Photoinitiation Mechanisms in Photopolymer Layer

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Quenching of imidazoyl radicals (Im •) in photoinitiator systems comprising an aminostyryl dye and a radical generating reagent by acrylate monomers in a poly(methyl methacrylate) (PMMA) film was investigated by a laser flash photolysis using a total reflection cell, as well as quenching of Im • by oxygens in the presence and absence of poly(vinyl alcohol) (PVA) over layer as an oxygen varrier.

Keywords: Imidazoyl radical, photopolymerization, sensitization, acrylate monomer, oxygen.

1. Introduction

The photoinitiation mechanisms for photopolymer layer containing a 2-[p-(diethylamino)styryl]naphtho[1,2-d]thiazole (NAS) and 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,1'-bi-1H-imidazole (BI), in the presence and absence of pentaerythritol triacrylate (PETA) in a poly(methyl methacrylate) (PMMA) under an air atmosphere and under the condition of poly(vinyl alcohol)-over layer were investigated by an laser flash photolysis using a total reflection cell [1,7]. The combination of NAS and BI affords high speed photoinitiators for visible laser imaging systems equipped with 488 nm argon ion laser (Fig. 1) [3-4,8].

We have already reported that a singlet excited state of NAS predominantly sensitized the decomposition of BI in a PMMA film [4]. The quenching processes of Im • by PETA and oxygen during short time, $10^{-9} \sim 10^{-4}$ s, after an excitation have not been clear yet except for some reports with respect to oxygen effects on photopolymerization kinetics in films during long time, $1 \sim 10^{3}$ s, after an excitation [2] though they are key processes which determine a sensitivity of photopolymers.

In this report, we present the quenching process of Im • resulted from NAS-sensitized photolysis of BI by PETA in a PMMA film, and also of the quenching process of Im • by oxygen with and without an PVA-over layer as an oxygen-varrier layer.

2. Experiments

The dye, NAS, was prepared by the condensation of 2-methylnaphtho[1,2-d]thiazole with 4-(diethylamino) benzaldehyde [5], and BI, prepared according to the reported procedure [6], and PETA was purchased from Aldrich Chemical Company, Inc.

Photophysical Measurement of the Photoinitiation Systems

The instrument for the laser flash photolysis

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using a total reflection cell is shown in Fig. 1 [1,7]. The cyclohexanone solutions containing 10 wt % of PMMA (weight average of molecular weight \( M_w \); \( M_w = 5 \times 10^4 \)), 0.039 mol dm\(^{-3}\) of NAS, 0.004 mol dm\(^{-3}\) of BI, and 0 ~ 0.1 mol dm\(^{-3}\) of PETA were coated with a 1.2 \( \mu \)m thickness on a sapphire cell (10 \( \times \) 30 mm, 1mm thickness, and both short sides were cut at an angle of 45°). A monitor light beam from a xenon lamp was introduced through a multi-reflection 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 TYPE R928) or to a SMA system (Princeton Instruments, Inc. Model TRY-700G/R/Par). The excitation light pulse (20 n sec, 355 nm, 10 mJ per pulse) from a YAG laser (Spectron Laser Systems Model SL 402) was expanded and exposed all over the sample cell. The measurement was repeated three times with less than 5 wt % of the decomposition of NAS 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 NAS, and NAS was homogeneously photoexcited in the film due to their low absorbance, less than 0.35 at 355 nm.

3. Results and Discussions

**Laser flash photolysis in a PMMA film.**

On an excitation of MMA film containing NAS...
by 355 nm laser pulse under an air atmosphere, strong fluorescence and significantly-weak-transient absorption, which was not assigned yet, were detected as described in earlier investigation [3-4,8]; the fluorescence was statically quenched by BI at the quenching distance (Rf), Rf = 11 Å.

Fig. 2 shows the transient absorption in a PMMA film containing NAS, 0.39 mol dm⁻³, and BI at the quenching distance (Rf).

Fig. 3. Decay of Im⁺ on 560 nm for a PMMA film containing NAS and BI at various concentrations of PETA without PVA-over layer (a) ~ (c), and with PVA-over layer (d) ~ (f). a) Substance concentration: NAS; 0.39 mol dm⁻³, BI; 0.04 mol dm⁻³ and PETA; 0, 0.5, and 1 mol dm⁻³. b) Excitation wavelength: 355 nm.

Fig. 4. Quenching of Im⁺ -initial absorption on 560 nm for a PMMA film containing NAS and BI by PETA without PVA-Over layer ( - ■ - ) and with PVA-over layer ( - ◆ - ). a) Substance concentration: NAS; 0.39 mol dm⁻³, BI; 0.04 mol dm⁻³ and PETA; 0 ~ 1 mol dm⁻³. b) Excitation wavelength: 355 nm. c) ABS: initial absorbance, ABS⁰: initial absorbance in the absence of PETA.

Fig. 5. Decay of Im⁺ resultant from direct photolysis of BI in a PMMA film.

a) Substance concentration: BI; 0.42 mol dm⁻³ in a PMMA.

b) Excitation wavelength: 355 nm, detection wavelength: 560 nm.

BI, 0.04 mol dm\(^{-3}\) under an air atmosphere (Fig. 2 (a)) and under the condition of PVA-over layer (Fig. 2 (b)). The transient absorption profile with absorption maximum, ca. 550 nm, at different times, 1 ~ 3, and 80 \(\mu\) s after an excitation of 355 nm laser pulse was almost same, and was assigned as Im \(\cdot\) from the comparison of the spectrum of Im \(\cdot\) reported by X. Z. Qin et al \[9\].

Fig. 3 depicts the decays of Im \(\cdot\) on 560 nm detected in a PMMA film containing NAS, 0.39 mol dm\(^{-3}\), and BI, 0.04 mol dm\(^{-3}\) at various concentrations of PETA under an air atmosphere (Fig. 3 (a) ~ (c)) and under the condition of PVA-over layer (Fig. 3 (d) ~ (f)). In the absence of PETA, both initial absorbances (absorbance during 1 ~ 3 \(\mu\) s) under an air atmosphere and under the condition of PVA-over layer were almost same, and decreased with the concentration of PETA. The quenching mechanism of Im \(\cdot\) by PETA was not clear yet, however logarithmic plots of both initial absorbances at various concentrations of PETA were apparently fitted to Perrin plots equation \[11\] as shown in Fig. 4, exhibiting a static quenching. If we assume a static quenching mechanism with respect to the quenching, the quenching distances (R\(i\)) were obtained, R\(i\) = 1.8 and 1.4 Å for the condition under an air atmosphere and PVA-over layer from the slopes of the Perrin plots. When assuming a diffusion-controlled quenching of Im \(\cdot\) by PETA, the initial intensity of the decay for decay time, \(\tau\) 2 and \(\tau\) 3, should not be changed and only the decay times, \(\tau\) 2 and \(\tau\) 3, were reduced with the concentration of PETA.

In the decays of Im \(\cdot\) under an air atmosphere in Fig. 3, Im \(\cdot\) decayed with both decay times of 20 \(\mu\) s (\(\tau\) 1) during 0 ~ 30 \(\mu\) s and 72 \(\mu\) s (\(\tau\) 2) during 40 ~ 80 \(\mu\) s in the absence of PETA, and the decay signal did not go back to the original-base line; ca. 30 % of initial Im \(\cdot\) signal remained 100 \(\mu\) s after an excitation. Under the condition of PVA-over layer, Im \(\cdot\) decayed single-exponentially with the decay time of 70 \(\mu\) s (\(\tau\) 3) in the absence of PETA, and the decay signal also did not go back to the base line; ca. 50 % of initial Im \(\cdot\) remained 100 \(\mu\) s after 355 nm excitation. When incorporating PETA from 0 to 1 mol dm\(^{-3}\), the intensity of fast decay with the intensity of decay with the decay times, \(\tau\) 2 decay time, \(\tau\) 1, was significantly attenuated, and \(\tau\) 3, was gradually attenuated, however the decay times of \(\tau\) 2 and \(\tau\) 3 were almost same.

In the comparison of \(\tau\) 1 with \(\tau\) 2 and \(\tau\) 3, \(\tau\) 1 was much shorter than \(\tau\) 2 and \(\tau\) 3. The origin of the shorter decay time of \(\tau\) 1 under an air atmosphere was considered due to Im \(\cdot\) quenching by oxygen. Under the PVA-over layer, PVA-over layer suppressed the oxygen-permeation from air atmosphere into photopolymer layer, so that the decay for the decay time, \(\tau\) 2, disappeared. From the decay time, \(\tau\) 1 = 20 \(\mu\) s, for the fast quenching of Im \(\cdot\) by oxygen, a quenching rate constant (k\(q\)), k\(q\) = 1.2 \(\times\) 10\(^7\) mol\(^{-1}\) dm\(^3\) s\(^{-1}\), was estimated using an equilibrium oxygen concentration, 0.003 mol dm\(^{-3}\) which was founded in Refs. 11 and 12. For O\(_2\) permeability coefficient (P) at 25 °C, P\(_s\) = 1.15 and 0.0089 \(\times\) 10\(^{10}\) cm\(^3\) (STP) cm cm\(^{-2}\) s\(^{-1}\) (cm Hg)\(^{-1}\) for PVA and poly(ethyl methacrylate) are described in Ref. 14, and a part of oxygens in the photopolymer layer were exhausted by dark reactions such as slow decomposition of photo-initiators at room temperature (25 °C) \[10\]. Thus equilibrium-oxygen concentration in the photopolymer layer under an air atmosphere became higher than that under the PVA-over layer, leading to that Im \(\cdot\) was quenched by oxygens during ca. 20 \(\mu\) s under an air atmosphere; ca. 30 % of initial Im \(\cdot\) in photopolymer layer under an air atmosphere was
quenched during 20 µs by oxygens in the absence of PETA.

In the slow quenching corresponding to the decay with decay time, \( \tau_2 \) and \( \tau_3 \): ca. 70 µs (Fig. 3), the slow quenching was accounted by the

\[
\text{NAS}^* + \text{BI} \rightarrow \text{NAS}^+ + \text{Im}^* + \text{ImH} \quad (1) \ 	ext{much fast (less than ns)}
\]

\[
\text{Im}^* + \text{Im}^* \rightarrow \text{BI} \quad (2) \ 	ext{slow (70 µs)}
\]

\[
\text{Im}^* + \text{O}_2 \rightarrow \text{Im-oo}^* \quad (3) \ 	ext{fast (20 µs)}
\]

\[
\text{Im}^* + \text{PETA} \rightarrow \text{Im-PETA}^* \quad (4) \ 	ext{much fast (less than 1 µs)}
\]

\[
\text{Im-PETA}^* + \text{O}_2 \rightarrow \text{Im-PETA-oo}^* \quad (5) \ 	ext{much fast (less than 1 µs)}
\]

Fig. 6 Scheme in quenching of \( \text{Im}^* \) by oxygen (\( \text{O}_2 \)).

recombination of \( \text{Im}^* \) [9], since both decay times, \( \tau_2 \) and \( \tau_3 \), in photopolymer layer both without and with PVA-over layer were almost same; the results indicated the quenching was not dependent on oxygen. Moreover in laser-flash photolysis of BI in a PMMA film under an air atmosphere, a fast decay with decay time, ca. 20 µs due to quenching by oxygen and a almost-same- slow decay with decay time, ca 70 µs was observed (Fig. 5).

In the fast decay with the decay time, \( \tau_1 \), under an air atmosphere, the decay intensity was reduced with increasing the concentration of PETA, the result suggests a possibility of oxygen-trapping mechanism dependent on PETA as described in Eqs. 1 – 6 in Fig. 6.

\( \text{Im}^* \), which was obtained from singlet-sensitized decomposition of BI by NAS during less than ns (Eq.1), behaves as follows, \( \text{Im}^* \) is slowly quenched by recombination of \( \text{Im}^* \) during ca. 70 µs after an excitation (Eq. 2), fast quenched by oxygen during ca. 20 µs (Eq. 3), or much fast quenched by \( \text{Im-PETA}^* \) during less than 1 µs (Eq. 4) which was derived from the much-fast reaction of \( \text{Im} \) with PETA during less than 1 µs (Eq. 5).

In the presence of PETA\( \cdot \), which scavenged oxygen, leading to the low PETA, PETA reacted with \( \text{Im} \) forming \( \text{Im}\)-concentration of oxygen immediately; that is within the rise time of \( \text{Im}^* \). Thus the fast decay with decay time, ca. 20 µs under an air atmosphere was decreased with the increase of PETA.

As for the deviation of static quenching rate with the hardness change of photopolymer layer by incorporating PETA into the photopolymer layer, we discussed the effect of static quenching rate with the decreasing hardness of photopolymer layer in the previous report of Ref 1-d; when incorporating 25 weight % (wt %) of dimethyl phthalate (DMP) as a plasticizer against the total-solid into the photopolymer layer containing keto-coumarin- and coumarin sensitizer dyes and a peroxide as a radical generating reagent, ca. 10 % of a static-quenching distance was increased. Thus a deviation of the quenching distance (Ri) by the decreasing hardness of photopolymer layer containing 30 wt % of PETA was considered as less than ca. 10 %. Moreover we
were considered as less than ca. 10%. Moreover we carried out control experiments for comparison: 1) a quenching of NAS’s fluorescence in a PMMA film by incorporating 25wt % of PETA and DMP, and 2) a quenching of Im • resulted from NAS-sensitized photolysis of BI by DMP. NAS’s fluorescence intensities for photopolymer with PETA and DMP were almost same, and the initial intensity of Im • was not changed by incorporating DMP. Thus the deviation of initial intensity of Im • by decreasing hardness of photopolymer layer with the concentration PETA practically be ignorable.

Finally it is concluded that PETA predominately quenched the initial absorption of Im • .

References