Sensitization Mechanisms of Photopolymer Coating Layer using Infrared Dye

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Photoinitiation mechanisms of photopolymer coating layer containing a heptamethine cyanine dye and a radical generating reagent were investigated by laser flash photolysis using a total reflection cell. From fluorescence quenching studies, it was found that singlet static sensitization process was predominant for CDB-TCT systems.

Keyword: infrared photoinitiator, photopolymer, sensitization, infrared dye.

1. Introduction

The photoinitiation mechanism for photopolymer coating layer containing a heptamethine cyanine dye 2-[2-[2-chloro-3[2-(1,3-dihydro-3,3-dimethyl-1-methoxyethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-3,3-dimethyl-1-methoxyethyl-1H-indolium tetrafluoroborate (CDB) and a radical generating reagent 2,4,6-tris (trichloromethyl)-1,3,5-triazine (TCT) was investigated by laser flash photolysis using a total reflection cell as depicted in Fig. 1.

It is well known that infrared cyanine dyes are used for fluorescence probes in biochemical procedure[1], sensitizer dyes of silver halide photography[2], dyes for dye laser technology [3], and abration dyes for write-once-optical-memory discs.

The character of photopolymer sensitization of cyanine dyes was not reported except for some reports [4, 5]. In our earlier investigation, [4] 20 mJcm⁻² of sensitivity was obtained at 830 nm, and the sensitization mechanisms are not clear yet.

According to the rapid development of high-power-laser diodes, the infrared-light-responsible photopolymers are demanded for new imaging systems equipped with laser diode with compact side, low price, and long shelf life compared to visible laser imaging systems.

Sanchez-Galvez et al. described the calculation of potential energy surface for visible and infrared cyanine dyes, and discussed an ultrafast radiationless deactivation process of the dyes by comparing results of calculation with that of photolysis in solution[5]. The ultrafast

Fig. 1. Laser flash photolysis.

Fig. 2. Absorption spectrum of CDB in acetonitrile a), and in PMMA b).
Substance concentration: 3.1×10^{-6} and 1×10^{-1} mol dm $^{-3}$ for CDB in acetonitrile and in PMMA.

radiationless deactivation process was a relaxation process through twisted intramolecular charge transfer (TICT) state from photoexcited singlet state accompanied with a rotation of polymethyne group, and the fast process made the decrease in fluorescence emission, which resulted in a low-fluorescence quantum yield (Φ_f) for cyanine dyes such as $\Phi_f = 0.06-0.4$ [5]. The low efficiency of fluorescence and low sensitivity of photodetector in infrared light region such as photomultipliers make it difficult to analyse the fluorescence using a normal fluorescence spectrometer.

A multi-reflection cell in the laser flash photolysis works as a collector of fluorescence lights. The fluorescence lights emitted from the photoexcited dyes in photopolymer coating layer are multi-reflected in the cell, efficiently directing to both sides of the cell. The fluorescence passing through the cell was easily measured by the detector equipped with an optical fiber head, contacted to the sidewall of the cell.

In this paper we present the sensitization processes using an infrared cyanine dye of similar concentration to commercial products in the photopolymer systems.

2. Experimental

CDB was purchased from Nippon Kayaku. 2,4,6-Tris(trichloromethyl)-1,3,5-triazine (TCT) was purchased from Midori Chemical. Poly(methylmethacrylate) (PMMA, Mw = 40000), was estimated by GPC (RI). All solvents were spectrograde and purchased from Wako Pure Chemical Industries.

UV-NIR spectra were recorded with a

Fig. 3. Fluorescence spectra of CDB in PMMA.
Substance concentration: 1×10^{-1} mol dm $^{-3}$ for CDB; excitation wavelength 355 nm.

Hiatchi U-3000 spectrophotometer. Laser flash photolysis in film was performed using a total reflection sapphire cell (10 × 30 mm, 1 mm thickness, and both short sides were cut at a 45 degree angle.). Films were spin-coated to form photopolymer layer as depicted in Fig. 1. Details concerning the apparatus are described elsewhere. [6,7] An excitation light pulse (20 ns, 355 nm and 10 mJ/cm 2 per pulse) from a YAG laser (Spectron Laser System Model SL 402) was exposed over the entire sample cell. A monitoring light from a xenon lamp was passed through the multireflection cell which was connected to the head of an optical fiber attached to a monochromator (Instruments Digikrom 240)

$$K_i = [\text{CDB-iTCT}] / \{[\text{TCT}][\text{CDB-(i-1)TCT}]\}, i = 1, 2, 3, \dots \quad (2)$$

$$I_f^0 / I_f = \{ (1 + k_q \tau_f^0 [\text{TCT}]) (X + k_q \tau_f^0) / \{ X + k_q \tau_f^0 [\text{TCT}] + [(X k_q^1 \tau_f^0 - k_q \tau_f^0 [\text{TCT}]) \exp(-VN [\text{TCT}]) \} \} \quad (13)$$

$$I_f^0 / I_f = (1 + k_q \tau_f^0 [\text{TCT}]) \exp(VN [\text{TCT}]) \quad (14)$$

Where I_f^0 and I_f are the fluorescence intensities in the absence and presence of the quencher (TCT), τ_f^0 is the life time in the absence of the quencher, k_q is the dynamic quenching rate constant, k_q^1 is the static quenching constant and $k_q^1 = i k_q^1$, $K_i = i K_i = VN$. V is the quenching sphere, $V = 4\pi R_f^3/3$. N is Avogadro's number. R_f is the quenching radius. $X = K_1 \sum [(\text{CDB-(i-1)TCT})] + 1$. [11-b,e]

equipped with a photomultiplier (Hamamatsu Photonics R 928 photomultiplier tube), or to a spectral multichannel analyzer (SMA) system (Princeton Instruments, Inc. model TRY-700G/R/Par). Films were prepared as follows. A 10 wt % PMMA solution containing 0.01 mol dm^{-3} of CDB and $0 - 0.035 \text{ mol dm}^{-3}$ of TCT was made up in cyclohexanone. Films were $1.2 \text{ }\mu\text{m}$ in thickness prepared by spin-coating the solution onto a sapphire cell.

3. Result and Discussion

Laser flash photolysis in PMMA film.

The maximal absorption for CDB were found at 780 and 790 nm in acetonitrile and a PMMA film respectively, as depicted in Fig. 2. The maximal fluorescence, 875 nm in a PMMA film with 355 nm excitation in Fig. 3.

On the excitation of a PMMA film containing CDB by 355 nm pulse, a weak fluorescence was observed, but any transient absorption was not observed. The fluorescence decay would be too short to be determined by 20 ns laser pulse.

Fig. 4 shows the quenching of fluorescence at various concentrations of TCT at an excitation of 355 nm. The fluorescence intensity was decreased as the concentration of TCT changed from 0 to 0.32 mol dm^{-3} .

As for quenching reduction of fluorescence in film, Kaneko et al. reported a multistep equilibrium model (Eqs. 1-12)[8]. In the equations, the multistep equilibrium between one CDB and more than two TCTs within a quenching sphere is assumed (Eqs. 1-2). CDB and (CDB-iTCT) is photoexcited to an excited singlet state ^1CDB (Eq. 3) and $^1(\text{CDB-iTCT})$ (Eq. 8) by absorbing a laser pulse. ^1CDB undergoes i) radiative (Eq. 5) and nonradiative deactivation (Eq. 4), ii) intersystem crossing (Eq. 7), and iii) dynamically sensitized decomposition of TCT, forming radicals such as chloro and dichloromethyl radicals (Eq. 6). $^1(\text{CDB-iTCT})$ undergoes i) radiative (Eq. 10) and nonradiative deactivation (Eq. 11), ii) intersystem crossing (Eq. 12), and iii) statically sensitized decomposition of TCT, forming radicals such as chloro and dichloromethyl radicals (Eq. 9). The attenuation of fluorescence by TCT in film is described as Eq. (13). When $^1(\text{CDB-iTCT})$ does not emit fluorescence, k_q^1 is much larger than any other decay rate. Eq. 13 is described as a combination equation (Eq. 14) of dynamic and static quenching term (perrin type [9]).

The logarithmic plots of the fluorescence intensity at various concentrations of TCT was fitted to Perrin Equation. The quenching radius (R_f) was $7.8 \text{ \AA}$ for CDB, which was determined from the slope of the logarithmic plots. The quenching radius is rather short compared to that obtained for photosensitization systems in which an exothermic electron transfer from photoexcited dyes to radical generators takes place; for examples, $R_f = 15 \text{ \AA}$ for 3-(9-julolidinyl)-1-

Fig. 4. Fluorescence Quenching of CDB by TCT in PMMA.

Substance concentration: $1 \times 10^{-1} \text{ mol dm}^{-3}$ for CDB; excitation wavelength: 355 nm; detection wavelength 890 nm.

pnenyl-2-propen and TCT, and $R_f = 14 \text{ \AA}$ for 2-(9-julolidinyl)methylene-1-indanone and TCT [7-e]. The short quenching radius would be due to the low-singlet-excited energy of infrared dye, which made the energy of electron transfer less exothermic. It is concluded that the singlet static sensitization process is predominant in the photopolymer layer containing an infrared dye, CDB, and TCT.

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