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PHOTOCALORIMETRIC SPECTROSCOPY OF ERYTHROSINE AND EOSIN IN EPOXY RESIN

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Abstract Photocalorimetric measurements using thermistor is applied to study the heat generation by nonradiative processes in erythrosine and eosin dyes in epoxy resin. Photocalorimetric spectra of them agree with photoacoustic ones in low concentration and the former are different from the latter in high concentration cases. The light intensity dependence of heat generation of both dyes in epoxy resin was linear although the optical absorption spectra showed nonlinear character. The experimental results were analyzed by four-level model to show that the difference of light intensity dependence between photocalorimetric intensity and optical absorption was based on triplet-triplet transitions.

INTRODUCTION

Erythrosine and eosin are xanthene dyes which are same class as rhodamine 6G (R6 G) and is used as materials for sensitizer. R6G is most widely used and investigated dye for many applications. Its optical properties are of particular interest. R6G forms solid solutions in non-polar plastic materials and inorganic glasses.[1,2] On the other hand, erythrosine and eosin are considered as one of the candidates for low power phase conjugation by degenerate four-wave mixing recently.[3,4] Erythrosine and eosin are of interest in that a long lifetime of the triplet state (of the order of milliseconds) and a strong absorption at wavelength of an Ar ion laser enables us to generate cw conjugate wave. Generation of a phase conjugated wave by degenerated four-wave mixing is attractive for applications to real-time holography, turbulence correction, and improvement of high-power laser-beam quality. Although several investigations have been carried out on the optical absorption and photoluminescence, and nonlinear properties of those dyes in non-polar plastic materials[5], there are few investigations on the heat generation by nonradiative processes except the work by thermal-lens measurements.[6,7] Study of heat generation by nonradiative processes is important because heat generation is related to irreversible bleaching in high light power

region. We present here the experimental results of heat generation spectra and the light intensity dependence of heat generation using photocalorimetric spectroscopy apparatus which measures direct detection of temperature changes[8] together with optical transmission measurements. Also photoacoustic spectra were measured in order to study the validity of photocalorimetric spectroscopy. It is worthwhile to investigate direct detection of temperature changes resulting from nonradiative processes following light energy absorption for short period light irradiation to avoid irreversible bleaching of dyes. The direct temperature measurements allow a more flexible sample cell arrangement than photoacoustic cell.

EXPERIMENTAL

Optically homogeneous films of epoxy resin having erythrosine and eosin dyes concentration of 10^{-4} to 10^{-1} mol/l were made with the thickness of about 100 μm. For photocalorimetric signal (PCS) measurements, we employed a thermistor as a sensor for temperature measurements.[8,9] In order to eliminate the effect of temperature changes of surrounding air, a differential thermistor was used to compensate for changes in ambient temperature. The thermistor has a nominal resistance of 12 kΩ and a sensitivity of 480 Ω/K at 20℃. For photoacoustic signal (PAS) measurements, we applied conventional microphone method.[10] PCS and PAS measurements were carried out over the range from 350 nm to 820 nm using 500 W xenon lamp. For PCS measurements, the light was permitted to irradiate the cell for 7 seconds. Neither thermistor was irradiated directly by the exciting beam during the experiment. The PCS and PAS intensities were always divided by the light intensity measured by carbon black sheet for normalization. The modulation frequency for PAS measurements was 30Hz. The light intensity dependence of the direct temperature changes was measured by using an Ar ion laser beam with a wavelength of 514.5 nm in which HOMO-LUMO transition was shown in erythrosine and eosin dyes. In order to avoid irreversible bleaching, irradiation time is restricted to 0.1 seconds.

RESULTS AND DISCUSSION

Figure 1 shows the optical transmission spectra of erythrosine and eosin dyes in epoxy resin for two different concentrations. Absorption peak near at 2.3 eV can be seen which indicates HOMO-LUMO transition in singlet states for both cases The general features can be understood in the framework of the Jabronski energy diagram. A peak at 2.5 eV is observed for both cases and it might be related to the association of erythrosine and eosin in epoxy resin. Figure 2 shows the photocalorimetric spectra for erythrosine and eosin in epoxy resin for two different concentrations. Two peaks at 2.3 eV and 2.5 eV are also observed in both cases in photocalorimetric spectra, indicating that the heat generation by nonradiative processes in erythrosine and eosin in epoxy resin are related to

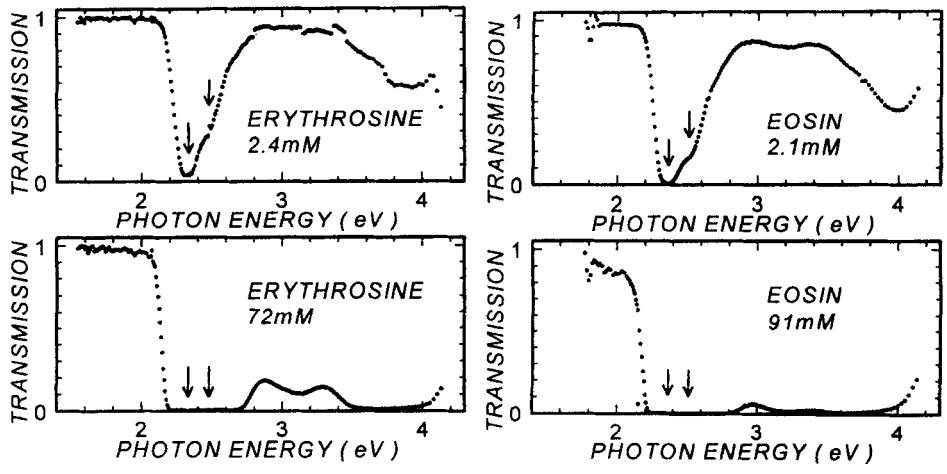

FIGURE 1 Optical transmission spectra for erythrosine and eosin dyes in epoxy resin for two different concentrations.

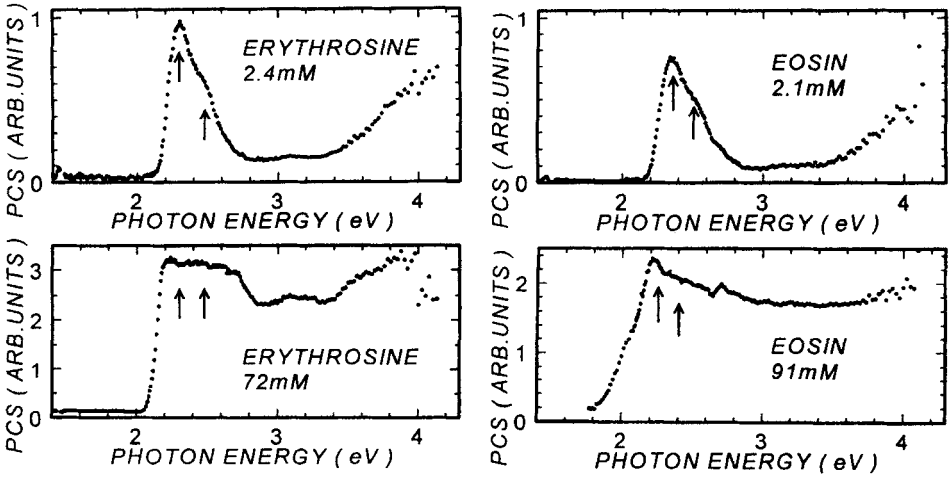

FIGURE 2 Photocalorimetric spectra (PCS) for erythrosine and eosin dyes in epoxy resin for two different concentrations.

optical absorption. Figure 3 shows photoacoustic spectra for erythrosine and eosin dyes in epoxy resin. The PCS and PAS band shapes depend on the dye concentration. That of PCS agreed with that of PAS in low concentration case and the former is different from the latter in high concentration case because of the thermal diffusion length concerned.

Figure 4 shows the incident light intensity dependence of the transmission spectra of erythrosine and eosin dyes in epoxy resin for different concentra-

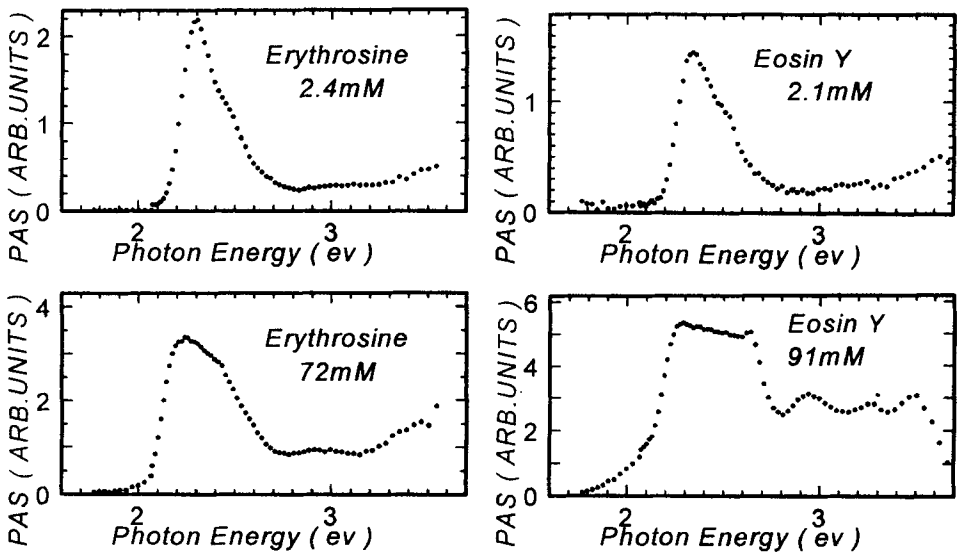

FIGURE 3 Photoacoustic spectra (PAS) for erythrosine and eosin dyes in epoxy resin for two different concentrations.

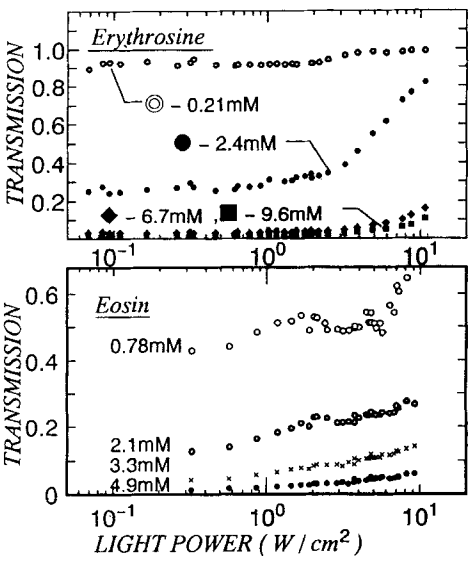

FIGURE 4 Light intensity dependence of the transmission for erythrosine and eosin dyes in epoxy resin.

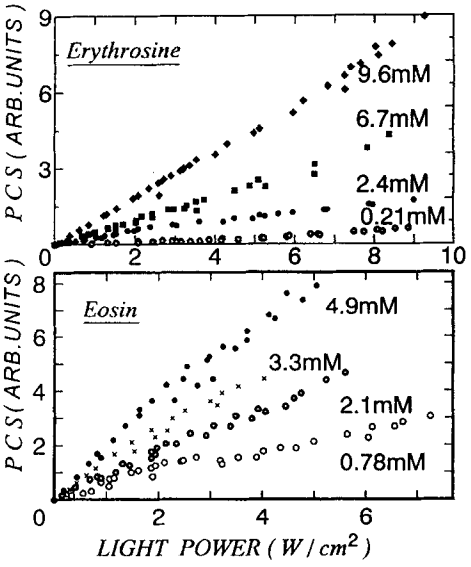

FIGURE 5 Light intensity dependence of the PCS for erythrosine and eosin dyes in epoxy resin.

tions. They display increasing transmission up to a final level, which is below unity. The measured saturation intensities (onset of saturation) are approximately 2.0 W/cm² and 0.6 W/cm² for erythrosine and eosin dyes, respectively, for

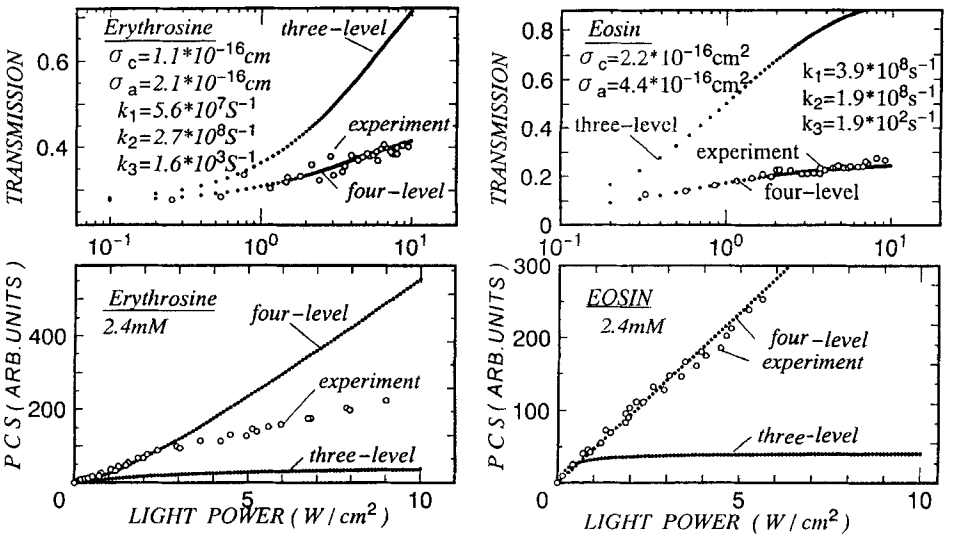

FIGURE 6 Comparison of experimental points with transmission and PCS curves derived from numerical calculations for erythrosine and eosin dyes in epoxy resin.

different dye concentrations. These values are close to those reported by Silberberg and Bar-Joseph.[3] Figure 5 shows the incident light intensity dependence of PCS for erythrosine and eosin dyes in epoxy resin for different concentrations. Figure 5 indicates that the heat generation by nonradiative processes in erythrosine and eosin dyes in epoxy resin shows linear dependence although the signal saturation in transmission (or absorption) occures as the pump laser intensity is sufficiently high. We calculated transmission (T) and PCS (P) by using rate equation analysis proposed by Giuliano and Hess.[11] They reported the light intensity dependence of transmission for several dyes using three-level scheme including two singlet and first triplet sates. Figure 6 shows that a simple three-level scheme is inadequate to describe the light intensity dependence of transmission and PCS of erythrosine and eosin dyes in epoxy resin. We included triplet-triplet transition in the rate equation and modified the model of reference 11. When light intensity is high, triplet-triplet transition have to be taken into account because energy difference between triplet-triplet transition is close to that of singlet-singlet (HOMO-LUMO) transition. According to Kasha's rule, we proposed that triplet-triplet transition is entirely nonradiative process. The stedy-state solution to the rate equation in which triplet-triplet transition is taken into account then becomes

$$T(I) = \exp(-\sigma_s A(I) IcL) \exp(-\sigma_T C(I) IcL)$$

$$P(I) = \alpha \sigma_s A(I) + \beta k_3 C(I) + \gamma \sigma_T IC(I)$$

where σ_S and σ_T are cross sections of ground state and first excited triplet state, A(I) and C(I) are populations of ground state and first excited triplet state as a function of light intensity, respectively, and c, L, k_3 are dye concentration, light pass length and triplet-singlet rate constant, and α, β, γ are constant coefficients for erythrosine and eosin dyes, respectively. Figure 6 shows the theoretical curves using the values of parameters and they show in good agreement between the experimental points and the four-level fitting curves in transmission and PCS except the case of PCS at high light intensity region for erythrosine dye in epoxy resin. The experimental points are smaller than theoretical curve in the PCS case for erythrosine. The cause of the difference between the experiments and theoretical calculations are the treatment of nonradiative process in triplet-triplet transition and the uncertainties of the values of parameters in erythrosine dye in epoxy resin. The results of our analysis are in agreement qualitatively with the phase-conjugated reflectivity calculation using four-level model by Miyanaga et al.[12]

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