Three-Component Photo Radical Initiating Systems
-The Effect of Accelerator-

Shota Suzuki, Toshiyuki Urano\textsuperscript{ab}, Nobukazu Miyagawa, Shigeru Takahara, and Tsuguo Yamaoka

Department of Information and Image Science, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522 Japan
\textsuperscript{a) Research Center, Mitsubishi Kagaku Corporation, Aoba-ku, Yokohama 227 Japan \textsuperscript{b) Center for cooperative research, Chiba University, Inage-ku, Chiba 263-8522, Japan}

Keywords: N-phenylglycine, accelerator, imidazolyl radical, photopolymerization, laser imaging

1. Introduction

Recently, with the rapid development of laser imaging technology, such as Computer to Plate and hologram, photofunctional materials have been developing. One of the most important factors that affect the sensitivity of photopolymer is the initial reaction of photo-initiating system. So there are a lot of research groups that have focus on various initiating systems and most of the initiating systems are composed of two or three components \cite{1}.

We already reported the photosensitive initiating system that was composed of sensitizer, 2-[p-(diethylamino)styryl]naphtho[1,2-d]thiazole (NAS), radical generating reagent, 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,1'-bi-1H-imidazole (BI), and accelerator, 2-mercaptobenzothiazole (MBT)\cite{2,3}. We studied mainly by laser flash photolysis using total reflection cell in poly(methyl methacrylate) (PMMA) film\cite{2-10} and the results showed that the combination of NAS and BI in the presence of MBT afforded high sensitivity for Argon ion laser. The enhancement of sensitivity was caused by the increase of imidazolyl radical (Im • ). It was suggested that MBT works as an accelerator because of increasing the initial concentration of Im • by slowing down the back-electron transfer from BI anion to NAS cation, and also works as a radical (Im • ) quencher because of abstracting a hydrogen from MBT to Im •.

In this paper, N-phenylglycine (NPG) was used as an accelerator instead of MBT and the effect of accelerator was studied from the data of MBT and NPG.

2. Experimental

2.1 Materials

The sensitizer, NAS was prepared by the condensation of 2-methylnaphtho[1,2-d]thiazole with p-diethylamino-benzaldehyde. The radical generating reagent, BI was prepared according to the reported procedure \cite{2,3}. The accelerator, NPG and MBT were purchased from Tokyo Chemical Industry Co. LTD.
2.2 Absorption and fluorescence spectra

UV-visible spectra were recorded using Hitachi U-3000 spectrophotometer. Fluorescence spectra were recorded using F-4500 spectrophotometer. For all the quenching experiments, the NAS concentration was adjusted to have an absorbance of 0.1 and concentration of quenchers were normally in the order of $10^{-2}$ to $10^{-3}$ mol/dm$^3$.

2.3 Laser flash photolysis

Transient spectra and decay were carried out using nanosecond laser flash photolysis. The cyclohexanone solution including 10wt% of PMMA, 0.57mol/dm$^3$ of NAS, 0.06 mol/dm$^3$ of BI, and 0~0.22 mol/dm$^3$ of MBT or NPG were coated to form the 1.2 µm thickness on a sapphire cell (10 × 30 mm, 1mm thickness, and both short sides were cut at 45 degree angle). A monitor light beam from a Xenon lamp was introduced through a multi-reflection cell and then captured onto the head of an optical fiber that directs the beam to a monochrometer (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/Par). The 355nm light (10mJ/pulse) from a YAG laser (Specron Laser Systems Model SL402) was used for excitation. More than 90% of the 355nm light absorbed in the sample film was absorbed by the dye, and the dye was homogeneously photoexcited in the film due to their low absorbance, less than 0.25 at 355nm.

2.4 Sensitivity

The cyclohexanone solution composed of poly- (benzylmethacrylate-co-methacrylic acid), pentaerythritol triacrylate (PETA), NAS, BI, and accelerator was prepared. The weight ratio of poly-(BzMA-co-MAA), PETA, NAS, BI, and accelerator was 100:100:1:10:5. Then the solution was coated on 5 × 5cm glass plates or aluminium plates that had been electrolyzed and oxidized and prebaked at 100°C for 2 minutes. The plate was exposed to an Argon ion laser (488nm) through a step tablet (Kodak No.2). After exposure, the plate was developed with a solution of 2.38% tetrarmethylammonium hydroxide (TMAB) for 30 seconds. After washing with water, the image was obtained and the sensitivity was determined from the images.

3. Results and Discussion

New characteristic absorption band wasn't observed when BI or NPG was added to NAS (Fig.1). It suggests that BI and NPG have no interaction with NAS in the ground state and there isn't an effect of static quenching.

![Figure 1(a,b). Absorption spectra of (a) NAS and BI (b) NAS and NPG in PMMA film.](image1)

Fig 2 shows the quenching of bimolecular reaction in PMMA film. In the presence of BI, the radius of the quenching sphere, which was determined using Perrin equation, was 12.8 Å. In the case of NPG, it was 7.37 Å. So the combination of NAS and BI is more effective for the quenching than that of NAS and NPG.

![Figure 2(a,b). Quenching of bimolecular reaction in PMMA film ($\lambda_{ex} = 355nm$). The concentration of NAS is held fixed (3.35×10$^{-2}$ mol/dm$^3$) and the concentration of BI (a) and NPG (b) is varied.](image2)
Fig. 3 shows the transient absorption spectra in the absence and presence of NPG. The absorption maximum (550 nm) was almost the same even at 80 µs after the laser excitation. As compared with the spectrum of imidazolyl radical (Im•) reported by X.Z. Qin et al [11], the transient absorption spectra we observed were assigned as Im•.

Fig. 4 shows the effect of NPG, which was obtained from the transient decay at 560 nm. The initial absorption of the decay increased from 0.19 to 0.31 with the concentration of NPG increased from 0 to 0.22 mol/dm³.

Fig. 5 shows the quenching of imidazolyl radical by NPG. The quenching rate constant was determined $5.7 \times 10^3$ mol⁻¹ dm³s⁻¹.

Summarizing the above discourse, NPG can increase the initial concentration of imidazolyl radical and work as a radical quencher. Both two works are similar to the case of MBT[2,3].

Taking these results into consideration, the sensitivity of photopolymer was measured on aluminum plate (Table 1.) at first. Both of the accelerators could enhance the sensitivity, but NPG was superior to MBT.

<table>
<thead>
<tr>
<th></th>
<th>NAS and BI</th>
<th>NAS, BI, and NPG</th>
<th>NAS, BI, and MBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al plate</td>
<td>12.3</td>
<td>8.93</td>
<td>6.32</td>
</tr>
<tr>
<td>glass plate</td>
<td>17.8</td>
<td>12.3</td>
<td>12.3</td>
</tr>
</tbody>
</table>

unit: mJ/cm²

Table 1. The sensitivity of photopolymer

Fig. 3. Transient absorption spectra of PMMA film including two or three-component. (a) 0.57 mol/dm³ NAS and 0.06 mol/dm³ BI, (b) 0.57 mol/dm³ NAS, 0.06 mol/dm³ BI, and 0.22 mol/dm³ NPG.

Figure 4. Transient decay of PMMA film including NAS and BI with various concentration of NPG monitored at 560 nm. (a) 0.57 mol/dm³ NAS, (b) 0.57 mol/dm³ NAS and 0.06 mol/dm³ BI (c) ~ (e) the concentration of NAS and BI is held fixed, and the concentration of NPG is varied (0.05 ~ 0.22 mol/dm³).

Figure 5. Quenching of imidazolyl radical by NPG
There are a lot of factors that affect the sensitivity, but it was not so difference between NPG and MBT on the initial reaction of photo radical initiating system. So we focused on another factors such as adhesion to know the difference between two accelerators and tried other plates such as glass plate. Table 1 shows the results. In the case of glass plate, the sensitivity was also enhanced, but the ratio of enhancement was almost the same between two accelerators. So it is suggested that NPG affects something between the photopolymer coating layer and the aluminium plate.

4. Conclusion
NPG can work as an accelerator because the sensitivity of the photopolymer including NPG is 1.9 times higher than that of not including system. Viewed in photochemistry, the effect of accelerator is almost the same as MBT, but take a developing process into consideration, NPG has something peculiarly its own. It is suggested that NPG affects something such as adhesion between the photopolymer coating layer and the aluminium plate. Currently, we are continuing our study on the effect of accelerator in PMMA film.

5. References