Sensitization Mechanisms of Subphthalocyanine in Photopolymer Coating Layer

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The sensitization mechanisms for photoinitiators comprising a subphthalocyanine dye and a radical generating reagent; 2,4,6-tris(trichloromethyl)-1,3,5-triazine (TCT) in a poly(methyl methacrylate) film have been investigated by laser flash photolysis using a total reflection cell. Keyword: photopolymerization, sensitizer, laser, subphthalocyanine

1. Introduction

The photoinitiation mechanisms for photopolymer coating layer containing a subphthalocyanine and a radical generating reagent; 2,4,6-tris(trichloromethyl)-1,3,5-triazine (TCT) in a poly(methyl methacrylate) (PMMA) have been investigated by laser flash photolysis using a total reflection cell as depicted in Figure 1 [1]

Phthalocyanines (Pcs) are generally low soluble against organic solvents, and used in colorants, and organic-photoconductor pigments for electrophotography copiers. The Pcs with specific substituents, which are soluble in organic solvents, are applied to electrochromism [2], write-once-optical-memory discs [2], laser dyes, chemical sensors [3], nonlinear optics [4],

![Photoinitiation system](image)

Fig. 1. Laser flash photolysis in film.

Received July 12, 2000
Accepted November 24, 2000

679
Subphthalocyanines (Subpc) were reported as an intermediator for preparation of asymmetric Pcs by Kobayashi et al., [7] in which Subpc’s physical and chemical characters were also described. Subpc has a good solubility against organic solvents due to their pyramidal chemical structure; the nonplaner chemical framework prevents an association between Subpc molecules, affording the good solubility.

However no applications of Pcs and Subpcs as a sensitizer for photoinitiators has been reported as far as I know. The combination of Subpc and TCT afforded high speed photoinitiator systems, which are applied to the photopolymers for visible laser imagings [10]; the sensitivity at 550 nm was 2 mJcm$^{-2}$.

In this report, we first present a new character of Subpcs as a sensitizer, and discuss photochemical characters of Subpcs in photopolymer coating layer.

2. Experimental

The Subphthalocyanine (Subpc) was prepared according to the literature procedure.[8] 2,4,6-Tris(trichloro-methyl)-1,3,5-triazine (TCT) was purchased from Midori Chemical Ltd. Poly(methyl methacrylate) (PMMA), M$_w$ = 40000, was estimated by GPC (RI), and all solvents were spectrograde and purchased from Wako Pure Chemical Industries, Ltd.

UV-VIS spectra were recorded with a Hitachi U-3000 spectrophotometer, and fluorescence spectra with a Hitachi F-4500 fluorescence spectrometer by using a solid sample holder, which was also used for a solution sample in order to minimize the effect of an internal light filter.

Laser flash photolysis in films was performed using a total reflection sapphire cell (10 X 30 mm, 1 mm thick, and both short sides were cut at a 45 degree angle), which was spin-coated with a 1.2 μm thick photopolymer film as depicted in Fig. 1. Details concerning the apparatus are described elsewhere [9]. An excitation light pulse (20 ns, 355 nm and 10 mJ per pulse) from a YAG laser (Spectron Laser Systems Model SL 402) was expanded and exposed over the entire sample cell. A monitoring light from a xenon lamp passed through the multireflection cell which was connected to the head of an optical fiber attached to a monochromator (Instruments Digikrom 240) equipped with a photomultiplier (Hamamatsu Photonics K.K. photomultiplier tube type R 928) or to a spectral multichannel analyzer (SMA) system (Princeton Instruments, Inc. model TRY-700G/R/Par). The measurement was repeated five times within less than 3 wt % of the decomposition of the dye and TCT; more than 90 % of the 355 nm-laser light absorbed in the sample film was absorbed by the dye.
Films were prepared as follows. A 10 wt % PMMA solution was made up in cyclohexane. Subpc was added to this solution either by dissolving the dyes directly in polymer solution or by mixing a portion of concentrated dye solution. Films were adjusted to be 1.2 μm thick by spin-coating a solution onto a sapphire cell.

The photosensitivity of the photoinitiator systems was measured as follows: the sensitive layer which was prepared by coating a cyclohexanone solution of the photosensitive composition containing 5 wt % of the Subpc, 5 wt % of TCT, 45 wt % of trimethyrolpropane triacrylate and 45 wt % of poly(methylmethacrylate-methacrylic acid) (90:10 mol %, Mw= 50000) onto a grained aluminum plate and dried at 80 °C to produce a 1 μm thick film, was exposed at 550 nm by the use of a xenon lamp, which was isolated using a monochrometer (Narumi ltd.). The incident energy required to insolubilize the last step of the layer was defined as sensitivity [10]. The incident energy was measured by a photoelectric cell (The Epplly Laboratory Inc).

3. Result and Discussion

Absorption and fluorescence spectra of Subpc were reported in the reference [2], in which absorption and fluorescence maximum were 564 and 569nm in benzene respectively.

Absorption and fluorescence maximum for Subpc (0.03 mol dm⁻³) in a PMMA film was 564 and 574nm, respectively and the spectrum profile was analogous to that in benzene.

Laser flash photolysis in a PMMA film.

On the excitation at 355 nm pulse of a PMMA film containing Subpc, fluorescence peak and transient decay were observed (Fig. 2), and the transient absorption was reasonably assigned as a triplet reported by Del Rey et al. [2] The fluorescence decaytime for Subpc was too short to be determined by a 20 ns laser pulse.

Figure 3 shows the quenching of fluorescence at various concentrations of TCT on an excitation at 550nm using the fluorescence spectrometer. The fluorescence intensity was reduced with the concentration of TCT from 0 to 0.15 M.

As for the reduction of fluorescence by quencher in films, Kaneko et al. reported a multistep equilibrium model (Eq. (1)-(11)). [11] In the equations, the multistep equilibrium between a subpc and more than two TCT within a quenching sphere are assumed (Eq. (1)-(2)).

![Graph 3: Quenching of Subpc fluorescence on 572 nm in PMMA. Substance concentration; 0.03 mol dm⁻³. Excitation wavelength; 550 nm.]

![Graph 4: Quenching of triplet absorption intensity on 450 nm of Subpc by TCT in PMMA. Substance concentration; 0.15 mol dm⁻³ for Subpc. Excitation wavelength 355 nm.]

Subpc and (Subpc-TCT) is photoexcited to an excited state * Subpc (Eq. (3)) and (*Subpc-TCT) (Eq. (8)) by absorbing a laser pulse. *Subpc 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 radicals and dichloromethyl type radicals.
(Eq. (6)). (*Subpc-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 radicals and dichloromethyl type radicals (Eq. (9)). The attenuation of fluorescence with the concentration of TCT in film is described as an Eq. (13). When (*Subpc-iTCT) does not emit fluorescence, meaning $k_q'$ is much larger than any other decay quenching term (Perrin type [12]).

The logarithmic plots of the fluorescence intensity at various concentrations of TCT exhibits a good linear relationship, indicating a (Perrin type) static quenching process [12]. The quenching radius (Rf) determined from the slope of the logarithmic plots was 15 Å.

Figure 4 depicts triplet decays with various concentrations of TCT from 0 to 0.15 mol dm$^{-3}$ in a PMMA film. The initial absorption of

\[
[\text{Subpc} - (i-1)\text{TCT}] + \text{TCT} \xrightarrow{K_i} (\text{Subpc-iTCT}), i = 1,2,3... (1)
\]

\[
K_i = [\text{Subpc-iTCT}]/([\text{Subpc}][\text{Subpc}-(i-1)\text{TCT}]), i = 1,2,3... (2)
\]

\[
\begin{align*}
\text{Subpc} & \xrightarrow{h\nu} * \text{Subpc} (3) \\
* \text{Subpc} & \xrightarrow{k_d} \text{Subpc} (4) \\
* \text{Subpc} & \xrightarrow{k_{isc}} \text{Subpc} + h\nu (5)
\end{align*}
\]

\[
* \text{Subpc} + \text{TCT} \xrightarrow{k_q} \text{Subpc} + \text{radicals} (6)
\]

\[
* \text{Subpc} \xrightarrow{k_{isc}} \text{Triplet} (7)
\]

\[
(\text{Subpc-iTCT}) \xrightarrow{h\nu} (*\text{Subpc-iTCT}) (8)
\]

\[
(*\text{Subpc-iTCT}) \xrightarrow{k_q^i} (\text{Subpc} + (i-1)\text{TCT}) + \text{radicals} (9)
\]

\[
(*\text{Subpc-iTCT}) \xrightarrow{k_i^i} (\text{Subpc-iTCT}) + h\nu (10)
\]

\[
(*\text{Subpc-iTCT}) \xrightarrow{k_{isc}^i} (\text{Triplet-iTCT}) (12)
\]

\[
I_f^0/I_f = \{(1 + k_q \tau_{i,0} [\text{TCT}])/(X + k_q \tau_{i,0})\}/(X + k_q \tau_{i,0} [\text{TCT}]+ [Xk_q^i \tau_{i,0} k_q \tau_{i,0} [\text{TCT}])\exp(-VN [\text{TCT}]) \} \quad (13)
\]

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

Where $I_f^0$ and $I_f$ are the fluorescence intensities in the absence and presence of the quencher (TCT). $\tau_{i,0}$ is the life time in the absence of the quencher. $k_q$ is the dynamic quenching rate constant. $k_q^i$ is the static quenching constant, $k_q^i = i k_q$. $K_i = i K_q = VN$. $V$ is the quenching shere, $V = 4 \pi Rf/3$. N is Avogadro's number. $Rf$ is the quenching radius. $X = K_i \Sigma [(\text{subpc}-(i-1)\text{TCT})] + 1.11-b,e)$. 

rate. Eq. 13 is described as a combination of dynamic and static the triplet decay was decreased with the concentration of TCT. However, the decrease of
triplet-decay time was not observed. The logarithmic plots of the initial absorption at various concentrations of TCT was fitted to Perrin Eq. The quenching radius (Rt) obtained from the slope of the logarithmic plots was 13 Å, which was almost same as that of fluorescence quenching radius, 15 Å. A triplet state generally comes from a fluorescent singlet state, and the initial-triplet concentration is reduced with the decrease of the singlet state. Hence the almost same quenching radiiuses between the fluorescence and the triplet suggest the attenuation of initial-absorption on the triplet decay with the concentration of TCT was due to the quenching of the fluorescent-singlet-excited state.

Finally it is suggested that the static-singlet-quenching process from the singlet photoexcited Subpc to TCT is predominant in the sensitization.

References