Mechanistic Analysis of Photopolymerization Reactions in the Presence of HABI / Hydrogen Donor Photoinitiating System

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The comparative efficiency of two multi-component photoinitiating systems (PIS): EAB/C1-HABI/NPG and C1/C1-HABI/NPG (where C1-HABI is a bisimidazole derivative, EAB an aminobenzophenone, NPG N-phenylglycine, C1 coumarin 1) are investigated through real time FT-IR, time-resolved laser spectroscopy and steady state analytical techniques. The investigation of the excited state processes in these multi-component photoinitiating systems, the elaboration of a general picture for the mechanisms encountered in the different PIS and a discussion on the relative efficiency of these PIS are presented.

Keywords: photoinitiating system, real time FT-IR, bisimidazole, coumarin

1. Introduction

Conventional lights and laser beams induced processes in organic monomers / oligomers / polymers materials are concerned with applications in the imaging area to inks, printing plates, computer-to-plate laser writing, direct laser patterning of printed circuit board, three dimensional machining and optical elements. [1] Among various factors, which affect the efficiency of the reaction, the role of the photoinitiator has been recognized as a key factor that governs, to some extent, the rate and degree of polymerization. [2] Recent papers show the behaviour of selected one- or two- or three-component photoinitiating systems. [3] Three-component photoinitiating system based on combinations of a bisimidazole derivative, a hydrogen donor (2-mercaptobenzothiazole) and a singlet photosensitizer (coumarin 1 referred as C1) was shown to be able to efficiently start the polymerization of methacrylate monomers in the photoimaging applications. [4] The present paper intends to understand the compared behaviour of three-component photoinitiating systems (PIS)

which can be also put in relation with the results obtained in related systems. [5-8]

2. Experimental

The different compounds used are C1-HABI (2-chlorohexaarylbiimidazole), EAB (N,N'-tetraethyl-4,4'-diaminobenzophenone), NPG (N-phenylglycine) and C1 (7-diethylamino-4-methylcoumarin).

The photopolymerizable formulation consists in Ebecryl 605 (epoxyacrylate / TPGDA) from UCB (Belgium). The different components of the photoinitiating system have typically (except otherwise stated) the following concentrations: 2 weight part of C1-HABI, 0.1 weight part of EAB, 0.1 weight part of C1 and 0.5 weight part of hydrogen donor (NPG).

The photopolymerization reaction was performed on 50µm films in laminated conditions to avoid the diffusion of oxygen, which is a strong inhibitor in radical polymerization.

The sample was irradiated with the light emitted by a UV Xe/Hg lamp (Hamamatsu). The UV light was passed through a bandpass filter centered at 366

nm having a bandwidth of 20 nm. The intensity of the light after the filter was in the range of 10 mW cm⁻² and the light beam can be attenuated by using a diaphragm. The geometry of the apparatus allows to record FT-IR spectra during the UV irradiation and provide real time kinetics. The sample is contained between two polypropylene films spaced by a Teflon spacer of 50 µm, inserted between two round BaF₂ windows which are fixed onto an aluminium cell. The cell is placed horizontally to prevent any drift of the sample.

The photopolymerization kinetics, recorded with a FT-IR spectrometer (Nexus 870, Nicolet), running in the rapid-scan mode with a spectral bandwidth of 4 cm⁻¹, were obtained by the following decrease of the absorption band of the monomer C=C stretching bands at 1620 and 1645 cm⁻¹. The initial rate of polymerization R_p and the final rate of conversion were deduced as usual from the conversion curves. The quantum yield of initiation Φ_i is assumed to be proportional to $R_p^2 / (1 - 10^{-OD})$ where OD is the optical density of the sample at the irradiation wavelength.

Absorption spectra were recorded on a Beckmann DU-7 spectrophotometer. The redox potentials (reduction potential E_{red} and oxidation potential E_{ox}) were measured, as described in [5], in acetonitrile by cyclic voltammetry with 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte at scan rate 1 V/s.

3. Results and Discussion

3.1. Rates of Polymerization

The monomer conversion is followed as a function of time (see Figure 1 for a typical example). The rates of polymerization R_p of the polymer formed as well as the limit conversion (%) in the presence of multi-component systems based on various combinations of EAB/CI-HABI/NPG and CI/CI-HABI/NPG are summarized in Table 1. In Table 1, the rates of polymerization are expressed as the slope of the conversion vs time curve. The quantum yields of initiation are written in arbitrary units because the absolute rates of polymerization and the value of the incident light are not available. Under the 366 nm irradiation, the CI-HABI/NPG combination leads to a higher R_p than that of EAB/NPG and exhibits an efficiency almost similar (within the experimental errors) to that of the EAB/CI-HABI/NPG system. The CI/CI-HABI/NPG combination is noticeably better than the EAB/CI-HABI/NPG combination.

Figure 1 Typical polymerization profiles.

Table 1 Rates of polymerization, final conversion and quantum yields of initiation.

PIS	R_p	Conv(%)	Φ_i (a.u.)
EAB / NPG	3.4	60	15
CI-HABI / NPG	7.5	78	370
EAB / CI-HABI / NPG	7	76	53
CI / NPG	0.1	10	(*)
CI / CI-HABI	(*)	11	(*)
CI / CI-HABI / NPG	10.9	83	140

* not calculable. The difficulty encountered in the reproducibility of the experiments leads to estimate that R_p s cannot be confidently given with an error better than 10 %.

3.2. The EAB / CI-HABI / NPG based and CI-HABI / NPG System

3.2.1. The excited state processes

The different pathways of evolution of the excited state processes in the CI-HABI/EAB/NPG system – obtained recently through time-resolved laser spectroscopy techniques [6] – are recalled in Scheme 1. $L^\bullet$, $NPG^{\bullet-H}$ (or $A^\bullet$), $EABH^\bullet$ (or $K^\bullet$) and L_2 refer to the lophyl radical, the amine derived radical, the EAB ketyl radical and CI-HABI respectively (in this scheme, the $L^\bullet$ quenching by NPG is much more efficient than the recombination process). These results and the data gained from the present photopolymerization measurements lead us to discuss the role of the different components of PIS in the photoinitiation step of the polymerization reaction. As already stated [6], all these conclusions, however, are derived from photopolymerization experiments carried out in film and excited state processes data obtained in acetonitrile. The extrapolation of the kinetics observed previously in fluid media for the excited states should be taken with care. In addition to the decrease of the rate constants with the increase of viscosity, some specific behaviours in bulk (where the diffusion

limits the mobility of the transient species) are expected.

Scheme 1

3.2.2. The role of the different photoinitiating systems

As already observed [9], in the Cl-HABI based system, the excited singlet state of Cl-HABI dissociates into two lophyl radicals, which can poorly initiate a polymerization. In the NPG based system, NPG presumably can lead to the generation of radicals under light excitation but nothing is really known on the photodecomposition of this compound. In the EAB based system, generation of radicals may occur through self-quenching. In all these systems, almost no polymerization occurs.

In the Cl-HABI/NPG based system, a good efficiency is obtained. In addition to the photodissociation process of Cl-HABI in the S_1 state, one could expect (by analogy with the Cl-HABI/2-mercaptobenzoxazole system) an electron transfer between Cl-HABI and NPG (the ΔG of the reaction is evaluated to -0.5 eV), which results in the generation of a radical ion pair and then in the formation of an amine derived radical and a lophyl radical. This bimolecular process, however, should not compete efficiently with the fast generation of $L^\bullet$ ($\sim 5 \times 10^8 \text{ s}^{-1}$) followed by the formation of $A^\bullet$.

On the opposite, the EAB/CI-HABI based system leads to a low efficiency. Both electron transfer ($\Delta G \sim -0.4$ eV) and energy transfer ($E_T(\text{EAB}) - E_T(\text{CI-HABI}) \sim 0.7$ eV) can account for the interaction process. Only $L^\bullet$ radicals are generated, which explains why the reactivity of CI-HABI and EAB/CI-HABI based systems is almost similar. The very classical EAB/NPG based system leads to a good efficiency. The mechanism involves a well-known electron transfer followed by a proton transfer. NPG efficiently reacts with the

ketyl radical of EAB (no efficient generation of new radicals is expected through this process) and allows to scavenge this radical which is known as a terminating agent of the growing macromolecular chains. [2]

The EAB/NPG/Cl-HABI based system has a good efficiency. The $^3\text{EAB/Cl-HABI}$ interaction is very strong and is mostly ascribed to an electron transfer process but *i)* the yield in $\text{L}^\bullet$ through the electron transfer process is not known in the present working media (but was found in benzene very similar to that obtained in the direct excitation of Cl-HABI) and *ii)* the generation of $\text{L}^\bullet$ from $^3\text{Cl-HABI}$ is a low efficiency process (see [6,9]). Moreover, the $\text{NPG}^{\bullet-}_{-\text{H}}/\text{Cl-HABI}$ and $\text{L}_2^{\bullet-}/\text{EAB}^{\bullet+}$ interactions lead to an additional production of $\text{L}^\bullet$ radical.

Cl-HABI appears as an efficient scavenger species of the EAB ketyl radicals so that the contribution of route ② (in Scheme 1) remains an important way to generate initiating radicals (the detrimental ketyl radicals are scavenged). Route (b) can be neglected compared to route (a) for the initiation itself if Cl-HABI behaves as HABI (*i.e.* the cleavage yield in the triplet state is low [10]) but route (b) leads to a detrimental competition to route (a). According to a reaction proposed in the eosin / amine system [11], one could also assume to have an electron transfer from NPG to the radical cation of EAB, which might generate an amine derived radical.

3.2.3. The direct photoinitiation vs the photosensitized initiation

The absorption of the excitation light at 366 nm by the different components of the photoinitiating system is due to EAB (see Table 2). EAB absorbs 10 times more light than Cl-HABI (the overall absorption is $\sim 90\%$). Thus, there are two kinds of initiation processes: *i*) the first initiation process corresponds to a direct photoinitiation process based on Cl-HABI, *ii*) the second one is related to a photosensitized initiation process in which EAB is a photosensitizer and Cl-HABI is a photoinitiator. Moreover, in that case, the direct excitation of EAB is also followed by efficient interactions with NPG

3.3.The C1 / Cl-HABI / NPG based Systems

3.3.1. Ground state information and excited state processes

The UV absorption spectra of the compounds are reported in Figure 2 and the molar extinction coefficients are gathered in Table 2.

Figure 2 Absorption spectra of (a) Cl-HABI,(b) EAB. (c) C1. (d) NPG in acetonitrile.

Table 2 Molar extinction coefficients of the compounds used (in $\text{M}^{-1} \text{cm}^{-1}$ in acetonitrile. The ϵ_{max} of C1 in methanol is $25400 \text{ M}^{-1} \text{cm}^{-1}$ [12]).

	ϵ_{166}	ϵ_{max}	λ_{max} (nm)
Cl-HABI	400	2790 ^[B0]	265
EAB	4400	4600 ^[B]	352
Cl	26730	26880	367
NPG	100	1200 ^[B]	241

Quenching rate constants of the C1 singlet state by Cl-HABI and NPG, determined from fluorescence measurements and the corresponding Stern Volmer plots, are listed in Table 3. These rate constants are diffusion-controlled. Therefore, the efficiency of the deactivation by Cl-HABI will depend on the concentration ratio of Cl-HABI vs NPG.

Table 3 Quenching rate constants (in $10^{-10} \text{ M}^{-1}\text{s}^{-1}$) of the C1 singlet state by Cl-HABI and NPG in acetonitrile (singlet state lifetime of C1 is 3.4 ns [13]).

Compound	kq
NPG	1.6
Cl-HABI	2.3

The redox properties are described in Table 4. The calculated free energy changes are -0.73 eV and +0.14 eV for C1/CI-HABI and C1/NPG respectively thereby supporting an electron transfer mechanism.

Table 4 Redox properties of C1 determined in acetonitrile (in eV).

Compound	$E_{\text{ox}}^{p/2}$ (V/SCE)	$E_{\text{red}}^{p/2}$ (V/SCE)
C1	+1	-2.1

The evolution of the excited state processes in the C1/C1-HABI/NPG system is summarized in Scheme 2 (the $L^{\bullet}$ quenching by NPG is much more efficient than the recombination process).

Scheme 2

3.3.2. The role of the different photoinitiating systems

In the absence of H-donor, the C1/CI-HABI based system leads to a very low efficiency. Electron transfer in the excited singlet state of C1 ($\Delta G \sim -0.73$ eV) accounts for the interaction process as observed in other coumarin derivatives. [5,7] Energy transfer is ruled out ($E_s(\text{C1}) - E_s(\text{CI-HABI}) \sim -0.2$ eV). The C1/NPG based system leads to a poor efficiency because the mechanism presumably involves an electron transfer process ($\Delta G \sim +0.14$ eV), which cannot be followed by a proton transfer.

The C1/Cl-HABI/NPG based system is more efficient than the Cl-HABI/NPG based system for the initiation of the polymerization reaction. The C1/Cl-HABI interaction is very strong and competes with the C1/NPG interaction. Taking account of the concentration of the photoinitiators ([Cl-HABI] = 0.035 M; [NPG] = 0.04 M; [C1] = 0.005 M; [EAB] = 0.0036 M), the corresponding first order rate constant in solution for the C1/NPG and C1/Cl-HABI interactions are very similar ($\sim 8 \times 10^8 \text{ s}^{-1}$). As a consequence, this C1/NPG interaction might appear as a detrimental route for the initiation step. However, according to what is observed with the radical cation of EAB, one could also assume to have an electron transfer *i*) from NPG to the radical cation of C1 which can generate an amine derived radical after reaction with the lophyl anion or *ii*) from the lophyl anion to the radical cation of NPG.

3.3.3. The direct photoinitiation vs the photosensitized initiation

The absorption of the excitation light at 366 nm

by the different components of the photoinitiating system is due to C1 (see Table 2). The overall fraction of light absorbed by the system is ~ 85 % and C1 absorbs ~ 10 times more than Cl-HABI. Thus, there are two kinds of initiation processes: *i*) the first initiation process corresponds to a direct photoinitiation process based on Cl-HABI, *ii*) the second one is related to a photosensitized initiation process in which C1 is a photosensitizer and Cl-HABI is a photoinitiator. Moreover, in that case, the direct excitation of C1 is also followed by efficient interactions with NPG, which do not lead to any initiating radical as shown by the corresponding low R_p .

3.4. Comparison of the three-component Photoinitiating Systems

In the C1 based system, there is only one main initiation pathway through the C1/Cl-HABI interaction. The C1/NPG interaction, which could appear as a detrimental pathway (no amine derived radicals are generated) might help to improve the overall efficiency by providing new additional pathways through secondary reactions of the C1 radical cation.

In the C1/Cl-HABI/NPG system, in addition to the secondary reactions with the radical cation, there is only one process (the C1/Cl-HABI electron transfer), which yields the lophyl radicals. The EAB based system is more complicated. Indeed, in the EAB/Cl-HABI/NPG system, there is still a similar EAB/Cl-HABI interaction, which yields lophyl radicals, but also a competitive EAB/NPG interaction, which yields detrimental ketyl radicals (that could be also partly scavenged by NPG and Cl-HABI), so that the initiation efficiency might decrease, when going from the C1/Cl-HABI/NPG system to the EAB/Cl-HABI/NPG system. Moreover, the EAB/Cl-HABI interaction in solution appears to be predominantly an electron transfer. If energy transfer occurs to some extent, the decrease of efficiency is expected since the Cl-HABI triplet state poorly leads to the generation of lophyl radicals. On the opposite, in highly viscous matrixes nothing is known on *i*) the possible balance between the energy/electron transfer processes *ii*) the evolution of the rate constants as a function of the chemical nature of the medium and *iii*) the diffusion ability of the different partners. In our opinion, the main difference between the EAB/Cl-HABI/NPG and C1/Cl-HABI/NPG systems originates from these points.

An evaluation of the relative efficiency of the

direct initiation route vs the sensitized route can be tentatively done. In a general way, the following relationship holds true,

$$R_p^2 = K^2 I_0 f_{abs} \Phi_i^{over}$$

where I_0 is the incident light intensity, Φ_i^{over} the overall initiation quantum yield and f_{abs} the fraction of light absorbed. If several compounds absorb in the formulation, one can write as follows.

$$R_p^2 = K^2 I_0 \sum_j \Phi_i^j f_{abs}^j$$

One can consider the following scheme 3,

Scheme 3

and write for the EAB/Cl-HABI/NPG system.

$$\Phi_i^{over} f_{abs}^{over} = \Phi_{i,d}^{EAB} f_{abs}^{EAB} + \Phi_{i,s}^{Cl-HABI} f_{abs}^{Cl-HABI} + \Phi_{i,d}^{Cl-HABI} f_{abs}^{Cl-HABI}$$

Calculations at $\lambda = 366$ nm are reported in Table 5 (from values of Table 1).

Table 5 Fractions of light absorbed by the different compounds and calculated quantum yields for the direct initiation routes at $\lambda = 366$ nm.

	f_{abs}			$\Phi_{i,d}$			Φ_i^{over}
	EAB	Cl-HABI	C1	EAB	Cl-HABI	C1	
EAB/NPG	0.82			15			15
Cl-HABI/NPG		0.25			370		370
EAB/Cl-HABI/NPG	0.85	0.07					53
C1/Cl-HABI/NPG		0.075	0.805				140
C1/NPG							0

It clearly appears that the efficiency of Cl-HABI is largely higher than that of EAB.

$$\Phi_{i,d}^{EAB} = 15 \text{ and } \Phi_{i,d}^{Cl-HABI} = 370$$

The quantum yield for the sensitized route is thus deduced as:

$$\Phi_{i,s}^{Cl-HABI} = 12$$

A similar calculation gives:

$$\Phi_{i,s}^{C1} = 119$$

These calculations show that the quantum yield of the EAB/CI-HABI sensitized route is noticeably lower than that of the CI/CI-HABI route which is in agreement with the discussion on the excited state processes (see above). Taking into account the fraction of light absorbed, the contributions of the direct route vs the sensitized route are expressed as follows and this result is summarized in Table 6.

$$\Phi_{1,d}^{EAB} f_{abs}^{EAB} + \Phi_{1,d}^{CI-HABI} f_{abs}^{CI-HABI} \text{ vs } \Phi_{1,s}^{CI-HABI} f_{abs}^{EAB}$$

Table 6 Contribution of the direct route vs the sensitized route (in %)

	Direct route	Sensitized route
EAB/CI-HABI/NPG	80	20
CI/CI-HABI/NPG	22	78

4. Conclusion

All the results obtained have led to a general discussion on the role played by the different compounds and to a proposal of a general picture for the different mechanisms encountered in the photoinitiating system. The whole rates of the polymerization measurements obtained as a function of the components of the photoinitiating system are well explained from the knowledge of the excited state processes. An explanation for the understanding of the comparative efficiency of the EAB/CI-HABI/NPG and CI/CI-HABI/NPG systems has been proposed. Interacting photosensitizers for the decomposition of CI-HABI should work in their singlet state or triplet state (in this last case, exclusively through electron transfer). Moreover, the behaviour of various coumarins in the presence of CI-HABI/thiol derivatives has been described in [5,7] and the role of the substitution on the HABI backbone has been discussed in. [8]

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