Mechanistic Studies of the Photo-decomposition of Substituted Bis(trichloromethyl)-1,3,5-triazine Sensitized by Merocyanine Dye

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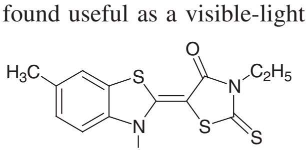
The photochemistry of a merocyanine dye (**1**)/triazine (**2**) two-component system that could be used as a visible light radical generator in photopolymerization formulations has been investigated. The electron transfer from excited merocyanine to triazine to generate a reactive photoinitiating radical was proposed based on fluorescence quenching experiments and a product analysis study.

The search for efficient photoinitiating systems operating under visible-light excitation has been extensively studied because of their wide applications to typical practical fields, such as high-speed photopolymers in computer-to-plate laser imaging and 3D polymerization systems.[1] Bis(trichloromethyl)-1,3,5-triazines, an important class of photoinitiators, are used in many photopolymerization formulations. However, as most triazines show absorption only in the UV region, it is necessary to use an appropriate sensitizer in order to extend the spectral sensitivity to the visible-light region. In fact, such systems consisting of triazines and various sensitizers have appeared in patents and reports, but full understanding of the detailed photochemical process from a mechanistic viewpoint is still lacking.[2] Recently, the detailed photochemical behavior of triazine was reviewed,[3] but nothing is yet known about the detailed interaction in a merocyanine/triazine photoinitiating system.

Here, we wish to report our mechanistic study on the photochemistry of a mixture consisting of triazine, 4-(4-methoxycarbonylphenyl)-2,6-bis(trichloromethyl)-1,3,5-triazine (**2**, $\lambda_{\max} = 284$ nm in THF), as a radical-generating species, and a merocyanine dye, benzothiazolylidene-rhodanine (**1**, $\lambda_{\max} = 431$ nm in THF), as a light absorbing species, which we have developed and found useful as a visible-light-sensitive initiating system.[4]



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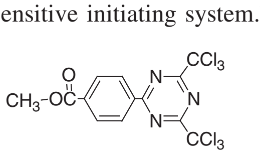

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In order to confirm that vinyl polymerization is actually induced by visible-light excitation of the initiator mixture, the progress of the reaction was monitored as a function of time by using an FTIR spectrophotometer. Thus, irradiation of the photopolymerization film[5] containing a polymeric binder, polyfunctional acrylates, and the initiator mixture with 430 nm wavelength light resulted in a smooth decrease in the intensity of the band at 1409 cm^{-1} due to the double bond of the acrylate (Figure 1). It is to be noted here that no such change was observed when the polymerization film was irradiated in the absence of the merocyanine dye, indicating that the initiator radical is generated by sensitization of the dye.

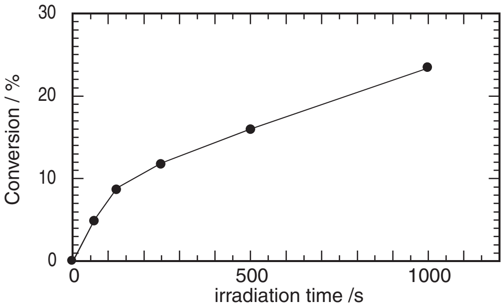


Figure 1. Conversion (%) of acrylate double bonds as a function of time upon irradiation (430 nm, 34 µW/cm^2) of photopolymer coatings containing **1** (24 mmol/dm^3) and **2** (24 mmol/dm^3) as photoinitiators.

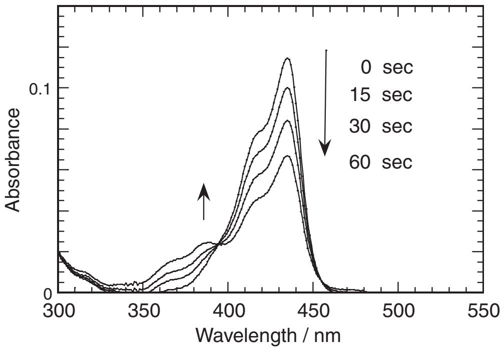


Figure 2. Spectral change upon irradiation (430 nm) of photopolymer coatings containing **1** (24 mmol/dm^3) and **2** (24 mmol/dm^3).

This is further confirmed by measuring the UV-vis spectral change of the film as a function of time. The band at 435 nm characteristic of the dye disappeared, and a new band showing its maximum at 385 nm appeared with an isosbestic point at 390 nm (Figure 2). In order to achieve a deeper insight into the possible mechanism of radical generation, the photodecomposition products were analyzed by HPLC. HPLC showed two new products, **P1** (major) and **P2** (minor), together with the starting materials. The major photo-product **P1** ($\lambda_{\max} = 381$ nm) was identical to oxo-rhodanine **4** (Scheme 1), which was prepared by a non-photochemical synthetic route.[6] The formation of **4** as a photo-product indicates that a single-electron transfer from the rhodanine dye to triazine took place upon irradiation.

Fluorescence spectra were also measured in a photopolymer coating film, where the intensity of fluorescence decreased with the addition of triazine. Assuming that the fluorescent and quenching molecules do not change their positions during the lifetime of the fluorescent molecule, the fluorescence intensity of the molecules is expressed by the Perrin Eq 1,

$$I_0/I = \exp(NV[\mathrm{Q}]) \qquad (1)$$

where I_0 is the emission intensity in the absence of a quencher, I is the observed emission intensity, N is Avogadro's number, [Q] is the concentration of a quencher, and V is the volume of the "quenching sphere." The quenching data fit Eq 1 reasonably well, as shown in Figure 3. The result demonstrates the total inhibition of diffusion in these systems. From the slope of this plot, the "active-quenching radius," R_q, can be estimated to be 13.7 Å. This electron-transfer distance is similar to the previous reports on electron-transfer reactions in photoinitiating systems.[7]

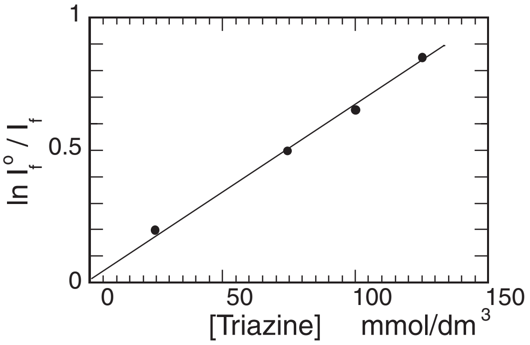


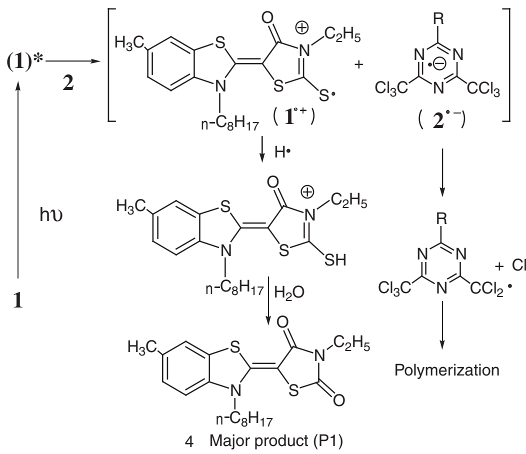
Figure 3. Relative intensity of the fluorescence of **1** (10 mmol/dm^3) vs the concentration of triazine **2** in the photopolymer film.

The fluorescence life time of merocyanine alone and in the presence of triazine (50 mmol/dm^3) was measured in photopolymer coating.[8] The decay curve of the films did not show a single-exponential decay but could be analyzed by a double-exponential decay. The major component obtained here was 70% and the decay time (τ_1) was 0.4 ns, and almost the same decay time was observed even in the presence of triazine. This result supports the static quenching mechanism in this system.[9]

UV-vis absorption spectra of **1** + **2** in the photopolymer film did not show, over a wide range of concentrations, charge-transfer complex formation between **1** and **2**. Therefore, we would conclude that there is no significant interaction between **1** and **2** in the ground state.

The free-energy change for the electron transfer from an excited donor D to an acceptor A in the ground state is expressed by the Rehm–Weller equation. By using the oxidation potential of merocyanine (+0.82 V vs SCE), the excitation energy of merocyanine (2.70 eV), and the reduction potential of triazine (−0.94 V vs SCE),[10] the ΔG value is estimated to be −0.94 eV for the present system. The large negative value of the free-energy change supports the idea that electron transfer is a likely mechanism.

Thus, all the data both product analysis and the fluorescence quenching experiments are in accord with the mechanism outlined in Scheme 1, in which the electron transfer takes place from the excited state of **1** to **2** to generate merocyanine cation radical ($\mathbf{1}^{\cdot+}$)–triazine anion radical ($\mathbf{2}^{\cdot-}$) pairs. The latter then could form a chloride anion and a triazine radical, which enters into the polymerization reaction, and the former can decompose to give oxo-rhodanine **4** via hydrogen abstraction, followed by hydrolysis. The present mechanism is also compatible with that reported for the analogous dye–triazine photosensitization by Sciano et al.[3]



Scheme 1.

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References and Notes

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[5] Preparation of films. The photoinitiator (a merocyanine/triazine combination) and equal amounts of a polyfunctional acrylate monomer (Pentaerythritol tetraacrylate; Shin-Nanamura Chemical) and a polymeric binder (copolymers of methacrylic acid and benzyl methacrylate; mole ratio 20/80, $M_w = 24000$) were dissolved in a 1:1 mixture of solvent (methylethyl ketone/1-methoxy-2-propanol, w/w), and the solution was cast on a glass or on a grained-surface aluminum plate, dried at 100 °C for 1 min. The thickness of the film thus prepared was about 2 µm. A thin layer of polyvinyl alcohol was over-coated to the film to prevent the diffusion of atmospheric oxygen. The light source was a 0.5-kW xenon lamp (Ushio Electric Instruments, UI 501C) and band-pass filters (Kenko Co., Ltd) were used to irradiate merocyanine alone in all irradiation experiments ($\lambda = 430$ nm).

[6] Oxo-rhodanine **4** was prepared by the hydrolysis of 3-ethy-5-(3-octyl-6-methyl-3*H*-benzothiazol-2-ylidene)-2-ethylsulfanyl-4-oxo-4,5-dihydrothiazolium tetrafluoroborate. Pale orange crystal. mp 114.8–115.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37 (s, 1H), 7.17 (d, $J = 8.6$ Hz, 1H), 7.00 (d, $J = 8.6$ Hz, 1H), 4.13 (t, $J = 8.4$ Hz, 2H), 3.84 (q, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 1.84 (m, 2H), 1.48–1.26 (m, 13H), 0.89 (t, $J = 6.6$ Hz, 3H); [$\lambda_{\mathrm{abs}}{}^{\mathrm{max}}$, nm ($\varepsilon$, $10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) THF]: 379 (4.40); HRMS calcd for $C_{21}H_{28}N_2O_2S_2$ *m/z* 404.15923, found 404.16267.

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[8] The fluorescence decay was measured by a time-correlated single photon counting apparatus (Horiba NAES-550) equipped with a hydrogen lamp. The emission was monitored through a cutoff filter (HOYA filter Y-46) to minimize the scattering.

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