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Laser Flash Photolysis in High–Speed Photopolymer Coating Layers : Elucidation of Radical Generated from Coumarin Dye Sensitized Photo–initiator Systems

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Radical generation from photoinitiation systems containing carbonylbiscoumarin dye with a radical–generating reagent, 3,3'–carbonylbis[7–(diethylamino)–2H–1–benzopyran–2–one](KCD–DA), with 2,2'–bis(2–chlorophenyl)–4,4',5,5'–tetraphenyl–1,1'–bi–1H–imidazole (BI) in a poly(methyl methacrylate) (PMMA) film have been investigated by laser flash photolysis using a total reflection cell.

Imidazolyl radical(Im ·) was predominantly generated from carbonylbis–coumarin triplet sensitized decomposition of BI, the quantum yield, $\Phi^0_{Im\cdot}$ of Im · at an infinite concentration of BI was measured, $\Phi^0_{Im\cdot} = 0.5 \sim 1.4$. The high quantum yield, $\Phi^0_{Im\cdot}$ implies an efficient KCD–DA triplet sensitized photoinitiation system containing BI.

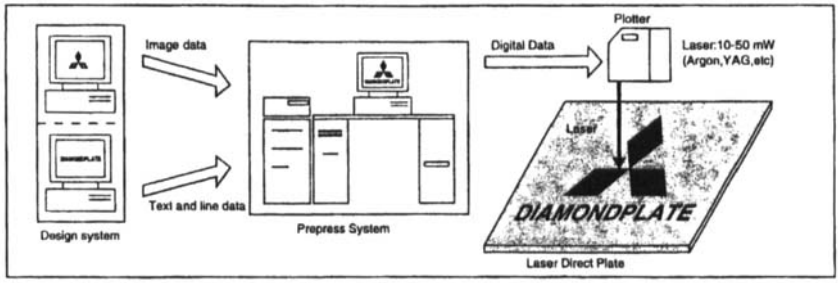
Keywords: laser flash photolysis; high–speed photopolymer; quantum yield; carbonylbiscoumarin; imidazolyl radical

Introduction

In recent years, the computerizaton of photopolymer plate systems has developed rapidly. Mitsubishi Chemical supplies computer–to–photopolymer plates (CTPs) available for air–cooled argon–ion lasers at 488 nm and YAG lasers at 532 nm, as shown in Fig.1.

The combination of the dye with BI affords a high speed photoinitiator for a visible laser photopolymerization system that can be used for high speed laser imaging systems.

Though it is difficult to discuss the photoinitiation mechanisms in polymer films based on the data obtaind from laser flash photolysis in solution, because of much difference in mobility of substances beween in solution and in polymer, [1–a] a laser analysis using a total reflection cell of the photopolymer, which contained photoinitiators with the same content as that of commercial products, could provide direct informations about photo–excited dyes, and about radicals resultant from sensitized decomposition of BI under the condition of negligible amount of sample destruction. The practically high–optical–pass length enable to detectthe short–life–transient states formed in photo–chemical reaction containing rapidly photo–decomposing substances by the laser pulse exposure



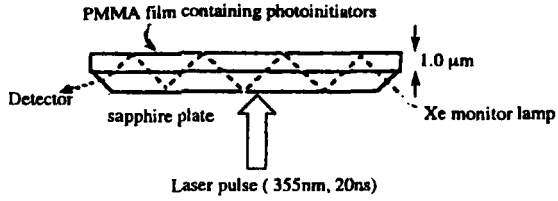
LA-1

- Air-cooled Argon laser (488 nm) exposure
- Sheet-fed and web offset,high quality color printing and business form printing
- Run-length: 100,000 to 200,000 sheets
- UV-ink printing possible without baking
- Plate Thickness: 0.20 mm, 0.24 mm and 0.30 mm

LY-1

- Air-cooled YAG laser (532 nm) exposure
- Sheet-fed and web offset printing,high quality color printing and business form printing
- Plate Thickness: 0.20 mm, 0.24 mm, 0.30 mm

Fig. 1 MCC's computer to photopolymer plate.



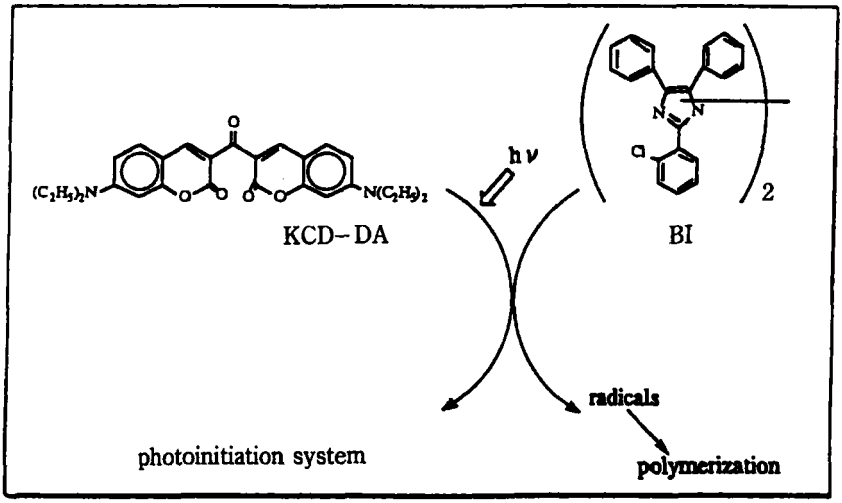


Fig. 2 Laser flash photolysis in film.

with low density of light energy.

KCD-DA is an efficient triplet sensitizer dye in solution systems, [2] and we reported previously that it undergoes static singlet and static triplet sensitisation against 1, 3, 5-triazine with low reduction potential, -0.94 V vs. SCE, as a radical reagent in a PMMA film, [1-a] and predominant static singlet sensitization and minor nonstatic triplet sensitization against 3, 3', 4, 4'-tetrakis (t-butyldioxy-carbonyl)benzophenone (BTTB) with medium reduction potential -1.18 V vs. SCE, [1-d] as well as nonstatic triplet sensitization against BI with high reduction potential, -1.35 V vs. SCE .

In the dye-sensitized decomposition of BI in blue light region, A. D. Liu, etc. reported that BI is predominantly decomposed through singlet sensitization process, giving imidazolyl radicals, Im · , and triplet sensitized decomposition of BI is minor process, [3] which is contrast to the predominant triplet sensitized photo-initiation process in high speed photoinitiation system containing KCD-DA and BI in earlier investigation. [1-f] To more reveal the photoinitiation process, We evaluate the quantum yield($\Phi^{0}_{Im\cdot}$) of Im · resultant from triplet-sensitized dissociation of BI by KCD-DA.

The result shows that high speed sensitivity of photopolymer containing KCD-DA and BI was due to the efficient-triplet-sensitized dissociation of BI.

Experimental

The dye KCD-DA was purchased from Nihon Kanko Shikiso Corporation. BI was prepared according to the reported procedure. [4]

Absorption spectra of the dye was recorded by a UV-visible absorption spectrometer (HItachi Spectrometer U-3000). A total-reflection cell in laser flash photolysis experiments is shown in Fig. 2. [1] The cyclohexanone solutions containing 10 wt% of PMMA, 0.099 mol dm^{-3} of the dye, and 0 ~ 0.185 mol dm^{-3} of BI were coated to 1.0 μ m thickness on a sapphire cell (10 × 30 mm, 1 mm thickness, and both short sides were cut at a 45 degree angle). A monitor light beam from a xenon lamp was introduced through a multireflection cell onto the head of an optical fiber that directs the beam to a monochromator (Instruments Digikrom 240) with a photomultiplier (Hamamatsu Photonics K. K. photomultiplier tube TYPER928) or to a SMA system (Princeton Instruments, Inc. Model TRY-700G/R/Par). The excitation light pulse (20 ns, 355 nm, 10 mJ per pulse and 3 mJ cm^{-3}) from a YAG laser (Spectron Laser Systems Model SL 402) was expanded and exposed all over the sample cell. The measurements was repeated five times within less than 3 wt% of the decomposition of the dye and BI ; the data of the five measurements were averaged. More than 90 % of the 355 nm laser light absorbed in the sample film was absorbed by the dye, and the dye were homogeneously photo-excited in the film due to their low absorbance, 0.01-0.06 on 355 nm. Fluorescence spectra in solution and in films were recorded by the laser flash photolysis using a SMA system.

RESULT AND DISCUSSION

The absorption and the fluorescence spectrum of KCD–DA were previously reported in earlier investigations [1-d] ; it was suggested that the fluorescence comes from intramolecular charge transfer (ICT) state of the coumarin with a nontwisted 7–dialkylmino group followed by undergoing intersystem crossing to a triplet, or by undergoing a nonemissive intramolecular charge transfer with a twisted 7–dialkylamino group, twisted intramolecular charge transfer (TICT). [5] In our previous report on laser flash photolysis in a PMMA film containing KCD–DA and BI, the fluorescence and the initial intensity of triplet absopion were not quenched by BI. The triplet decay time of the dye was quenched by BI at k_q of 0.60×10^6 mol^{-1} dm^3 S^{-1}, [1-f] suggesting a predominant–n onstatic–sensitization process from the triplet of the dyes to BI, Figure 3 and 4s hows the decay and transient spectrum of the dyes on the 355 nm laser excitation, in the presence of BI, the initial transient absorption spectrum was similar to that of the triplet absorption of the dye, and after 100 μ s, most features assigned to triplet of the dye disappeared and the spectrum in 540 ~ 600 nm was determined as an Im · absorption (Fig. 4) ; in comparison of the spectrum with Im · spectrum in dichloromethane in literature, [3] the transient spectrum in 540 ~ 600 nm formed by KCD–DA triplet–sensitized decom–position of BI in a PMMA film exhibited a good fitting to the spectrum of Im · for direct–photodecomposition of BI in dichloromethane [3] except for a small reduction of the spectrum in 550 ~ 570 nm, which could be attributable to the absorption of KCD–DA ground state. Im · decayed at a decay time of more than 200 μ s. After 100 μ s quantum yield of Im · , $\Phi_{Im\cdot}$, was obtained at various concentrations of BI. [6] From the scheme of triplet sensitization decomposition of BI in eq. 1 ~ 3, the relationship of the reciprocal of the quantum yield and the reciprocal of the concentration of BI is explained by eq. 3. The quantum yield at an infinitive concentration of BI, $\Phi^0_{Im\cdot}$ was determined from the intercept of $\Phi_{Im\cdot}^{-1}$ plots against the reciprocal of various concentrations of BI (Fig. 5), and from incorporating $k_q = 0.60 \times 10^6$ mol^{-1} dm^3 S^{-1}, [1-f] and $k_d = 1/\tau_T = 0.86 \times 10^6$ mol^{-1} dm^3 S^{-1} into the slope = 0.914 of $\Phi_{Im\cdot}^{-1}$ plots, $\Phi^0_{Im\cdot} = 0.5$ and 1.4 for the intercept andf or the slope (A and B in Fig. 5). The reciprocal plot of $\Phi^0_{Im\cdot} = 1.4$ has a good relationship with $\Phi_{Im\cdot}^{-1}$ plots in Fig. 5. The difference between $\Phi^0_{Im\cdot}$ s was explained due to the small value of intercept, $\Phi_{Im\cdot}^{-1}$, which should contain large deviation compared to the slope, when considering small absorbance of Im · (Fig. 3).

The high quantum yield $\Phi^0_{Im\cdot}$ implies an efficient dissociation of BI resultant from triplet sensitization by carbonybiscoumarin dye, and the contrast result to low–dissociation efficiency of BI through triplet sensitization, reported in Ref. 3. Finally, we conclude that the efficient–triplet–sensitized dissociation of BI contributes to the high speed sensitivity of photopolymer containing carbonylbiscoumarin and BI.

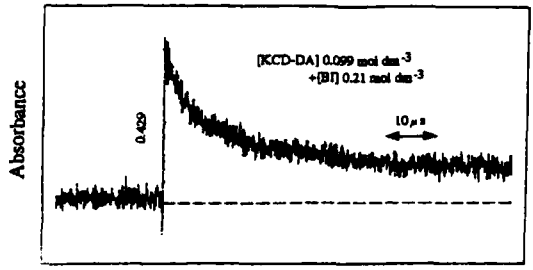


Fig. 3 Decay of KCD–DA triplet and growth of Im · for KCD–DA and BI in PMMA film at 580 nm.

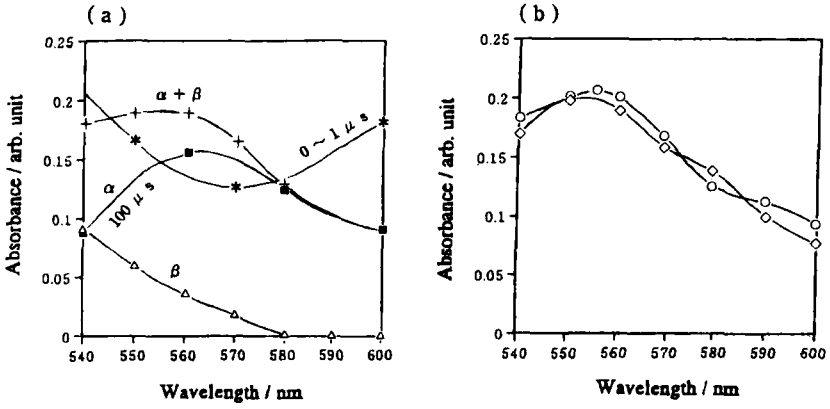


Fig. 4 Transient absorption spectra for KCD–DA and BI, [a] transient absorption spectrum during 0 ~ 1 μ s (– * –) and at 100 μ s (– ■ –) after 355 nm laser irradiation for KCD–DA and BI, [a] in a PMMA film, and absorption spectrum of KCD–DA ground state [b] (– △ –), as well as the plots (– + –); addition of (– ■ –) and (– △ –) (a), transient absorption spectrum of Im · (– ○ –) for direct photolysis of BI in dichloromethane [3-a] and (– □ –) for sensitized decomposition of BI in dichloromethane [b] (b). a) Subsrate concentrations are 0.099 and 0.21 mol dm $^{-3}$ for KCD–DA and BI. b) Substrate concentration is 0.099 mol dm $^{-3}$, c) 2,5–bis[(2,3,6,7–tetrahydro–1H,5H–benzo[ij]quinolizin–1–yl)–methylene]–cyclopentanone (JAW).

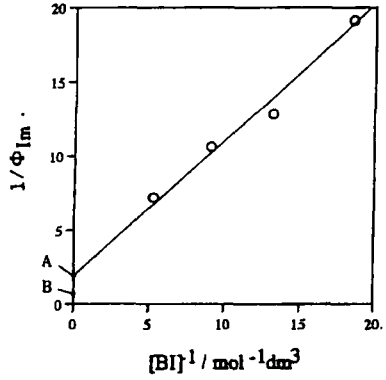
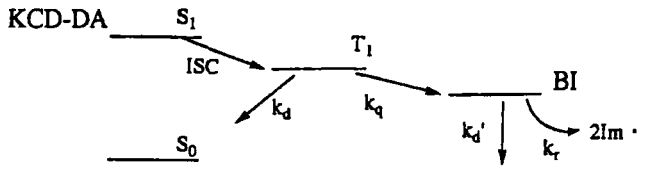


Fig. 5 Concentration dependence of the quantum yield of sensitized dissociation of BI for KCD–DA in 355 nm laser flash photolysis at 580 nm.
A ; $\Phi^{0}_{Im\cdot} = 0.5$ obtained from the intercept of $\Phi_{Im\cdot}{}^{-1}$ plots,
B ; $\Phi^{0}_{Im\cdot} = 1.4$ from incorporating k_d = 0.60×10^{5} mol $^{-1}$ dm ^{3} S $^{-1}$, [1-f] and $k_d = 0.86 \times 10^{5}$ mol $^{-1}$ dm ^{3} S $^{-1}$ [1-f] into the slope.



$$\Phi_{Im\cdot} = \Phi_{ISC}\{kq[BI]/(kd+kq[BI])\}\{2kr/(kd'+kr)\} \quad \text{eq.1}$$

$$1/\Phi_{Im\cdot} = (1/\Phi_{ISC})\{(kd'+kr)/2kr\}+(1/\Phi_{ISC})(kd/kq)\{(kd'+kr)/2kr)\}/[BI] \quad \text{eq.2}$$

$$= 1/\Phi^{0}_{Im\cdot} + (1/\Phi_{ISC})(kd/kq)\{(kd'+kr)/2kr\}/[BI] \quad \text{eq.3}$$

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[6]Quantum yield of was obtained using the quantum yield of Im · formation ($\Phi^{0}_{Im\cdot} = 1.2$ [3-b]) in direct photodecomposition of BI in dichloromethane and absorption coefficient of BI ($\varepsilon = 404$ mol^{-1} dm^{2} at 355 nm) in a PMMA film.