Photochemistry and Polymerization Efficiency of Bis-imidazole based Photoinitiator Systems

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Photopolymerization efficiency of an acrylate formulation (Ebecryl 605) under light irradiation at 365 nm has been evaluated by using RTFTIR. The role of various multicomponent photoinitiating systems based on bis imidazole derivatives, in the presence or not of an aminobenzophenone, N-phenylglycine and several iodonium salt derivatives has been emphasized. Excited state processes in these two-, three- or four- component systems have been investigated through time resolved laser spectroscopy. The different photophysical processes and photochemical reactions involved are defined and the role of each partner is discussed : this helps to explain the high performance of the three- and four- component photoinitiating systems.

Keywords: photoinitiator system, bisimidazole, time resolved laser spectroscopy

1. Introduction

Three- and four- component photoinitiating systems - based on various combinations of a bis imidazole derivative (HABI), an aminobenzo phenone (EAB), an iodonium salt (IOD) and an amine (NPG : N-phenyl glycine) - were recently shown to be able to efficiently start the polymerization of acrylate monomers [1-2]; excited state processes involved in the various combinations of these compounds have been characterized [3]. These systems can be very helpful in the Radiation Curing and Laser Imaging areas where the applications are ever increasing [4-5]. Discussion on the behaviour of other multicomponent photoinitiating systems also appeared (see e.g. recent papers [6] and references therein). The present paper will *i)* show how the introduction of substituents on the starting molecules (bisimidazole HABI and iodonium salt IOD) can affect the efficiency of both the photophysical / photochemical processes and the polymerization reaction and *ii)* help to understand

the photochemical reactivity observed in the model formulation used to check the high practical performance of these multi component photoinitiating systems.

2. Experimental

The studied compounds are shown in Chart 1. The photopolymerization was performed on 50 micron films, in laminated conditions. The sample is irradiated with the filtered light emitted by a UV Xe lamp at 366 nm, as described elsewhere [2]. The photopolymerization profiles (obtained, as usually, by following the decrease of the absorption of the monomer C=C stretching bands at 1620 and 1645 cm^{-1}) were recorded with a FTIR spectrometer, running in the rapid-scan mode with a spectral bandwidth of 4 cm^{-1} . The initial rate of polymerization R_p and the final percent of conversion % Conv were deduced from the conversion curves; the efficiency of the polymerization reaction takes into account the fraction of energy absorbed and is expressed by Ef

which is proportional to the quantum yield of initiation [4b]:

$$Ef = R_p^2 / (1 \cdot 10^{-OD})$$

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 [3], in acetonitrile by cyclic voltammetry with 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte and at scan rate 1V/s.

The nanosecond transient absorption setup is based on a pulsed solid state tunable Nd:Yag laser (excitation: $\lambda = 353\text{nm}$) [2-3]. The instrument response is about 7 ns using a transient digitizer (TDS 340, Tektronix).

Chart 1. Molecules studied

3. Results and Discussion

3.1. Rates of polymerization

Monomer conversion is followed as a function of time (see typical profiles in Fig. 1). The rates of polymerization and the limit % conversions as well as the polymerization efficiencies in the presence of a set of various multi-component systems are summarized in Table 1. These data show the effects of *i*) the iodonium salt derivative on the well-known EAB / NPG two-component system, *ii*) the HABI derivative on EAB / NPG, *iii*) the HABI derivative on NPG, *iv*) the iodonium salt derivative on EAB / NPG / Cl-HABI, *v*) the HABI derivative on EAB/NPG/BIP-T. Some changes are observed as a function of the substitution on the HABI and iodonium salt skeletons. Three- and four-

component photoinitiating systems appear as the most reactive.

Fig.1. Typical photopolymerization profiles: % conversion as a function of time. Cl-HABI: 2% weight part, EAB: 0.1%, NPG: 0.5%, DPI-Cl: 1%

Table 1. Role of the photoinitiating system on the final percent conversion, rate of polymerization and efficiency. See text. HABI: 2% weight part, EAB: 0.1%, NPG: 0.5%, IOD: 1%

Photoinitiating System	Conv (%)	R _p (a.u.)	Ef
EAB/NPG	54	3	11
EAB/NPG/BIP-T	74	10	117
EAB/NPG/BBI-102	75	9.7	109
EAB/NPG/MPI-105	76	10.7	126
EAB/NPG/DPI-Cl	76	17.8	375
EAB/NPG	54	3	11
EAB/NPG/Cl-HABI	72	6.1	40
EAB/NPG/MMF-HABI	73	10	109
EAB/NPG/EO-HABI	76	9.4	101
EAB/NPG/2,6-F-HABI	69	7.2	59
NPG/Cl-HABI	72	7	445
NPG/MMF-HABI	73	12.7	301
NPG/EO-HABI	75	11.1	423
NPG/2,6-F-HABI	70	7.3	382
EAB/NPG/Cl-HABI	72	6.1	40
EAB/NPG/Cl-HABI/BIP-T	76	12.5	185
EAB/NPG/Cl-HABI/BBI-102	75	10.3	119
EAB/NPG/Cl-HABI/MPI-105	77	13.7	213
EAB/NPG/Cl-HABI/DPI-Cl	77	13.6	205
EAB/NPG/BIP-T	74	10	117
EAB/NPG/BIP-T/Cl-HABI	76	12.5	185
EAB/NPG/BIP-T/MMF-HABI	74	9.5	94
EAB/NPG/BIP-T/EO-HABI	76	8.6	77
EAB/NPG/BIP-T/2,6-F-HABI	74	11.0	141

In a general way, the four component systems exhibit the highest efficiency (except EAB/NPG/DPI-Cl which is better than EAB / NPG / Cl-HABI / DPI-Cl). The best HABI seems to be Cl-HABI itself in the four component systems and MMF-HABI in the three component systems. DPI-Cl is the best iodonium salt derivative.

3.2. Electrochemical properties

All the results concerning the electrochemical analysis are gathered in Table 2, including some of the compounds already reported [3].

Table 2. Redox properties of the compounds studied ; Solvent : acetonitrile.

Compound	E_{red} (V/SCE)	E_{ox} (V/SCE)
MMF-HABI	-1.35	1.46
L'(MMF-HABI)	-	0.38
2,6-F-HABI	-1.38	1.55
L'(2,6-F-HABI)	-	0.35
EO-HABI	-1.54	1.29
L'(EO-HABI)	-	0.14
Cl-HABI[3]	-1.37	1.48
L'(Cl-HABI)[3]	-	0.29
EAB[3]	-	+0.95
NPG[3]	-	+1.14
BIP-T[3]	-0.82	-
BBI-102	-0.82	>1.7
DPI-Cl	-0.63	1.14
MPI-105	-0.63	>1.5

HABI derivatives exhibit a clear substituent effect: electron withdrawing substituents as fluoro or chloro- groups increase both E_{red} and E_{ox} . On the contrary, electron donating groups (ethoxy- on EO-HABI) lead to a decrease of these redox potentials. The E_{ox} of the lophyl anion L' created during the reduction process was also measured. Although the oxidation of L' was irreversible, the value represents to some extent the standard potential of the redox couple $L'/L^{\bullet}$. The E_{ox} value decreases when going from electron withdrawing to electron donating substituents.

The four iodonium salts (IOD) exhibit high reduction potentials. As expected, BIP-T and BBI-102 are characterized by the same reduction potential, this property being mainly attributable to the iodonium cation and not to the anion. DPI-Cl and MPI-105 also exhibit similar reduction potentials, although one of the phenyl groups of MPI-105 was substituted with an electron donating

group.

3.3. Absorption properties

The singlet excitation energy E_{S1} of the HABIs used can be approximated by the $E_{ox} - E_{red}$ difference : E_{S1} is nearly the same for the four studied derivatives (2.81 eV, 2.93 eV, 2.83 eV and 2.85 eV for MMF-, 2,6-F-, EO- and Cl- HABI, respectively, the latter value being in agreement with the singlet energy level of Cl-HABI estimated at about 3 eV [7]).

The absorption spectra of the different lophyl radicals ($L^{\bullet}$) measured by photolysis of the HABIs are shown in Fig. 2.

Fig.2. Absorption spectra of irradiated acetonitrile solutions of HABI derivatives : the lophyl radical absorption.

Large substituent effects are observed for the different compounds : EO- $L^{\bullet}$ strongly absorbs in the visible range ($\lambda_{max} = 620$ nm), and 2,6-F- $L^{\bullet}$ exhibits an absorption band centered at 540 nm ; MMF- $L^{\bullet}$ absorbs in the blue range, and exhibits an absorption that falls down around 400 nm, with a slight absorption tail up to 500 nm ; Cl- $L^{\bullet}$ has been already reported to exhibit an absorption band centered at 540 nm in benzene [3].

3.4. Excited state processes

3.4.1. Lophyl radical reaction with additives

Excitation of HABIs leads to a fast homolysis resulting in the formation of two lophyl radicals $L^{\bullet}$. This one-photon process occurs with a high yield from the singlet state [7-8], e.g. 0.95 ± 0.01 in methanol under 347 nm laser excitation [9]. The efficiency of the lophyl radical generation from the triplet state of HABI is very low : the sensitized decomposition of the parent compound (hexaarylbiimidazole) in the presence of the benzophenone triplet state occurs with a low probability (~ 0.075) [7]. In the following, the

reactivity of 2,6-F-HABI, EO-HABI and MMF-HABI is assumed to behave similarly.

The reactions between the Cl-HABI derived lophyl radical (Cl-L[•]) and amines (AH) were already reported [3]. This reaction yields initiating aminoalkyl radicals A[•]. The values of the rate constants for the reactions between the other lophyl radicals and NPG are reported in Table 3.

Table 3. Bimolecular rate constants for the reaction between the lophyl radicals and NPG in acetonitrile

Compound	k_q ($\times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$)
Cl-L [•]	1.2
2,6-F-L [•]	1.8
EO-L [•]	3.7
MMF-L [•]	2.8

The rate constants are generally slightly higher than that for Cl-L[•]. No significant reaction between lophyl radicals and iodonium salts was detected, as already reported for the system Cl-L[•] / BIP-T [3].

3.4.2. Lophyl formation under sensitized conditions

The sensitized formation of lophyl radicals through a reaction of the HABIs with the EAB triplet state has been already pointed out [8] and recently demonstrated in the case of Cl-HABI [3]. Indeed, the relative quantum yield $\phi_{L^{\bullet}}^{\text{rel}}$ of formation of Cl-L[•] in sensitized conditions was found to reach unity when compared to that obtained under direct excitation. EO-HABI, 2,6-F-HABI, and MMF-HABI were investigated according to the procedure described in [3]. Typical transient absorption signals showing the decay of the EAB triplet state and the build up of the lophyl radicals are displayed in Fig. 3.

Fig.3. Transient absorption signals obtained when exciting EAB in benzene at $\lambda = 353\text{nm}$, in the presence of 2,6-F-HABI at different concentrations (analysing wavelength : 540nm).

Table 4 gathers the results obtained. The homolysis of Cl-HABI and 2,6-F-HABI is efficiently sensitized through the reaction with ³EAB, the yield of lophyls being close to that obtained in the direct excitation of HABI. On the contrary, the sensitization of EO-HABI was found less efficient, with a relative quantum yield in lophyl radicals of 0.5. In the case of MMF-HABI, the absorption band of MMF-L[•] overlaps that of the EAB ground state, thereby preventing any accurate measurement.

Table 4. Relative quantum yields $\phi_{L^{\bullet}}^{\text{rel}}$ in L[•] obtained in the sensitized homolysis of HABIs in the presence of EAB, in benzene.

Compound	$\phi_{L^{\bullet}}^{\text{rel}}$
Cl-HABI[3]	1.0
2,6-F-HABI	1.05
EO-HABI	0.5
MMF-HABI	-

3.4.3. Reactivity of ³EAB and EAB ketyl radical

The photochemistry of EAB and Michlers ketone (MK) has been previously reviewed [3]. The intersystem crossing quantum yields ϕ_{ISC} in benzene were found to be 0.95 ± 0.05 for both molecules, and the triplet energy of EAB was determined as 3.0 eV. The rate constants for the O₂ quenching are in the range $10^{10} \text{ M}^{-1}\text{s}^{-1}$. Quenching by monomers occurs with rate constants about $3\text{--}4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and do not yield any initiating radicals. Reaction of ³EAB with NPG ($k_q = 1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) leads to the formation of an aminoalkyl radical A[•] and a EAB ketyl radical (EABH[•]) [3]. Table 5 gathers the rate constants k_q of interaction between the triplet state of EAB or EABH[•] with the different additives. The rate constants obtained are slightly lower than with Cl-HABI for the interaction of ³EAB with the HABIs. Similarly, ³EAB efficiently react with IODs, as reported for the EAB / BIP-T system [3].

An electron transfer process accounts for the quenching of EABH[•] by NPG. In the presence of HABIs, an electron of EABH[•] is transferred and a dissociation of HABIs into a lophyl radical and a lophyl anion occurs with high rate constants. IODs exhibit a high reactivity with EABH[•] (Table 5) : this reaction is expected to yield new initiating phenyl radicals [3].

Table 5. Rate constants of interaction between ^3EAB or its ketyl radical $\text{EABH}^\bullet$ with the HABI or iodonium salts derivatives, in acetonitrile.

Compound	^3EAB $k_q (\times 10^{-9} \text{ M}^{-1} \text{ s}^{-1})$	$\text{EABH}^\bullet$ $k_q (\times 10^{-9} \text{ M}^{-1} \text{ s}^{-1})$
Cl-HABI	6.0	5.7
2,6-F-HABI	3.3	-
EO-HABI	4.1	0.9
MMF-HABI	5.7	~1.1
BIP-T	6.0	1.3
BBI-102	5.0	0.7
DPI-Cl	4.0	0.6
MPI-105	7.0	1.3

3.4.4. Diagram of evolution of the excited state processes

From the whole results, the primary processes taking place after excitation and efficiently leading to initiating radicals are summarized in Scheme 1.

Scheme 1.

3.5. Discussion on the excited state processes / polymerization efficiency relationships

The role of the different components of the photoinitiating system in the photoinitiation step of the polymerization reaction can be discussed on the basis of the data obtained. As stated elsewhere [2-3], photopolymerization experiments were carried out in film and excited state processes data gained in acetonitrile: extrapolation of the kinetics observed for the excited states in fluid media should be taken with precaution.

In the efficient HABIs / NPG based system, the

photodissociation process of the HABIs in the S_1 state is fast (as indicated for HABI itself [7]) and leads to the generation of $\text{L}^\bullet$ followed, through a reaction with NPG, by the formation of the amine derived radical $\text{A}^\bullet$. On the opposite, the Cl-HABI and EAB / Cl-HABI based system lead to a low efficiency: both electron transfer and energy transfer can account for the interaction process, as discussed previously [3]; only $\text{L}^\bullet$ radicals are generated which explains why the reactivity of Cl-HABI and EAB / Cl-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 was also shown [3] to efficiently react with $\text{EABH}^\bullet$ (but 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 (see reference to this question in [5]). In the HABIs / NPG / IODs, a quenching of $\text{A}^\bullet$ by the IODs can occur [2]. This quenching process luckily leads to new initiating phenyl radicals.

In the EAB / NPG / IODs based system, one observes an improvement of the efficiency, compared to that of EAB / NPG: the $\text{EABH}^\bullet$ / BIP-T interaction decreases the concentration of the scavenging $\text{EABH}^\bullet$ radicals, as observed in similar three component systems [5] and an electron transfer from the EAB triplet state to the iodonium salt occurs, as already suggested in [3] (new substituted phenyl initiating radicals are also formed). The EAB / NPG / HABIs based system appears also as efficient for the initiation of polymerization reactions. The ^3EAB / Cl-HABI interaction is very strong and is mostly ascribed to an electron transfer process. Moreover, the $\text{EABH}^\bullet$ / Cl-HABI interaction and the $\text{L}_2^{\bullet-} / \text{EAB}^{\bullet+}$ interaction lead to an additional production of $\text{L}^\bullet$ radical [3]. The EAB / NPG / IODs / HABIs based system generally exhibits an efficiency better than that of the EAB / NPG / IODs systems or the EAB / NPG / HABIs systems. The interactions between the EAB triplet state and HABIs appear as the most important but their relative contributions decrease because of the EAB triplet state quenching by IODs. As stated elsewhere for Cl-HABI itself [3], the HABIs are efficient scavenger species of $\text{EABH}^\bullet$ under our experimental conditions. Upon addition of IODs, the contribution of the EAB / NPG interaction which generates the detrimental $\text{EABH}^\bullet$ radicals

should be less important so that a lower amount of EABH[•] radicals is formed thereby reducing the further detrimental effect of these radicals. Moreover, IODs which are good electron acceptors can also react through an out of cage process, with the lophyl anion formed after the electron transfer between EAB and HABIs and followed by the generation of an ionic pair (EAB cation radical / HABIs anion radical) [3] : this is not possible in an in- cage process which only leads to two lophyl radicals. The efficiency of the process originating from the energy transfer between EAB and HABIs can be neglected because the cleavage yield in the triplet state of HABIs is low [7-8], but this process obviously leads to a detrimental competition to the useful EAB/ HABIs electron transfer reactions.

The overall behaviour of the present photoinitiating systems is very similar to that encountered in the parent compound based systems [2-3]. Under irradiation at 365 nm, direct excitation of HABIs (followed by the generation of L[•] and A[•] after reaction with NPG) occurs. Most of the light at 365 nm in a EAB / Cl-HABI based system is, however, absorbed by EAB and the main processes are i) a photosensitized excitation of HABIs (through electron transfer from EAB), followed by the generation of two L[•] radicals and then A[•] radicals after reaction with NPG and ii) a direct excitation of EAB which leads to a A[•] radical through an interaction with NPG or to phenyl radical through an interaction with IODs. The main role of HABIs is its direct participation in the photoinitiation step and the quenching of the ketyl radicals which are known as scavenging species towards the growing macromolecular chains. The main role of IODs is the quenching of the ketyl radicals and their direct participation in the photoinitiation reaction where they contribute to both a decrease of the ketyl radical concentration and an increase of the initiating radical amount.

4. Conclusion

Multi component photoinitiating systems allow highly efficient initiation steps for acrylate polymerization reactions. The primary processes involved have been studied in real time. No striking differences in the excited state processes are noted when modifying the starting compounds. The improvement of the polymerization efficiency in a model matrix reflects however the more favourable balance between the different reactions which have been pointed out: unfortunately, it is almost impossible to quantitatively express the true

correlation existing between the polymerization efficiency and the chemical nature of the photoinitiating systems. Although there is no clear effect that can be *a priori* expected from this excited state processes investigation, introduction of carefully selected substituents on known chemical skeletons leads to even more efficient systems in patterning experiments [1] : in addition to a possible more favourable photochemistry, the role of specific reactions due to the monomer / oligomer / polymer matrix should play a role.

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