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Three-component photo radical initiating system—the effect of 2-mercaptobenzothiazole as a co-initiator in polymer matrix

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Abstract

We studied the sensitization mechanism in a photo initiating system that consists of an aminostyryl sensitizing dye, 2-[*p*-(diethylamino)styryl]naphto[1,2-d]thiazole (NAS), and a radical generator, 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1, 1′-bi-1*H*-imidazole (HABI). In a photopolymer bearing NAS/HABI system, an improvement of the photosensitivity was observed by the addition of co-initiator, 2-mercaptobenzothiazole (MBT), to the initiating system. Photochemical and photophysical behavior of the three-component initiating system, NAS/HABI/MBT, in the PMMA film was studied by means of a nanosecond laser flash photolysis method employing a total reflection sapphire plate. It is considered that MBT can enhance to generate the triplet state of NAS, which is hardly observed by the direct excitation, and the mechanism of both singlet and triplet electron transfer from NAS to HABI is suggested.

Keywords: Three-component initiating system; Co-initiator; Imidazolyl radical

1. Introduction

In recent years, with the rapid development of laser direct imaging technology such as computer-to-plate technology (CTP), much attention has been paid to photofunctional materials. One of the most important factors that affect the photosensitivity of photopolymer is the initial reaction in the photo initiating system. In this field, the photopolymer mainly consists of a binder polymer, an acrylate monomer, the radical generator, and the sensitizing dye. The sensitizing dye absorbs the light of the corresponding visible laser at first, then reacts with the radical generator by energy or electron transfer to generate an initial radical which can react with the monomer. Many research groups have focused on the photo initiating systems and lots of reports concerning a novel photo initiating system, sensitization mechanism in solution, and the photochemical and photophysical behavior in solution or polymer matrix [1–13] have been proposed so far. However, there are few reports concerning the sensitization mechanism in polymer matrix that is closer to the system currently employed in CTP or other microlithographic processes.

We have already studied the photochemical and photophysical behavior of each component, NAS, HABI, and MBT, as summarized in Table 1. Fluorescence lifetime of NAS was very short similar to other polymethyne dyes and stokes shift was very large, 4602 cm^{-1}. It is considered that the twisted intramolecular charge transfer (TICT) occurs mainly in the excited state of NAS [15–18]. Moreover, by applying the picosecond laser flash photolysis method for NAS, S–S absorption and very weak transient absorption that might be assigned to the triplet state [17] were observed. In the case of HABI, the long-lived imidazolyl radicals, which were assigned from the comparison of the spectrum reported by X.Z.Qin [19], were observed. No transient species were obtained by the direct excitation of MBT even at high concentration. Sensitization mechanisms for the NAS/HABI and NAS/HABI/MBT system in the PMMA film were also studied by means of the nanosecond

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Table 1
Photophysical properties of each component

	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})	$\varepsilon_{355\ nm}$(M^{-1} cm^{-1})	E_{max} (nm)	τ_f (ps)
NAS	415	28,200	4500	513	100[a]
HABI	269	21,400	480	–	–
MBT	326	20,600	580	–	–

[a] Ref. [17].

laser flash photolysis method employing the total reflection sapphire plate [14]. Singlet electron transfer is considered as the main reaction pathway for the NAS/HABI system and the improvement of the photosensitivity was observed by the addition of MBT and the effect of MBT is suggested as an electron donor toward NAS that loose an electron by singlet electron transfer to HABI or hydrogen donor toward imidazolyl radicals [15–18].

In this report, we describe the sensitization mechanisms for the NAS/MBT and NAS/HABI/MBT system in the PMMA film by means of spectroscopic techniques and the laser flash photolysis method in the PMMA film and propose another important role of MBT in the improvement of the photosensitivity, which is neither electron donor nor hydrogen donor and is observed especially in polymer matrix.

2. Experimental section

2.1. Materials

The sensitizing dye, NAS, was synthesized by the condensation of 2-methylnaphto [1,2-d]thiazole with *p*-diethylamino-benzaldehyde [15–18]. The radical generator, HABI, was provided by Mitsubishi Chemical Corporation and used without further purification. The co-initiator, MBT, was purchased from Tokyo Kasei and recrystallized twice from ethanol. Their corresponding structures are shown in Fig. 1. The binder polymer, PMMA ($M_w = 76{,}000$, $D = 1.82$), was purchased from Wako Chemicals and used as received. A cyclohexanone solution for dissolving the PMMA was also purchased from Wako Chemicals. A copolymer of a methyl methacrylate (MMA) and a methacrylic acid (MAA) for photosensitivity measurement was synthesized by the copolymerization using 2,2′-azobis(isobutyronitrile) (AIBN) as a thermal initiator. Pentaerythritol triacrylate mono-mer (PETA) was purchased from Aldrich and used as received. A triplet sensitizer, Michler's ketone (MK), was purchased from Wako Chemicals and recrystallized from ethanol.

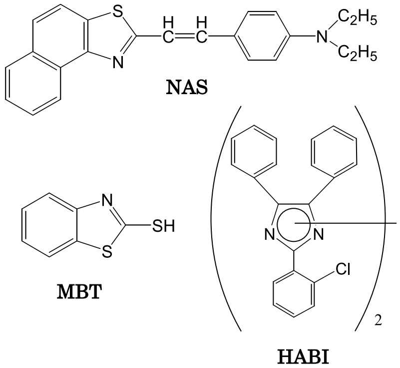


Fig. 1. Chemical formulae of the three-component photo initiating system.

2.2. Absorption and fluorescence spectrum

Ground state absorption and fluorescence spectra in the PMMA film were recorded on a Hitachi U-3000 spectrophotometer and a Hitachi F-4500 spectrophotometer, respectively.

The cyclohexanone solution including 10 wt% of PMMA was coated (2000 rpm, 1 min) by the spin-coater (Techno Staff, MY SPINNER) on a quartz plate. After evaporating the solvent at 100 °C for 5 min (iuchi, MULTI HOTPLATE MH-180), polymeric films of 1.2 μm thickness were obtained.

In all the quenching experiments, the concentration of NAS was adjusted to have an absorbance of ca. 0.1 and the concentration of the radical generator, HABI, was normally in the order of 10^{-2}–10^{-1} mol/dm^3.

2.3. Nanosecond laser flash photolysis method in the PMMA film

Transient absorption spectra and decay kinetics in the PMMA film were carried out using the nanosecond laser flash photolysis method. The cyclohexanone solution including 10 wt% of PMMA, various concentration of NAS, HABI, and MBT were coated to form the 1.2 μm thickness on the sapphire plate (10×30 mm, 1 mm thickness and both short side were cut at 45°). A monitor light beam from a Xenon lamp was introduced through the total reflection sapphire plate and then captured onto the head of an optical fiber that directs the beam to a monochrometer (Instrument Digikrom 240) with a photomultiplier (Hamamatsu Photonics K.K. photomultiplier tube type R928) or a SMA system (Princeton Instruments, Inc. Model TRY-700G/R/Par). The third harmonic of a nanosecond Nd:YAG laser (355 nm, 18 ns, 10 mJ/pulse) (Spectron Laser System Model SL402) was used for excitation. The experimental arrangement is schematically shown in Fig. 2. More than 90% of the 355 nm light was absorbed by the sensitizing dye and it was homogeneously excited in the PMMA film due to its low absorbance, less than 0.35 at 355 nm.

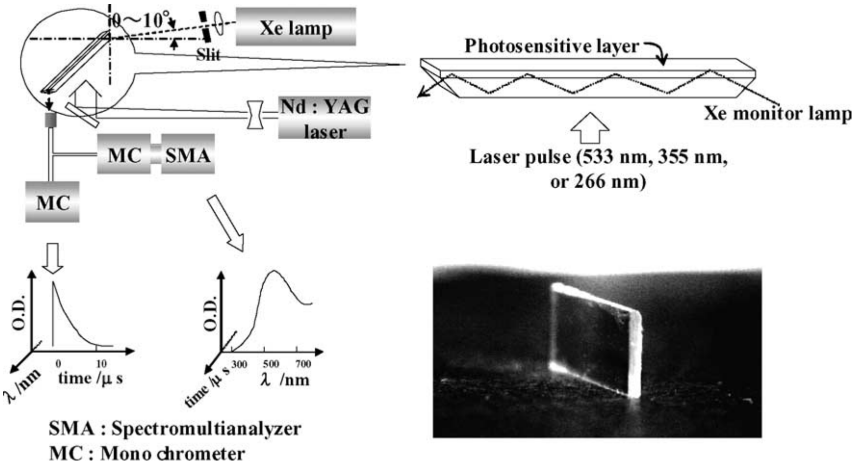


Fig. 2. Schematic of the laser flash photolysis system in the polymer matrix. Inset photograph: actual sapphire plate (10×30 mm, 1 mm thickness and both short side are cut at 45°).

2.4. Photosensitivity measurement

The sensitizing dye, NAS, was typically used in formulations consisting of the MMA–MAA copolymer, the acrylate monomer, the radical generator, the sensitizing dye, and the co-initiator combined in a weight ratio of 100:100:10:1:8 and they were dissolved in cyclohexanone (11.1% by weight of solids). The photopolymer solution was deposited on a grained Al plate and baked at 100 °C for 5 min (1.2 μm thickness), and then 10 wt% polyvinyl alcohol (PVA) aqueous solution was coated on the photopolymer layer to avoid the oxygen inhibition (2.0 μm thickness after baking). The photosensitive layer was flood-exposed by an argon ion laser (1.2 mJ/cm^{2}sec, 488 nm) through a step tablet (Kodak, photographic step tablet no.2) which contains the optical density, 0.15 each from 0 to 3.05, followed by the removal of the PVA overcoat layer, it was developed in a 2.38 wt% aqueous solution of tetramethylammonium hydroxide (TMAH) for 1 min. The photosensitivity, that is, lowest exposure energy (E) to polymerize the photopolymer was determined using the following equation:

$$E = I_0 \times t \times 10^{-\mathrm{OD}}$$

where I_0 is the incident light energy of the argon ion laser (1.2 mJ/cm^2 s), t and OD is the lowest exposure time and optical density of the step tablet image that remains polymerized on the developed layer, respectively [6].

3. Results and discussion

3.1. NAS/MBT system

In the presence of MBT, slight red shift in the ground state absorption spectrum of NAS was observed (Fig. 3). It is suggested that static quenching occurred in the PMMA film; therefore, we did a quenching experiment for the NAS/MBT system as shown in Fig. 4. The fluorescence of NAS was efficiently quenched with increasing MBT concentration and the radius of the quenching sphere in the system was determined from the following Perrin equation [20,21].

$$I_{f0}/I_{fq} = (4\pi R^3/3)N[\mathrm{MBT}]$$

where I_{f0} and I_{fq} represent the fluorescence intensity in the absence and presence of the quencher (MBT), respectively. R is the quenching radius, N is the Avogadro's number, and [MBT] is the concentration of MBT. The Perrin model assumes that the sensitizing dye and the radical generator cannot undergo displacements in space during the lifetime of the excited state of the sensitizing dye (S*), there exists a volume in space so-called quenching sphere about S* whose radius is R, and if a quencher molecule is within this quenching sphere, then S* is deactivated with unit efficiently [20]. These assumptions are suitable for our experimental condition in the PMMA film; therefore, we applied the Perrin equation and the quenching radius of

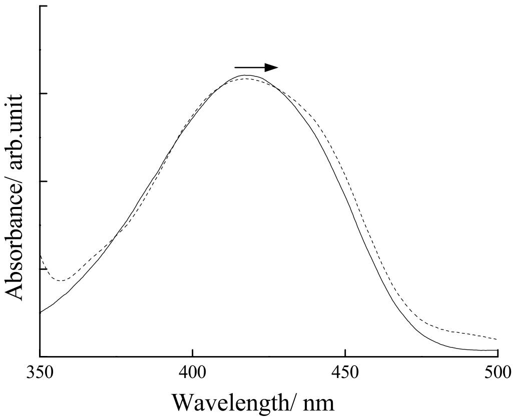


Fig. 3. Change in the ground state absorption spectra of NAS (0.21 mol/dm^3) in the absence (solid) and presence of MBT (broken, 0.55 mol/dm^3) in the PMMA film.

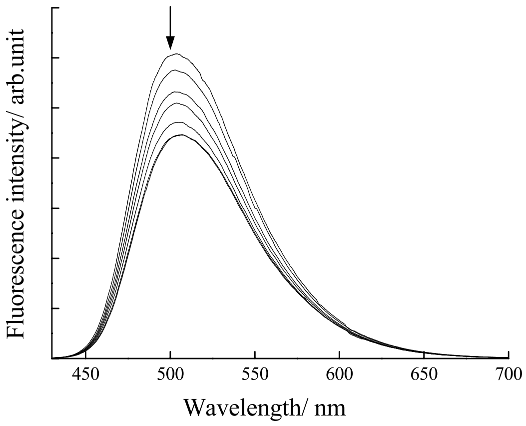


Fig. 4. Fluorescence quenching of NAS in the NAS/MBT system in the PMMA film. [NAS]: 0.21 mol/dm^3, [MBT]: 0–0.68 mol/dm^3.

6.67 Å was obtained as shown in Table 2. Though this value is low compared with the NAS/HABI system (12.8 Å), we considered some kinds of reaction might occur in the NAS/MBT system, and then measured the transient absorption spectrum (Fig. 5) and the change in decay kinetics (Fig. 6) in the PMMA film. The transient absorption spectrum was similar to that of the direct excitation of NAS (Fig. 5, inset) to some extent and the initial absorption increased significantly with increasing MBT concentration. Two possibilities are considered about the transient species.

Scheme 1 shows the possibility of donating the electron from MBT to NAS, which is thermodynamically allowed [15–18], and a generated thiyl radical was reported to have good ability to induce radical polymerization [13]. Another possibility was that we might observe the triplet state of NAS (Scheme 2). The transient species were strongly affected by oxygen, that is, when the PVA over coat layer was coated, which is often used to protect the oxygen inhibition in the field of CTP, the faster component of the decay disappeared and the decay time became longer. To confirm the possibility of the path to generate the triplet state (Scheme 2), we applied triplet–triplet energy transfer from MK to NAS. MK originally has high triplet quantum yield and triplet energy [22]; therefore, triplet–triplet energy transfer is easily induced in this bimolecular reaction. We investigated the triplet state of MK in the PMMA film at first since there are few reports concerning it in polymer matrix. Fig. 7 shows the transient absorption spectra of MK in the PMMA film by the 355 nm laser pulse irradiation. R.G. Brown and G. Porter already reported the triplet state of MK in solution [23] and our result was similar to their report, accordingly obtained transient absorption spectra were assigned to the triplet state of MK, then we tried the triplet–triplet energy transfer from MK to NAS. In this experiment, the concentration of MK was adjusted to have much higher absorbance than that of NAS and the concentration of NAS was changed in the range of 0–0.21 mol/dm^3. The decrease in triplet absorption of MK was monitored at 480 nm, a wavelength region where no transient absorption of NAS was observed, and the increase in triplet absorption of NAS was monitored at 540 nm, respectively. Fig. 8 shows the triplet state of NAS obtained from triplet–triplet energy transfer. It is notable that the profile of the triplet state of NAS is very similar to that of the transient absorption obtained from the NAS/MBT system

Table 2
Quenching radius and photosensitivity in each combination

	Quenching radius (Å)	Photosensitivity (mJ/cm^2)
NAS/MBT	6.67	–[a]
NAS/HABI	12.8	12.3
NAS/HABI/MBT	–	6.32

[a] Upper limit: 1.2 J/cm^2.

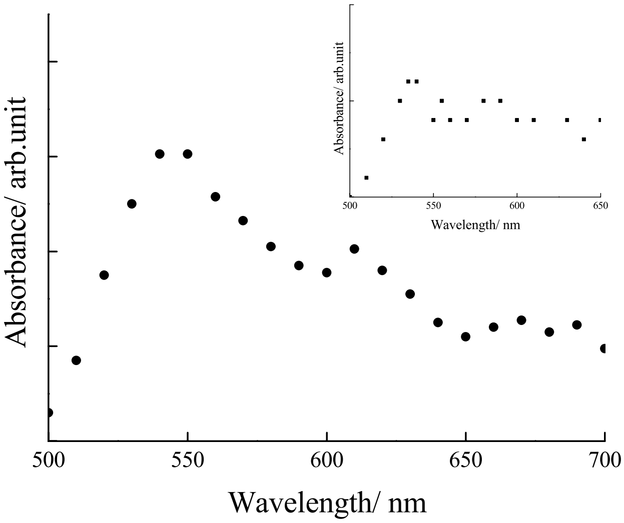


Fig. 5. Transient absorption spectrum in the NAS/MBT system: 3 μs after the laser pulse. Inset: transient absorption spectrum of NAS in the PMMA film.

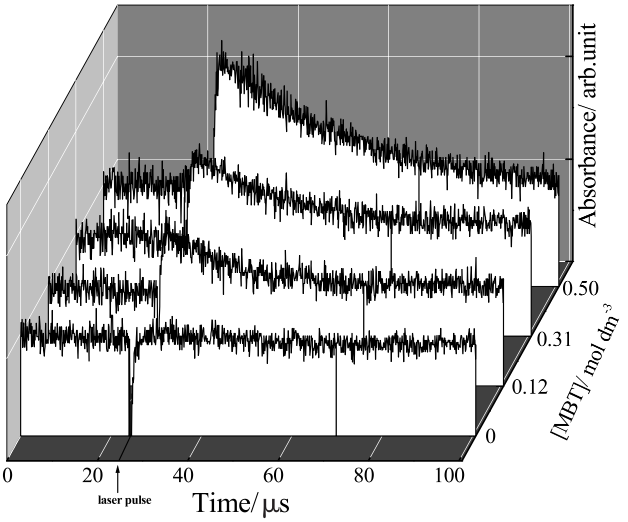
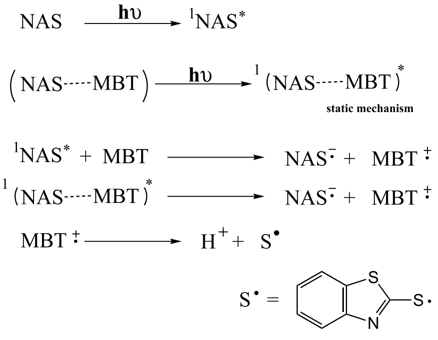


Fig. 6. The change in decay kinetics in the NAS/MBT system in the PMMA film monitored at 540 nm. [MBT]: 0–0.50 mol/dm^3.

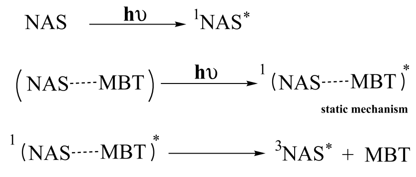


Scheme 1.

(Fig. 5). Taking this similarity into consideration, it is suggested that the obtained transient spectrum might be the triplet state of NAS (Scheme 2), and besides, if Scheme 1 occurred mainly, in other words, we observed a radical anion of NAS or its related intermediate, thiyl radicals should be generated more or less and the photopolymer bearing NAS and MBT should exhibit the photosensitivity, however, this combination did not give it at all (Table 2), accordingly, we consider the mechanism as shown in Scheme 2 might occur, that is, triplet state of NAS is enhanced by the addition of MBT.

3.2. NAS/HABI/MBT system

In the case of three-component photo initiating system, the considerable transient species are as follows: (1) Imidazolyl radical (obtained from the NAS/HABI system), (2) Triplet state of NAS (obtained from the NAS/MBT system), (3) New transient species. It is not so difficult to distinguish the possibility (1) from (2) since both decay profiles are different and the transient absorption spectrum of (1) does not possess significant absorption around 600 nm in comparison with (2). Figs. 9 and 10 show, respectively, the transient absorption spectra and the change in decay kinetics in the NAS/HABI/MBT system. Both transient absorption spectra and decay kinetic were similar to that of imidazolyl radial (Im•), accordingly we assigned it to Im• as well as the case of the NAS/HABI system. It is surprising that the initial absorption of Im• in the case of NAS/HABI/MBT system is 2.75 times higher than that of NAS/HABI system at the maximum (Fig. 10). As we mentioned before, the difference of these two systems are that the triplet state of NAS might be enhanced by the MBT addition as regards the three-component system. For the purpose of confirmation, we investigated the photochemical behavior in the HABI/MBT system by means of absorption spectrum and laser flash photolysis method. However, no spectral changes and transient species originated from the bimolecular reaction between HABI and MBT were observed. Hence we concluded that the increase in imidazolyl radicals were exceedingly concerned with the triplet state of NAS and suggest the following sensitization mechanism, both singlet and triplet electron transfer from NAS to HABI might occur by the addition of MBT (Scheme 3).



Scheme 2.

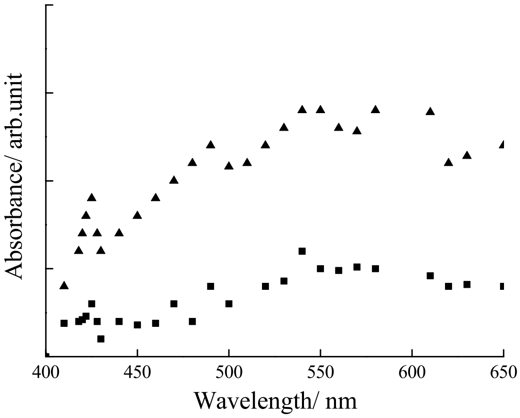


Fig. 7. Transient absorption spectra of MK: 3 μs (triangle) and 80 μs (square) after the laser pulse.

3.3. Photosensitivity

Table 2 shows the photosensitivity in the photopolymer bearing NAS/MBT, NAS/HABI, or NAS/HABI/MBT system. It is often said that imidazolyl radicals are relatively stable and only initiate polymerization with low efficiency [13]; however, NAS/HABI system could exhibit high photosensitivity. Moreover, by incorporating MBT, the photosensitivity was improved about 1.95 times in comparison with two-component system. This result corresponds with that of the increase of Im• in the laser flash photolysis experiment.

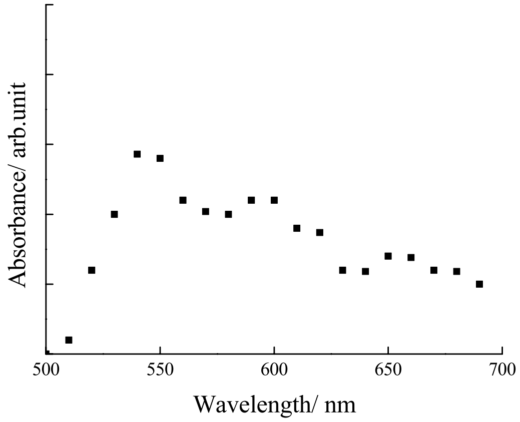


Fig. 8. Transient absorption spectrum in the MK/NAS system: 3 μs after the laser pulse.

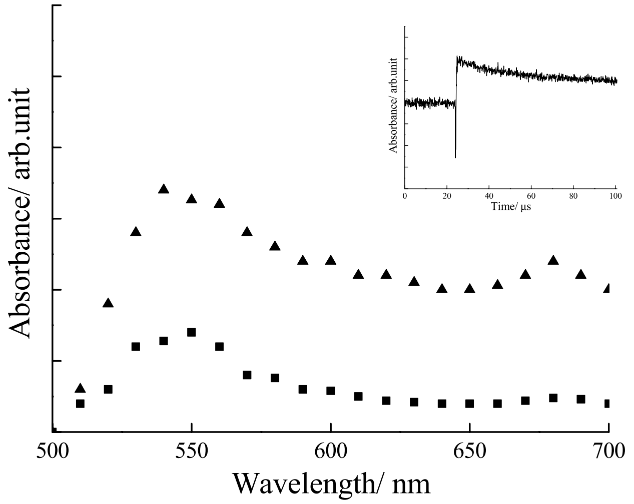


Fig. 9. Transient absorption spectra in the NAS/HABI/MBT system: 3 µs (triangle) and 80 µs (square) after the laser pulse. Inset: decay kinetic.

4. Conclusion

We studied the sensitization mechanisms in the NAS/MBT and NAS/HABI/MBT system in the PMMA film. The transient species that might be assigned to the triplet state of NAS was observed as regards the NAS/MBT system and the initial absorption of the transient increased with increasing the MBT concentration. In the case of three-component system, the initial absorption of imidazolyl radicals was also increased by the addition of MBT. It is suggested that the triplet state of NAS was enhanced by MBT and additional sensitization, that is, triplet electron transfer from NAS to HABI might occur. Finally, we conclude that electron transfer occur via both singlet and triplet state of NAS, resulting in the improvement of the photosensitivity.

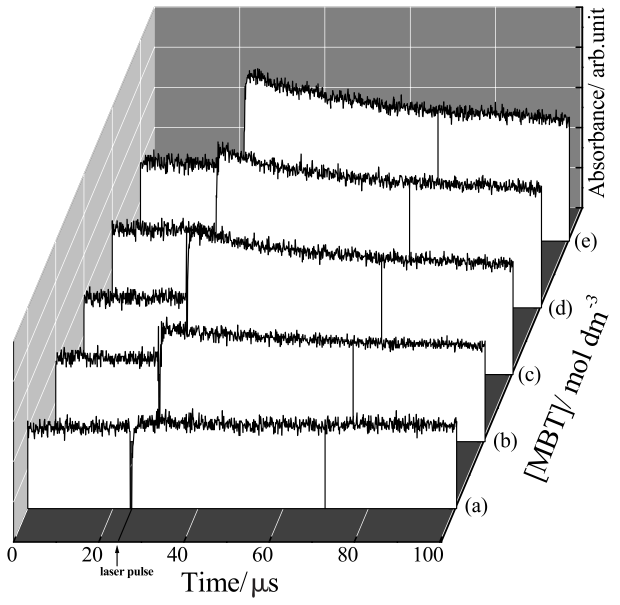


Fig. 10. The change in decay kinetics in the NAS/HABI/MBT system monitored at 540 nm. (a): NAS (0.21 mol/dm^{-3}), (b): NAS (0.21 mol/dm^{-3}) and HABI (0.27 mol/dm^{-3}), (c)–(e): NAS (0.21 mol/dm^{-3}), HABI (0.27 mol/dm^{-3}), and MBT (0.12, 0.31, and 0.55 mol/dm^{-3}).

$$\begin{aligned}
&\mathrm{NAS} \xrightarrow{h\upsilon} {}^{1}\mathrm{NAS}^{*}\\
&(\mathrm{NAS}\cdots\mathrm{MBT}) \xrightarrow{h\upsilon} {}^{1}(\mathrm{NAS}\cdots\mathrm{MBT})^{*}\\
&(\mathrm{NAS}\cdots\mathrm{HABI}) \xrightarrow{h\upsilon} {}^{1}(\mathrm{NAS}\cdots\mathrm{HABI})^{*} \quad \text{static mechanism}\\
&{}^{1}(\mathrm{NAS}\cdots\mathrm{MBT})^{*} \longrightarrow {}^{3}\mathrm{NAS}^{*} + \mathrm{MBT}\\
&{}^{1}\mathrm{NAS}^{*} + \mathrm{HABI} \longrightarrow \mathrm{NAS}^{+\bullet} + \mathrm{HABI}^{-\bullet}\\
&{}^{1}(\mathrm{NAS}\cdots\mathrm{HABI})^{*} \longrightarrow \mathrm{NAS}^{+\bullet} + \mathrm{HABI}^{-\bullet}\\
&{}^{3}\mathrm{NAS}^{*} + \mathrm{HABI} \longrightarrow \mathrm{NAS}^{+\bullet} + \mathrm{HABI}^{-\bullet}\\
&\mathrm{HABI}^{-\bullet} \longrightarrow \mathrm{Im}^{-} + \mathrm{Im}^{\bullet}
\end{aligned}$$

Scheme 3.

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