Visible-Light Photoinitiating Systems for Laser Imaging Using Pyrromethene Dyes

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In this paper, a new three-component photoinitiating system based on pyrromethene dyes was shown to exhibit high performance for laser imaging at 532 nm. Pyrromethene dye was used with a reductant coinitiator (Amine) and oxidant coinitiator (Triazine). The initial mechanism of reaction depends on the relative concentration of the oxidant and the reductant. After reaction between the excited dye and the coinitiator, secondary reactions involving the second redox additive take place, leading to beneficial effects— such as dye ground-state recovery and formation of additional initiating species. The efficiency of these processes is deeply investigated, and the effect on the polymeric network formation is detailed.

P hotopolymerization technology has gained prominence as an attractive alternative to traditional polymerization processes due to a large variety of benefits. As an efficient, low-cost and environmentally friendly method, photopolymerization has led to remarkable expansion in a variety of applications such as coatings, adhesives, composites, graphics arts, laser imaging, microelectronics, optics, rapid prototyping and rapid manufacturing. More recently, this technology has entered the biomedical arena, leading to very attractive and elegant achievements.[1-10]

Many different photoinitiating systems are commercially available, covering a wide range of applications mainly using UV-irradiation sources. Due to the harmful effects of UV radiation, the use of visible light is preferable for biological applications, such as dental restorations,[11] orthopedics and polymer scaffolds for tissue engineering.[6-10, 12] In addition,

the evolution in laser technologies makes the choice of visible lights preferable for different applications, such as holography, color printing and microencapsulation.[13] However, the development of visible-light photoinitiating systems has always been considered quite challenging. Different methods have been proposed and among them is the use of additional redox additives, leading to the so-called three-component photoinitiating systems.[14]

Three-component photoinitiating systems typically consist of a dye that works as a photosensitizer; a coinitiator; and a third redox component. The choice of the coinitiators is based on their redox properties. The choice of the dye makes a whole host of reactions possible in three-component photoinitiating systems. In fact, the reactions that take place in these systems seem to depend on the precise nature of the components chosen as well as the physical properties of the monomer.

FIGURE 1

Reaction mechanism of a three-component photoinitiating system based on dye/electron donor (D)/electron acceptor (A)
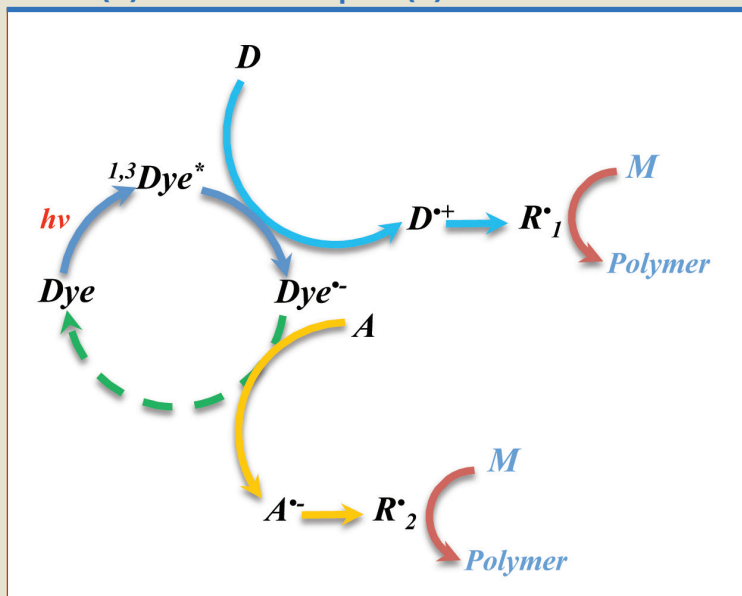
According to the literature,[14-19] the general reaction mechanism expected (Figure 1) for these systems involves a deactivation of the excited states of the dye via a photoinduced electron transfer reaction from an electron donor (D). This induces the formation of the dye anion radical (semi-reduced form of dye) and the radical cation of electron donor ($D^{\bullet+}$). Thus $D^{\bullet+}$ undergoes a reaction leading to the formation of a radical $R_1^{\bullet}$ that will initiate the polymerization reaction. A low-efficient direct reaction is expected between the excited states of dye and the electron acceptor. The semi-reduced form of the dye then reacts with the electron acceptor (A), inducing the formation of the anion radical of electron acceptor that could lead to the formation of a new initiating radical $R_2^{\bullet}$. This beneficial side reaction leads to the recovery of the dye ground state and limits its photobleaching via a quasi photocatalytic cycle.

Experimental Materials

2,6-diethyl-8-phenyl-1,3,5,7-tetramethylpyrromethene BF_2 complex (EPP) was used as pyrromethene dye[20-22] together with ethyl-4-dimethylamino-benzoate (EDB) as a reductant coinitiator and 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA) as an oxidant. The molecules are depicted in Figure 2.

Table 1 shows the photophysical and electrochemical properties of the EPP dye.[20, 23]

Techniques

Infrared Spectroscopy

The Real Time Fourier Transform Infrared spectroscopy was used to measure the photopolymerization kinetics of studied systems. In addition, UV-visible spectroscopy and cyclic voltammetry experiments provide the photochemical and electrochemical data to establish the general criteria and thermodynamic considerations. The fluorescence spectroscopy and laser flash photolysis were used to study the reactivity of reactive species and to propose a reaction mechanism for the systems studied.

Results and Discussion

Figure 3 shows the evolution of the photopolymerization kinetics against the irradiation time. The main characteristics are collected in Table 2—i.e., inhibition time t_{inh}, polymerization rate $Rp/[M]_0 \times 100$, where $[M]_0$ stands for the initial concentration in double bonds, and final conversion (Conv). As can be seen, the two-component

FIGURE 2

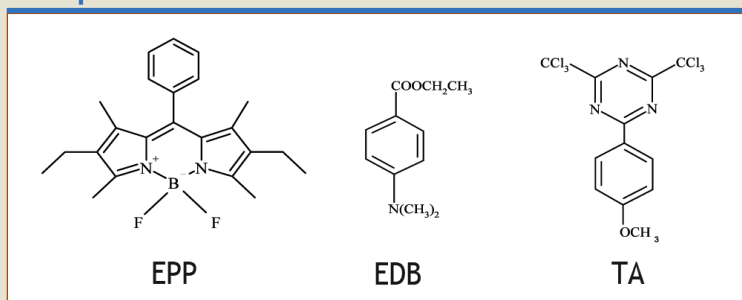### Molecular structures of compounds used in experiment

TABLE 1

The photophysical and electrochemical properties of the EPP dye.[20, 23]

Maximum wavelengths of absorption λ_{max} and emission λ_{max}^{EM}, maximum extinction coefficient ε_{max}, energies of the first excited singlet E_S and triplet E_T states, corresponding excited state lifetimes τ_S and τ_T and fluorescence quantum yield $\o_f$

	EPP
λ_{max} (nm)	521
λ_{max}^{EM} (nm)	538
ε_{max} (M^{-1} sec^{-1})	72,000
E_S (kcal/mol)	54.0
τ_f (ns)	5.8
$\o_f$	0.77
E_T (kcal/mol)	37.5
τ_T (µs)	39

photoinitiating systems based on EPP/EDB exhibits poor results, with a very low rate of polymerization and low final conversion. The system based on EPP/TA exhibits better results, with a good rate of polymerization and good final conversion.

However, the best results are noted for the three-component photoinitiating system EPP/EDB/TA. The performance of the EPP/EDB system increases after the addition of TA. In addition,

the efficiency of this system is related to the molar concentration of TA present in the formulation. Increasing the concentration of TA induces an increase of the polymerization rate and a decrease of the inhibition time, suggesting that the presence of TA is crucial to achieve a high monomer conversion.

According to the redox properties of the dyes and the coinitiators, a photoinduced electron transfer

reaction is expected between the excited states of EPP and the coinitiators. The values of the Gibbs free energy ΔG_{et} were calculated using the Rhem Weller equation $\Delta G_{et} = E_{ox} - E_{red} - E^* + C$ where E_{ox} and E_{red} are the half-wave oxidation and reduction potentials for the donor (EDB, E_{ox} = 1.07 V/SCE) and the acceptor (TA; E_{red} = -1.12 V/SCE), respectively, and E* is the energy of the excited state of dye. The coulombic term C is usually neglected in polar solvent. The calculated values were grouped in Table 3. As can be seen, the intermolecular singlet electron transfer reactions are thermodynamically favorable, indicating that EPP can be reduced in the presence of EDB or oxidized with TA.

In addition, the quenching rate constants of the excited states of EPP with EDB and TA were studied (Table 3). The quenching rate constants of the singlet excited state k_q^S show high values close to the diffusion rate constant in acetonitrile ($k_d = 2.10^{10}$ M^{-1}s^{-1}). Laser flash photolysis (LFP) experiments were also carried out in order to study the triplet state ^{3}EPP reactivity at 440 nm.[20] The triplet-state quenching rate constants (k_q^T) show that the quenching of EPP triplet-excited state

TABLE 2

Sample formulation, EDB/TA Molar ratio, inhibition time t_{inh}, polymerization rate $Rp/[M]_o$x100 and final conversion (Conv) obtained after 15 min. irradiation

# of Sample	Molar ratio (EDB/TA)*	t_{inh} (s)	$Rp/[M]_0$x100(s^{-1})	Conv (%)
EPP 1	1/0	**	**	28.6
EPP 2	0/1	10.7	0.9	42.1
EPP 3	5/1	8.4	1.2	50.3
EPP 4	1/5	4	2.2	56.6
EPP 5	1/1	2.4	5.1	74.1

* A molar ratio of 1/1 corresponds to 2.5 wt% of EDB and 1 wt% of TA.

Figure 3

Photopolymerization kinetics of different formulations based on EPP/EBD/TA
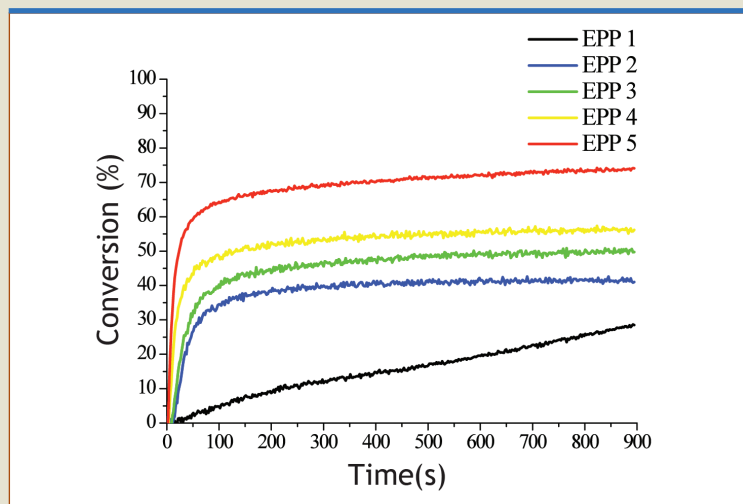
is less efficient than the quenching of its singlet excited state. This is in line with the positive calculated values of ΔG_{et}. However, the high lifetime of ^{3}EPP can lead to a significant contribution of the triplet state quenching in the formation of initiating species.

From these results, one can conclude that EPP reacts with the coinitiators EDB or TA from both the singlet and the triplet-excited states. The reaction proceeds through the formation of a germinate radical ion pair, which can recombine through a back electron transfer process or separate into free ions. The latter

process explains the formation of the radical anion of the dye when EDB is used as quencher or the radical cation of the dye when TA is used instead. The formation of these species was observed using LFP and time-resolved photoconductivity experiments (not reported here).

The study was completed for the three-component photoinitiating system where the transient absorption spectroscopy at 400 nm shows that the signal of EPP$^{•+}$ formed from the interaction EPP/TA decreases under the addition of EDB. This indicates that the amine reacts with the radical

cation of EPP formed from the interaction of EPP excited states with TA. In addition, the recovery of EPP ground state was observed. Similarly, if the deactivation of excited states of the dye proceeds through a photoinduced electron transfer with EDB, the radical anion of the dye is formed. The latter can react with TA leading to the recovery of EPP. In this case, one can assume that the oxidation potential of EPP$^{•-}$ is -1.16 V/SCE. This leads to the calculation of ΔG_{et} values of -0.04 eV, showing that this reaction is exergonic enough to be operative.

According to these results, the mechanisms of reaction of three-component photoinitiating systems based on EPP/EDB/TA can be proposed, in which the former photochemical reaction with the excited dye will depend on the relative EDB/TA molar ratio (Figure 4).

Conclusion

The visible photopolymerization efficiency of two- and three-component photoinitiating systems based on EPP/EDB/TA was described in this paper. It was found that TA is more efficient than EDB to initiate polymerization reaction. Moreover, the three-component photoinitiating system was proved to be the most efficient in terms of polymerization rate and final conversion.

Table 3

Fluorescence k_q^S and triplet state k_q^T quenching rate constants, Gibbs free energy ΔG_{et} for the photochemical reaction of EPP with EDB and TA in acetonitrile

	^{1}EPP		^{3}EPP	
	ΔG_{et} (eV)	k_q^S (M^{-1}s^{-1})	ΔG_{et} (eV)	k_q^T (M^{-1}s^{-1})
EDB	-0.11	$7.0\ 10^9$	+0.6	$8.0\ 10^6$
TA	-0.12	$1.7\ 10^{10}$	+0.59	$2.0\ 10^6$

FIGURE 4

Mechanisms of three-component photoinitiating system reactivity based on EPP/EDB/TA depending on the EDN/TA molar ratio—(a) low EDB/TA molar ratio and (b) high EDB/TA molar ratio.
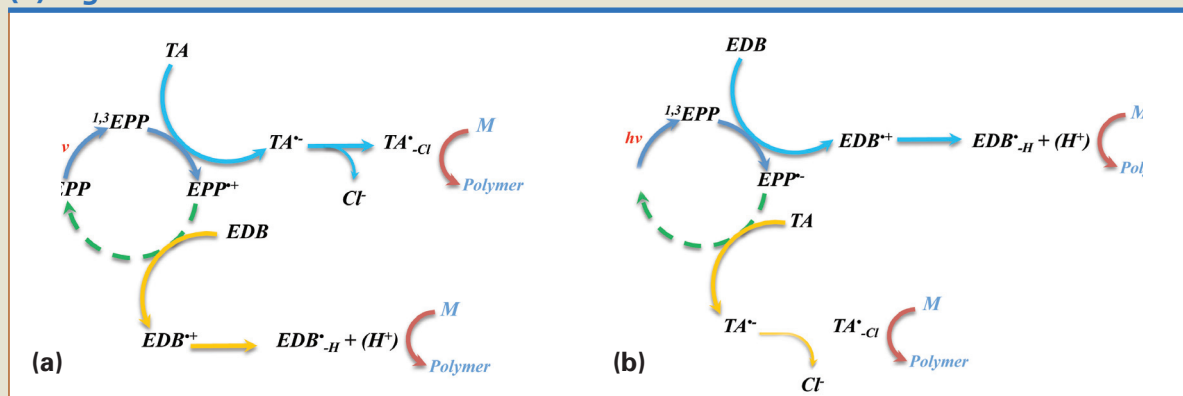
Spectroscopic studies were made to explain the obtained results of photopolymerization kinetics. The dye reacts mainly through a singlet electron transfer mechanism from the dye to the triazine and from the amine to the dye. Secondary reactions inducing the recovery of dye ground state were observed. The influence of the concentration of coinitiators on the performance of systems was also investigated. ◗

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