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Polymer 44 (2003) 3671–3677
polymer
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Visible light induced photopolymerization: speeding up the rate of polymerization by using co-initiators in dye/amine photoinitiating systems

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Received 17 October 2002; received in revised form 18 March 2003; accepted 27 March 2003

Abstract

The activity of six newly designed three-component systems (containing a dye, an amine and a triazine derivative) for the initiation of the photopolymerization of multifunctional acrylates under visible light has been evaluated. The selection of the dyes was based on thermodynamic considerations. A discussion of the photochemical reactivity of these systems reveals the role played by thermodynamics and outlines different aspects concerned with kinetics.

Keywords: Photoinitiator; Photopolymerization; Dye

1. Introduction

In recent years, photoinitiators that operate in the visible region of the spectrum have been developed. This is mostly due to the fact that visible light is cheap, safe and possesses higher penetration ability (compared to ultraviolet light) in the presence of UV absorbing monomers, pigments and substrates [1].

In addition to a few one-component systems such as the bis-acylphosphine oxides [2] or the titanocenes [2], two-component systems, working through electron transfer/proton transfer (e.g. dyes/amines) or energy transfer (e.g. ketone/ketone), were first used as photoinitiators of radical polymerization under visible light. For example, dyes such as Rose Bengal (RB) or Eosin (EO) are employed as photosensitizers in the presence of free radical sources [3–5]. To improve the efficiency of the polymerization and the sensitivity of such systems, multi-component combinations have been developed. For example, the use of three-component systems, the analysis of the mechanisms involved, the photochemical behaviour and the evaluation of the photopolymerization activity have been discussed in our previous studies [6] of a large variety of combinations:

- ketone (benzophenone, thioxanthone)/amine/CBr_4 or organic bromo compound;
- ketone (benzophenone, thioxanthone, ketocoumarin)/amine/onium salt;
- dye (thioxanthene dye or eosin)/amine/onium salt;
- ketone (coumarin or ketocoumarin derivatives)/amine/ferrocenium salt;
- ketone (coumarin or ketocoumarin derivatives)/bis-imidazole derivatives/thiol derivatives;
- ketone (thioxanthone derivative)/amine/photoinitiator
- dye/amine/photoinitiator.

Recent work has appeared on other three-component systems (xanthenic dye/amine/onium salt [7a] and methylene blue/amine/onium salt [7b] and four-component systems dye (Rose bengal)/amine/ferrocenium salt/hydroperoxide [8].

Photoinitiating systems containing triazine derivatives have received considerable interest in the patent literature but few papers have dealt with these systems (see e.g. Refs. [9,10]). In a previous paper [9] it was demonstrated that the addition of a bis(trichloromethyl)-substituted-1,3,5-triazine (Tz) to a dye/amine photoinitiating system clearly leads (in well defined experimental conditions and in model systems) to an increase in the efficiency of the polymerization under visible light irradiation. A reaction mechanism was elaborated which shows that Tz mainly acts as an inhibitor scavenger. The involved inhibitor is the reduced dye arising

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doi:10.1016/S0032-3861(03)00286-6

from the first photochemical reaction between the excited states of the dye and the amine.

The aim here is to report the polymerization activity of other three-component systems that are based on the dye/amine/Tz derivative, to discuss the results as a function of the thermodynamic parameters and the spectroscopic properties of the dye and to see if it is possible to design, a priori, such a three-component system.

2. Experimental

2.1. Materials

(i) 2-(4′-Methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA) was obtained from the PCAS company (Produits Chimiques Auxiliaires et de Synthèses, Longjumeau, France). The purity of this triazine (>99%) was checked by HPLC. Erythrosin B (ERB) (from Aldrich), Acridine Orange (AO) (from Aldrich), Acriflavine (AF) which contains ~65% 3,6-diamino-10-methylacridinium chloride and ~35% 3,6-diaminoacridinium chloride (from Fluka), 3-butoxy-5,7-diiodo-6-fluorone (DIBF) (from Spectra Group limited, Inc.) and 3-hydroxy-2,4,5,7-tetraiodo-6-fluorone (TIHF) (from Spectra Group limited, Inc.) and the *N*-methyldiethanolamine (MDEA) were used as received. Safranin O (SO) (Aldrich) was purified by column chromatography. The formula are displayed in Scheme 1. Acetonitrile (MeCN) (Fluka UV-grade) was used as received.

(ii) The polymerizable formulation contained Actilane 20 (poly(urethane diacrylate) from the SNPE company, France), Sartomer 344 (poly(ethylene glycol) 400 diacrylate from Cray Valley company, France), HDDA (1,6-hexane diol diacrylate from the Cray Valley company) and Sartomer 506 (isobornyl acrylate from Cray Valley company), with a weight percentage ratio of 55:24:12:9, respectively. Sartomer 344 was incorporated into the formulation to increase the solubility of charged compounds, such as xanthenic dyes. The viscosity of this mixture was 2050 mPa s at 25 °C. The stabilizers were not removed from the monomers. The formulation was applied as an approximatively uniform layer of 50 μm thickness using a calibrated wire-wound bar. Laminate experiments were carried out between two poly(propylene) films to prevent diffusion of atmospheric oxygen. For all the combinations of dye/MDEA/TA, the weight percentages of each component were the same (dye: 0.07 wt%, MDEA: 2.5 wt%, TA: 0.3 wt%).

2.2. Techniques

(i) Ground state absorption spectra were measured on a Beckman DU7 spectrophotometer.

(ii) Redox potentials were determined by cyclic voltammetry in N_2-saturated acetonitrile solutions, containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. A platinum working electrode (0.1 cm^2) was used. The reference electrode was a saturated calomel electrode (SCE) connected to the sample solution through a fritted glass bridge that contained the supporting electrolyte, in methanol. Calibration of the reference electrode was carried out with the ferrocenium/ferrocene couple, used as an internal reference. Redox potentials data were taken equal to half-peak potentials in the case of irreversible systems.

(iii) The light source was a 150 W metal halide mercury lamp (continuous light emission $\lambda > 300$ nm) and the total light intensity was equal to 42 mW/cm^2. Cut-off filters were used to irradiate the dye alone in all polymerization experiments ($\lambda > 425$ nm : $I_0 = 20$ mW/cm^2). The mean light intensity remained constant within ± 10% in the 420–650 nm wavelength range.

(iv) The curing was monitored by using a modified IFS 28 FT-IR Brucker spectrophotometer working in the rapid-scan mode, allowing an average 5 scans/s collection rate (with 8 cm^{-1} resolution). The kinetics of the polymerization were measured as described elsewhere [9] by following the disappearance of the IR absorption of the acrylic double bond at 810 cm^{-1} (=CH_2 twisting).

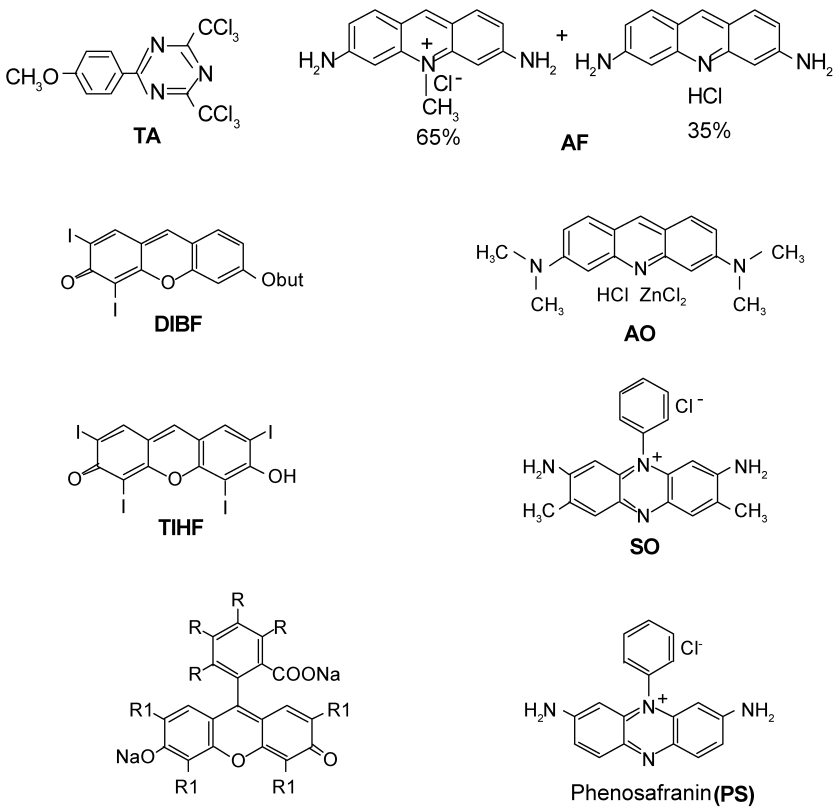
3. Results and discussion

3.1. Efficiency of dye/amine/TA photoinitiating systems in radical polymerization

Several combinations of dye/MDEA/TA were tested as photoinitiating systems for the polymerization of the acrylate monomers. Six dyes (ERB, SO, DIBF, TIHF, AF, AO) (see Chart 1) were used with the same amine (MDEA) and the same triazine derivative, TA. These sensitizing dyes absorb light at higher wavelengths than TA ($\lambda^{max} = 327$ nm in acetonitrile). Therefore, irradiation of the dye alone (at >425 nm) is made possible by using a cut-off filter (Fig. 1). The kinetics of the polymerization for different dye/MDEA/TA combinations, under irradiation with a filtered visible light, is shown in Fig. 2. The inhibition times, the observed rates of polymerization (R_p/M_0) and the double bonds conversion yield after 40 s of irradiation are shown in Fig. 3.

It appears that the dyes/TA systems are not able to initiate a radical polymerization as did other dye based systems (Rose Bengal or Eosin Y or Phenosafranin/TA) under the same irradiation conditions [9]. This means that under sensitization conditions and using these dyes as sensitizers, the interaction between the dye and TA does not efficiently lead to initiating species.

The apparent efficiency of the well known two component dye/amine photoinitiating system is dependent



Scheme 1.

on the dye as expected (Figs. 2 and 3). Some of the combination such as AO/MDEA or SO/MDEA behave very inefficiently, leading to a long inhibition time and low conversion yields.

The addition of TA to the dye/amine leads to an enhancement of the polymerization efficiency for all the systems studied. The polymerization rate and the final acrylate conversion increase (compared to those noted in the presence of the two component dye/amine system) and the inhibition time decreases.

TA has the most striking effect on the photoinitiating system that contain Acridine Orange (AO): the inhibition time is close to zero and the curing rate exhibits a sixfold increase in the presence of TA (Fig. 3). AO is used as sensitizer for the decomposition of onium or sulfonium salts in cationic or mixed cationic/radical polymerizations and has not been reported for use with an amine as radical photoinitiating system. With the addition of a small amount of TA (0.3%), the AO/MDEA photoinitiating system becomes better that the well known EO/MDEA or RB/MDEA mixtures that are widely used in imaging systems. Moreover, under the low light intensity that was used in these studies, AO/MDEA/TA shows the highest final double bond conversion yield among all the studied systems (Fig. 2).

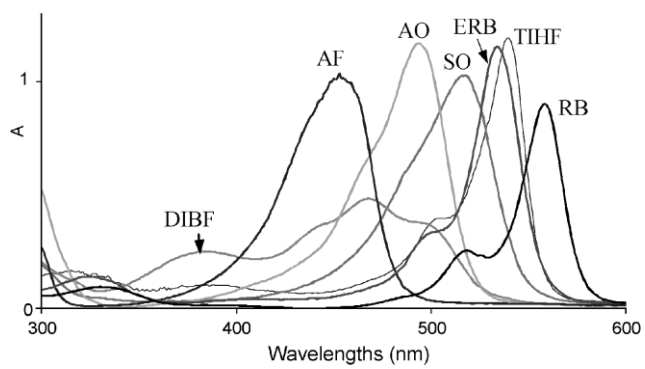


Fig. 1. Absorption spectra of the dyes in acetonitrile.

The system based on the fluoronone dyes (DIBF and TIHF) exhibits a different behaviour pattern (Fig. 2). The efficiency of the system TIHF/MDEA/TA is low whereas, in the presence of the photoinitiating system containing DIBF, the efficiency is excellent. The maximum of acrylic bond conversion is reached within 10 s of irradiation (both with and without TA). In addition, the final film is almost near colourless (in contrast to what was observed with the other photoinitiating systems). This last three-component system appears to be the most efficient when compared to the efficiency of the other three-component systems that were investigated previously. In fact the apparent rates of

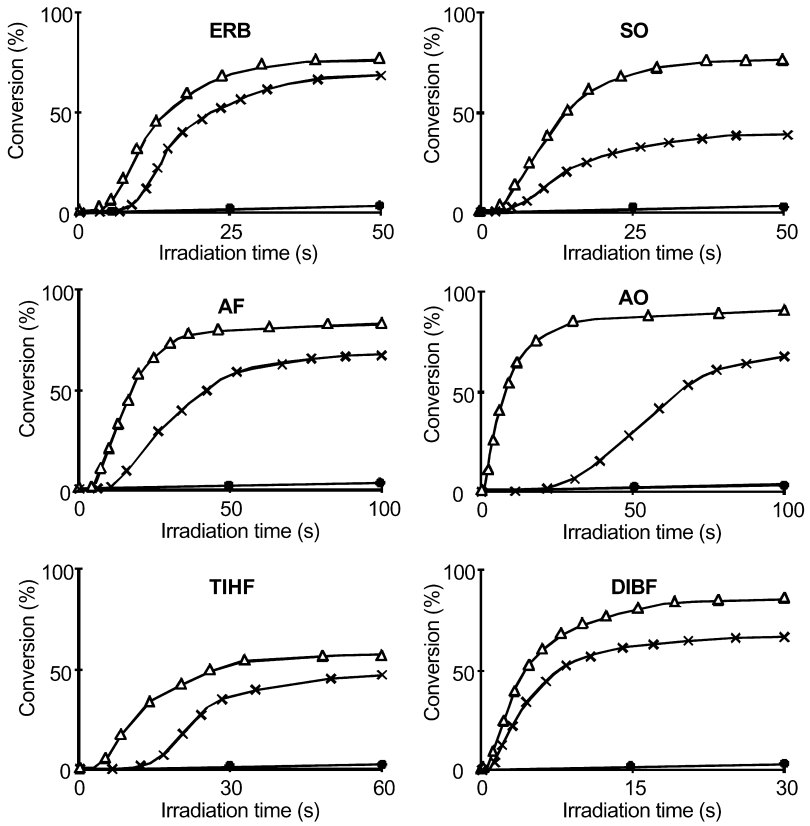


Fig. 2. Influence of the photoinitiating system used in the polymerization of a multi-acrylate formulation exposed to a visible irradiation: $\lambda > 425$ nm; (●) Dye/TA; (×) Dye/MDEA; (△) Dye/MDEA/TA; [Dye] = 0.07 wt%, [MDEA] = 2.5 wt%, [TA] = 0.3 wt%; Laminate-Film thickness = 50 μm.

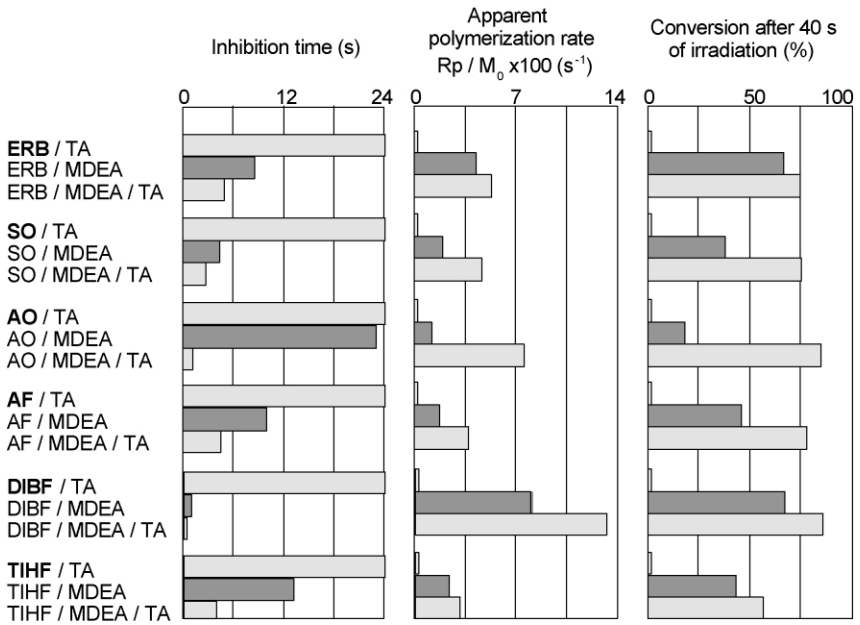


Fig. 3. Comparison of the polymerization characteristics for different visible photoinitiating systems. Irradiation with filtered visible light ($\lambda > 425$ nm, $I_0 = 20$ mW/cm^2); [Dye] = 0.07 wt%, [MDEA] = 2.5 wt%, [TA] = 0.3 wt%; Laminate-Film thickness = 50 μm.

Table 1
Apparent rates of polymerization ($R_p/[M]_0 \times 10^2$ s^{-1}) of an acrylate formulation containing several Dye/MDEA photoinitiating systems in the presence or not of TA

Dye/MDEA	No TA	With TA
Rose Bengal (RB)	3.2	8
Eosin (EO)	3	6.7
Phenosafranin (PS)	0.8	6.8

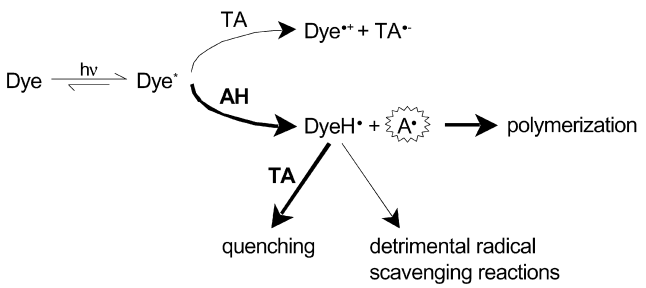
polymerization ($R_p/[M]_0 \times 10^2$ s^{-1}) that were observed in the presence of these other dyes (Table 1) were acquired for the same experimental conditions [9].

3.2. Criteria of selection for the dye in the system dye/amine/TA

Addition of bis(trichloromethyl)-substituted-1,3,5-triazine to a classical dye/amine photoinitiating system (in which the dye is the only absorbing species) clearly leads to an increase in the polymerization of acrylic monomers. This confirms the results that were obtained when Rose Bengal (RB), Eosin (EO) and Phenosafranin (PS) [9] were present. The synergistic effect was only observed in the case of amines that were capable of readily donating a proton, after oxidation by the excited dye, through a primary electron transfer reaction. The interactions between these three compounds (dye, MDEA, TA) were studied and detailed reaction pathways were determined. The following Scheme 2 holds true in the investigated dye based systems:

After light absorption by the dye, the excited states of the dye are quenched by MDEA and TA (with different rate constants) but only the interaction with the amine leads to the generation of initiating radicals (the neutral aminoalkyl radical, A˙). This last reaction also leads to the reduced dye (DyeH˙) that has been recognized in many three-component systems as being a terminating agent of the growing macromolecular chains, during the polymerization reaction (see e.g. Ref. [6a–e] and references therein). The importance of the inhibition effect of DyeH˙ is dependent on the efficiency of its interaction with TA. DyeH˙ being a reducting species, the reaction with TA is probably a reduction of the latter, leading to the recovery of the dye: $DyeH^{\cdot} + TA \rightarrow Dye + TA^{\cdot -} + H^{+}$

A comparison of the excited state energies of the dyes



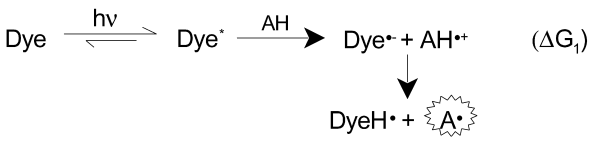
Scheme 2.

(Table 2) with that of TA ($E_S = 3.4$ eV, $E_T = 2.9$ eV [9]) reveals that no energy transfer from the excited states of the dye to the triazine can take place. As a consequence, it appears that the efficiency of the photoinitiating system dye/amine/TA lies on the involvement of electron transfer reactions between the dye, the tertiary amine and TA.

All the dyes studied exhibit the same kind of photophysics and photochemistry [1e,7a,11–17]. They possess a short lived singlet excited state and a rather long lived triplet state. Amine interaction occurs in both excited states and generates an aminyl radical and a DyeH˙ radical. In view of the redox potentials of TA, one tempted to assume that TA can act as an electron acceptor toward the excited states of the different dyes, and react then with the DyeH˙ radical formed when the amine is present, as shown in Scheme 1.

The a priori selection of efficient systems should obey at least to three major criteria:

(i) the interaction between the excited states of the dye and the amine AH must be important in order to generate a large number of initiating radicals:



(ii) the inhibition of the excited states of the dye by TA, through an electron transfer reaction, must be as weak as possible in order not to compete with the amine quenching:

$$Dye \overset{h\nu}{\rightleftharpoons} Dye^{*} \overset{TA}{\rightarrow} Dye^{\cdot +} + TA^{\cdot -} \qquad (\Delta G_2)$$

(iii) the interaction between the reduced dye and TA must be as efficient as possible to reduce the inhibition effect of DyeH˙. Unfortunately this interaction cannot be evaluated because the redox properties of DyeH˙ are usually not known.

ΔG_1 and ΔG_2 denote the free energy changes in the schemes identified, respectively.

It appears that the first condition (i) involves a reduction of the excited states of the dye by AH whereas (ii) is the oxidation of the same excited states of the dye by TA. Since the two reactions are governed by two different redox parameters, reduction and oxidation potentials of the dye, it should be possible to select a dye that would be usable in such three-component systems, on the basis of these properties.

An analysis based on the calculated free energy changes of the electron transfer reactions mentioned above (ΔG_1 and ΔG_2) was carried out for various dyes (Table 2). According to the Rehm–Weller model [18], significant quenching rate constants through electron transfer ($> 10^9$ M^{-1} s^{-1}) should

Table 2
Calculated free energies (ΔG) of the electron transfer reaction between the singlet and the triplet excited states of the dyes and MDEA or TA

	E_{ox} (V/SCE)	E_{red} (V/SCE)	E_S (eV)	E_T (eV)	ϕ_{ISC}	Dye reduction by MDEA[a]		Dye oxidation by TA[b]	
						$^{S}\Delta G$ (eV)	$^{T}\Delta G$ (eV)	$^{S}\Delta G$ (eV)	$^{T}\Delta G$ (eV)
Rose Bengal	+0.65[c]	−1.00[c]	2.2[c]	1.8[d]	0.8[e]	−0.5	−0.1	−0.6	−0.2
Phenosafranin	+0.90[c]	−0.65[c]	2.34[c]	1.77[d]	0.1[f]	−1.0	−0.4	−0.4	+0.1
Eosin Y	+0.60[c]	−1.05[c]	2.33[c]	1.84[d]	0.33[f]	−0.6	−0.1	−0.7	−0.2
Erythrosin B	+0.76[d]	−1.05[d]	2.3[g]	1.9[g]	0.7[d]	−0.5	−0.1	−0.5	−0.1
DIBF	+1.35[c]	−1.00[c]	>2.4[c]	2.3[h]	>0.1[h]	<−0.7	−0.6	< 0.0	+0.1
TIHF	+1.34[h]	−0.99[h]	2.3[c]	1.83[i]	0.87[j]	−0.6	−0.1	+0.1	+0.5
Acridine Orange	+0.77[k]	−1.08[k]	2.52[k]	2.13[k]	0.10[l]	−0.7	−0.3	−0.8	−0.4
					0.37[l]				
Acriflavine	+0.74[k]	−1.05[k]	2.57[f]	2.22[d,f]	0.53[m]	−0.8	−0.5	−0.9	−0.5
			2.81[d]			−1.0		−1.1	
Safranin O	+0.86[n]	−0.62[k]	2.41[n]	1.83[n]	0.5[k]	−1.1	−0.5	−0.6	0.0

[a] Calculated free energy changes (ΔG) in acetonitrile: calculated by $^{S,T}\Delta G = E_{ox}(\text{MDEA}) - E_{red}(\text{dye}) - (E_S \text{ or } E_T)$ with $E_{ox}(\text{MDEA}) = +0.72$ V/SCE [8c].
[b] Calculated free energy changes (ΔG) in acetonitrile: calculated by $^{S,T}\Delta G = E_{ox}(\text{dye}) - E_{red}(\text{TA}) - (E_S \text{ or } E_T)$ with $E_{red}(\text{TA}) = -1.00$ V/SCE [9], the coulombic stabilization term is negligible in polar solvents like MeCN, MeOH.
[c] Ref. [9].
[d] Ref. [3b].
[e] Ref. [11].
[f] Ref. [19].
[g] Ref. [12].
[h] Ref. [1e].
[i] Ref. [13].
[j] Ref. [14].
[k] Ref. [15].
[l] Ref. [20].
[m] Ref. [21].
[n] Ref. [22], E_{ox} in H_2O pH 7.

be observed when ΔG values are negative. Table 1 shows that the reaction between the excited state of the dyes and the amine is thermodynamically favorable for all selected dyes, both in their singlet and triplet states. This roughly correlates the good efficiency of the dye/amine system (Fig. 2).

It also appears that it is unfortunately difficult to find dyes for which the excited state interaction with TA is thermodynamically not favorable. Only TIHF meets this requirement (ΔG_2 is >0) and one could expect, on this ground, a high reactivity of the TIHF based system. This is not the case. However, the TIHF/MDEA system shows the most important decrease in the inhibition time in the presence of TA, proving that TA plays its role but be enhanced for a system whose the intrinsic reactivity is low compared to that of other dye/amine systems. However, the lack of reactivity that was observed with TIHF could be related to the observed solubility issues for the dye in the acrylic monomers.

In fact, the interaction between the dye, in its excited state, with TA will lead to detrimental competition towards the production of initiating radicals, in three-component systems. In fact, the thermodynamic conditions that have to be fulfilled on ΔG are necessary but not enough. Kinetics play an important role, as demonstrated in the previous complete study, where the excited state processes have been carefully investigated [9]. The values of the rate constants of interaction between the different partners will govern the production of the initiating radicals, as schematically depicted. If the dye*/TA reaction is allowed ($\Delta G_2 < 0$), the concentration of TA must be optimized and kept as low as possible in order to reduce the dye*/TA interaction. As an example, 0.3% of TA in RB/MDEA leads an increase in R_p by a factor 2.5 but with 3% of TA the R_p gains only 15% more.

In a similar way, the efficiency of the quenching of the DyeH$^{\cdot}$ radicals by TA will strongly be dependent on the rate constants. Moreover, a balance between a singlet mechanism and a triplet mechanism for the primary steps of the processes, is to be expected. Even with dyes such as AO or DIBF (where ΔG_1 values for the triplet state are very favorable), the contribution (to the initiation of the polymerization) of the electron transfer in the triplet state will be less important. This is because of the low quantum yield for intersystem crossing (Φ_{ISC}).

4. Conclusion

This paper describes the factors that are of relevance to

the acceleration of the curing rates in several three-component systems that are used for the initiation of a radical photopolymerization, under visible lighting by the addition of a triazine. Dyes showing very poor efficiency in dye/amine photoinitiating systems, such as AO, show very interesting reactivity in the presence of TA. Moreover, the maximum of absorption of AO (493 nm in acetonitrile) matches very well the 488/514 nm emission lines of Ar + laser that is used in imaging applications and could be very useful in such applications. Considerations on the kinetics of the excited states could help to provide a better understanding of the difference in reactivity that is observed in the various studied systems. The experimental determination of all these kinetic data, however, is rather tedious and difficult. This paper suggests that consideration of the thermodynamic aspect of the processes can be successfully applied as a first approach, to provide screening of potentially efficient photoinitiating systems.

Acknowledgements

The authors thank Prof. D.C. Neckers (Bowling Green State University) and Dr D.Martin (Spectra Physics, USA) for the gift of DIBF (Hnu-470) and THIF (Hnu-535).

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