

A Novel Visible Light Photo-Induced Acid-Generation System

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ABSTRACT: A novel, visible light, photo-induced acid-generation system composed of four types of intramolecular charge transfer compound and substituted bis(trichloromethyl) triazine was studied in this work. The photo-induced electron transfer process between electron donor and electron acceptor was studied by the methods of fluorescence quenching and the change of fluorescence intensity with the time of irradiation. In the acidity measurement, the chemical reaction of acid formation of the studied system can be observed clearly. The acid-induced cross-linking reaction of m-cresol resin and 2,4,6-tris-[*N,N*-di(methoxymethyl) amino] triazine (HMMM) has also been studied. A clear negative image can be obtained after irradiation and developing by solvent. The possible mechanism of reaction has been discussed before. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 909–915, 2002; DOI 10.1002/app.10103

INTRODUCTION

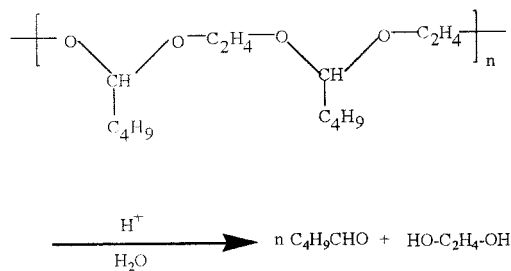
Recently, the study of photo-initiation polymerization through the electron transfer process has attracted more and more attention. This study is concerned with the development and extensively practical application of photo-polymerization and with the rapid and continuous evolution of new kinds of lasers, which are an important light source for polymerization. In the traditional photo-induced electron transfer process,^{1,2} the active radical, as the main species formed, initiates the monomer's polymerization. Hence, if this process is used in imaging science, a negative image can be obtained. In recent years, a new photo-induced acid-generation system has been developed³ that is able to initiate either polymer degradation or polymer cross-linking to obtain the positive or negative image, respectively. It has been demonstrated that this is a quite important

photosensitive system and could be applied very extensively. For instance a negative-image system—m-cresol resin/HMMM^{4,5}—and a positive one—polyacetal⁶—could be degraded and cross-linked in acidic environment, respectively. They can be incorporated with the photo-induced acid generation system to obtain different imaging results. The reactions of these systems are shown as Schemes 1 and 2.

It should be noted that this type of photosensitive system has a special function—that of chemical amplification—that enables this process to have a rather higher quantum yield than other processes. As a consequence, this method is very important in the field of photo polymerization. Scaiano and others^{7,8} studied the mechanism of the photo-acid generation process in detail. In their work, they used phenothiazine as a sensitizer and different substituted bis(trichloromethyl) triazines as electron acceptors, composing a high-efficiency photo-acid generation system. But it should be noted that the absorption peak wavelength of phenothiazine is too short, and the selection of new sensitizers with longer peak wave-

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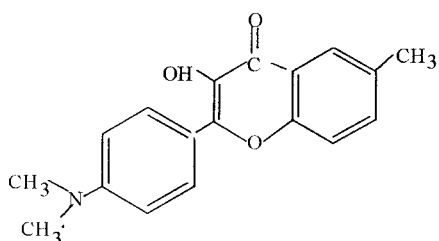
Scheme 1 The acid-induced degradation reaction of a positive polyacetal.

lengths is important. The selection of a sensitizer with a suitable wavelength that can match the emission wavelength of the laser used is especially attractive. Thus, the substituted bis(trichloromethyl) triazine possesses clear advantages as an electron acceptor. In this article, the photo-physical behavior of some new photo-acid gener-

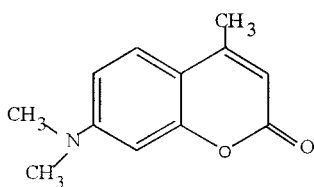
ation systems composed using triazine and different intramolecular charge-transfer compounds or some dyes as electron donors has been studied carefully. Some interesting results were obtained and discussed.

EXPERIMENTAL

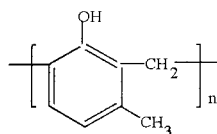
The intramolecular charge-transfer compounds 1 and 2 were synthesized in our laboratory. The methods of synthesis have been published elsewhere. Two other compounds used are coumarin derivatives—coumarin 311 and 153—obtained from Aldrich. The 2-phenyl-4,6-bis(trichloromethyl) triazine was the gift from Dr. D. Burr, EFI. The m-cresol resin and the HMMM are gifts from Professor Y. Y. Yang of this institute. The structures of the compounds studied in our work are as follows:



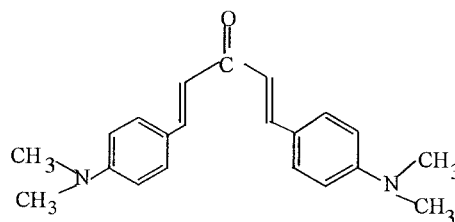
2-N,N-dimethylamino-phenyl-3-hydroxy-6-methyl-flavone. (compound 1)



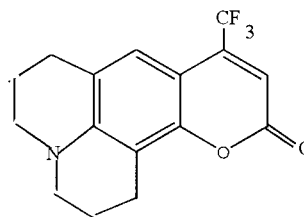
Coumarin 311,



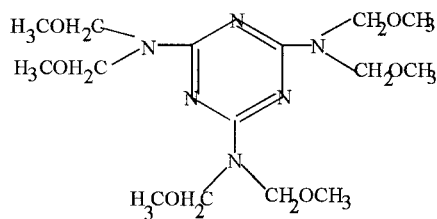
Cresol resin,



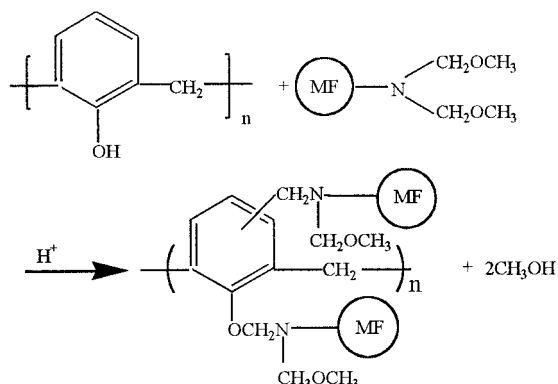
Bis(N,N-dimethylamino-benzilidene) acetone (compound 2)



coumarin 153



2,4,6-Tris-[N,N-di(methoxy-methyl) amino] triazine (HMMM)



Scheme 2 The acid-induced cross-linking reaction of negative cresol resin/2,4,6-tris-[*N,N*-di(methoxymethyl) amino] triazine system.

The fluorescence emission spectra were measured on a Hitachi MPF-4 fluorescence spectro-photometer. Dichloroethane was used as the solvent, and the concentration of solution studied was 2×10^{-5} mol/L. Absorption spectra were recorded on a Hitachi 330 UV-Vis spectro-photometer. The peak wavelengths in both fluorescence and absorption spectra were listed in Table I.

The acidity of the solutions in the studied systems was measured on a pH S-2-type pH meter (from the Shanghai Second Factory of Analytical Instruments, Shanghai). The light source used in this work was a xenon lamp (USHIO, Inc.; 450 W), and the distance between the lamp and the samples was 25 cm. A cutting-off filter was used to remove the light that had a wavelength of < 380 nm.

RESULTS AND DISCUSSION

Figures 1 and 2 are the fluorescence-quenching spectra of compounds 1 and 2, respectively. These figures show that the fluorescence of both compounds effectively can be quenched by triazine.

According to the absorption wavelength of triazine, it is less than those of all the sensitizers studied in this work. This may demonstrate that the observed fluorescence quenching was unable to be used as an energy transfer quenching process and that it should belong to the electron transfer quenching mechanism. The fluorescence of two coumarin derivatives can also be quenched by triazine. But the quenching efficiency is less than that of compounds 1 and 2. The fluorescence-quenching spectra of coumarin derivatives are similar to compounds 1 and 2 and are not shown here. The results obtained from fluorescence-quenching spectra were treated with the Stern-Volmer relationship as follows:

$$I_0/I = 1 + k_{sv}[Q] = 1 + k_q\tau[Q]$$

where I_0 and I are the fluorescence intensity of the studied compounds in the absence and presence of the quencher, respectively; k_{sv} is the Stern-Volmer constant, and k_q is the quenching constant. According to the fluorescence life, time, τ_f and the slope from the linear relation in the Stern-Volmer plot, k_q value can be calculated. All results obtained are listed in Table II.

It can be seen from Table II that all k_q listed are $< 10^{12}$ in order of magnitude and are similar to the diffusion rate constant. This table demonstrates that the quenching process studied is controlled with the diffusion process. It corresponds highly to the usual electron transfer quenching process. This result further demonstrates that the quenching process studied here is indeed an electron transfer process. It is worth noting that the quenching rate constants of compounds 1 and 2 are approaching to 10^{13} and 10^{14} in order of magnitude. It may be explained by the fact that these two compounds form a complex with triazine in the ground state and make the quenching rate constants have such higher values than those of diffusion constant. In Figure 4, the

Table I Absorption and Fluorescence Peak Wavelengths of the Compounds Studied

Compounds	Absorption Peak Wavelength (nm)	Fluorescence Peak Wavelength (nm)
Compound 1	369	565
Compound 2	410	550
Coumarin 311	360	420
Coumarin 153	420	498
Triazine (electron acceptor)	350	—

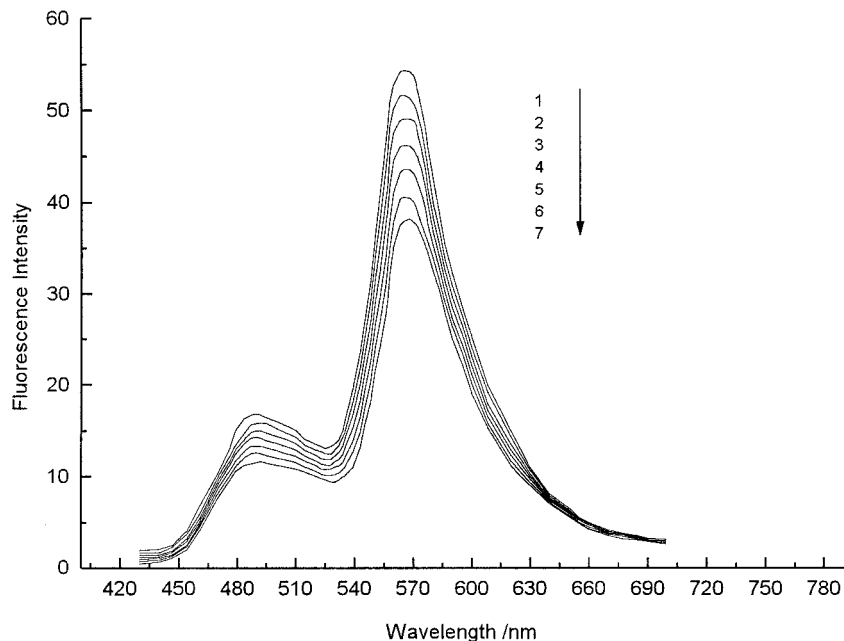


Figure 1 The fluorescence spectra of Compound 1 quenched by triazine. Concentration of Compound 1: 2×10^{-5} mol/L. Concentration of quencher: (1) 0; (2) 1×10^{-6} ; (3) 2×10^{-6} ; (4) 3×10^{-6} ; (5) 4×10^{-6} ; (6) 5×10^{-6} ; (7) 6×10^{-6} .

change of fluorescence intensity of compound 1 in dichloroethane solution mixed with a certain amount of triazine was plotted as a function of irradiation time. This experiment shows that the fluorescence intensity decreases gradually with irradiation time. Meanwhile, the color of the so-

lution also changed dramatically, which indicated that, under irradiation, a chemical reaction between compound 1 and triazine definitely occurred.

To prove that the reaction generated acid, the change of the pH value of the mixed solution

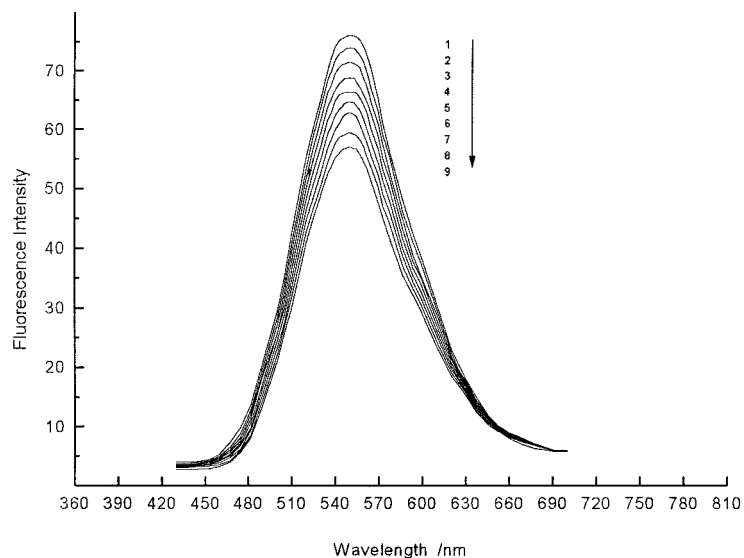


Figure 2 The fluorescence spectra of Compound 2 quenched by triazine. Concentration of Compound 2: 2×10^{-5} mol/L. Concentration of Quencher: (1) 0; (2) 1×10^{-6} ; (3) 2×10^{-6} ; (4) 3×10^{-6} ; (5) 4×10^{-6} ; (6) 5×10^{-6} ; (7) 6×10^{-6} ; (8) 7×10^{-6} ; (9) 8×10^{-6} .

Table II Fluorescence Quenching Rate Constants of Emission Compounds Quenched by Triazine (in Dichloroethane Solution)

Compounds	k_{sv}	τ_f (ns) ^{9,10}	k_q
Compound 1	6.7×10^4	2.0	3.4×10^{13}
Compound 2	4.0×10^4	0.09	4.4×10^{14}
Coumarin 311	1.1×10^4	3.4	3.2×10^{12}
Coumarin 153	1.2×10^4	5.6	2.1×10^{12}

studied has been measured under photo-irradiation. For the sake of convenient pH value measurement, the mixed solvent—acetonitrile and water (80 : 20)—was used instead of dichloroethane. The result obtained is depicted in Figure 5 and indicated that the pH value of mixed solution will be changed rapidly and dramatically from the beginning pH of 6.2 to pH 2.3 in a very short irradiation duration. It should be noted that in the measurement of the pH, the solvent used was different from that in the measurement of the spectrum. Evidently, the trend of changing two measurements should also be different. In the measurement of pH, the polarity of the solvent used is much higher than that of the solvent used in spectrum measurement. It will be an advantage for the electron transfer process between the electron donor and the electron acceptor and will result in the reaction occurring rapidly. The result obtained indicates that all sensitizers used in this work are able to generate acid that can initiate some prepolymer to cross-linking or degradation under photo-irradiation.

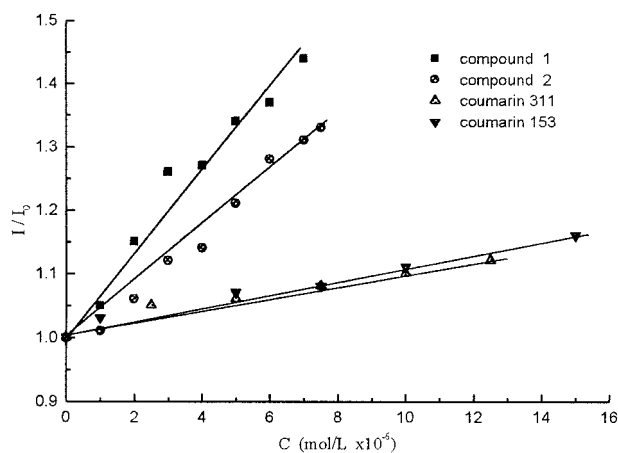


Figure 3 The Stern–Volmer plots of fluorescence quenching of Compound 1, Compound 2, Coumarin 311, Coumarin 153.

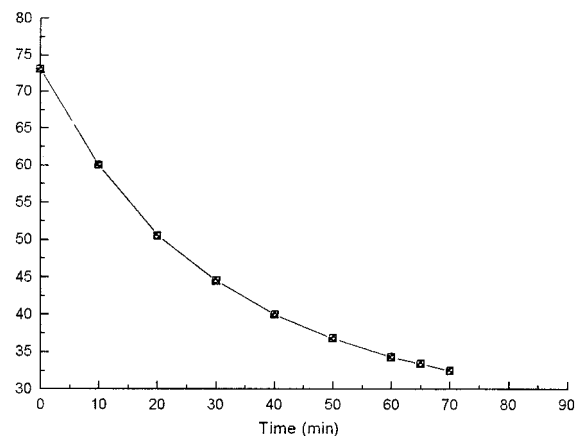


Figure 4 In the presence of Triazine, the change of fluorescence intensity of compound 1 with irradiation time.

According to a published method,^{4,5} the mixed solution of cresol resin and HMMM in ethoxyethyl acetate was prepared. The photo-acid generation system was then added to the mixed solution in a darkroom. The formulation of this negative-imaging system has been listed as follows: cresol resin, 3–5 g; HMMM, 1–2 g; compound 2, 0.2–0.4 g; substituted bis(trichloromethyl) triazine, 0.4–0.6 g; ethoxy-ethyl acetate, 50–100 mL.

The mixed solution was coated on an anode-oxidized aluminum plate and then dried in an oven and kept in a dark place. The prepared sensitive plate was covered by a mask and exposed under light from a Xenon lamp for 2 min. Then the exposed plate was heated in a 140°C oven for another 2 min. The plate was washed and devel-

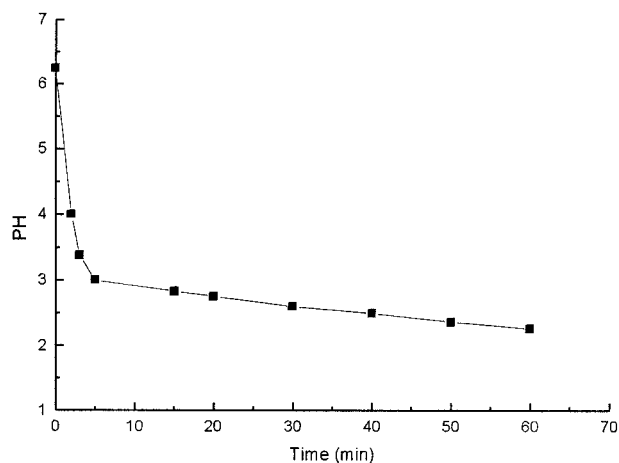
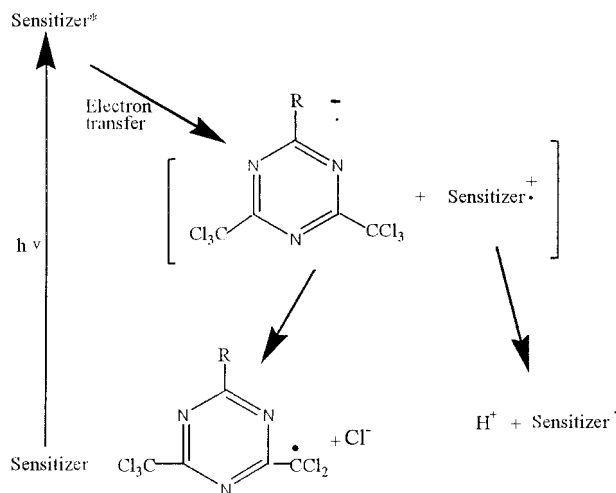


Figure 5 The change in acidity of mixed solution of compound 1/triazine with irradiation time.



Scheme 3 (a) 2-*N,N*-dimethylamino-phenyl-3-hydroxy-6-methyl-flavone. (compound 1); (b) bis(*N,N*-dimethylamino-benzilidene) acetone (compound 2); (c) coumarin 311; (d) coumarin 153; (e) cresol resin; (f) 2,4,6-tris-*[N,N*-di(methoxymethyl) amino] triazine (HMMM).

oped in a 2% NaOH solution in mixed solvent (ethanol : water, 1 : 4). A clear image was obtained (see Scheme 4).

This work shows that the systems studied here possesses the photo-induced electron transfer character. These systems are sensitive when irradiated by visible light with different wavelengths and generate acid through the process of photo-induced electron transfer. The acid formed can

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Scheme 5 The photo-induced electron transfer process of sensitizer/triazine system, and the photo-acid generation reaction.

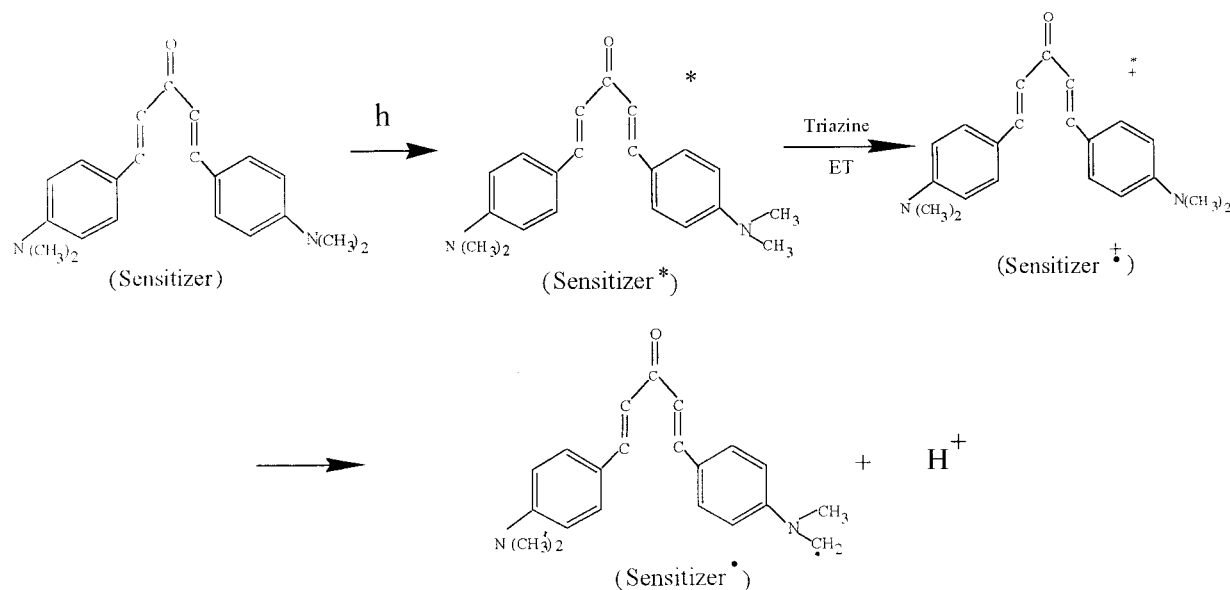
initiate a cross-linking reaction of the *m*-cresol resin/HMMM system, and a clear negative image can thus be obtained.

According to Scaiano's point of view, the mechanism of photo-acid generation reaction can be described as follows:

In Scheme 5, it can be seen that after irradiation, the sensitizer enters the excited state. Then the triazine could accept an electron from the excited sensitizer through the electron transfer process, simultaneously forming a triazine anion radical and a sensitizer cationic radical. The former could form a chloride and a triazine radical, and the latter can decompose to a proton and a sensitizer radical. The formed proton can initiate the cross-linking reaction of the prepolymer system to form an image. A possible mechanism of the electron transfer process for the acid formation of sensitizer compound 2 is illustrated in Scheme 4.

CONCLUSION

A new system of visible light, photo-induced acid generation has been studied in this work. Be-



Scheme 4 An example of electron transfer used to create sensitizer compound 2.

cause HMMM can be used as a very strong electron acceptor, it is able to be create, with different kinds of sensitizer that have different absorption wavelengths, an electron transfer acid generation system, so as to initiate some monomer polymerization via the cationic or radical polymerization process. The visible light initiation process is important for the image recording process. A polymerized image was prepared in this work and is shown in Scheme 6. Further study of this process is in progress.

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