intensities.

The scattering anisotropy factor $g$ was determined by irradiating the disk-shaped sample placed at the center of a circular goniometer table. A He–Ne laser (Uniphase model 1101P) with a power of 1 mW and the beam diameter of 2 mm was used to excite the sample and an Oriel model 70680 photomultiplier tube (PMT) mounted at the edge of the table as shown in Fig. 1 was used to measure the scattered light. The laser beam was aligned at a 90° angle with respect to the plane of the sample, and the PMT was attached to an adjustable pointer which could be rotated around the table for measuring the scattered intensities at different angles. The scattered light intensity was measured between 0° and 180° at an increment of 1° from 0° to 10° of the scattering angle, and at an increments of 5° from then on. Since the scattered light intensity can also be in the backward direction, the measurements between 170° and 180° were made at 1° increments as well. Using the values obtained, the scattering anisotropic factor ($g$) was calculated and found to be 0.95. The measurement was repeated three times and the values of $g$ were found to vary less than 5%.

### Table I. The wavelength dependent index of refraction of $C_{28}H_{20}N_2O_2B_2F_4H_2O$ dye in a plastic host. Sellmeier coefficients: $S = 1.301$ and $\lambda_0 = 152.793$ nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$n_{exp}$</th>
<th>$n_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>632.8</td>
<td>1.547</td>
<td>1.543</td>
</tr>
<tr>
<td>575.0</td>
<td>1.549</td>
<td>1.549</td>
</tr>
<tr>
<td>532.0</td>
<td>1.551</td>
<td>1.555</td>
</tr>
<tr>
<td>514.5</td>
<td>1.554</td>
<td>1.558</td>
</tr>
<tr>
<td>501.7</td>
<td>1.559</td>
<td>1.560</td>
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<tr>
<td>488.0</td>
<td>1.564</td>
<td>1.563</td>
</tr>
<tr>
<td>476.5</td>
<td>1.570</td>
<td>1.565</td>
</tr>
</tbody>
</table>

The values of the constants, $S$ and $\lambda_0$, obtained from the least-squares fit of the experimental data to Eq. (6), were then used to recalculate the values of the index of refraction at all wavelengths.
D. Total diffuse reflectance and transmittance measurements

The total diffuse reflectance and total diffuse transmittance measurements were taken using double-integrating spheres (Oriel model 71400). The prepared solid sample was placed in a sample holder mounted in between the two spheres. The measurements were performed on the sample at different wavelengths. The light sources used for these measurements were an argon ion laser (476.5, 488.0, 501.07, and 514.5 nm), Nd:YAG (second harmonic: 532.0 nm), and He–Ne laser (632.8 nm). The detailed specifications of the lasers employed in this study can be found in Ref. 15.

The schematic of the experimental setup employed to measure the total diffuse reflectance and total diffuse transmittance is shown in Fig. 2. The laser was directed into the entrance port A of the first integrating sphere whose exit port C is equipped with the sample. The port C is coupled with the entrance port of the second integrating sphere. The transmission from the sample was collected into the second integrating sphere whose exit port B was capped with a reflective surface identical to that of the interior of the integrating sphere. The reflecting baffles within the spheres shielded the PMT’s from direct photons from the sample. The diameters of the spheres were 6 in. and each of the ports had a diameter of 1 in. The reflected and transmitted light intensities were detected by the PMT’s attached to the respective measuring ports. The PMT’s were powered by a high voltage power supply (Bertan, model 215). The signals from the PMT’s were taken to digital multimeters (Fluke, Series II). The measured light intensities were then utilized to determine the total diffuse reflectance \( R_d \) and total diffuse transmittance \( T_d \) by

\[
R_d = \frac{X_r - Y_1}{Z - Y_1} \quad \text{and} \quad T_d = \frac{X_r - Y_2}{Z - Y_2},
\]

where \( X_r \) is the intensity detected by the PMT-1, \( X_r \) is the intensity detected by the PMT-2 with a reflective surface at B, \( Z \) is the intensity detected by the PMT-2 with no sample at C and a reflective surface at B, \( Y_1 \) and \( Y_2 \) are the correction factors measured by the PMT-1 and PMT-2, respectively, with no sample at C and no reflective surface at B. The linearity of the PMT’s was checked and found to be linear over the entire range of visible wavelengths of our interest.

E. Collimated transmittance measurement

The unscattered collimated transmittance \( T_c \) was measured to determine the total attenuation coefficient. The collimated laser beam intensities were measured by placing the integrating sphere approximately 2 m from the sample so that the photons scattered off the sample would be prevented from entering the small aperture (approximately 3 mm in diameter) at A. The sample was aligned at 90° relative to the incident beam for all measurements taken. The collimated transmittance \( T_c \) was calculated by

\[
T_c = \frac{X_c}{Z_c},
\]

where \( X_c \) is the collimated light intensity and \( Z_c \) is the incident light intensity.

According to the Beer’s Law, the total attenuation coefficient \( (\mu = \mu_a + \mu_s) \) can be determined from

![FIG. 1. Schematic of the experimental setup for the measurement of \( g \); DM is the digital multimeter, PS is the power supply, and PMT is the photomultiplier tube.](image1)

![FIG. 2. Schematic of the experimental setup for the measurements of \( T_d \) and \( R_d \).](image2)

![FIG. 3. Room-temperature total attenuation spectrum of \( C_3H_5N_2O_2B_2F_4H_2O \) dye in plastic host, sample thickness was 0.51 cm.](image3)
where \( t \) is the physical thickness of the sample and is measured in cm.

### F. Total attenuation and fluorescence measurements

The room-temperature total attenuation spectrum ranging from 450 to 750 nm was taken on the solid plastic host containing \( \text{C}_{28}\text{H}_{20}\text{N}_{2}\text{O}_{2}\text{B}_{2}\text{F}_{4}\text{H}_{2}\text{O} \) dye using a Cary-14 spectrophotometer upgraded by On-Line Instrument Systems. The spectral bandwidth was set at 0.5 nm, and the instrument was internally calibrated to an accuracy of 0.3 nm. The sample thickness was 0.51 cm. The total attenuation spectrum displayed in Fig. 3 shows two strong broad band absorptions peaking at 580 and 630 nm. The attenuation coefficients of these peaks are about 6 cm\(^{-1}\) and 7 cm\(^{-1}\), respectively.

The room-temperature fluorescence spectrum ranging from 600 to 800 nm was taken on the solid-state dye sample using a Photon Technology International fluorometer and is presented in Fig. 4. The sample was excited with 560 nm and the spectral resolution was 0.25 nm. A personal computer equipped with a software (ALPHASCAN) was used to control the fluorometer and collect and analyze the data. The spectra were analyzed and plotted by using the computer software package SIGMA PLOT.

### III. RESULTS AND DISCUSSION

The indices of refraction \((n)\) of the laser dye in solid plastic host were measured at the wavelengths 476.5, 488.0, 501.7, 514.5, 532.0, 575.0, and 632.8 nm; the index of refraction decreases with increasing wavelength. The index of refraction data were least-square fitted to the Sellmeier’s equation. The experimental and theoretical values of \( n \) are given in Table I; the experimental values are plotted in Fig. 5. The root-mean-square deviation of the \( n \) values provided in Table I has been found to be less than 1%.

The total diffuse reflectance, diffuse transmittance, and collimated transmittance were measured on a solid-state dye sample at 476.5, 488.0, 501.7, 514.5, 532.0, and 632.8 nm. These measurements were repeated three times and the data were in good agreement to within 5%. These values were then used to calculate the Kubelka–Munk coefficients which were used to obtain the absorption and scattering coefficients. These values are tabulated in Table II. The total attenuation coefficients are also determined from the collimated transmission \( T_c \) and given in Table III. The total attenuation coefficients at these wavelengths were obtained from the Cary-14 measurement are also given in Table III for comparison. A visual comparison can be seen in Fig. 6. These values were found to be in good agreement. The scattering anisotropy factor \( g \) was determined to be approximately 0.95; this clearly indicates that the scattering in the

![FIG. 4. Room-temperature fluorescence spectrum of \( \text{C}_{28}\text{H}_{20}\text{N}_{2}\text{O}_{2}\text{B}_{2}\text{F}_{4}\text{H}_{2}\text{O} \) dye in plastic host excited at 560 nm.](image)

![FIG. 5. Index of refraction at various wavelengths for \( \text{C}_{28}\text{H}_{20}\text{N}_{2}\text{O}_{2}\text{B}_{2}\text{F}_{4}\text{H}_{2}\text{O} \) dye in plastic host.](image)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Experimental</th>
<th>Kubelka–Munk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_d )</td>
<td>( T_d )</td>
</tr>
<tr>
<td>632.8</td>
<td>0.006</td>
<td>0.064</td>
</tr>
<tr>
<td>532.0</td>
<td>1.402</td>
<td>1.630</td>
</tr>
<tr>
<td>514.5</td>
<td>0.889</td>
<td>3.151</td>
</tr>
<tr>
<td>501.7</td>
<td>0.506</td>
<td>3.470</td>
</tr>
<tr>
<td>488.0</td>
<td>0.679</td>
<td>3.510</td>
</tr>
<tr>
<td>476.5</td>
<td>0.498</td>
<td>3.489</td>
</tr>
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</table>
plastic host containing C$_{28}$H$_{20}$N$_{2}$O$_{2}$B$_{2}$F$_{4}$H$_{2}$O dye molecules is highly forward scattering.

The anisotropy factor $g$ was also determined using the Kubelka–Munk method, and was found to vary approximately from 0.7 to 0.9. The measured value is in agreement with the calculated values within the uncertainty of experimental measurements.

The scattering coefficient at all wavelengths below 632.8 nm was found to be significantly higher than the absorption coefficient. The loss due to scattering in laser design is a serious drawback. It is therefore critical to determine the loss of the pump energy by scattering in any potential laser medium. Therefore, further studies on more suitable polymeric hosts doped with this dye should be done.

The room-temperature fluorescence spectrum shows two broad bands peaking at around 645 and 695 nm. Because of the strong and broad emission ranging from 600 to 750 nm, this dye in plastic host would be a likely candidate for tunable solid state laser device. The values of the optical properties reported in this article are of significant importance to the laser community and can be considerably useful for the design of the tunable solid state dye laser system.

**ACKNOWLEDGMENTS**

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TABLE III. A comparison of the total attenuation coefficients obtained from the Kubelka–Munk method, collimated transmittance, and the Cary-14 measurements for C$_{28}$H$_{20}$N$_{2}$O$_{2}$B$_{2}$F$_{4}$H$_{2}$O dye in a plastic host.

<table>
<thead>
<tr>
<th>Wavelength ($\lambda$) (nm)</th>
<th>Kubelka–Munk ($\mu_s$ (cm$^{-1}$))</th>
<th>Collimated transmittance ($\mu_s$ (cm$^{-1}$))</th>
<th>Cary-14 ($\mu_s$ (cm$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>632.8</td>
<td>6.803</td>
<td>6.900</td>
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<tr>
<td>532.0</td>
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<td>3.646</td>
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<td>501.7</td>
<td>3.714</td>
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<td>3.764</td>
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<tr>
<td>488.0</td>
<td>3.660</td>
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<td>476.5</td>
<td>3.735</td>
<td>3.820</td>
<td>3.975</td>
</tr>
</tbody>
</table>

FIG. 6. Comparison of obtained total attenuation coefficients for C$_{28}$H$_{20}$N$_{2}$O$_{2}$B$_{2}$F$_{4}$H$_{2}$O dye in plastic host obtained from Cary-14 spectrophotometer, collimated transmission measurements, and Kubelka–Munk method.