

VISIBLE LASER POLYMERIZATIONS WITH THE SULFONIUM BORATE - STYRYL DYES AS NEW PHOTOINITIATOR SYSTEMS

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Abstract – New photoinitiator systems of dimethylphenacylsulfonium butyltriphenylborate (DMPSB) as a donor-acceptor initiator and styryl dyes have been investigated for free radical polymerization of an acrylate with visible lasers (488, 514 and 647 nm). DMPSB was able to be sensitized by many styryl dyes. When polymerized with pentaerythritol triacrylate, the sensitivity value of the photosensitive layer containing DMPSB was higher than that of a tetrabutylammonium butyltriphenylborate (TBAB) as an electron donating initiator or a dimethylphenacylsulfonium tetrafluoroborate (DMPS) as an electron accepting initiator. The sensitivity values of the photosensitive layer containing the photoinitiator systems had a close relation to the free energy changes between the excited singlet styryl dyes and DMPSB.

INTRODUCTION

In recent years, visible photopolymerization have been investigated and developed to use in the field of imaging technologies, particularly for laser imaging,^{1,2} holography³ and stereography.⁴ Visible photoinitiator systems produce polymerization of monomers with visible light and give significant effect to the sensitivity of the polymerization. Though many visible photoinitiator systems have been described,⁵⁻¹³ more efficient visible photoinitiator systems were required in the field.

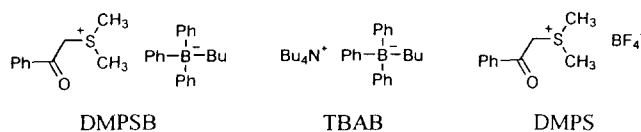
Recently, we reported the onium borates as novel donor-acceptor initiators.¹⁴ The initiators have both an onium cation (electron accepting radical generator) and a borate anion (electron donating radical generator) within the same compound and initiate efficiently free radical photopolymerization of an acrylate.

On the other hand, It is well known that styryl dyes absorb light over visible region. The wavelength of absorption of the styryl dye is tunable the number of conjugated alkene units in the styryl dye.

In the present paper we report herein new visible photoinitiator systems with the onium borate initiator and styryl dyes and deal with visible laser photopolymerization of an acrylate with the photoinitiator systems.

MATERIALS AND METHODS

Materials. Dimethylphenacylsulfonium butyltriphenylborate (DMPSB) and tetrabutylammonium butyltriphenylborate (TBAB) were prepared according to the reported procedure.¹⁴ Dimethylphenacylsulfonium tetrafluoroborate (DMPS) and



Structural formula of the initiators

tetrabutylammonium perchlorate were obtained from Tokyo Chemical Industries Co., Ltd.. All styryl dyes were used as received (Nippon Kankoh-Shikiso Kenkyusho Co., Ltd.). Poly(methylmethacrylate) (PMMA, MW=996,000) and poly(vinylalcohol) (PVA, 99% hydrolyzed, MW=124,000-186,000) were obtained from Aldrich Chemical Co., Inc.. Pentaerythritol triacrylate (PE3A) was purchased from Osaka Organic Chemical Industry Ltd.. 1,1,2,2-Tetrachloroethane (TCE), ethyl acetate and acetonitrile were obtained from Kanto Chemical Co., Inc..

Instruments. Absorption spectra and fluorescence spectra were recorded on a Jasco V-530 UV/VIS spectrophotometer and a Jasco FP-770F spectrofluorometer, respectively. Redox potentials of styryl dyes and initiators were measured by cyclic voltammetry on a CV-50W voltammetric analyzer (BAS Inc.) by the reported procedure.¹⁵ All the measurements were carried out with 100 mV/s of scan rate in dry acetonitrile under argon at room temperature. The electrode was calibrated with ferrocene using its known reduction value (0.06 V)¹⁶ and converted to those relative to SCE by the addition of 0.337 V. 488 and 514 nm laser beam were obtained from an argon ion (Ar⁺) laser (Lexel Model 95, laser beam diameter: 1.3 mm). 647 nm laser beam were obtained from a krypton ion (Kr⁺) laser (Coherent Innova 70, laser beam diameter: 1.4 mm).

Measurement of Sensitivity. The sensitivity value of the photosensitive layer was measured by reference to the methods described.¹⁰ A TCE solution of photosensitive

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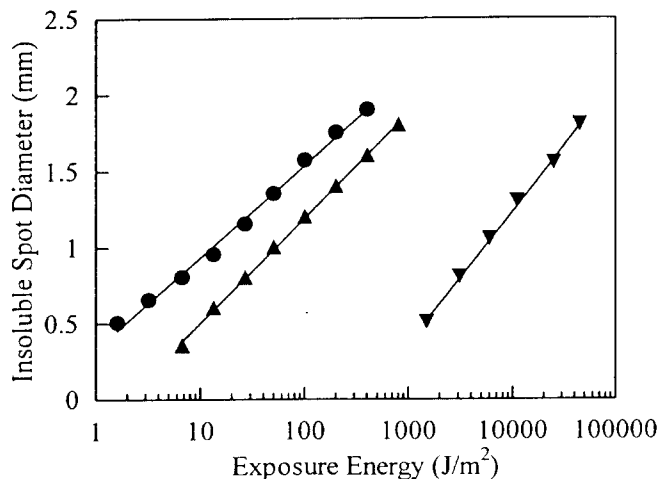


Figure 1. Characteristic curves of the photosensitive layer by using of St3a and various initiators for Ar⁺ laser (514 nm). DMPSB (●), TBAB (▲), DMPS (▼).

composition was prepared by mixing initiator, styryl dye, PE3A, PMMA and TCE; typical weight ratio was DMPSB: St1a: PE3A: PMMA: TCE = 5.77: 4.0: 100: 100: 2400 (wt/wt). A photosensitive layer was prepared by coating the TCE solution of the composition onto a glass plate and drying it at 60 °C, producing a 2 μm film. In addition, it was given an overcoat of 2 μm PVA. The exposed photosensitive layer was developed in tap water and in toluene at 20 °C. Laser exposure was carried out with Ar⁺ or Kr⁺ laser with the laser beam diameter, at which the energy is $1/e^2$ of the peak energy. The sensitive layer was exposed to the laser beam spot by spot with varying exposure time at constant laser power. The incident energy required to insolubilize a spot size equal to the beam diameter was defined as the sensitivity.

RESULTS

Structures and photophysical properties of the styryl dyes are shown in Table 1. The singlet energies of the dyes (E_{00}) are taken as the point where the normalized absorption and fluorescence spectra overlap. Since the absorption spectra of the styryl dyes exhibit strong absorption in visible region, the photosensitive layer containing the styryl dye can be expected absorbing the visible laser light (488, 514 and 647 nm).

The photosensitive layer consists PMMA as binder, PE3A as monomer, the initiator and the styryl dye as the sensitizer. The sensitivity value of the photosensitive layer for the laser light was measured by varying the laser power, and the characteristic curve for the laser light exposure was obtained by plotting the insoluble spot diameter after development against the incident laser energy. To compare with different initiator for the sensitivity value of the photosensitive layer, we chose and used TBAB as an electron donating initiator and DMPS as an electron accepting initiator. Fig. 1 shows

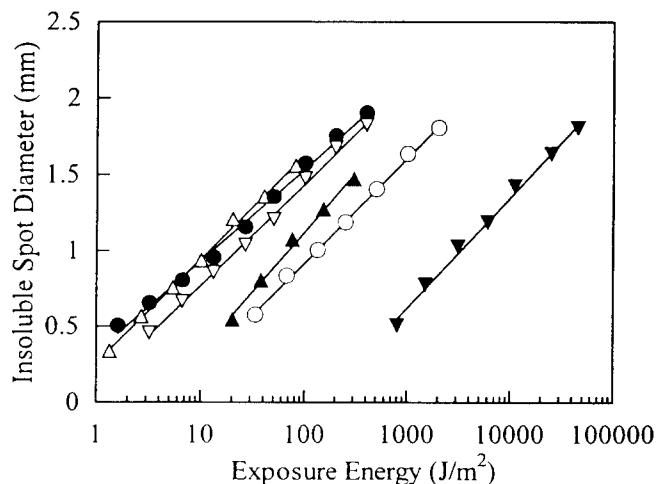


Figure 2. Characteristic curves of the photosensitive layer by using of DMPSB and various styryl dyes for Ar⁺ laser (488 or 514 nm). St1a (△), St2a (▲), St3a (●), St4a (▽), St4b (○), St5a (▼).

the characteristic curve of the photosensitive layer by using of the styryl dye St3a and various initiators for Ar⁺-laser (514 nm). It is especially noteworthy that the sensitivity value of the photosensitive layer containing DMPSB as an initiator exhibited much higher than that of TBAB or DMPS. DMPS was not so effective as initiator. Fig. 2 shows the characteristic curve of photosensitive layer by using of DMPSB and various styryl dyes for Ar⁺-laser (488 or 514 nm). The

Table 1. Structures and photophysical properties of styryl dyes.

St	W ⁺	n	X ⁻	λ _{max} ^a	λ _{fl} ^a	E ₀₀
				(nm)	(nm)	
St1a		1	I ⁻	493	557	228
St2a		2	I ⁻	568	693	190
St3a		1	I ⁻	547	593	211
St3b		2	ClO ₄ ⁻	608	692	184
St4a		1	I ⁻	529	627	208
St4b		2	I ⁻	558	723	187
St5a		1	ClO ₄ ⁻	597	737	180
St5b		2	ClO ₄ ⁻	608	811	169

^a in methanol

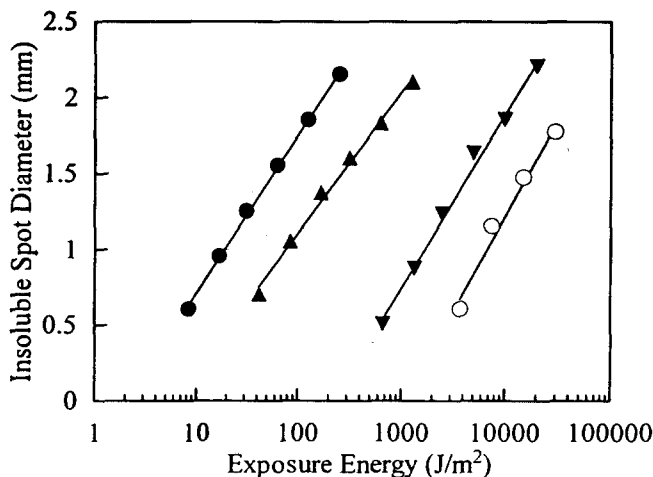


Figure 3. Characteristic curves of the photosensitive layer by using of DMPSB and various styryl dyes for Kr^+ laser (647 nm). St2a (▲), St3b (●), St5a (▼), St5b (○).

photosensitive layer containing St1a gave the highest sensitivity value (9 J/m^2). The sensitivity value containing St3a and St4a were about two-fold lower than that containing St1a. More, The sensitivity value containing St4b and St5a were 1000 J/m^2 order and were not virtually effective as sensitizer.

Fig. 3 shows the characteristic curves of photosensitive layer by using of DMPSB and various styryl dyes for Kr^+ -laser (647 nm). The photosensitive layer containing St3b gave highest sensitivity value (20 J/m^2). The sensitivity value using the styryl dyes containing benzopyran ring, St5a and St5b were ineffective as sensitizer.

DISCUSSION

In Fig. 1, we can show that the sensitivity value of the photosensitive layer containing DMPSB as an initiator is clearly much higher than that of TBAB or DMPS. It is likely that the sensitivity value containing DMPSB was affected by both dimethylphenacylsulfonium and butyltriphenylborate in DMPSB. This is the same results using other sensitizers in our communication.¹⁴

We shall discuss the photoreaction between the excited styryl dye and DMPSB, we would like to consider why the sensitivity value was observed. The deactivation processes for most of excited polymethine dyes (styryl,^{17,18} cyanine,¹⁹ etc.) are fluorescence and torsional rotation. Intersystem crossing to the triplet states of the dyes was usually unlikely. Since we observed that the fluorescences of the styryl dyes in the photosensitive layers were quenched by DMPSB, it is likely that the reaction were between the excited singlet state of styryl dyes and DMPSB.

The free energy changes (ΔG_{et}) for the electron transfer

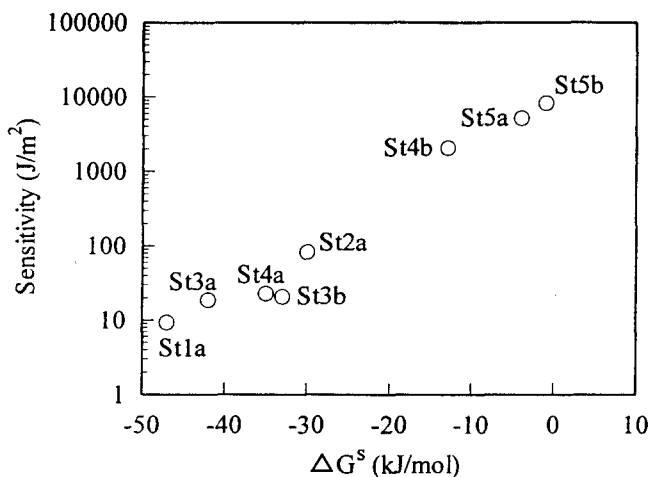


Figure 4. Relationship of the sensitivity values of the photosensitive layer with free energy changes (ΔG^0) for electron transfer reactions from DMPSB to excited singlet styryl dyes.

process can be calculated using Rehm-Weller equation²⁰ (Eq. 1),

$$\Delta G_{\text{et}} = E_{\text{ox}}(\text{D}/\text{D}^+) - E_{\text{red}}(\text{A}^-/\text{A}) - E - Z e^2 / \epsilon \gamma \quad (1)$$

where $E_{\text{ox}}(\text{D}/\text{D}^+)$ is the oxidation potential of the electron donor, $E_{\text{red}}(\text{A}^-/\text{A})$ is the reduction potential of the electron acceptor; E are excitation energy of the sensitizers, $Z e^2 / \epsilon \gamma$ is the Coulombic energy, which is the free energy gained by bringing the radical ions to an encounter distance γ in a solvent with dielectric constant ϵ . Butyltriphenylborate and dimethylphenacylsulfonium cation serve as an electron donor ($E_{\text{ox}} = 0.84 \text{ V vs SCE}$) and an electron acceptor ($E_{\text{red}} = -1.01 \text{ V vs SCE}$), respectively. The styryl dyes can serve not only as a donor but also as an acceptor to be affected from the property of the coexisting DMPSB, however, the electron transfer from butyltriphenylborate to the excited singlet states of styryl dyes would energetically occurred rather than the electron transfer from the excited singlet states of styryl dyes to dimethylphenacylsulfonium cation. Hence, we considered the electron transfer from butyltriphenylborate to the excited singlet states of styryl dyes. To obtain ΔG_{et} between the styryl dye and DMPSB, we approximated Eq.1 to Eq. 2 as below,

$$\Delta G^0 = E_{\text{ox}}(\text{Bo}^-/\text{Bo}^\cdot) - E_{\text{red}}(\text{St}^\cdot/\text{St}^+) - E_{00} \quad (2)$$

where $E_{\text{ox}}(\text{Bo}^-/\text{Bo}^\cdot)$ is the oxidation potential of butyltriphenylborate, $E_{\text{red}}(\text{St}^\cdot/\text{St}^+)$ is the reduction potential of the styryl dye; E_{00} is excitation energy of the styryl dye. The excited singlet states of the styryl dyes and DMPSB are summarized in Table 2.

It is noteworthy that Fig. 4 gives a correlation of the sensitivity values of the photosensitive layer with ΔG^0 for electron transfer reactions from DMPSB and excited singlet styryl dyes. The result in Fig. 4 presents us an

Table 2. Sensitivity values of the photosensitive layer by using of DMPSB and styryl dyes, reduction potentials (E_{red}) of styryl dyes and free energy changes (ΔG^{\ominus}) for electron transfer reactions from DMPSB to excited singlet styryl dyes.

St	$\lambda_{\text{irr}}^{\text{a}}$ (nm) ^d	E_{red} (V vs SCE)	Sensitivity (J/m ²)	ΔG^{\ominus} (kJ/mol) ^b
St1a	488	1.03	9	47
St2a	514	0.81	80	30
St3a	514	-0.90	18	-42
St3b	647	-0.72	20	39
St4a	514	0.94	22	35
St4b	514	-0.96	2000	13
St5a	514	-0.97	5000	4
St5b	647	-0.89	8000	-1

^a λ_{irr} : irradiation wavelength

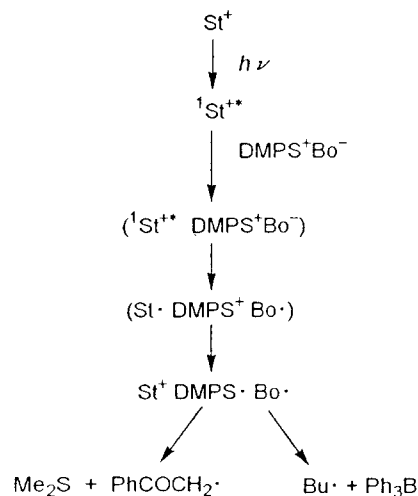
^b Calculated from $\Delta G^{\ominus} = E_{\text{ox}}(\text{Bo}^{\cdot-}/\text{Bo}^{\cdot-}) - E_{\text{red}}(\text{St}^{\cdot+}/\text{St}^{\cdot+}) - E_{00}$

useful information to design an effective photoinitiator system with DMPSB. Thus, the lower ΔG^{\ominus} , the higher the sensitivity values. Moreover, as the number of methine n in the styryl dyes was increased, the sensitivity values were decreased. The main reason would be that the ratio of deactivation process by torsional rotation in styryl dyes was much higher than that of other deactivation process.

From the above results, the proposed mechanism for the initial step of photopolymerization with DMPSB initiators sensitized by styryl dyes is summarized in Scheme 1. The excited singlet state of styryl dye is formed from the ground states of the styryl dye by irradiating of visible laser. Subsequently, the excited singlet styryl dye was reduced by butyltriphenylborate anion of DMPSB. It admits of no refutation from the fact that the fluorescence of the styryl dye was quenched by DMPSB in the photosensitive layer. As a consequence the radical of the styryl dye and butyltriphenylboranyl radical is formed. Since the lifetime of butyltriphenylboranyl radical is less than nanosecond time scale,^{21,22} it rapidly dissociates to give butyl radical (and triphenylborane). On the other hand, the radical of the styryl dye immediately reduces dimethylphenacylsulfonium cation of DMPSB. As a result, the styryl dye is reformed and phenacyl radical (and dimethylsulfide) is generated via dimethylphenacylsulfonium radical. Accordingly, in the case of coexistence of PE3A as an acrylate, phenacyl radical and butyl radical initiate polymerization of PE3A. In the case of using TBAB instead of DMPSB, the photosensitivity value is lower because phenacyl radical does not generate.

CONCLUSION

In this paper we have shown useful photoinitiator systems (DMPSB / styryl dye) for visible laser photo-



(St⁺: styryl dye cation, DMPS⁺: Me₂S⁺CH₂COPh, Bo⁻: BPh₃Bu)

Scheme 1. Proposed mechanism for styryl dye sensitized radical-generation using DMPSB.

polymerization. DMPSB was able to be sensitized by many styryl dyes. The sensitivity value of the photopolymerizable layer containing DMPSB was higher than that of a tetrabutylammonium butyltriphenylborate (TBAB) as an electron donating initiator or a dimethylphenacylsulfonium tetrafluoroborate (DMPS) as an electron accepting initiator.

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