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Photoreaction and photopolymerization studies on squaraine dyes/iodonium salts combination

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Abstract

A novel visible photosensitized system, squaraine dye (SQ)/iodonium salt (On) combination, used as a radical photogeneration source has been suggested and studied. The thermodynamic data and experimental results show that the SQ/On combination readily undergoes photoreaction via fast intramolecular ion-pair electron transfer within the short time scale of excited lifetime of SQ, simultaneously resulting in a photobleaching of SQ dye and a generation of active radical species released by subsequent decomposition of onium product. Some important factors that affect the formation of ion-pair complex between SQ dye and onium salts, such as solvent polarity, nature of counter anion, concentration of SQ dye and onium salt, show a large influence on the photoreaction kinetics. Based on the results of primary photoreaction, the visible photopolymerization using SQ/On combination as photoinitiator was studied in the solution and film. The synchronous photopolymerization and photobleaching behaviors were found in the polymerization process. The dye-sensitized photoreaction mechanism of SQ/On system was also proposed and discussed.

Keywords: Squaraine dye; Iodonium salt; Electron transfer; Photobleaching; Photopolymerization

1. Introduction

Squaraine dyes have unique photophysical and photochemical properties and have been found many specialized uses as a kind of important functional dyes for diversely technological applications in xerography, optic recording, non-linear optic and organic solar cells, etc. [1,5–10]. From MNDO and CNDO calculations [3], we known that the squaraine dyes both in the ground state and excited states exhibit intramolecular donar-acceptor-donar (D-A-D) change-transfer form [2] with partially negative charge located at the oxygen atom on central four-member ring [3].

Considering the active electron structure of the squaraine dye, it is possible to construct a new photoinduced radical generation system for polymerization and organic synthesis in combination with suitable component. In addition, by alternation of substitution group their absorption spectrum can cover all the visible and near IR region with very high molar absorption coefficient ($\varepsilon > 10^5$) and small half band width (∼30 nm) [4]. Therefore, this combination can be used as a photoinitiation system for visible photopolymerization and has potential application in three-dimensional fabrication and holographic information recording.

In generation, the dye sensitized photopolymerization is based on the generation of initiating species through either photoreduction or photooxidation reactions of dye with coinitiator [11]. In view of the very short excited singlet state lifetime and very low quantum yield of intersystem crossing for the squaraine dye, it is difficult to proceed the photoreaction efficiently with coinitiator through ordinary diffusion-controlled bimolecular reaction process, specially in the high viscous or rigid polymeric reaction system, since the molecular mobility is very low. In order to reduce this drawback, the linking of photosensitization dye with coinitiator by various chemical forces was suggested and realized, in which two components bonded together by electrostatic interaction seem to be more convenient one. In earlier studies [12,13], a series of ion-pair type xanthens dye/iodonium salt combination photosensitization systems have been reported (expressed in Scheme 1). On exposure to visible light, they rapidly undergo intra-ion-pair electron transfer reaction, but these works are mostly limited to triplet-excited reaction.

In this paper, we design a new photoreaction system that consists of squaraine dyes as photosensitizer and iodonium

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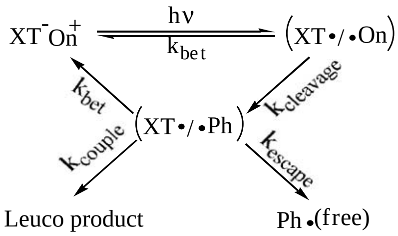


Scheme 1.

salts as co-initiator. The photophysical and photochemical properties of this system was investigated with absorption and fluorescence spectroscopes. The photopolymerization are further studied kinetically in the solution and the film.

2. Experiment

Two squaraine dyes, bis(1,2,3,3-tetramethylindolenium-2-ylidene) squaraine (SQP) and bis(3-methylbenzothiazol-2-ylidene) squaraine (SQT), and three diphenyliodonium salts (OPPIP, OPPIA and OPPIT) expressed in Scheme 2 were prepared by reported procedures [14,15].

Methyl methacrylate (MMA) was obtained from Tianjin Chemical Reagent Institute and purified according to conventional methods and vacuum distilled before use. Epoxy acrylate (CN124) and trimethylolpropane triacrylate (TMPTA) were offered by Satomer Company and UCB Company and used as received. Other reagents were treated with the common purification processes.

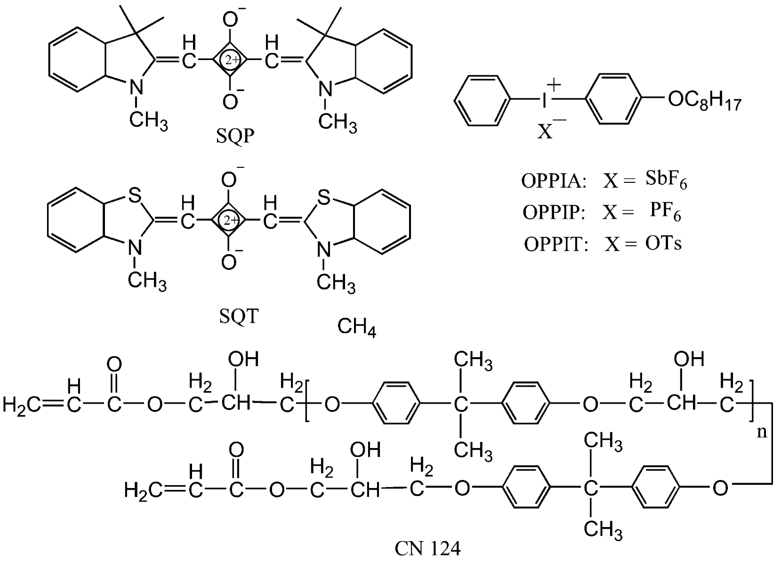
The absorption spectra were recorded on HITACHI-330 and the emission spectra were taken on HITACHI/MPF-4. The excited lifetime was conducted on Horiba NAED-1100.

The light source for photobleaching and photopolymerization was 400 W Xenon lamps, light below 300 nm was filtered out with pyrex glass and the intensity of irradiation was 68 m W cm^{-2}. The polymerization rates were measured with dilatometers (composed of a 10 mm diameter cylinder glass bottle and a capillary above it), which rotated around the light source at 4 rpm on merry-go-round set in a thermostatical photoreaction bath (303 K). The MMA solutions were prepared by dissolving MMA into the of squaraine dye/iodonium combination solution in different solvent and bubbled with high purity nitrogen for 40 min. The experimental data were treated by a least-squares method. The photocurable films were prepared by evenly coating the formulations containing dye and iodonium with constant concentration on a polyester film base, covering tightly with thin plastic film. The film thickness was controlled to be about 20 μm. Gas chromatography/mass spectrometry analysis were performed in a FINNIGAN-4201C system. IR spectra were recorded on a Perkin-Elmer model 983 IR spectrometer.

3. Results and discussions

3.1. Photophysical properties

The absorption spectra of the squaraine dye/iodonium salt combination (SQ/On) were shown in Fig. 1, it can be seen that there are two absorption bands, one at visible region, λ_{max} 632 nm for SQP dye and another at deep UV region, λ_{max} 227 nm for iodonium salt OPPIA, which correspond to the absorption peaks of single SQ dye and On salt, respectively. Thus, only the SQ dyes absorb the irradiation under expose to visible light. In order to estimate thermodynamically the activity of the squaraine dye/iodonium salt photoreaction, the values of free energy change (ΔG) for the electron transfer reaction were calculated according to the



Scheme 2.

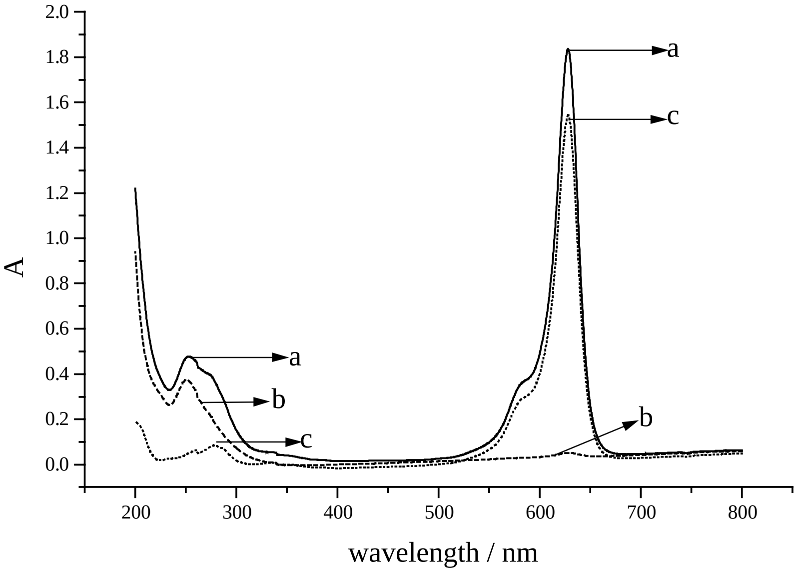


Fig. 1. Absorption spectra of SQP and OPPIA and their combination [SQP] $= 1 \times 10^{-5}$ mol/l, [OPPIA] $= 2 \times 10^{-5}$ mol/l, in acetonitrile: (a) OPPIA + SQP, (b) OPPIA, (c) SQP.

Rohm–Weller equation [16]. The thermodynamic parameters measured and calculated listed in Table 1 indicate that both SQP and SQT combination systems possess high driving force, $\Delta G^* < 0$ on exposure of light. It means that their photoelectron transfer reaction easily occurs through singlet excited state, while they are high thermal stable at non-irradiation condition, since $\Delta G > 0$ in ground state.

In this combination system, the photoinduced electron transfer reaction between SQ dye and iodonium salt may undergo via two possible reaction pathways: bimolecular and unimolecular reaction, the latter is a type of ion-pair complex of SQ dye/On salt likely formed at the oxygen atom sites on the squaric ring. In order to estimate the contribution of two reaction routes to the photoreaction of SQ/On combination, respectively, the fluorescence quenching experiment of squaraine dyes by iodonium salt was further performed at room temperature. From Stern–Volmer equation plot, as shown in Fig. 2, the rate constants of quenching reaction were obtained to be $1.95 \times 10^{11}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $6.7 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for SQT and SQP, respectively, which are nearly 2 orders of magnitude larger than that of diffusion controlled bimolecular reaction constant ($\sim 2 \times 10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$). These results obtained give fine evidence that the onium salt is a very effective fluorescence quencher for excited SQ dye and the fast quenching occurs predominantly through the intramolecular ion-pair pathway.

Table 1
Thermodynamic data for SQ/On systems

	E_{ox} (eV)	E_{s} (kJ/mol)	T_{S_1} (ns)	ΔG (kJ/mol)	ΔG^* (kJ/mol)
SQP	0.43	183.08	1.3	60.74	−122.35
SQT	0.22	175.56	3.2	40.50	−139.24

E_{red} (eV) $= -0.2$ for OPPIP [17].

Owing to the energy of excited SQ dye lower than that of On salt, the energy transfer from excited SQ to On is impossible. Therefore, it is reasonable to consider that upon irradiation the photoinduced electron transfer reaction between excited SQ dyes and On occurs via intramolecular pathway, which have a strong driving force and large reaction rate as thermodynamic calculation and fluorescence quenching experiments described above.

3.2. Photochemical reaction

When the SQ/On combination system is exposed to visible light, the bleaching phenomenon of SQ dye was observed, and the absorption peak of squaraine dye (SQP) decreased with irradiation time (Fig. 3). In the absence of On, the absorption of dye is stable. It demonstrates that photoinduced electron transfer reaction occurs between dye and iodonium salt and results in the oxidation of dye to the colorless form.

Therefore, the photoreaction kinetic study can be carried out by monitoring the relative change in the optical density of SQ dye absorption maximum with irradiation time. As shown in Fig. 4, the photobleaching reactions of different SQ dyes with onium salt OPPIA were carried out in the same experimental condition. It can be seen that the photobleaching rate R_{b} ($R_{\mathrm{b}} = (\mathrm{OD}_0 - \mathrm{OD})/(\mathrm{OD}_0 \times t)$) for SQT is higher markedly than that of SQP, which is consistent with the order of fluorescence quenching rate obtained above, because the SQT possesses a lower redox potential and higher driving force for photoelectron transfer related to the SQP.

The effect of iodonium salts with different counter anion on the photobleaching of SQ dye was also examined. As presented in Fig. 5, the photobleaching rate of different On salts is in the order: OPPIA > OPPIP > OPPIA. This result can be attributed to the difference in size of counter anion

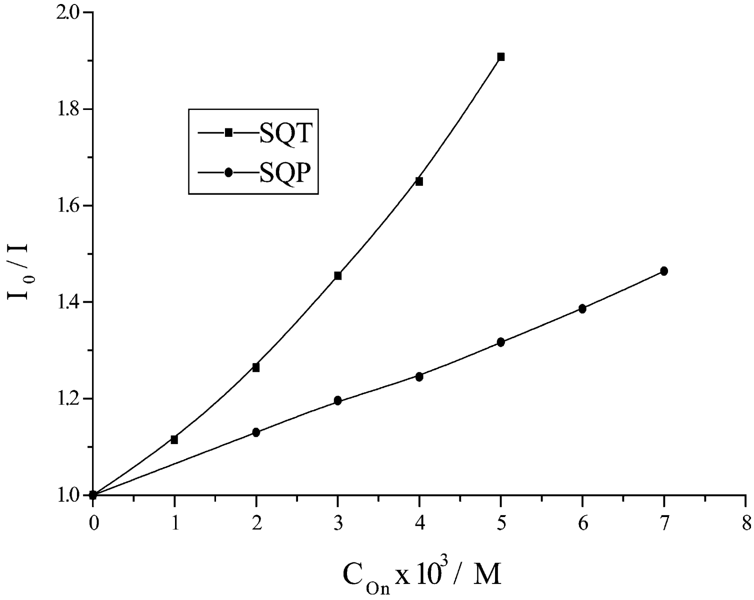


Fig. 2. Stern–Volmer plot of fluorescence quenching of SQ dye by onium salt [SQ] = 8×10^{-6} mol/l, [OPPIA] = 0 to 7×10^{-3} mol/l, in acetonitrile, N_2.

($SbF_6^- > PF_6^- > TsO^-$), which is large influence on the dissociation ability of onium salts to give free onium ionic species for formation of SQ/On ionic pair complex.

The effect of solvent nature on the photoreaction was examined by comparing the photobleaching reaction of SQ/On system in the different solvents. As Fig. 6 shows, the photobleaching rate for different solvents is in the order: chloroform > ethyl acetate > acetone > acetonitrile > ethyl alcohol (their π^* value are 0.58, 0.55, 0.71, 0.75 and 0.54, respectively [18]). These results implied that the photoreaction rate significantly depend on the polarity of solvent, which is closely related with the formation of SQ/On ion-pair complex, In addition, the hydrogen bonding also plays an important role because the alcohol solvents are known that can form hydrogen bonded complex with dye, leading to decrease of their electron donating ability [19]. Thus, the lowest result was observed in the alcohol solution.

To exclude the influence of other solvent nature, the different proportions of acetonitrile and ethyl ether mixture were utilized for determination of polarity effect. The

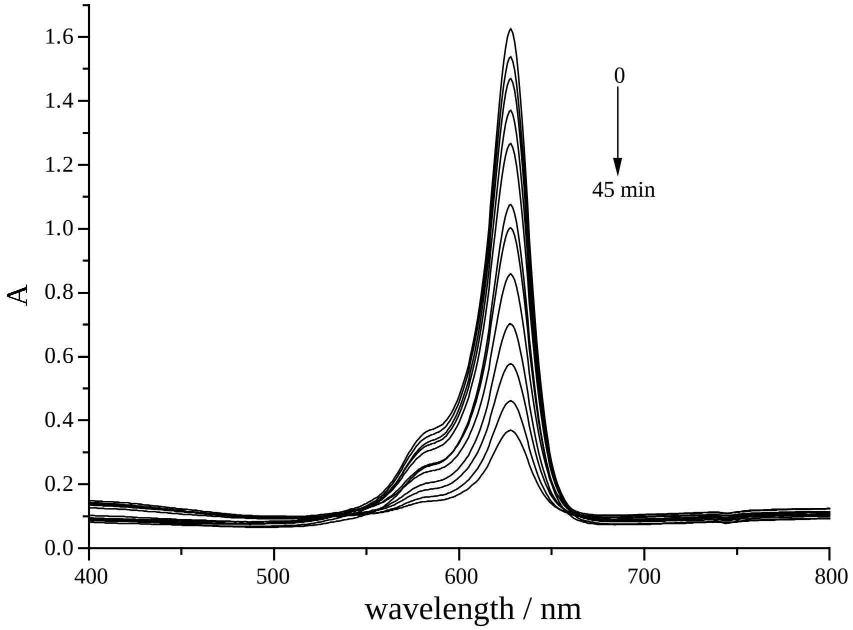


Fig. 3. Change of absorption peak for SQP/OPPIA combination with irradiation time [SQP] = 1×10^{-5} mol/l, [OPPIA] = 2×10^{-5} mol/l, in acetonitrile, N_2.

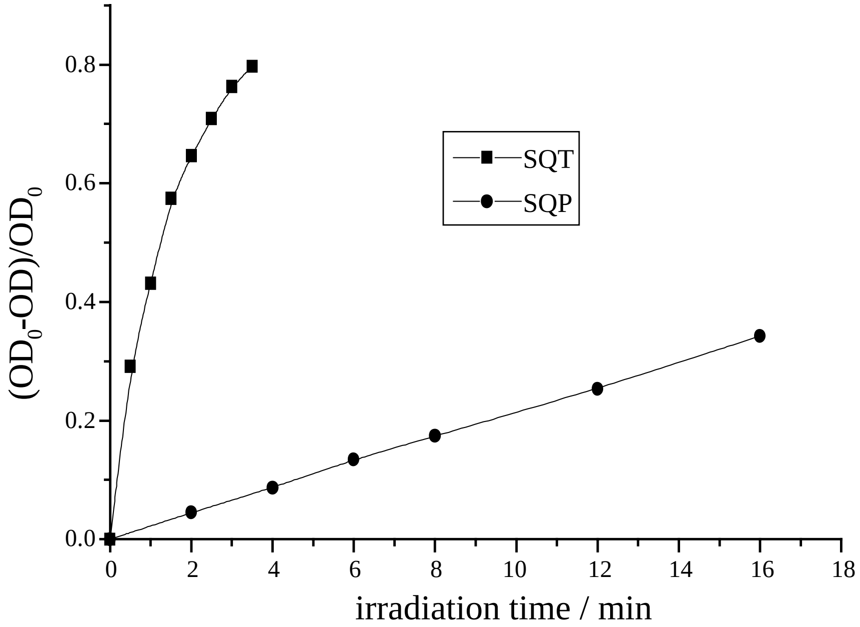


Fig. 4. Photobleaching of different squaraine dyes with iodonium salt [SQ] = 1×10^{-5} mol/l, [OPPIA] = 1×10^{-4} mol/l, in chloroform, N_2.

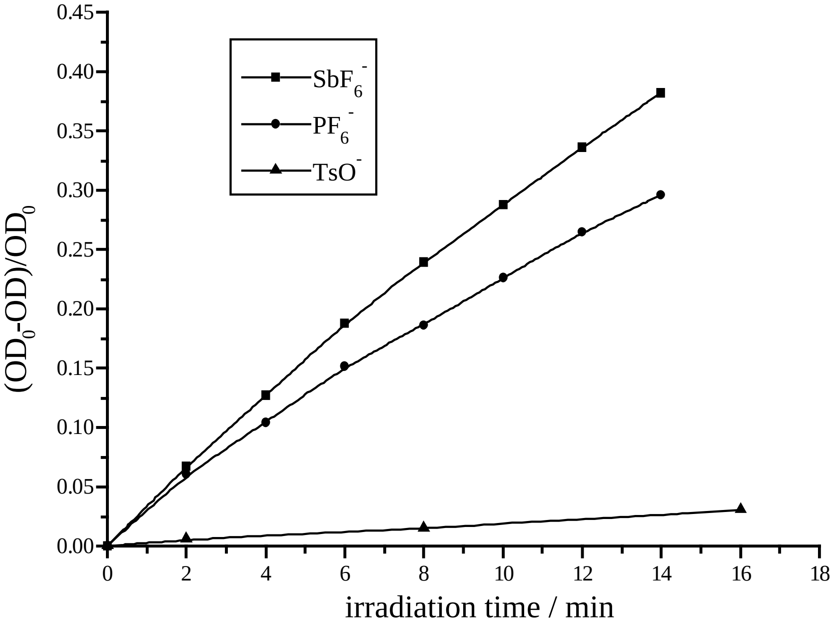


Fig. 5. Influences of counter anion of iodonium salt on the photobleaching rate [SQP] = 8×10^{-6} mol/l, [OPPIA] = 1×10^{-4} mol/l, in chloroform, N_2.

photobleaching data of SQ/On listed in Table 2 indicate that following the decreasing in acetonitrile content, the photobleaching rate markedly increases. Obviously, the decrease in polarity of solvent causes the movement of equilibrium towards to formation of ion-pairs complex, which will greatly promote the electron transfer between SQ and On molecules upon irradiation. The similar rate-enhancement was also obtained as the concentration of On salt increases at constant level of SQ dye.

Table 2
Photobleaching reaction rate in different ratio mixture of acetonitrile and ethyl ether

Acetonitrile/ethyl ether (v/v)	R_b ($\times 10^2$ min^{-1})
1/9	5.66
5/5	3.07
3/7	2.36
9/1	1.42

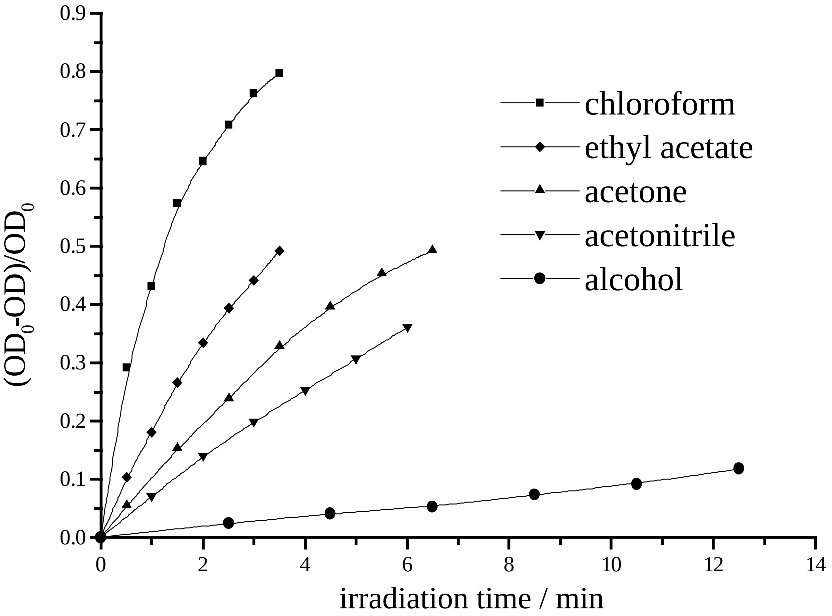


Fig. 6. Influence of polarity of solvent on the photobleaching rate [SQT] = 8×10^{-6} mol/l, [OPPIA] = 1×10^{-4} mol/l, N_2.

The oxygen quenching effect on the photoreaction of SQ/On was conducted in the air and nitrogen saturated solution separately. As shown in Fig. 7, it can be found that they exhibits same photobleaching rate in early stage, indicating the excited singlet state to be assigned to control the sensitization reaction of SQ dye. The some deviant appeared in the late stage between them may be explained by the oxidative degradation of SQ dye occurred.

Analytical results of the volatile products of photochemical reaction of SQ/On system using GC–MS was given in Table 3. The data showed that the main products were the species of On salt. This result is evidence that the cleavage of onium salt occurs in the process of photosensitization reaction of SQ/On. The similar results were reported in our easier work about photoreaction of xanthene dye/onium salt system [20].

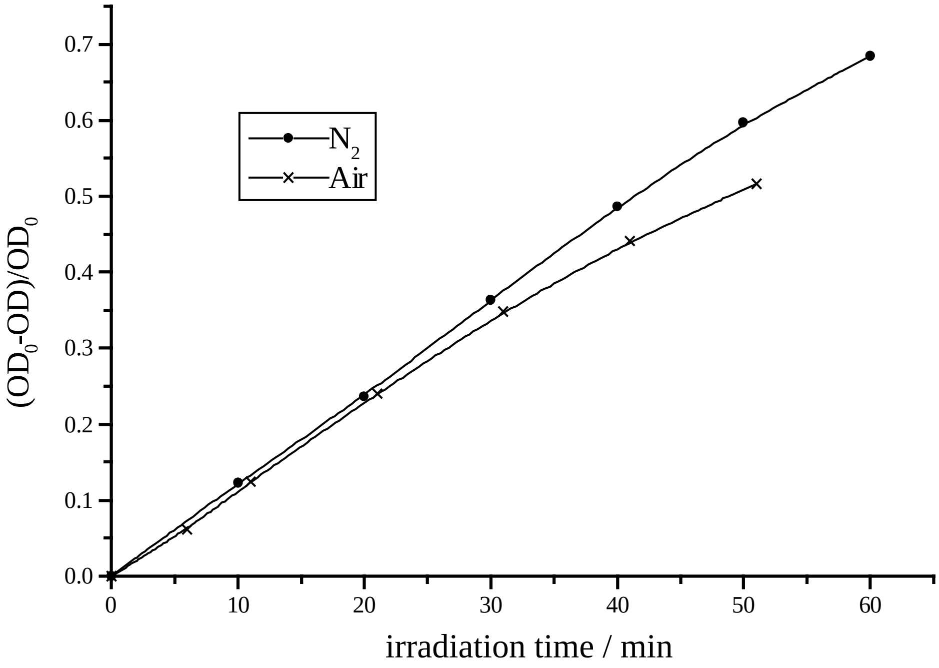
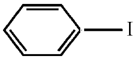
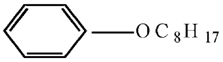
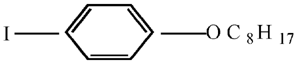
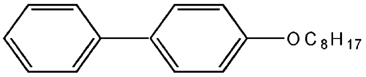


Fig. 7. Influence of oxygen on the photobleaching rate [SQT] = 4×10^{-6} mol/l, [OPPIA] = 1×10^{-4} mol/l, in chloroform.

Table 3
GC–MS analysis result of photoreaction product

m/e	Species
204	
206	
242	$C_8H_{17}OC_8H_{17}$
332	
282	

Based on the above results, the following photochemical reaction mechanism of SQ/On system is proposed:

In the SQ/On system, there exist freely solvated SQ and On^+ ions, and their ion-pair complex, their proportion depending on the polarity of solvent. During photoreaction, they may undergo inter or/and intra-molecular electron transfer, pathways I and II. In view of the very small S_1–T_1 intersystem crossing efficiency ($\varphi_T < 10^{-3}$) and very short S_1 excited life time ($\tau \sim 10^{-9}$ s) of SQ dye, the photoreaction cannot proceed effectively via diffusion-controlled bimolecular reaction pathway II within the small scale of excited lifetime. Thus, it can be considered that upon irradiation the fast electron transfer ($k_e \sim 10^{11}$ to $10^{12}\,M^{-1}\,s^{-1}$) between S_1 excited SQ dye and onium salt readily undergoes exclusively through intramolecular pathway I, then simultaneously leads to an oxidation of SQ dye to form photobleaching products and a reduction of On salts to give radical product, which subsequently undergoes cleavage to generation of phenyl radical species and iodine phenyl derivatives. It should note that the fast subsequent cleavage would effectively reduce the back electron transfer and deactivation in the solvent cages, resulting in a great increase in the photoreaction of SQ/On combination.

3.3. Photopolymerization

As presented above, the SQ/On combination can act as a radical photogeneration source; therefore they could be utilized as a useful photoinitiation system for visible photopolymerization.

The photopolymerization of MMA initiated by SQ dye/iodonium salts combination systems were firstly carried out in the CH_3CN solution. The result obtained as expressed in Fig. 8 indicated that SQ/On system can initiate the polymerization of the MMA efficiently, and the polymerization rate of SQT/OPPIP is larger than that of SQP/OPPIP, because of the difference of electron transfer rate and redox potential value between them as mentioned above.

The effect of SQ concentration on polymerization rate is expresses in Table 4. It can be seen that with increasing

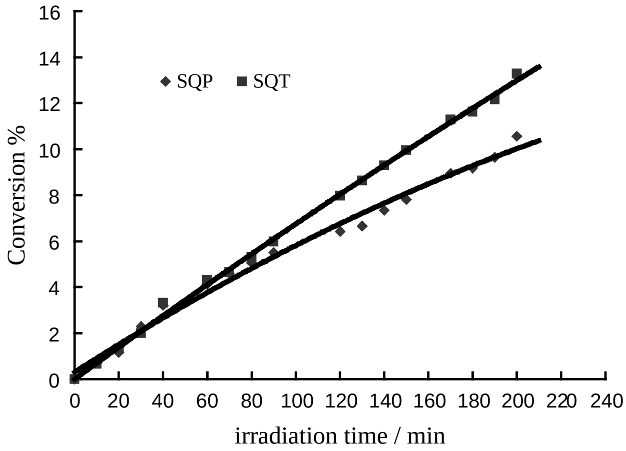


Fig. 8. Plot of polymerization initiated by SQ/On in solution $[SQ] = 2 \times 10^{-4}$ mol/l, $[OPPIA] = 2 \times 10^{-4}$ mol/l, $[MMA] = 3.76$ mol/l, in acetonitrile, N_2.

SQP concentration, the polymerization rate increases in the low concentration range, then slowly decreases in the high concentration range due to the inert light screening effect of dye, which is usually observed in the photosensitized polymerization system [21].

Photopolymerization in film was carried out at room temperature. The polymerizable resin formulation consists of 62.5 wt.% epoxy acrylate CN 124 and 37.5 wt.% multifunctional monomer TMPTA. All samples contain 1 wt.% SQ dye and 2 wt.% iodonium salt (OPPIA) on base of resin weight. Upon exposing with visible light, the polymerization was found readily to take place by SQ/On combination as photoinitiator resulting in a formation of crosslinked polymer along with the occurrence of dye bleaching.

To elucidate the relationship between photopolymerization and photobleaching in photocurable film, the polymerization process was determined by monitoring the decrease of IR absorbance at $810\,cm^{-1}$, which corresponds to the twisting vibration of the acrylic double bond. The kinetic profiles of polymerization are shown in Fig. 9. As expected, on the basis of chain mobility considerations, the polymerization was found to develop very quickly in the initial viscous state then the rate decreases gradually, from the semi-solid state to the rigid solid state with the progress of crosslinked network formation.

Table 4
Effect of SQ concentrations on polymerization rate of MMA

[SQP]/M	lgRp + 4
5×10^{-6}	0.23
1×10^{-5}	0.30
2×10^{-5}	0.70
4×10^{-5}	0.65
8×10^{-5}	0.62
1×10^{-4}	0.60

[OPPIP]: 2×10^{-5} M, [MMA]: 3.76 M.

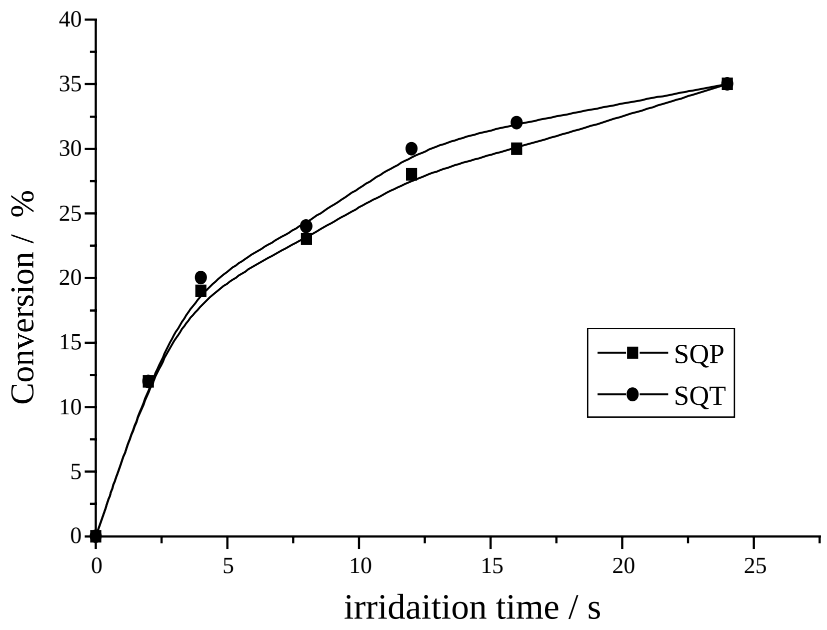


Fig. 9. Plot of photopolymerization initiated by squaraine dye and iodonium salt system in film [SQP] = 1 wt.%, [OPPIA] = 2 wt.%, film thickness: 20 μm.

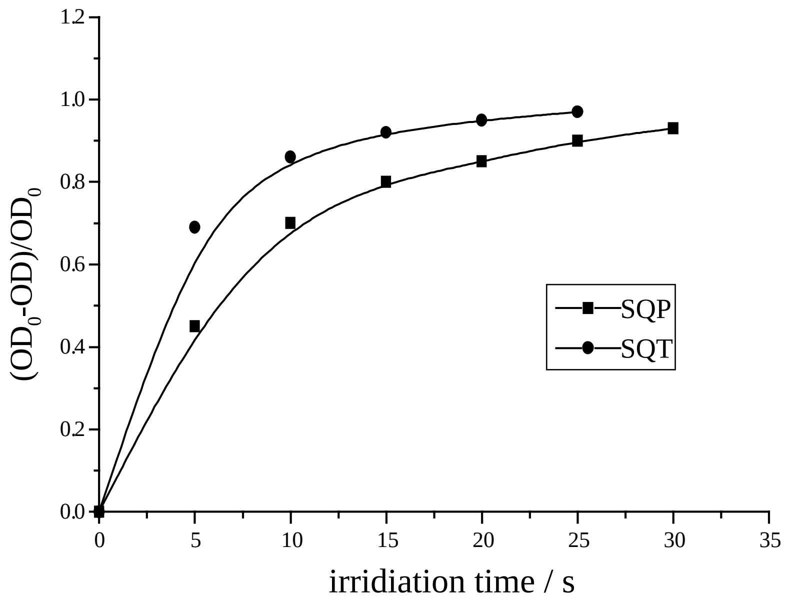
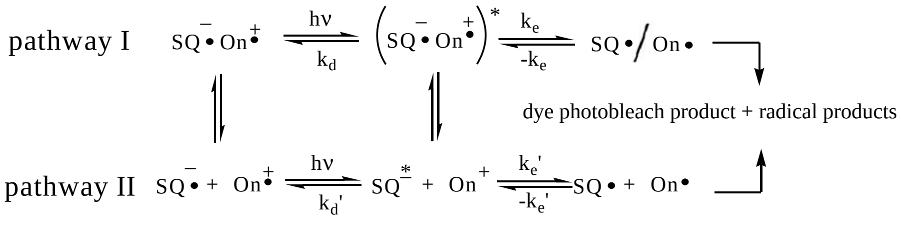


Fig. 10. Plot of photobleaching of squaraine dye and iodonium salt system in photocurable film [SQP] = 1 wt.%, [OPPIA] = 2 wt.%, film thickness: 20 μm.



Scheme 3.

A similar pattern of the kinetic plot of photobleaching was also obtained from the identical photocurable samples. As shown in Fig. 10, the photobleaching rate of SQT in film is somewhat greater than that of SQP. Their photobleaching rate is fast in the beginning and then becomes more and more slow. These synchronous photopolymerization and photobleaching behaviors of such photosensitized polymerization system further verified the photochemical reaction mechanism of SQ/On combination (Scheme 3) as mentioned above and make them suitable to use for deep photopolymerization.

4. Conclusion

The SQ/On combination system can readily undergoes photosensitization reaction upon irradiation by visible light through intra-ion-pair electron transfer pathway, simultaneously results in a photobleaching of SQ dye and a generation of active radical species.

The intramolecular electron-transfer ($k_e \sim 10^{11}$ to $10^{12}\,M^{-1}\,s^{-1}$), much faster than the competitive process of S_1 excited decay ($k_d \sim 10^9\,M^{-1}\,s^{-1}$), and the rapid subsequent cleavage of On salt reduced product allow the photoreaction of SQ/On system proceeding effectively. Some important factors that affect the formation ion-pair complex between SQ and On, such as solvent polarity, counter anion nature and concentration of SQ and On compounds, exhibit a significant influence on the photoreaction kinetic. On the basis of the photoreaction results, the SQ/On combination can act as a radical photogeneration source and could be utilized as a useful photoinitiation system for visible photopolymerization. Their high initiation reactivity and concomitant dye photobleaching property in the photopolymerization process make them possible to be used for fabrication of deep photoresist and holographic recording devices.

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References

[1] K.Y. Law, J.S. Facci, F.C. Ballry, J.F. Yanus, J. Imag. Sci. 34 (1990) 31.
[2] T. Mori, K. Miyachi, T. Kichimi, Jpn. J. Appl. Phys. 33 (1994) 6594.
[3] R.W. Bigelow, H.J. Freund, Chem. Phys. 107 (1986) 159.
[4] J. Griffiths, J. Mama, Dyes Pigments 44 (2000) 9.
[5] A.B. Karl, Synth. Met. 124 (2001) 385.
[6] U.A. Engin, H. Emür, Talanta 58 (2002) 719.
[7] P. Ralf, T. Minquan, T. Satoshi, F. Makoto, Dyes Pigments 57 (2003) 43.
[8] K. Basak, U.A. Engin, Tetrahedron Lett. 40 (1999) 9125.
[9] M.A. Christine, O. Bernhard, S.W. Otto, Anal. Biochem. 305 (2002) 166.
[10] C.R. Chenthamarakshan, J. Eldo, A. Ajayaghosh, Macromolecules 32 (1999) 5846.
[11] T. Tanabe, A. Torres-Filho, D.C. Neckers, J. Polym. Sci., Part A: Polym. Chem. 36 (1995) 1691.
[12] W. Zhou, E. Wang, J. Photochem. Photobiol. A: Chem. 96 (1996) 25.
[13] Y. Bi, D.C. Neckers, J. Photochem. Photobiol. A: Chem. 74 (1993) 221.
[14] T. Lin, B. Peng, Dyes Pigments 35 (1997) 331.
[15] J.V. Crivello, J.L. Lee, J. Polym. Sci., Polym. Chem. Ed. 27 (1989) 3951.
[16] J. Paczkowski, M. Pietrzak, Z. Kucybala, Macromolecules 29 (1996) 5057.
[17] S.P. Pappas, L.R. Gatechair, J.H. Jilek, J. Polym. Sci., Polym. Chem. Ed. 27 (1984) 77.
[18] J.K. Mortimer, M.A. Jose-luis, H.A. Michael, R.W. Taft, J. Org. Chem. 48 (1983) 2877.
[19] S. Das, K.G. Thomas, R. Ramanathan, M.V. George, J. Phys. Chem. 97 (1993) 13625.
[20] J. He, M. Li, E. Wang, Chin. Sci. Bull. 41 (1996) 38.
[21] J. Nie, W. Zhou, E. Wang, L.A. Linden, J.F. Rabel, J. Funct. Polym. Chin. 11 (1998) 223.