Double-Amplified   Photoinitiator Systems

for Computer to Plates

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Abstract

Photoinitiation processes for photopolymer coating layers have been investigated with respect to quenching rates by a laser flash photolysis using a total reflection cell, as well as to decomposition-quantum yield of sensitizer dyes and radical-generating reagents by a gel permeative chromatographic analysis (GPC); the sensitizer dye,2-[p-(diethylamino)styryl]naphtho[1,2-d]-thiazole (DNT), and the radical-generating reagent, 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,1'-bi-1H-imidazole (BI).   Strong fluorescence and no transient absortion were observed at excitation of 355 nm laser pulse,and the fluorescence was statically quenched with a quenching distance, R=11 Å. The high-quantum yield of decomposition (Φ) were obtained as Φ(DNT)=2.5 and Φ(BI)=9.3 for DNT and BI in the presence of acrylate monomers, trimethrolpropanetriacrylate (TMPTA), at 488 nm exposure of 3 mJcm^{-2} required to form photo-hardened image, though no decomposition of DNT and BI were detected in the absence of TMPTA. The results imply that the photoinitiator system accelerated photo-polymerization of the acrylate monmers not only by the efficient-static-dye sensitization but also by chain decomposition of DNT and BI.

Introduction

Photoiniator systems which is composed of a sensitizer dye, 2-[p-(diethylamino)styryl]naphtho[1,2-d]thiazole (DNT) and a radical-generating reagent,

2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,1'-bi-1H-imidazole (BI), afford high-speed photopolymers to 488 nm-argon-ion laser, which can be applied to laser imaging systems,[1] as well as to 366nm and 420nm-high-pressure-mercury lamp, applied to colour photo-resists for liquid crystal displays (LCD).[9]

Though it is difficult to discuss the photoinitiation processes in commercial-photopolymer products based on the data obtained from laser flash photolysis in solution due to much different of the mobility of initiators and of their concentrations between in solution systems and in commercials photopolymer systems, the laser analysis of the photopolymer systems could reveal physical and chemical phenomina about photoexcited sensitizer dyes. In this paper we wish to describe dye-sensitized-photoinitiation mechanisms in photopolymer containing photoinitiators with the same content as that of commercial products, which have been investigated by the laser flash photolysis using a reflection cell and by the measurement of a quantum yield on decomposition of photo-initiators in a PMMA film.

Experimental

The dye DNT was prepared by the condensations of naphtho[1,2-d]thiazole with the corresponding diethylaminobenzaldehyde.[6] The BI was prepared from the procedure reported in Ref. 7.

A total-reflection cell used in laser flash photolysis experiments is shown in Fig. 1; detailes concerning the apparatus are described elsewhere.[1] The cyclohexanone solutions containing 10 wt% of PMMA containing 0 and 40 wt% of TMPTA, 0.03 moldm^{-3} of the dye, and 0-0.025 moldm^{-3} of BI were coated to 1.0 μ m thickness on a saphire cell (10X30 mm, 1mm thickness, and both short sides were cut at a 45 degree angle). A monitor light beam from a Xenon lamp was introduced through a multireflection cell onto the head of an optical fiber that directs the beam to a monochromator (Intriments Digikrom 240) with a photomultiplier (Hammatsu Photonics K.K. Photomultipler tube Type R928) or to a SMA system (Princeton Instruments, Inc. Model TRY-700G/R/Par). The excitation light pulse(20 ns, 355 nm, 10 mJ per pulse, and 3 mJcm^{-2}) from a YAG laser (Spectron Laser Systems Model SL 402) was expanded all over the sample cell. The measurement was repeated five times whithin less than 3 wt% of the decomposition of DNT and BI; the data of the five measurements were averaged. More than 90 wt% of the 355 nm laser light absorbed in the sample film was absorbed by the dye, and the dye was

homogeneously photoexcited in the film. Fluorescence spectra in film were recorded by the laser flash photolysis.

The photosensitivity of the photopolymer layer containing a TMPTA of 40 parts, a poly(methyl methacrylate - methacrylic acid) (the mol ratio of 90:10) of 60 parts, DNT of 2 parts, BI of 5 part, and MBT of 5 parts was measured. The sensitive layer was prepared by coating a cyclohexanone solution of the photosensitive composition onto a grained aluminum plate and drying it at 80 °C to produce a 1μ m thick film; then a 1μ m layer of poly(vinyl alcohol) was applied as an oxygen-gas barrier, was exposed through a step tablet (Kodak photographic step tablet no.2) by the 488 nm band of a high-pressure mercury lamp, which was isolated by using glass filters (Toshiba glass Corp. Y-47 and KL-49). The incident energy required to insolubilized the last step of the layer was defined as the seinitivity. The incident energy was measured by a photoelectric cell (The Eppley laboratry Inc.).

The decomposition-quantum yield of initiators in the photopolymer layer applied poly(vinyl alcohol) layer was measured from the decomposition yield of initiators devided by the number of photons on 488nm exposure, 3 mJcm^{-2}, for image-formation: the decomposition yields were determined by a gel permeative chromatographic analysis; Shimadzu Corp.,Liquid chromato graph LC-6A equipped with five columns of Toso Corp, Type G1000HXL using a tetrahydrofuran as an eluent.

Result and Discussion

Absorption spectrum with a maximum, 417 nm, and fluorescnce with a maximum, 510 nm, of DNT in a PMMA film, in the absence of a radical generating reagent and the experiments of laser flash photolysis in a PMMA film were reported together with that in solvents in earlier investigation[2]; strong fluorescence was detected and no transient absorption was observed. The decay time of the fluorescence could not be determined because of too short decay time of the fluorescence compared to 20 ns of excitation laser pulse.In the presence of BI, though no-new-transient absorption was detected, a new absorption with a decay time of longer than 100μ s of Xenon-monitor-light pulse, observed due to the generation of photoproducts which is considered as imidazolyl radical.[8-b)10)] The relaxation mechanism is suggested as depicted in Fig. 6; a planer singlet excited state(E1), obtained directly from the photoexcitation of DNT behaves as follows: E1

undergoes (i) twisting of the olefinic moiety to a phantom state (r1)[11], which decays nonradiatively, and (ii) twisting of the aminophenyl group to the TICT (r2) state,[3] which decays radiatively or nonradiatively, or is quenched by a radical-generating reagent.

Figure 3 shows logarithmic plots of fluorescence intensity at various concentrations of BI. The fluorescence reduced with the concentration of BI, and the logarithmic plots of fluorescence fitted to the perrin equation. From the slope of the equation, a quenching distance, R=11 Å, was obtained.

As to the measument of decomposition-quantum yields, Φs, in initiators, Figure 4 shows the results on the GPC peaks for DNT, BI and 2-mercapotbenzothiazole (MBT) as a radical-tranfer reagent in the photopolymer layer in the presence of the acrylate monomer, TMPTA. at 488nm-exposure of 3mJcm^{-2} for image-formation.In the presence TMPTA, the content of DNT and BI reduced with the exposure, and that of MBT was almost same,and Φ was estimated as Φ (DNT)=2.5 and Φ(BI)=9.3. However the content of DNT, BI and MBT did not change in the absence of TMPTA. The significantly-high quantum yields more than one in the presence of TMPTA suggests that the chain decomposition of photoinitiators was induced by addition of acrylate monomer or/and polyacrylate radicals, leading to generate active radicals which initiate polymerization of acrylate monomers.

Figure 5 shows a assumed-chain-decomposition mechanism of initiators; singlet excited dyes, ^{1}DNT*, sensitizedly decomsed BI generating active radicals, Rad·; DNT· and Im·, which induced polymerization of TMPTA, affording acrylate monomer radicals and polymer acrylate radicals, Rad-(TMPTA)n·. Though Rad· did not efficiently react with DNT and BI, Rad-(TMPTA)n· underwent the decomposition of DNT and BI, resulting in active radicals, Rad·, which again induced polymerization of TMPTA.

To evaluate an electron-transfer mechanism in the sensitizations, the redox potentials of DNT was measured by cyclic voltammetry.[4] The high E_{ox} of DNT, 0.72 V (VS. SCE), and the low E_{red} of BI, -1.35 V(VS. SCE),[8-b] corresponding to - 0.43 eV of the free energy change (ΔG) for electron transfer,[5] suggests the possibility of electron transfer from the singlet excited state of the dye to the ground state BI.

Finally the large quenching distance and the high quantum yield much more

than one in the photoinitator containing of DNT and BI suggest that photopolymerization system was double-amplified both by both the efficient-dye-sensitization and the chain decomposition of initiators.

Refeences

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4)For Eredox potential of reagents. we applied values obtained in acetnitrile solvent;E_{ox}=0.72 eV 2) and E_{red}=-1.35 eV (vs. SCE) [8-b)] for DNT and BI.

5)$\triangle G$ was obtained from the Rhem Weller equation reported in D. Rhem and A. Weller, Isr. J. Chem., 259(1970), $\triangle G=E_{ox}-E_{red}-E_{oo}-C$. where E_{oo} is the excitation energy of the DNT singlets. E_{oo}=2.7 eV, and C. coulombic term, usually assumed to value ca. 0.1 eV for acetonitrile solvent.

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11)For the transient absorption of sensitizer-dye-singlet phantom state with a twisted-olefine

group, see the report of R.J.Devoe, M.R.V.Sahyun, E.Schmidt, M.Sadrai, N.Serpone, and D.K.Sharama, Can. J. Chem., 67, 1565 (1989); a twisted-singlet-phantom state from photoexcited 1,5-bis[4-(dimethylamino)phenyl]-1,4-pentadien-3-one (DMPP) was observed in some solvents, and was quenched by a radical-generating reagent.
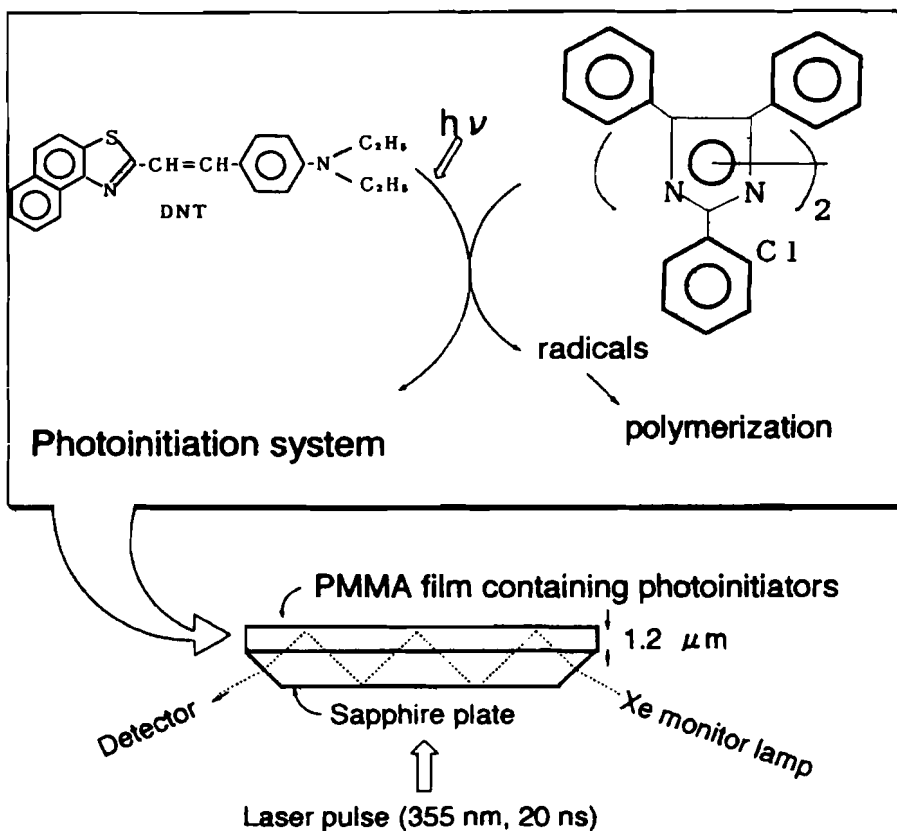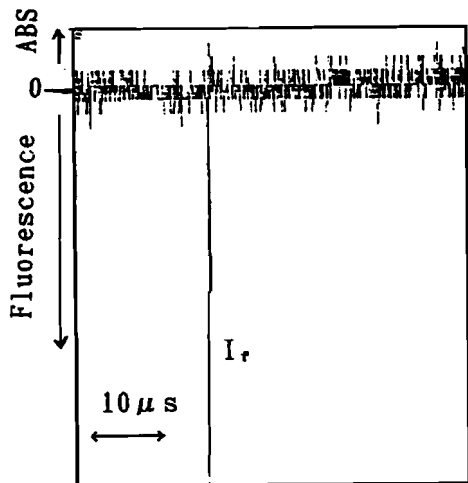

Fig. 1   Laser flash photolysis in film.

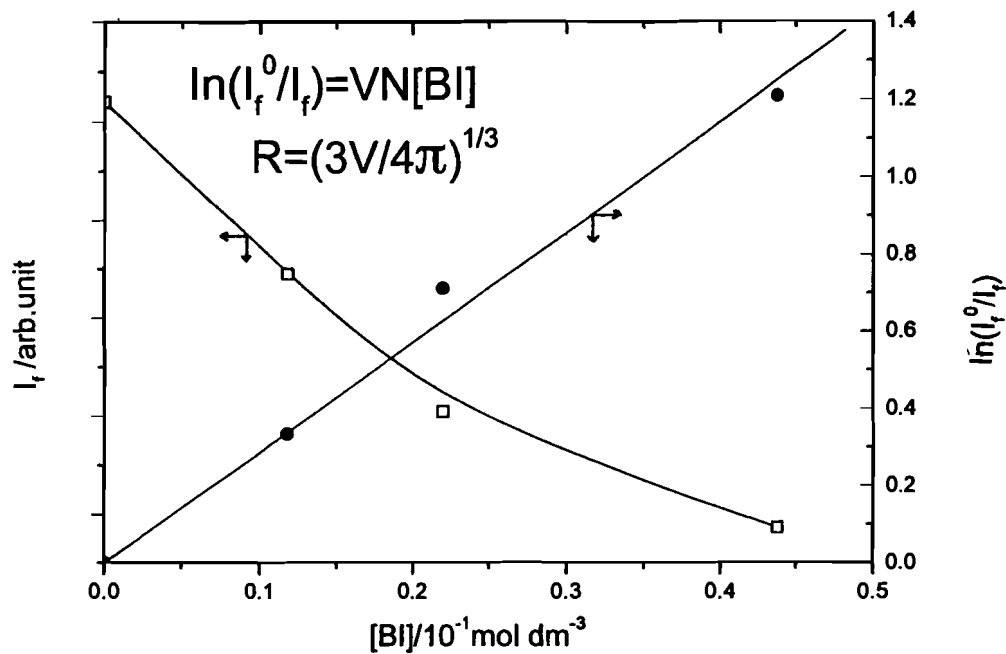Fig. 2. Measurement of fluorescence (If) and transient absorption (ABS) on 530nm for DNT at excitation of 355nm laser pulse.

Fig. 3. Fluorescence quenching of DNT (–O–) by BI in PMMA. a) Excitation wavelength 355nm, detection wavelength 530nm.
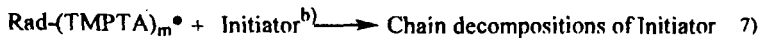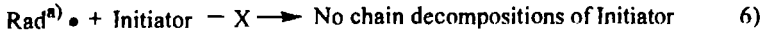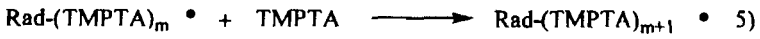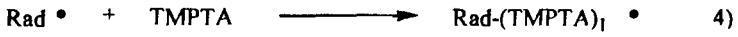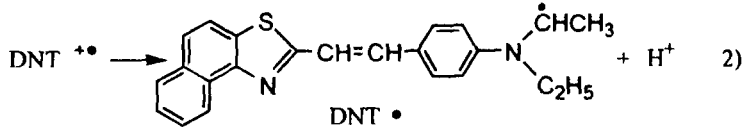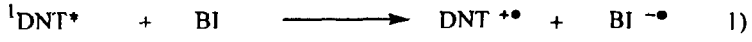
Fig. 4. Peaks of GPC output for DNT, BI and MBT in the presence of TMPTA before and after exposure, (A) and (B). a)Exposure wavelength 488nm, exposure energy 3 mJcm^{-2}, detection wavelength 350 nm.

^{1}DNT* + BI   ⟶   DNT$^{+•}$ + BI$^{-•}$ 1)

DNT$^{+•}$ ⟶ [benzothiazole–CH=CH–C$_6$H$_4$–N(ĊHCH$_3$)(C$_2$H$_5$)] + H$^+$ 2)

DNT •

BI$^{-•}$ ⟶   Im •$^{c)}$ + Im$^-$ 3)

Rad • + TMPTA   ⟶   Rad-(TMPTA)$_1$ •   4)

Rad-(TMPTA)$_m$ • + TMPTA   ⟶   Rad-(TMPTA)$_{m+1}$ •   5)

Rad$^{a)}$ • + Initiator $-$ X ⟶ No chain decompositions of Initiator   6)
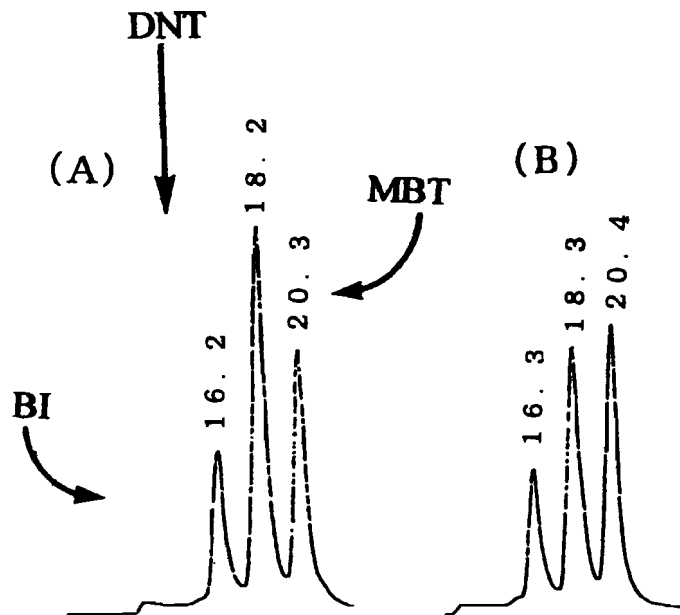
Rad-(TMPTA)$_m$• + Initiator$^{b)}$ ⟶ Chain decompositions of Initiator   7)

a) Rad•:Im • and DNT•   b) Initiator : DNT and BI,

c) Im •:

Fig. 5. Chain decomposition of photoinitiator.

TICT(r_2) E_1 TICT(r_3) S_1

$k_q{}^1$ (TCT)

T_1 k_{isc}

$k_d{}^2$ $h\nu_f$ $k_d{}^1$ $h\nu$ $k_d{}^3$

r_2 E_0 r_3 S_0

r_1 r_2 r_3

$-CH=CH-$ $N-$ C_2H_5 / C_2H_5
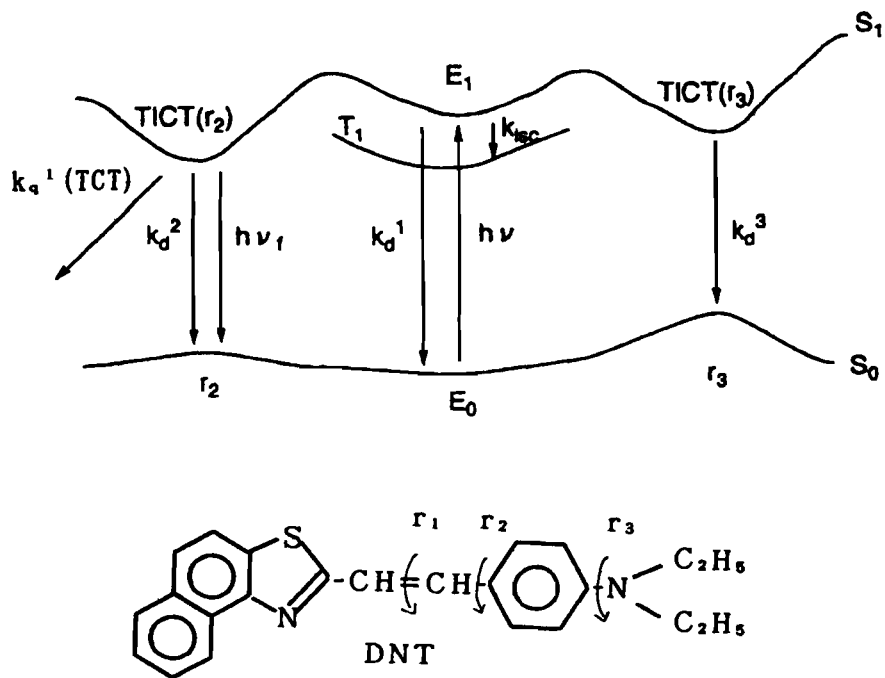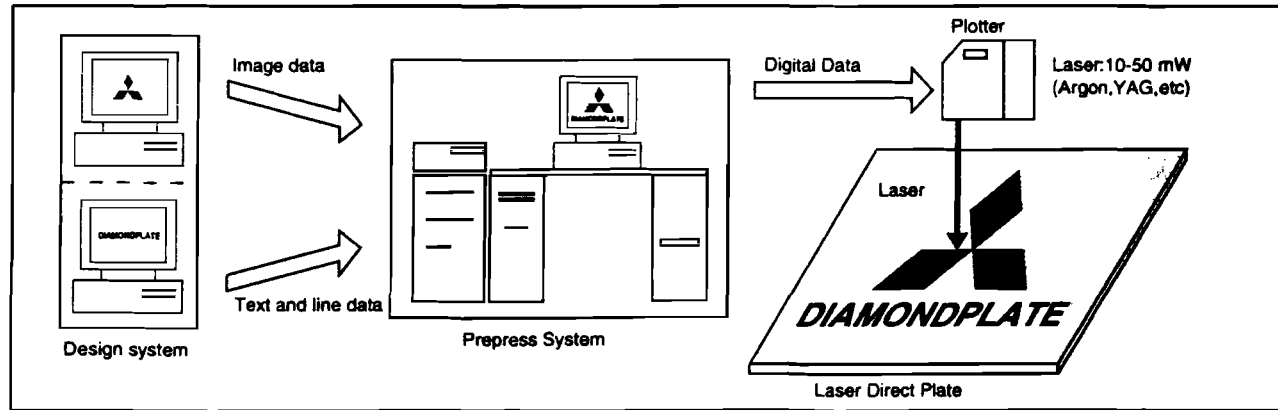
DNT

Fig. 6 Quenching scheme.

Fig. 7. Computer to photopolymer plate.

Fig. 1.   Laser flash photolysis in film.

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