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Photophysics of 2,6-bis(4′-diethylaminobenzylidene)cyclopentanone in a polymer matrix containing carboxyl groups

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Abstract

The photophysics of a photosensitizer, 2,6-bis(4′-diethylaminobenzylidene)cyclopentanone (DBC) in solvents and polymer matrices containing carboxyl groups is reported. In acetic acid, the fluorescence spectrum of DBC showed two bands of fluorescence with individual lifetimes. Two emitting species were also observed in polymer matrices containing carboxyl groups. The shorter and longer wavelength fluorescence bands are assigned to the emission from DBCs hydrogen bonded (HB) and protonated (PR) with the carbonyl group, respectively. As the concentration of DBC increased, the ratio of PR fluorescence intensity to HB fluorescence intensity increased, and the lifetime of HB fluorescence decreased. The energy level of HB in the excited state is dispersive depending on the magnitude of hydrogen bonding, resulting in the gradual red-shift of fluorescence spectra with the increase of carboxyl content and DBC concentration. Efficient energy transfer was observed from the HB to PR-DBC which acts as an energy trap in the polymer matrix containing carboxyl groups.

Keywords: Polymer matrix; Photopolymers; Photoprinting systems; Sensitizer

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1. Introduction

Photopolymers have been widely used in various areas of application, for example, printing plates, resists for printed circuit boards, and photocurable ink [1]. Recently photopolymers sensitive to visible laser light are being studied for direct imaging materials [2–5]. In these systems, visible dyes are used as sensitizers for photoinitiation [3–8], and polymers containing carboxyl groups are used as binders which are developable in aqueous alkali solutions [3]. 2,6-Bis(4′-diethylaminobenzylidene)cyclopentanone (DBC) (Scheme 1) is one of well-known sensitizers [9] and widely employed for photoprinting systems [10], although the photophysics of dyes in polymer matrix has not yet been clarified. In this article, we report photophysics of DBC in polymer matrix containing carboxyl group, and reveal the remarkable effect of hydrogen bonding on the deactivation processes of the excitation energies.

2. Experimental details

DBC is synthesized from 4-(*N*,*N*-diethylamino)benzaldehyde and cyclopentanone in the presence of sodium hydroxide, and recrystallized in a mixed solvent of benzene and hexane. Methyl methacrylate (MMA) and methacrylic acid (MAA) were copolymerized in a mixed solvent of methanol and ethyl acetate. The ratio of MMA/MAA in the copolymer is characterized by acid value. Polymer films containing DBC were cast by a mixed solvent of methanol, ethyl acetate, and DMF. The thickness of films obtained is 0.8 μm. Absorption spectra were measured with a Shimadzu UV–VIS 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 time-resolved fluorescence spectra were obtained from the decay curves recorded at every 3 nm of wavelength from 540 to 800 nm. The pulsed excitation light was obtained with a Spectra-Physics dye laser. The emission from the samples was detected with a microchannel plate photomultiplier (Hamamatsu R1564U-0l). The FWHM of the overall excitation pulse was 75 ps.

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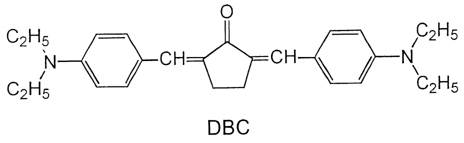


DBC

Scheme 1.

3. Results and discussion

3.1. Spectroscopy in solvents

The absorption spectra of DBC in various solvents are shown in Fig. 1. The bands around 450–500 nm are largely affected by the kind of solvents used. These bands are assigned to the intramolecular charge transfer transition from aminobenzene group to carbonyl group [11,12]. The absorption wavelength in DMF is longer than that in toluene. This is due to the stabilization of the excited states by increasing the polarity of solvents, because the excited intramolecular charge transfer state of DBC is polar compared with that of the ground state. However, the absorption wavelength in methanol is longer than that in DMF. This phenomenon is not due to the stabilization by increasing polarity of solvent, because DMF has larger dielectric constant than methanol. This result suggests that the hydrogen bonding between the hydroxyl group of methanol and the carbonyl group of DBC give rise to the red-shift of the absorption band. The molar extinction coefficient of absorption maximum in acetic acid is much smaller than those in other solvents, indicating that the interaction of DBC with acetic acid is different from other solvents. The absorption spectrum of DBC in toluene had a shoulder, on the other hand no shoulder was observed in polar solvents. This is due to the dipole–dipole interaction of the intramolecular charge-transfer state in polar solvents [9].

The fluorescence spectra of DBC in various solvents are shown in Fig. 2. The wavelength at fluorescence maximum is remarkably affected by the kind of solvent. The red-shift of fluorescence spectrum from that in toluene to that in DMF is again due to the stabilization of the excited states by increasing the polarity of the solvent. Stokes shift of DBC in methanol is 139 nm, which is much larger than 82 nm in DMF. This phenomenon indicates that some additional stabilization of excited DBC in methanol occurs during the excited lifetime. This stabilization seems to be caused by hydrogen bonding as suggested in the absorption spectra. DBC in acetic acid shows two fluorescence peaks at around 620 and 740 nm. The lifetime of these two fluorescence are different as shown in Table 1. These data indicate that these are fluorescence from different excited states. The shorter wavelength fluorescence is assigned to be one from excited DBC hydrogen bonded (HB) with carboxyl group, because the wavelength of the shorter fluorescence is close to that of the fluorescence in methanol. The longer wavelength fluorescence is supposed to be from excited DBC protonated (PR) by carboxyl group of acetic acid.

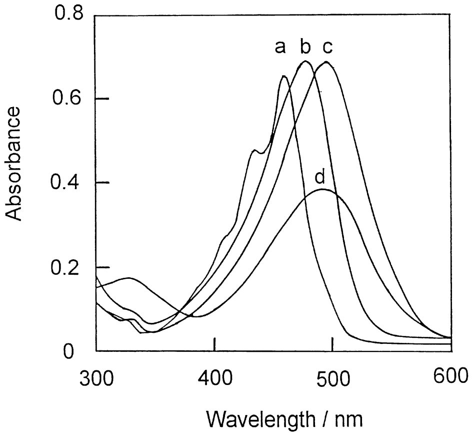


Fig. 1. Absorption spectra of 1.0×10^{-5} M DBC: a, in toluene; b, in DMF; c, in methanol; d, in acetic acid.

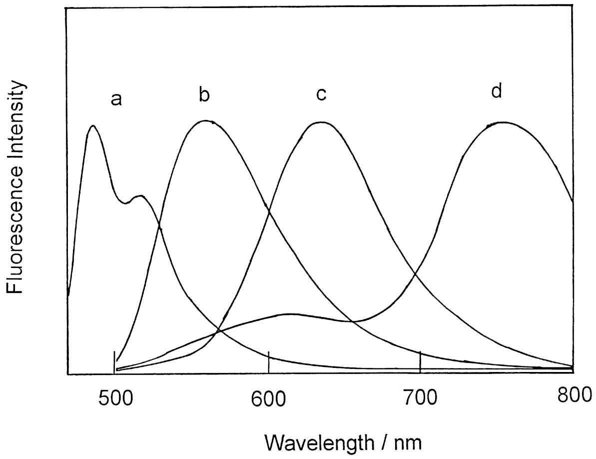


Fig. 2. Fluorescence spectra of DBC: a, in toluene; b, in DMF; c, in methanol; d, in acetic acid.

3.2. Photophysics in polymer matrix containing carboxyl groups

3.2.1. DBC spectra dependent on carboxyl content

Three kinds of polymers, polymer 1 (MMA/MAA=100/0 mol%), polymer 2 (MMA/MAA=77/23 mol%) and polymer 3 (MMA/MAA=27/73 mol%) were used as matrices. The absorption spectra of DBC in these three polymers are shown in Fig. 3. As the concentration of the carboxyl group

Table 1
Fluorescence lifetime of DBC in various solvents

Solvent	Fluorescence lifetime (ps)	
	627 (nm)	740 (nm)
Toluene	340	
DMF	770	
Methanol	160	
Acetic acid	63	220

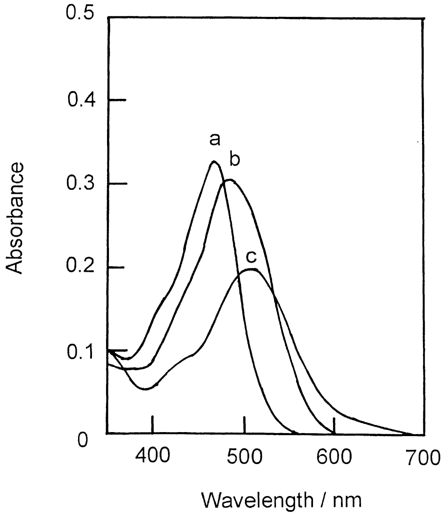


Fig. 3. Absorption spectra of 6.0×10^{-2} M DBC: a, Polymer 1; b, in Polymer 2; c, in Polymer 3.

increased, the absorption bands shifted to the red side and the extinction coefficient decreased. This trend is similar to that of solution systems as described above. The fluorescence spectra of DBC in these polymers are shown in Fig. 4. Although in polymer 1, DBC showed a simple fluorescence spectrum peaked at 550 nm, DBC in polymers 2 and 3 provided two bands at a shorter wavelength (emission 1) and a longer wavelength (emission 2).

Emission 1 in these two polymers locates at longer wavelengths than the emission of DBC in polymer 1. Judging from the result obtained in various solvents, the shorter emitting species in these two polymers is assigned to the excited DBC-HB between the carbonyl group of DBC and the carboxyl group of the matrix polymer. The peak wavelength of emission 1 in polymer 3 is further shifted to the red side compared to polymer 2. This can be explained by the degree of hydrogen bonding. Since the mobility of molecules in the polymer matrix is very low, the environment of each dye is different, molecule by molecule, resulting in the different degree of hydrogen bonding. This means that the energy level of DBC in the excited state must be dispersive. Due to the large content of carboxyl groups in polymer 3, the DBC molecules could find more suitable site for stabilization easily than those in polymer 2. The fluorescence lifetime of DBC in polymers 1–3 are shown in Table 2. The decay curves of these fluorescence are not of single component because of dispersion of interaction between DBC and polymers. The decay curves were fitted with a sum of two exponentials, and the weighed average lifetimes were calculated from these two decay constants.

Table 2
Fluorescence lifetime of DBC in poly(MMA-co-MAA) films[a]

Matrix polymer	MMA/MAA (mole ratio)	Fluorescence lifetime (ps) (567 nm)[b]
Polymer 1	100/0	710
Polymer 2	77/23	930
Polymer 3	27/73	1240

[a] DBC=1.8×10^{-3} M.

[b] Weighed average lifetimes calculated from two decay components.

Polymers 2 and 3 showed another emission (emission 2) at 710 nm. The peak wavelength of this emission is similar to that of DBC in acetic acid. Therefore, this emission can be assigned to the excited DBC-PR by carboxyl group of the copolymer.

3.2.2. Concentration dependence

The absorption spectra of 1.8×10^{-3} and 6.0×10^{-2} M DBC in polymer 2 were measured and no difference between these two spectra was observed. The fluorescence spectra of DBC at various concentrations in polymer 2 are shown in Fig. 5. As the concentration of DBC increased,

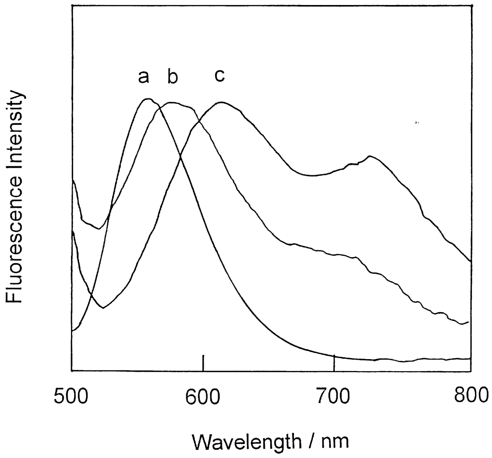


Fig. 4. Fluorescence spectra of 1.8×10^{-3} M DBC: a, in Polymer 1; b, in Polymer 2; c, in Polymer 3.

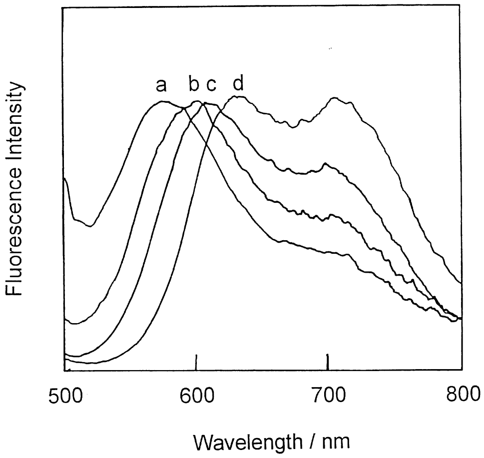


Fig. 5. Fluorescence spectra of DBC in Polymer 2: a, 1.8×10^{-3} M; b, 6.0×10^{-3} M; c, 1.8×10^{-2} M; d, 6.0×10^{-2} M.

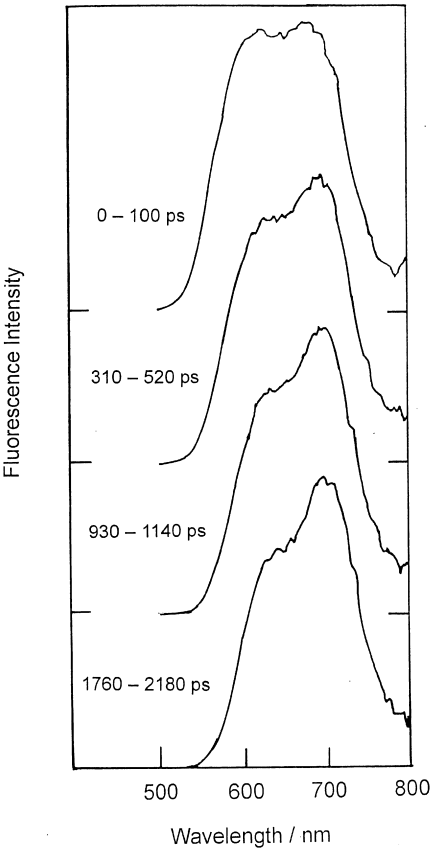


Fig. 6. Time resolved fluorescence spectra of 6.0×10^{-2} M DBC in Polymer 2.

the peak of emission 1 shifted to the red side and the ratio of emission 2 to emission 1 increased. This red-shift of emission 1 can be explained by the degree of hydrogen bonding mentioned above, and by the intermolecular energy migration from weakly HB species to more strongly HB species. The increase of emission 2 indicates that the efficient energy migration among HB species also increase the probability of the intermolecular energy transfer from HB species to PR species because of the short distance between DBC molecules at high concentrations.

The time-resolved fluorescence spectra of 6×10^{-2} M DBC in polymer 2 are shown in Fig. 6. Emission 2 already exists at 100 ps after the excitation, and emission 1 decays rapidly, being of very small intensity at 520 ps. This indicates clearly that emissions 1 and 2 are individual species.

The decay curves of emissions 1 and 2 are shown in Figs. 7 and 8, respectively. As the concentration of DBC increased, the lifetime of emission 1 decreased. On the other hand, the time-dependent fluorescence intensity curves for emission 2 provided rise-and-decay features; the rise components were 30–120 ps depending on the concentration of DBC, and the decay components were kept constant to 1.7 ns. This phenomenon means that the emitting species of emission 2 is not directly excited through photo-absorption. From these facts, it is safely said that the energy transfer from HB species to PR species occurs. The constant lifetime of emission 2 indicates that the PR species is the final excited state acting as an energy trap for the migrating energies in the polymer matrix.

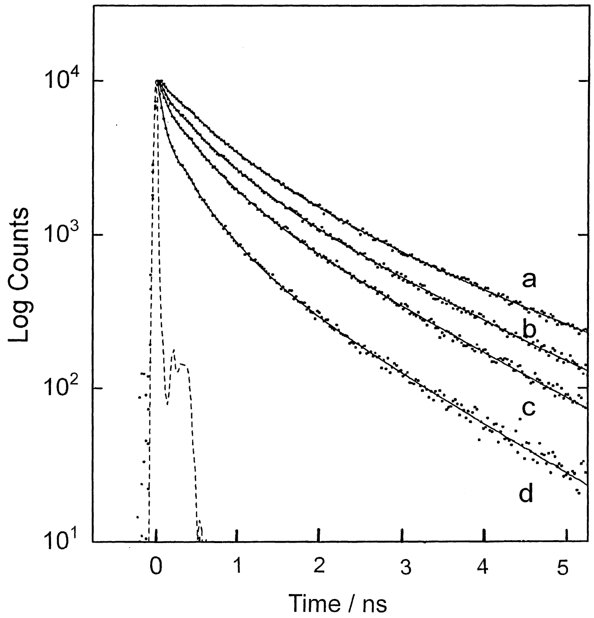


Fig. 7. Fluorescence decay curves of DBC in Polymer 2 observed at 567 nm. Concentrations of DBC are: a, 1.8×10^{-3} M; b, 6.0×10^{-3} M; c, 1.8×10^{-2} M; d, 6.0×10^{-2} M.

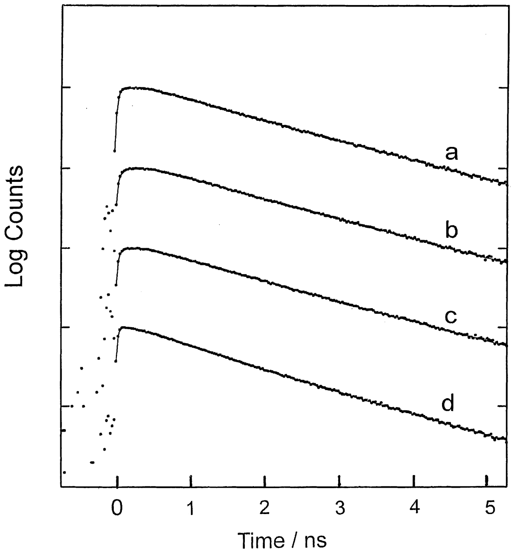
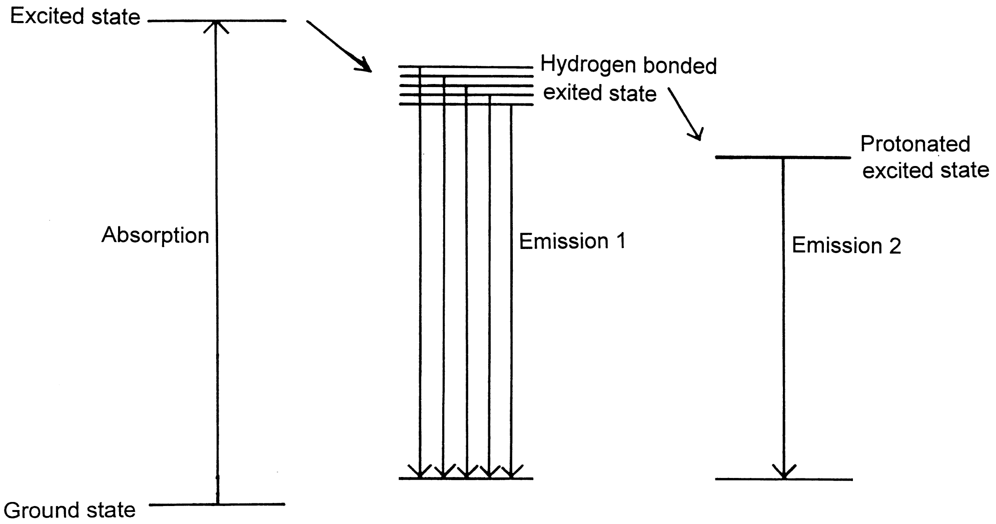


Fig. 8. Fluorescence decay curves of DBC in Polymer 2 observed at 740 nm. Concentrations of DBC are: a, 1.8×10^{-3} M; b, 6.0×10^{-3} M; c, 1.8×10^{-2} M; d, 6.0×10^{-2} M.



Scheme 2.

4. Conclusions

The photophysical processes of DBC in polymer matrices containing carboxyl groups were investigated by absorption and fluorescence spectroscopy. The excited state of DBC was remarkably affected by the polarity of surroundings, furthermore, showing two states, i.e. HB and PR ones with the carboxyl units. The energy diagrams in polymer solids studied are shown in Scheme 2, where the energy migration among HB state takes place efficiently with the increase of DBC concentration. The energy level of HB state is dispersive and finally the excitation energy transfers from HB species to PR species which acts as a trap site in the samples. These findings indicate that the polymer bearing carboxyl units serves not only as an alkali water-soluble matrix but as a significant factor determining the photophysics of the photosensitizer dye.

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