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# Energy transfer and trap site formation in a photopolymer film containing carboxyl groups and benzylidene ketone dyes

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## Abstract

The photophysics of the hydrogen-bonded (HB) state and the protonated (PR) state of a photosensitizer, 2,6-bis(4′-diethylaminobenzylidene)cyclopentanone (DBC) in a polymer matrix containing carboxyl groups was investigated by fluorescence spectroscopy and decay curve analysis. The fluorescence spectrum of the excited DBC HB with the carboxyl unit was composed of emission from two species peaking at 567 and 627 nm, which were assigned to the emission from the weakly HB state (HB1) and the strongly HB state (HB2) of DBC, respectively. The excitation energy is able to migrate through the HB1 states and then transfers to the HB2 site and the PR DBC site. At low DBC concentrations, not only PR but also HB2 acts as a deep trap of the excitation energy. The concentration of PR was estimated to be ca. 40% of DBC by the fluorescence decay analysis based on the Förster kinetics. These results indicate that the photoinitiation reaction of this photopolymer system proceeds in competition with the energy transfer to these large amounts of trap sites formed by interaction between the DBC dye and the carboxyl unit of the matrix polymer.

*Keywords:* Photopolymer; Energy transfer; Fluorescence decay analysis

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## 1. Introduction

Photopolymers sensitive to visible wavelength light have been widely investigated for the development of novel laser direct imaging systems. So far various photo-initiation systems have been proposed. Most of these systems are composed of a visible dye as a sensitizer and an initiator such as titanocene derivatives [1], *N*-phenylglycine [2–4], iron arene complex [5–7], dipheny iodonium salt [8–14], triazine derivatives [15–16], and peroxyester compound [17–20]. These initiators generate reactive species by the photon energy from an excited dye. In practical direct imaging systems, photopolymers are irradiated very shortly with a raster-scanned laser beam. Therefore, there is always a strong demand for sensitivity high enough to achieve the throughput required for commercial use. To raise the sensitivity of photopolymers, the absorbed photon energy should be efficiently utilized for the reaction of photo-initiator, which is often incorporated into a kind of light harvesting system based on energy transfer among dye molecules. Therefore, it is very important to clarify the photophysics of concentrated dyes doped in polymer matrices. However, in a solid system like a photopolymer, each molecule is not in the same environment because of inhomogeneity in location, orientation, polarity and so on, even if dye molecules take a statistically random distribution in the polymer film.

Nowadays, for conservation of environment, it is highly desirable not to use organic solvents in the photographic development process. Therefore, various photopolymers consisting of carboxyl groups have been explored as binder polymers for use in aqueous alkali solutions [13,16]. However, the protic nature of the carboxyl unit has additional effects on the photophysics of dyes, because of the interaction between the dye and the acid both in the ground state and in the excited state of the dye molecule. These factors further complicate the photophysics of photopolymers.

2,6-Bis(4′-diethylaminobenzylidene)cyclopentanone

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(DBC) is a sensitizer [21] widely employed as a dye for photoimaging systems [22]. Authors previously clarified the photophysical process of DBC in polymers containing carboxyl groups, and reported that some DBC are hydrogen-bonded (HB) and some are protonated (PR) with the carboxyl groups of the binder polymer [23]. In the present article, we focus on the energy transfer phenomena between HB and PR states. The role of these states and their amounts in the polymer matrix were investigated by fluorescence spectroscopy in order to show up the whole photophysical processes of this polymer system.

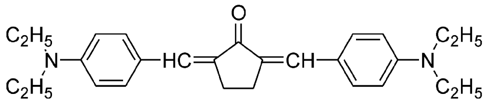
## 2. Experimental

### 2.1. Sample preparations

DBC was synthesized from 4-(*N*,*N*-diethylamino)-benzaldehyde and cyclopentanone in the presence of sodium hydroxide, and then recrystallized from a mixed solvent of benzene and hexane. Methyl methacrylate (MMA) and methacrylic acid (MAA) were copolymerized at a ratio of MMA/MAA = 77:23 in a mixed solvent of methanol and ethyl acetate. The ratio of MMA/MAA in the copolymer was characterized by acid value, and the weight-average molecular weight was measured to be 90,000 by GPC. The copolymer thus obtained was used as a matrix polymer for sample films, which were prepared on a glass plate by casting the mixed solution of DBC and the copolymer in methanol, ethyl acetate and DMF. The films were ca. 0.8 μm in thickness.

### 2.2. Photophysical measurements

Absorption spectra were measured with a Shimadzu UV–visible spectrophotometer UV-160. Corrected fluorescence spectra were measured with a Hitachi fluorescence spectrophotometer F-4100. Excitation band pass was 1.5 nm and emission band pass was 5.0 nm. Fluorescence decay curves were measured by a single-photon-counting method. The pulsed excitation light was obtained with a Spectra-Physics synchronously pumped mode-locked dye laser. The emission from the sample was detected with a microchannel plate photomultiplier (Hamamatsu R1564U-01). The overall response function of the photon-counting system had an fwhm of 75 ps.



DBC

Scheme 1.

### 2.3. Parameters in Förster kinetics

The probability of Förster type energy transfer per unit time, $W_{DA}$, from an excited donor molecule D to an acceptor molecule A, is given by Eq. (1) [24],

$$W_{DA} = 1/T_{DO}(R_{DA}/r_{DA})^6 \tag{1}$$

where $r_{DA}$ is the distance between D and A, and $R_{DA}$ is the critical transfer radius at which donor D has an equal probability of energy transfer to other decay processes, and $T_{DO}$ is the unquenched lifetime of D. This $R_{DA}$ is related to the overlapping of fluorescence spectrum of D and the absorption spectrum of A.

Given that the donor and acceptor molecules are randomly distributed in a solid matrix, the decay function of donor fluorescence is expressed by Eq. (2) [25–27],

$$I(t) = I_0 \exp(-t/T_{DO})\exp[-2g(t/T_{DO})^{1/2}] \tag{2}$$

where

$$g = [A]/C_{DA} \tag{3}$$

$$C_{DA} = 3000/(2\pi^{3/2}NR_{DA}^3) = (7.66\times 10^{-8}/R_{DA})^3 \tag{4}$$

In Eq. (3), [A] represents the concentration of the acceptor molecule and $C_{DA}$ is the critical concentration at which the efficiency of energy transfer from the donor becomes 76% of the whole deactivation processes.

## 3. Results and discussion

### 3.1. Absorption and fluorescence spectra of DBC

The absorption spectrum of $6.0\times 10^{-2}$ M DBC in the copolymer film gave a feature similar to the absorption spectra of DBC in organic solvents. The spectrum is almost independent of the concentration of DBC in a wide range of $10^{-3}$–$10^{-1}$ M. These results indicate that the DBC dyes have little intermolecular interaction even in the highly doped film, and also that they have no interaction with the carboxyl groups of the matrix polymer in the ground state.

The fluorescence spectra of films with DBC at $1.8\times 10^{-3}$ M, $6.0\times 10^{-3}$ M, $1.8\times 10^{-2}$ M, and $6.0\times 10^{-2}$ M, are shown in Fig. 1. As previously reported [23], this DBC-copolymer system is characterized by the formation of HB DBC and PR DBC, both of which are species in the excited state interacting with protons from the carboxyl units of the copolymer. Although the fluorescence spectra were markedly altered with the increase of DBC concentration, there was no difference in the absorption spectra as mentioned before, and also the excitation spectra monitored at the HB band (ca. 600 nm) and the PR band (ca. 720 nm) showed no difference and coincided in position with the absorption spectra of DBC. This behavior indicates that the corresponding ground states for HB and PR are the same as for DBC, and the interaction only in the excited

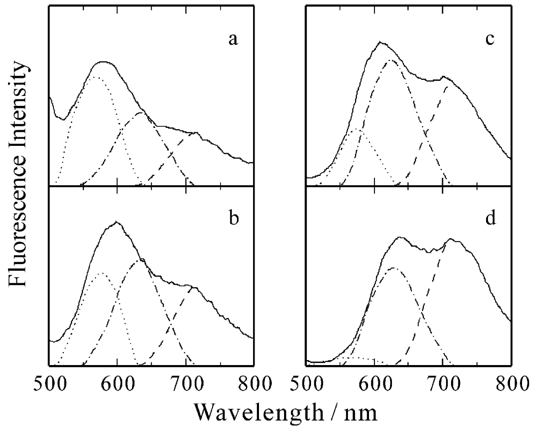


Fig. 1. Fluorescence spectra of DBC in the copolymer film: (a) $1.8 \times 10^{-3}$ M; (b) $6.0 \times 10^{-3}$ M; (c) $1.8 \times 10^{-2}$ M; (d) $6.0 \times 10^{-2}$ M. (- - -) component spectrum for HB1, (– – –) spectrum for HB2, (— — —) spectrum for PR.

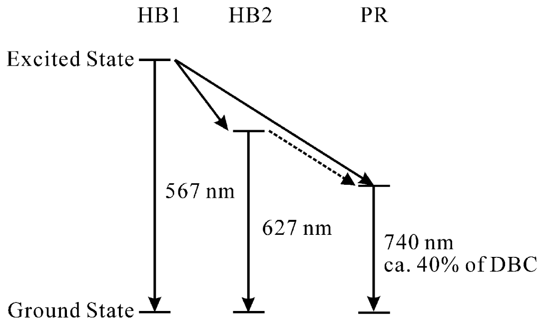
state gives rise to the drastic changes in the fluorescence spectra.

The spectra in Fig. 1 could be divided into the component spectra by a curve fitting procedure, yielding at least three components with peak intensities at 567, 620, and 720 nm. All spectra shown by solid lines in Fig. 1 were reproduced by summation of the three component spectra with their appropriate fractions as listed in Table 1. The HB band, which appeared as a broad band around 600 nm, was separated into two species, HB1 (567 nm) and HB2 (620 nm), in addition to the PR band at 720 nm. We assigned these plural HBs to the HB states because DBC in aprotic polymer matrices showed fluorescence at a shorter wavelength of 550 nm. Furthermore, the spectra shifted to longer wavelengths depending on the degree of interaction, in a manner similar to the spectra of DBC observed in alcoholic (proton donating) solvents. As shown in Table 1, the increase of DBC concentration in the polymer film resulted in a marked decrease of the HB1 fraction, instead of the steep rise of HB2 and PR fractions, although the PR/HB2 ratio was kept almost constant up to $1.8 \times 10^{-2}$ M DBC. These results suggest that the excitation energy on HB1 is transferred to the HB2 site and the PR site with a given probability, and the latter two act as the trap sites of energy in this film.

Taking into account these observations, the energy diagram of this system is illustrated in Scheme 2, which shows the energy levels of three representative species together with the energy dissipation routes among them. The solid arrows from HB1 to HB2 and PR represent the processes of energy migration and transfer. The broken arrow between HB2 and PR shows the energy transfer process that occurs only at high concentrations of DBC as described later. Scheme 2 provides an overview of this system, which is quite useful for understanding the photophysics of this system. However, the quantitative details of the energy consumption are unknown yet.

Table 1
Relative fluorescence intensities of HB1, HB2 and PR

| Concentration of DBC (M) | Relative fluorescence intensities | | | |
|---|---|---|---|---|
| | HB1 | HB2 | PR | PR/HB2 |
| $1.8 \times 10^{-3}$ | 0.39 | 0.32 | 0.29 | 0.91 |
| $6.0 \times 10^{-3}$ | 0.28 | 0.38 | 0.34 | 0.90 |
| $1.8 \times 10^{-2}$ | 0.15 | 0.44 | 0.41 | 0.93 |
| $6.0 \times 10^{-2}$ | 0.02 | 0.43 | 0.55 | 1.3 |



Scheme 2.

### 3.2. Fluorescence decay analysis

Fluorescence decay curves of DBC in the copolymer film were measured at 567, 627 and 740 nm by a picosecond laser-single photon counting system. The upper and middle parts of Fig. 2 show the decays for HB1 and HB2, respectively. The decay profile of HB1 was different from that of HB2; for example, the decay of HB1 became much faster as the DBC concentration increased, while the decay of HB2 was independent of the concentration up to $1.8 \times 10^{-2}$ M. This indicates that the excitation energy of HB1 transfers to the acceptor sites having lower energy levels (HB2 and PR), and the transfer process becomes faster at higher concentrations of DBC because of the increase of these acceptor sites. Although the fluorescence of HB1 shows non-single exponential decays due to the inhomogeneous distribution of DBC dyes both in the space and the energy levels, the average lifetime was rapidly shortened with the increase of DBC concentration. The energy migration and transfer through the HB1 states are responsible for this behavior.

On the other hand, the decay times for PR, which are shown in the lower part of Fig. 2, were almost constant irrespective of the large variation of the DBC concentration. The time profiles showed rise-and-decay features; the rise components were 30–120 ps depending on the concentration of DBC, but the decay components were around 1.7 ns for all samples. Therefore, the PR site is considered to be excited mainly through the energy transfer from the HB species, and then the energy is dissipated with its intrinsic decay rate without any intermolecular quenching, i.e. PR is the final stop of the excitation energy.

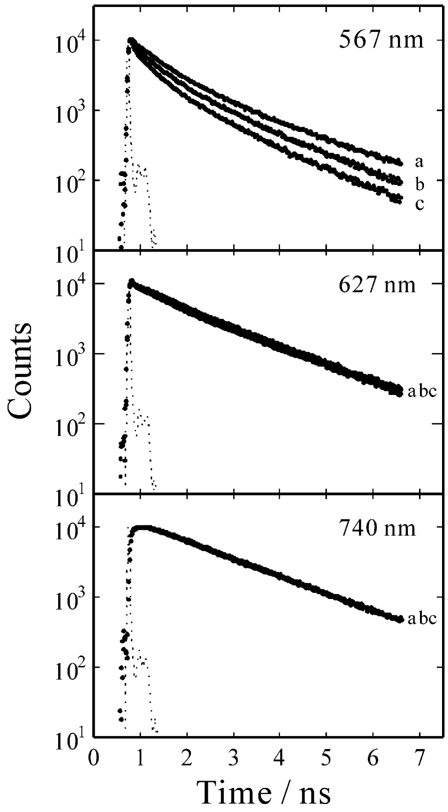


Fig. 2. Fluorescence decay curves of DBC in the copolymer film observed at 567 nm (upper part), 627 nm (middle part) and 740 nm (lower part). Concentration of DBC: (a) $1.8 \times 10^{-3}$ M, (b) $6.0 \times 10^{-3}$ M, (c) $1.8 \times 10^{-2}$ M.

### 3.3. Evaluation of the quantities of PR sites

Fig. 3 shows the decay curve of $6.0 \times 10^{-2}$ M DBC in the copolymer film at 627 nm. Comparing Fig. 3 and the middle part of Fig. 2 shows that further increase of the DBC to $6.0 \times 10^{-2}$ M resulted in a decrease of the HB2 lifetime, indicating that another energy transfer process from HB2 to PR started because of the large population of the PR site in the polymer matrices. As described above, the energy transfer from HB2 to PR occurs at DBC concentrations higher than $1.8 \times 10^{-2}$ M. Therefore, the fluorescence decay of HB2 (627 nm) was analyzed by Eq. (2) for the sample at $6.0 \times 10^{-2}$ M in order to evaluate the quantities of PR sites in the copolymer film. The parameters used in this analysis were as follows. The critical energy transfer radius for the Förster type transfer ($R_{DA}$) was calculated to be 2.0 nm from the overlapping area of the absorption spectrum and the fluorescence spectrum. The unquenched lifetime of HB2 ($T_{DO}$) was measured as 1.78 ns from the decay curve at a dilute concentration of $6.0 \times 10^{-3}$ M, at which the energy transfer from HB2 to PR did not occur as described above. Using these parameters, the decay curve, $I(t)$ in Eq. (2) was calculated as a function of the acceptor concentration [A]; the results were shown with the solid lines in Fig. 3. The actual decay curve of HB2 was fitted best at $[A] = 2.5 \times 10^{-2}$ M. This high concentration of PR site in the copolymer film indicates that about 40% of the doped DBC is converted to the PR site in the excited states.

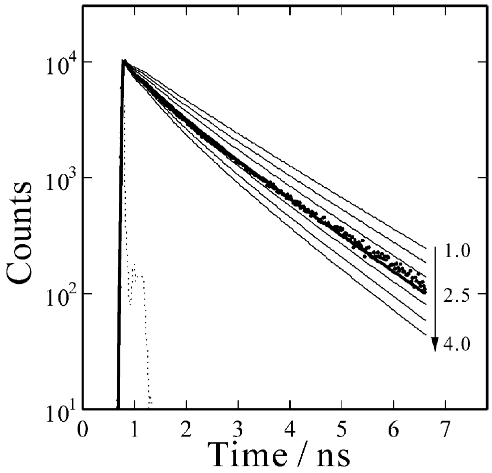


Fig. 3. Fluorescence decay curves of $6.0 \times 10^{-2}$ M DBC in the copolymer film observed at 627 and calculated lines as a function of the acceptor concentration.

### 3.4. Roles of the HB2 and PR in photopolymers

The first line in Table 1 shows the fraction of intensity for the HB1, HB2 and PR emission at $1.8 \times 10^{-3}$ M. Under such dilute conditions, the spectrum will be of the isolated dyes without any energy transfer effect. It is worth noting that the fractions were 0.3–0.4 for all species, suggesting that the excited states of DBC dyes have three degrees of interactions with a nearly equal probability, although uncertainty still remains in this estimation because of the lack of exact evaluation of fluorescence quantum efficiency for each species. Since, it was very difficult to determine the quantum efficiency of the fluorescent components, we used the time-resolving decay analysis based on energy transfer kinetics, which provided invaluable data for the amounts of them.

The current work has clarified the kinetic scheme of the photopolymer system. In actual use, an appropriate amount of initiator is incorporated into the dye–copolymer films, in which the photon energy absorbed by a dye is efficiently transferred to the initiator to start the chemical reaction. To achieve a highly sensitive photoreaction, it is crucially important to design highly efficient energy migration and transfer systems and also to reduce the amount of trap sites for the excitation energies as small as possible. In the present polymer system, DBC was employed as an energy donating chromophore, but it also yielded the HB2 and PR trap sites in the protic polymer matrices. It is expected that the sensitivity could be markedly improved by using aprotic polymers as a base polymer and by structural design of the dye molecule to prevent it from hydrogen-bonding and protonation.

## 4. Conclusions

The photophysics of DBC in polymer matrices containing carboxyl groups were investigated by absorption and fluorescence spectroscopy and time-resolving decay analysis. The energy diagram of DBC in this photopolymer system was clarified as shown in Scheme 2, in which the kinetics is characterized by the competitive energy migration and transfer to two kinds of trap sites: the HB2 site and the PR site. Both sites were formed with high rates of the doped DBC, showing strong interactions between the carboxyl unit and the dye molecule. These analyses clearly indicate that appropriate control of the dye–polymer interaction is needed to satisfy the requirements both of the enhanced sensitivity and development ability in practical use.

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