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Synthesis of benzylideneketone dyes and their photochemical properties as a sensitizer for alkali-developable photopolymerization systems

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Abstract

A series of benzylideneketone dye derivatives were synthesized and the relationship between their molecular structure and their photochemical characteristics as a sensitizer in photopolymerization systems was investigated. Although 2,5-bis(4-diethylaminobenzylidene)cyclopentanone (Dye-**1**) is widely used as a photosensitizer, it forms hydrogen bonds and is protonated in protic solvents in its excited state. As dyes having substituents with lower electron-donating ability than Dye-**1** did not form a hydrogen-bonded nor a protonated excited state, alkali-developable photopolymerization systems incorporating these dyes as sensitizer is expected to have high sensitivity, because the system possesses efficient absorbed photon energy migration. Benzylideneketone dyes having rigid amino groups showed red shifts in both their absorption and fluorescence spectra compared with Dye-**1**. In contrast, dyes having a six-membered ring structure at their center displayed blue shifts in absorption and fluorescence spectra. These phenomena are ascribed to an increase and decrease in degree of conjugation, respectively.

Keywords: Benzylideneketone dye; Sensitizer; Photopolymerization systems; Electron-donating ability; Rigidized amino group; Ketone ring structure

1. Introduction

Sensitivity in the visible region is required for photopolymerization systems used in direct laser imaging systems. In the various photoinitiation systems sensitive to visible light that have been investigated [1–20], the majority of the photochemical reaction systems are triggered by light absorption by sensitizing dyes incorporated in the system, which generate reactive species such as radicals and cations by reaction between the excited dye and the initiator in the system.

2,5-Bis(4-diethylaminobenzylidene)cyclopentanone (Dye-**1**) is a well-known sensitizing dye [21] that is widely employed in photoinitiation systems [22–26]. However, the photophysics of Dye-**1** and the role of its chemical components in the reaction mechanism in photopolymerization have not been investigated. Previous studies on the photophysical processes of Dye-**1** in a photopolymerization system comprising poly(methyl methacrylate-*co*-methacrylic acid), in which the carboxy unit was required for development in aqueous alkali solutions, revealed that the excited states are characterized by the formation of hydrogen-bonded and protonated states with the carboxy units [27,28]. The energy migration phenomenon among dye molecules plays a critical role in photoinitiation, which proceeds in competition with energy transfer to trap sites formed in hydrogen-bonded and protonated states.

In this study, several benzylideneketone dye derivatives were synthesized. Dye-**2** and Dye-**3** were designed from the viewpoint of the electron-donating ability of the substituent group whilst Dye-**4** and Dye-**5** were prepared to study the effect of the rigidity of amino groups; Dye-**6** and Dye-**7** have a linear conjugated ketone and a cyclohexanone structure,

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respectively, at the center of the dye molecule, instead of the cyclopentane ring present in Dye-**1**.

2. Experimental

2.1. Sample preparation

The dyes shown in Fig. 1 were synthesized as follows.

*2.1.1. 2,5-Bis(4-diethylaminobenzylidene)cyclopentanone (Dye-**1**)*

4-(*N*,*N*-Diethylamino)benzaldehyde (3.54 g) and cyclopentanone (0.98 g) were dissolved in 50 ml of 2-butanol containing 2.5 g of 25 wt% NaOH aqueous solution. The mixture was refluxed for 3 h and then was chilled and the precipitate collected and recrystallized in a mixed solvent of benzene and hexane (benzene/hexane = 10/90 wt%). ^{1}H NMR ($CDCl_3$) δ 7.51−7.47 (m, 6H), 6.69−6.65 (d, 4H), 3.44−3.34 (q, 8H), 3.04 (s, 4H), 1.21−1.14 (t, 12H).

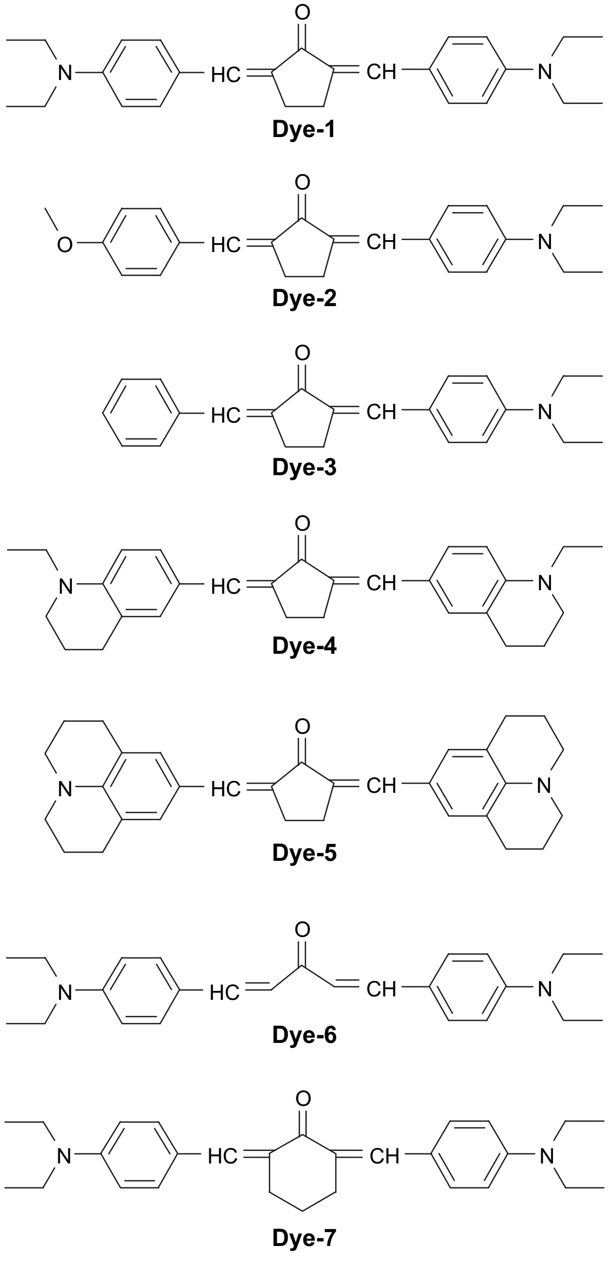

Fig. 1. Molecular structures of Dye-**1** to Dye-**7**.

*2.1.2. 2-(4-Diethylaminobenzylidene)-5-(4-methoxybenzylidene)cyclopentanone (Dye-**2**)*

2-(4-Diethylaminobenzylidene)cyclopentanone (473 mg), which was obtained by the reaction of 1-morpholino-1-cyclopentene with 4-(*N*,*N*-diethylamino)benzaldehyde, and 4-methoxybenzaldehyde (272 mg), were dissolved in 6 ml of 2-butanol containing 0.32 g of 25% aq. NaOH solution. The mixture was refluxed for 2 h and the product was collected and purified by chromatography with methylene chloride as eluent. ^{1}H NMR ($CDCl_3$) δ 7.59−7.44 (m, 6H), 6.98−6.64 (m, 4H), 3.82 (s, 3H), 3.53−3.26 (q, 4H), 3.05 (s, 4H), 1.30−1.12 (t, 6H).

*2.1.3. 2-Benzylidene-5-(4-diethylaminobenzylidene)-cyclopentanone (Dye-**3**)*

2-(4-Diethylaminobenzylidene)cyclopentanone (415 mg), which was obtained by the reaction of 1-morpholino-1-cyclopentene with 4-(*N*,*N*-diethylamino)benzaldehyde, and benzaldehyde (180 mg), were dissolved in 5.1 ml of 2-butanol containing 0.27 g of 25% aq. NaOH solution. The mixture was refluxed for 0.5 h and the product was purified by chromatography with methylene chloride as eluent. ^{1}H NMR ($CDCl_3$) δ 7.55−7.31 (m, 9H), 6.72−6.61 (d, 2H), 3.53−3.26 (q, 4H), 3.06 (s, 4H), 1.28−1.10 (t, 6H).

*2.1.4. 2,5-Bis{[6-(1-ethyl-1,2,3,4-tetrahydroquinolyl)]-methylene}cyclopentanone (Dye-**4**)*

1-Ethyl-1,2,3,4-tetrahydroquinoline was prepared by the reaction of 1,2,3,4-tetrahydroquinoline with ethyl iodide. 6-(1-Ethyl-1,2,3,4-tetrahydroqunolyl) aldehyde (9.17 g), which was obtained by the reaction of 1-ethyl-1,2,3,4-tetrahydroquinoline with $POCl_3$, and cyclopentanone (20.0 g) were dissolved in 115 ml of 2-butanol containing 5.7 g of 25% aq. NaOH solution. The mixture was refluxed for 3 h and then was chilled and the precipitate was collected. ^{1}H NMR ($CDCl_3$) δ 7.42−7.19 (m, 6H), 6.63−6.52 (d, 2H), 3.49−3.23 (m, 8H), 3.00 (s, 4H), 2.82−2.67 (t, 4H), 2.10−1.80 (m, 4H), 1.25−1.07 (t, 6H).

*2.1.5. 2,5-Bis[(6-julolidyl)methylene]cyclopentanone (Dye-**5**)*

6-Julolidylaldehyde (650 mg), which was obtained by the reaction of julolidyne with $POCl_3$, and cyclopentanone (137 mg), were dissolved in 8.1 ml of 2-butanol containing 0.41 g of 25% aq. NaOH solution. The mixture was refluxed for 3 h and the product was collected and washed with 2-butanol. ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 2H), 7.05 (s, 4H), 3.29−3.14 (t, 8H), 3.00 (s, 4H), 2.84−2.63 (t, 8H), 2.12−1.81 (m, 8H).

*2.1.6. 1,3-Bis(4-diethylaminobenzylidene)acetone (Dye-**6**)*

4-(*N*,*N*-Diethylamino)benzaldehyde (3.54 g) and acetone (0.58 g) were dissolved in 50 ml of 2-butanol containing

2.5 g of 25% aq. NaOH solution. The mixture was stirred at room temperature for 7 h and the product was collected. ^{1}H NMR ($CDCl_3$) δ 7.74–7.35 (m, 6H), 6.91–6.56 (m, 6H), 3.52–3.25 (q, 8H), 1.28–1.10 (t, 12H).

2.1.7. *2,6-Bis(4-diethylaminobenzylidene)cyclohexanone (Dye-**7**)*

4-(*N*,*N*-Diethylamino)benzaldehyde (3.54 g) and cyclohexanone (0.98 g) were dissolved in 50 ml of 2-butanol containing 2.5 g of 25% aq. NaOH solution. The mixture was refluxed for 4.5 h and the product collected and recrystallized in benzene. ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 2H), 7.46–7.23 (m, 4H), 6.70–6.60 (d, 4H), 3.51–3.24 (q, 8H), 2.93–2.84 (t, 4H), 1.88–1.75 (t, 2H), 1.23–1.10 (t, 12H).

2.2. *Measurements*

Absorption spectra were measured with a Shimadzu UV–vis spectrophotometer UV-160 in solutions of concentration in the range 10^{-5} M. Fluorescence spectra were measured with a Hitachi F-4100 fluorescence spectrophotometer and fluorescence quantum yields were measured by comparison with that ($\varphi = 0.9$) of fluorescein in 0.01 M KOH methanol solution; fluorescence lifetimes were measured using the single-photon-counting method. All fluorescence measurements were carried out in solutions with concentrations of $<1.0 \times 10^{-6}$ M. Cyclic voltammograms were measured in 5 mM benzonitrile solution containing 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte, using a carbon electrode as a working electrode, a silver chloride electrode as a reference electrode and a platinum electrode as a counter electrode, with a sweeping rate of 100 mV s^{-1}. Oxidation potentials were obtained using cyclic voltammetric measurement.

2.3. *Photopolymerization*

Photosensitive compositions containing 610 mg of poly (methyl methacrylate/methacrylic acid) (molar ratio of methyl methacrylate:methacrylic acid = 77:23), 490 mg of tetraethylene glycol dimethacrylate, 77 mg of initiator, 23 mg of dye, 1.48 g of methanol, 0.55 g of ethyl acetate and 2.50 g of DMF were prepared. Each composition was coated onto a transparent polyethylene terephthalate film of 100 μm thickness, having an undercoated layer, using a wire bar and was dried at 90 °C for 1 min to obtain a photosensitive layer of 2 μm thickness. Aqueous 7% polyvinyl alcohol solution (completely saponified, polymerization degree: 500) was applied to the film using a wire bar and dried at 90 °C for 1 min to obtain a PVA layer of 1 μm thickness on the photosensitive layer. The films were used as test specimens. A step tablet of gray film scale (Dainippon Screen Mfg. Co., Ltd.) was placed on the test specimen and the specimen was then exposed to light of 490 nm for 38 s provided by a UXL-500D-O xenon lamp (Ushio Electric Co., Ltd.) which had been monochromated using a KL-49 interference filter (Toshiba Glass Co., Ltd.) and Y-47 color glass filter (Toshiba Glass Co., Ltd.). The distance from the xenon lamp to the test specimen was 15 cm. The test specimen was dipped in aq. 0.7% Na_2CO_3 solution at 30 °C for 7 s and rinsed with water to remove uncured portions and was then dried. The sensitivity of the test specimens was calculated as the energies required to cure the test specimens.

3. Results and discussion

3.1. *Influence of electron-donating ability of the substituents*

The photophysical characteristics of Dye-**1** in various solvents have been discussed in previous papers [27,28]. Dye-**1** has an absorption band whose λ_{max} was markedly affected by solvent. This band is attributed to intramolecular charge transfer from the aminobenzene group to the carbonyl group [29]. Fig. 2a shows the fluorescence spectra of Dye-**1** in various solvents. The fluorescence spectrum in DMF was red shifted compared with ethyl acetate due to stabilization of the excited state by solvation in the polar medium, as the excited state is more polar than the ground state. The Stokes shift of Dye-**1** in methanol (dielectric constant $\varepsilon = 33.1$) was 139 nm, which was much larger than the value of 82 nm obtained in DMF ($\varepsilon = 36.7$). This phenomenon is caused by hydrogen bonding between the carbonyl group of the excited Dye-**1** and the hydroxyl group of methanol. Dye-**1** in acetic acid showed two fluorescence peaks at around 620 and 750 nm; the shorter wavelength florescence can be assigned to hydrogen-bonded state with the carboxy group of acetic acid and the longer wavelength fluorescence can be attributed to protonated state by acetic acid.

Fig. 2b and c shows the fluorescence spectra of Dye-**2** and Dye-**3** in various solvents, respectively. Peak wavelengths of absorption spectra and fluorescence spectra in various solvents of Dye-**1** to Dye-**7** are listed in Table 1.

The Stokes shift of Dye-**2**, in which one of the diethylamino groups in Dye-**1** was replaced by a methoxy group, was 117 and 134 nm in methanol and DMF, respectively, while that of Dye-**3**, having no substituent in one phenyl ring while having a diethylamino group in the other phenyl group was 115 and 141 nm, respectively. The Stokes shift of Dye-**1** was 139 and 82 nm, in methanol and DMF, respectively, indicating that stabilization of the excited states of Dye-**2** and Dye-**3** was caused predominantly by solvent polarity, and not by hydrogen bonding in methanol. In acetic acid, Dye-**2** and Dye-**3** showed no fluorescence peak at 750 nm, which appeared in the fluorescence spectrum of Dye-**1** in acetic acid. This indicates that the carbonyl groups in the excited states of Dye-**2** and Dye-**3** were not protonated in acetic acid. These findings can be explained by the electron density at the carbonyl group; the electron-donating ability of the methoxy group and the hydrogen atom is smaller than that of the diethylamino group.

Table 2 shows the fluorescence quantum yields and fluorescence lifetimes for Dye-**1** to Dye-**7**. Fluorescence quantum yields of Dye-**1**, Dye-**2** and Dye-**3** were 8, 8 and 10%, respectively. Substitution of one diethylamino group with a methoxy group or a hydrogen atom had little effect on the fluorescence

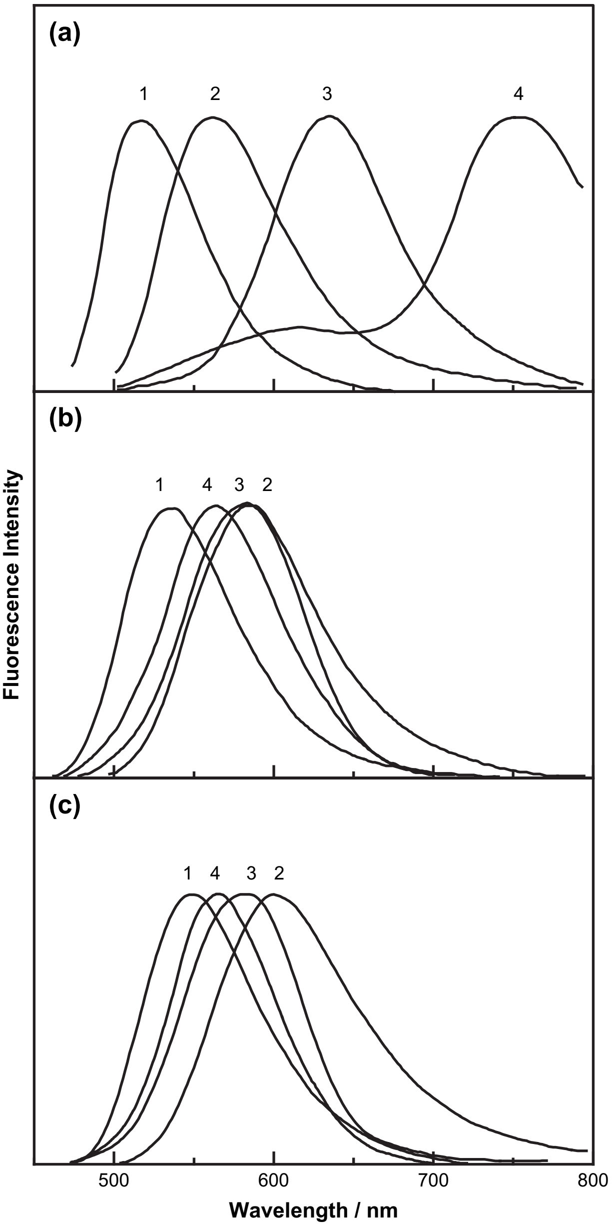

Fig. 2. Fluorescence spectra in solutions of: (a) Dye-**1**; (b) Dye-**2**; (c) Dye-**3**. Solvents used were 1, ethyl acetate; 2, DMF; 3, methanol; 4, acetic acid.

quantum yield, indicating that the excited states of the benzylideneketone dyes are mainly formed at the structure between the ketone group and one amino group, and that the other amino group simply donates an electron to the excited state.

Table 1
Peak wavelengths of absorption and fluorescence spectra of Dye-**1** to Dye-**7**

Dye	Peak wavelengths of absorption spectra/fluorescence spectra (nm)			
	In ethyl acetate	In DMF	In methanol	In acetic acid
Dye-**1**	459/514	477/559	494/633	459/616, 754
Dye-**2**	427, 441/534	452/586	463/580	476/559
Dye-**3**	434, 443/548	458/599	467/582	475/562
Dye-**4**	467/532	487/577	510/652	510/625, 774
Dye-**5**	475/542	493/596	517/668	527/>800
Dye-**6**	432/514	452/568	473/642	475/625, 757
Dye-**7**	430/505	445/560	470/612	460/591, 754

Table 2
Parameters of singlet excited states of Dye-**1** to Dye-**7**

Dye	φ^{a} (%)	τ^{b} (ps)	k_f^{c} (10^9 s^{-1})	k_n^{d} (10^9 s^{-1})
Dye-**1**	8	770	0.10	1.20
Dye-**2**	8	1070	0.07	0.86
Dye-**3**	10	500	0.20	1.80
Dye-**4**	10	830	0.12	1.08
Dye-**5**	17	590	0.29	1.41
Dye-**6**	8	700	0.11	1.29
Dye-**7**	0.5	230	0.02	4.28

[a] Fluorescence quantum yields in ethyl acetate.
[b] Fluorescence lifetimes in DMF.
[c] Rate constants of radiative decays.
[d] Rate constants of non-radiative decays.

Table 3 shows the oxidation potentials of Dye-**1** to Dye-**7**. Two oxidation waves were apparent in the cyclic voltammogram of Dye-**1** whereas only one oxidation wave was observed for Dye-**2** and Dye-**3**, as they have only one diethylamino group to be oxidized. The oxidation potentials of Dye-**2** and Dye-**3** were 0.85 and 0.88 V, respectively, which were larger than the first oxidation potential of Dye-**1**. This can be explained by the weaker electron-donating ability of the methoxy group and hydrogen atom compared with that of a diethylamino group.

From these findings, it can be concluded that the formation of the hydrogen-bonded and protonated states in the excited states is suppressed by substituting one diethylamino group with a group of lower electron-donating ability. Dye-**2** and Dye-**3** are efficient in energy migration from dye molecule to reaction site, and are superior sensitizing dyes in photopolymerization systems that contain carboxy groups because they have no energy trapping sites such as the hydrogen-bonded and protonated state of Dye-**1**, and show no change in fluorescence quantum yield.

3.2. Influence of rigid linkage of amino groups

The fluorescence spectra of Dye-**4** and Dye-**5** in various solvents are shown in Fig. 3a and Fig. 3b, respectively. The nitrogen atoms of the amino group of Dye-**4** are linked by one trimethylene chain to the *o*-position of the phenyl group. The Stokes shift of Dye-**4** in methanol was 142 nm, which was much larger than the value of 90 nm in DMF. This trend is similar to that of Dye-**1** and shows that the carbonyl group of Dye-**4** in the excited state forms hydrogen bonds with the hydroxyl group of methanol. The fluorescence spectrum of Dye-**4** in acetic acid shows

Table 3
Oxidation potentials of Dye-**1** to Dye-**7**

Dye	Oxidation potential (V)	
	First	Second
Dye-**1**	0.82	0.96
Dye-**2**	0.85	–
Dye-**3**	0.88	–
Dye-**4**	0.72	0.83
Dye-**5**	0.63	0.73
Dye-**6**	0.82	0.91
Dye-**7**	0.85	0.99

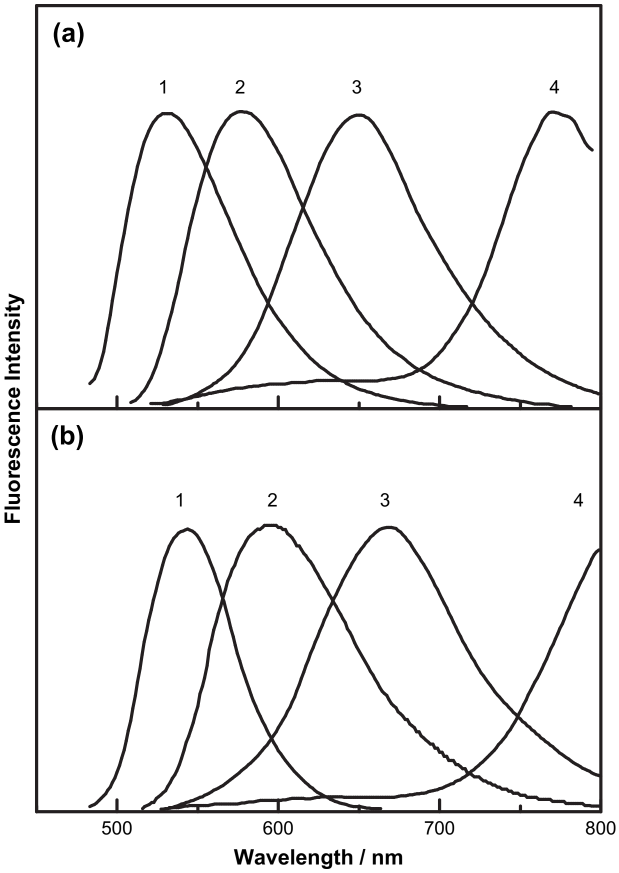

Fig. 3. Fluorescence spectra of: (a) Dye-**4**; (b) Dye-**5**. Solvents used were 1, ethyl acetate; 2, DMF; 3, methanol; 4, acetic acid.

a band at around 770 nm in addition to the band at around 630 nm, showing that the carbonyl group of Dye-**4** in the excited state forms both hydrogen-bonded states and protonated states in acetic acid as observed for Dye-**1**.

In Dye-**5**, the nitrogen atoms of the amino groups are linked by two trimethylene chains to the *o*-position of the phenyl group. The fluorescence spectra of Dye-**5** showed a behavier similar to that of Dye-**4**; this can be attributed to the carbonyl group of Dye-**5** in the excited state forming a hydrogen-bonded state with the hydroxyl group of methanol and the carboxy group of acetic acid; it is also partly protonated by acetic acid.

The peak wavelengths of both the absorption spectra and the fluorescence spectra of Dye-**4** were red shifted compared with Dye-**1** and those of Dye-**5** were further red shifted. This is probably due to the more planar conformation of the amino unit, which yields wider conjugation of π-electrons.

The fluorescence quantum yields of Dye-**1**, Dye-**4** and Dye-**5** were 8, 10 and 17%, respectively showing that the formation of a ring structure at the amino group increases fluorescence quantum yield. The phenomenon of this type has been reported in other dyes and is explained by the increased energy gap between the first excited singlet state and the lowest triplet state [30]. A similar energy level structure may also be formed in Dye-**4** and Dye-**5**.

Fig. 4 shows the cyclic voltammograms of Dye-**1**, Dye-**4** and Dye-**5**. The cyclic voltammograms of these dyes show two oxidation waves, indicating that the cationic radicals of these dyes are stable. The first oxidation potentials of Dye-**4** and Dye-**5** were 0.72 and 0.63 V, respectively, which were smaller than the 0.82 V of Dye-**1**. These phenomena are ascribed to stabilization of oxidized states by widening of the conjugation system.

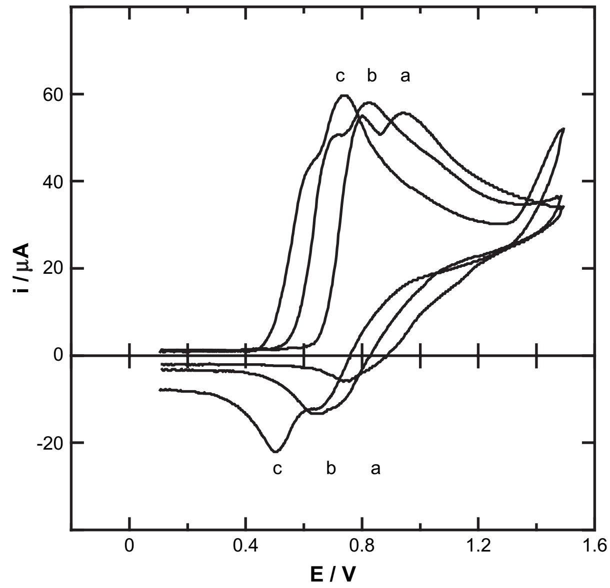

Fig. 4. Cyclic voltammograms of: a, Dye-**1**; b, Dye-**4**; c, Dye-**5**.

From the results above, photopolymerization systems incorporating Dye-**4** or Dye-**5** as a sensitizer are probably more sensitive at longer wavelengths than the systems incorporating Dye-**1**. These systems are also expected to have high sensitivity in combination with an electron-acceptor-type initiator because of the low oxidation potential of the dyes. The sensitivity of photopolymerization systems incorporating Dye-**4** and Dye-**5**, respectively, in combination with (η^6-cumene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate as initiator, was three times higher than that of the system incorporating Dye-**1**.

3.3. Influence of ketone ring structure

The fluorescence spectra of Dye-**6** and Dye-**7** in various solvents are shown in Fig. 5a and Fig. 5b, respectively. The ketone unit of Dye-**1** is linked to two double bonds through part of the five-membered ring structure at the center while the ketone of Dye-**6** is conjugated via two double bonds but does not form a ring at the center. The fluorescence spectrum, fluorescence quantum yield and oxidation potential of Dye-**6** were similar to those of Dye-**1**; this indicates that the conjugation system was not altered by the presence or absence of a five-membered ring structure.

Dye-**7** has a six-membered ring structure at its center instead of the five-membered ring structure in Dye-**1**. The fluorescence spectra in methanol and acetic acid revealed that the carbonyl group in the excited state of Dye-**7** forms hydrogen-bonded and protonated states as with Dye-**1**. However, the peak wavelengths of absorption and fluorescence of Dye-**7**

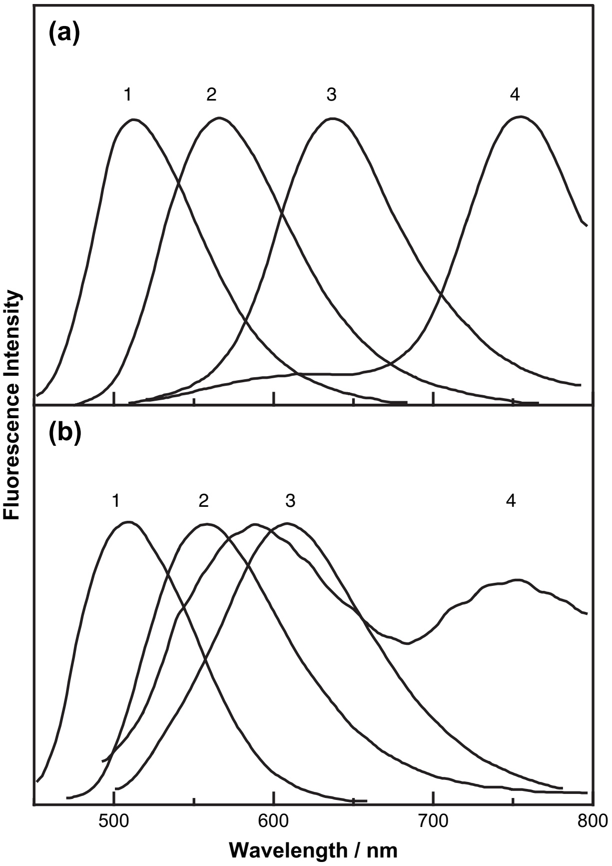

Fig. 5. Fluorescence spectra of: (a) Dye-**6**; (b) Dye-**7**. Solvents used were 1, ethyl acetate; 2, DMF; 3, methanol; 4, acetic acid.

were blue shifted compared to Dye-**1** due to a decrease in the extent of conjugation in the non-planar cyclohexane ring. This effect also appears in the relative intensities of fluorescence at around 750 nm to that at around 600 nm. Although Dye-**1** emits fluorescence mostly from its protonated state at around 750 nm, the major component of Dye-**7** is observed at 600 nm, which is from the hydrogen-bonded state.

From the fluorescence quantum yields and lifetimes, the rate constants of radiative and non-radiative decays were calculated to be 0.02×10^9 s^{-1} and 4.28×10^9 s^{-1} for Dye-**7**, and 0.10×10^9 s^{-1} and 1.20×10^9 s^{-1} for Dye-**1**, respectively, as listed in Table 2. The increased non-radiative decay rate of Dye-**7** seems to be caused by the lower stability of the excited state of Dye-**7** than Dye-**1**.

The first oxidation potential of Dye-**7** was 0.85 V, which was larger than that of Dye-**1** (0.82 V), indicating that the stability of the oxidized state of Dye-**7** was lower than that of Dye-**1**. These phenomena may also be explained by the decrease in degree of conjugation.

4. Conclusions

Benzylideneketone dyes having low electron density at the carbonyl groups do not form a hydrogen-bonded state nor protonated state in their excited states, in either methanol or acetic acid. Photopolymerization systems using these dyes as sensitizers have no energy trapping sites due to their interaction with carboxy groups, and are expected to have high sensitivity because of high energy migration efficiency. Benzylideneketone dyes having a rigid linkage at amino groups showed red shifts in both their absorption and fluorescence spectra as well as lower oxidation potentials compared to Dye-**1**. In contrast, benzylideneketone dyes having a six-membered ring at their center showed blue shifts and higher oxidation potentials compared with Dye-**1**. These findings are ascribed to a change in the extent of conjugation in the dyes. These findings will be helpful for designing dyes satisfying the requirements of photopolymerization systems.

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