

# New initiating systems for radical photopolymerization

*Xavier Allonas, Jacques Lalevée, Céline Dietlin,  
Mohamad El Roz, Jean-Pierre Fouassier*

*Department of Photochemistry, UMR7525, CNRS, University of Haute Alsace,  
ENSCMu, 3 rue Alfred Werner, 68093 MULHOUSE Cedex, France*

## Introduction

Apart from the photophysical and photochemical processes involved in the excited states of a photoinitiator PI for free radical photopolymerization reactions, the initiating radical plays a significant role. Different varieties of radicals are now clearly recognized as powerful polymerization initiating agents. This is for example the case of the benzoyl, phosphinoyl or aminoalkyl radicals [1]. The search for new radicals having enhanced or specific properties presents an outstanding interest. As known, according to the structure of a ketone chromophore based PI, the radicals are formed through i) a cleavage process from the lowest triplet state of type **I** PI leading to at least one initiating radicals  $R_i^\bullet$  (benzoin ethers, bis-acylphosphineoxides, hydroxyalkylphenyl ketones...) or ii) in the presence of a co-initiator co-I (AH) in type **II** PI, through an electron transfer followed by a proton transfer process leading to a ketyl radical  $PIH^\bullet$  and a  $A^\bullet$  radical (e.g. with benzophenone/amine...). Sulfur containing PI can be designed as cleavable compounds or as a co-initiator,  $A^\bullet$  being a thiyl radical.

The direct optical detection of radicals was formerly provided by using pulse radiolysis techniques, time-resolved laser absorption spectroscopy and time resolved FTIR vibrational spectroscopy. Indirect methods have been sometimes employed. Laser induced photoacoustic calorimetry (LIPAC) was shown as a powerful technique but all of the reactions cannot be studied [2].

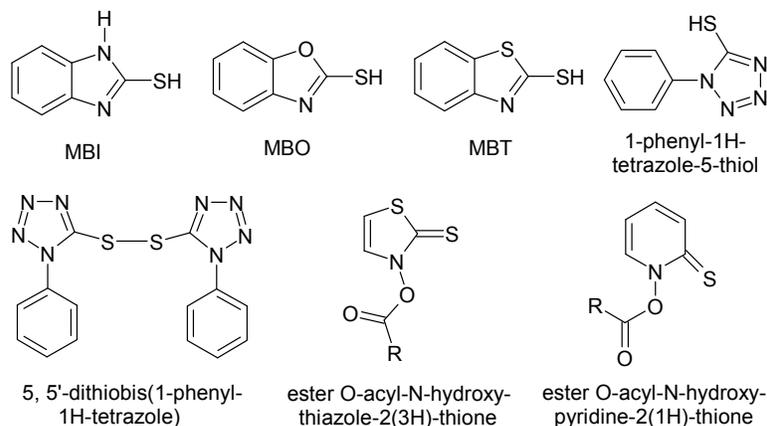
The new approach [3-4] we recently developed is done through three consecutive reactions: i) the generation of a tert-butoxy radical t-butO $^\bullet$  (by a photochemical decomposition of tert-butylperoxide), ii) the abstraction reaction between t-butO $^\bullet$  and an additive AH leading to the generation of a radical  $A^\bullet$ , iii) the addition of  $A^\bullet$  to the monomer M and generation of  $AM^\bullet$  (the initiation rate constant  $k_i$  is thus accessible). In contrast to  $M^\bullet$ , this  $AM^\bullet$  radical absorbs in the visible wavelength range and is easily detected.

Then, interaction rate constants with various compounds become also very easily accessible. This method was shown suitable for the investigation of carbon centred radicals such as the acrylate radicals, M being an acrylate monomer and AH an amine. In such a way, the interaction of an acrylate radical with oxygen, TEMPO, phenol derivatives was recently carried out [5]. In the same way, the recombination of two  $AM^\bullet$  radicals as well as the addition of  $AM^\bullet$  to M can be followed. This could mimic the determination of both the propagation  $k_p$  and recombination  $k_t$  rate constants in the early stages of the polymerization reaction. Many other radicals are currently investigated: sulfur, aminoalkyl, aminyl, silyl, germanyl, peroxy [6-8].

Quantum mechanical calculations allow to determine the molecular orbitals involved in the cleavage process (when the molecule is going from its triplet state to the separated

radicals through a transition state) and many parameters (bond dissociation energy BDE, reaction enthalpy, spin density, transition state, triplet energy...)

In this paper, we present a general discussion on the detection, analysis and reactivity of sulfur centered radicals of selected compounds (Scheme 1).



Scheme 1 : Examples of sulfur based molecules that can be used as PI.

## Thiyl radicals in mercaptobenzoxazole, mercaptobenzimidazole and mercaptobenzothiazole

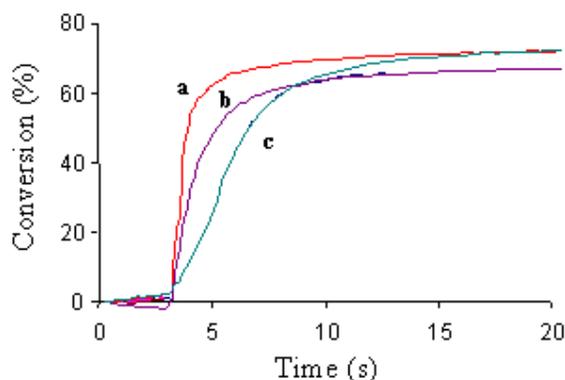
Mercaptans RSH such as mercaptobenzoxazole (MBO), mercaptobenzimidazole (MBI) and mercaptobenzothiazole (MBT) are used as co-initiators of polymerization, e.g. in thiol-ene chemistry (where the classical ketone/RSH photoinitiating system leads to photoreduction of the ketone and generates a  $RS^\bullet$  radical) or in direct laser imaging applications (where the bisimidazole derivatives HABI/RSH system allows to generate a  $RS^\bullet$  radical through a reaction of RSH with the lophyl radical formed upon the photolysis of HABI [10]). However, the addition properties of these  $RS^\bullet$  radicals to a monomer double bond M and the further back fragmentation reaction of the  $RSM^\bullet$  radical remain both largely unknown. The knowledge of the processes are obviously important for getting a high efficiency of the polymerization initiation step. The relative contribution of the polar and enthalpy effects as well as the factors which govern the fragmentation process are outstanding problems. The formation and the reactivity of three sulfur centered radicals derived from MBO, MBT and MBI toward four double bonds (methyl acrylate, acrylonitrile, vinyl ether and vinyl acetate) were investigated. The reversibility of the addition/fragmentation reaction was studied through the measurement of the corresponding rate constants by time resolved laser spectroscopy [9]. Contrary to previous studies devoted to other aryl thiyl radicals, it was found that the addition rate constants are governed by the polar effects associated with the very high electrophilic character of these radicals. However, interestingly the back fragmentation reaction is mainly influenced by the enthalpy effects with a direct relationship between the rate constant and the reaction enthalpy  $\Delta H_R$ . It appears that Molecular Orbital MO calculations offer new opportunities for a better understanding of the sulfur centered radical reactivity and can be a powerful tool for the design of new highly reactive radical structures.

## New thiyl radicals

Despite the two main advantages of thiyl radicals i.e. a high reactivity toward a large set of monomer double bonds and a low sensitivity to oxygen, these systems were not largely used to initiate a polymerization process because of the unpleasant smell of sulfur compounds preventing any widespread use for industrial applications. The general picture for the primary processes that occur in the precursor excited states are now well known: sulfur centered radicals are formed from the photocleavage of thiobenzoate derivatives in type **I** systems or from a thiol as the hydrogen donating compound in type **II** systems. Thiols have received much less attention than structures leading to the formation of carbon centered radicals such as amines; the same holds true for the direct and sensitized cleavage processes of disulfides which have been seldom investigated.

We have proposed a series of new sulfur containing compounds for the photoinitiation of the acrylate polymerization. They correspond to various thiols (bearing tetrazole, thiadiazole, imidazole, triazole or pyridine moieties) and disulfides (containing phenyl, propionic acid, pyridine, tetrazole or pyridine-N-oxide moieties) [10]. These compounds are considered as PI (the disulfides) or coI (the thiols). Various ketones were used as PI in the type II system (benzophenone, isopropylthioxanthone, camphorquinone, chloro-hexa-aryl bis-imidazole Cl-HABI) or photosensitizers PS (benzophenone and thioxanthone derivatives, coumarin and ketocoumarin derivatives).

Among the systems investigated, the disulfides photosensitized by isopropylthioxanthone as well as the tetrazole derived thiols in the presence of benzophenone, camphorquinone or isopropylthioxanthone are found highly reactive and, in some cases, even better than a reference type I or type II photoinitiator. These thiols can also be incorporated in a combination of Cl-HABI and a photosensitizer such as a coumarin or a ketocoumarin. A system based on a coumarin/Cl-HABI/tetrazoethiol derivative exhibits a higher reactivity than that of the corresponding photosensitizer/Cl-HABI/N-phenylglycine commonly used system (Figure 1) [10].



**Figure 1.** Conversion vs time curves for the photopolymerization of Ebecryl 605/HDDA (50/50 w/w). Irradiation at 366 nm. Role of the photoinitiating systems. Coumarin 1 (0.1%)/Cl-HABI (1%)/coI (0.5%) (w/w): a: phenyltetrazole thiol; b: methyltetrazole thiol; c: N-phenylglycine.

As expected, the thiol behaviors strongly depend on the chemical structures involved. It also appears that disulfides can be efficient photoinitiators provided that the effect of their weak absorption in the 350-400 nm spectral range is counterbalanced by the use of a polychromatic irradiation or a photosensitization process. A complete photochemical investigation of these compounds is likely necessary in a further step and the mechanistic aspects of all the reactions involved also deserve to be studied in detail. The role of the viscosity of the photopolymerizable medium on the quantum yields also remains a fascinating challenge: a better knowledge will probably allow to understand how the results gained in fluid media or solutions can be extrapolated to bulk media. Through this approach, the design of ever more reactive new structures should presumably be possible in the future.

## **A new sulfur centered radical derived from tetrazole**

The search for new radical structures having both a low selectivity and a high reactivity which can be of interest in polymer chemistry led us to propose a tetrazole derived thiyl radical TZ<sup>•</sup> [11]. Its reactivity toward ten alkenes, chosen among monomers (vinyl ethyl ether VE, vinyl acetate VA, methyl acrylate MA, acrylonitrile AN, allylbutylether ABE, acrylamide AAM, N-vinylpyrrolidone NVP, dimethyl fumarate FU, dimethyl maleate MAL, vinylcarbazole VC), have been studied using laser flash photolysis and quantum mechanical calculations. The TZ<sup>•</sup> radical was generated from the photodissociation of the corresponding disulfide (5,5'-dithiobis(1-phenyl-1H-tetrazole) under laser irradiation at 355 nm. The corresponding radical spectrum is centered at about 430 nm as known from previous studies. The S-S bond cleavage occurs within the rise time of our experimental set-up (<10 ns). The addition rate constants  $k_a$  are determined from a classical Stern-Volmer analysis. To determine the addition and fragmentation rate constants ( $k_a$  and  $k_{-a}$ ) and the equilibrium constant ( $K = k_a/k_{-a}$ ) of TZ<sup>•</sup> we used the selective radical trapping flash photolysis method.

The considered double bonds having very different electron acceptor/donor properties, strong enthalpy/polar effects have been observed on the addition reactions. The low selectivity and the high reactivity of TZ<sup>•</sup> toward both electrophilic and nucleophilic alkenes was outlined. The behavior of TZ<sup>•</sup> is particularly worthwhile. A remarkable low selectivity toward the addition process can be noted: the rate constants are higher than  $10^7 \text{ M}^{-1}\text{s}^{-1}$  for the complete range of monomer electronegativity going from electron rich  $\pi$  system (VE-NVP-VC...) to electron deficient alkenes (AN, MA, AAM...), except for the two bisubstituted acrylates FU and MAL (in that case, the steric hindrance destabilizes the adduct radical: the reaction is less exothermic than expected from their electronegativity). Comparatively, a carbon centered structure is found rather selective with an enhanced reactivity toward electron deficient alkenes, particularly for monomer exhibiting  $\chi > 4.5 \text{ eV}$ , and a very low reactivity toward electron rich structures ( $k_a \ll 5 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1}$ ). The behavior of TZ<sup>•</sup> probably corresponds to a unique feature. To the best of our knowledge, such a high reactivity associated with a very low selectivity has never been observed.

## **Sulfur centered radicals in controlled polymerization reactions**

The conventional radical polymerization terminates when the propagating intermediates are rendered inactive through bimolecular recombination reactions. The radical generation is irreversible without any possibility to control the final properties of the polymer formed such as the number average molecular weight  $M_n$  and the molecular weight distribution MWD. It is therefore difficult to achieve a highly uniform and well-defined product; the same holds true in specialized applications where a control is necessary.

Controlled thermal polymerization reactions represent one of the major emerging field in the polymer science area. In a controlled (or living) radical polymerization (CRP), radicals are reversibly generated. There are four major CRP methodologies: Atom Transfer Radical Polymerization (ATRP), Reversible Addition-Fragmentation Transfer (RAFT), Nitroxide-Mediated Polymerization (NMP) and use of iniferters, each method having advantages and disadvantages. However, the use of this concept in photopolymerization reactions has not received a large attention so far although there is a great interest to combine the advantages of CRP with those of the photopolymerization reactions (spatial resolution combined with higher polymerization rates). These two concepts can be unified through the use of photoiniferters as photoinitiating systems. The term “photoiniferter” refers to a compound that exhibits a combined function of photoinitiator, transfer agent and chain terminator; both the initiation and the reversible termination are photoinduced. This approach can be useful for photografting, photolithography applications, production of block copolymers, manufacture of multi layered photomaterials, spatial photomodification of polymer networks. The proposed systems, albeit powerful for these applications, lead to relatively broad  $M_n$  distribution.

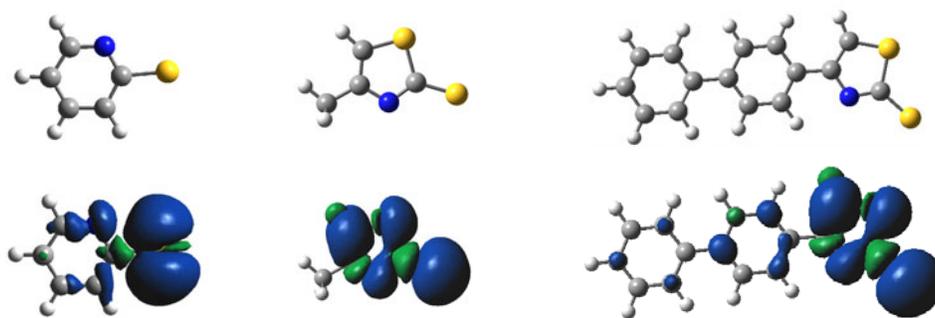
The mechanism observed in a usual living radical photopolymerization process involving a photoiniferter is based on a set of reactions: the first one corresponds to the photocleavage of the photoiniferter to produce an initiating ( $R^{\cdot}$ ) and a chain terminator radical ( $X^{\cdot}$ ). The second one relates to the initiation step and the further propagation step. The crucial difference with a non-controlled reaction lies on the recombination of  $X^{\cdot}$  and the propagating radical. This process is photochemically reversible leading to the living character of the reaction. This photodissociation of the polymer chain end and the further propagation repeatedly occur. As the exchange between the active  $R-Mn^{\cdot}$  and the dormant species  $R-Mn-X$  is fast in comparison with the propagation reaction, the molecular weight will increase with the conversion; the total number of chains is recognized as constant.

The new asymmetric disulfide photoiniferter based on thio-1-phenyl-1H-tetrazole and dithiocarbamate moieties was used for the control of the photopolymerization of methyl methacrylate MMA [12]. The polymerization proceeds in a noticeably efficient controlled or living way: the number average molecular weight  $M_n$  increases with the conversion (from 8000 to 18000). The molecular weight distribution MWD is also found better than for classical photoinitiators [12]. The addition of tetramethyl thiuramdisulfide still increases the performance (MWD = 1.6 for  $M_n$  between 4000 and 8000). Interestingly, polymeric photoiniferters corresponding to the structure proposed were also synthesized allowing the formation of MMA-Styrene copolymer through a sequential approach. Other copolymers can probably be formed using the low selectivity property of tetrazole derived radical towards monomers.

Four other new structures (o,o-diethyl dithiobis-thioformate, isopropylxanthic disulfide, tetramethyldicarbonotrithioic diamide, and phenylacetyl disulfide) were proposed as photoiniferters [13]. Their photochemical properties, their efficiency to control the photopolymerization of MMA as well as their ability for the photocrosslinking of a difunctional acrylate monomer HDDA were investigated. The rates of polymerization of MMA and HDDA, the molecular weights  $M_n$  and the polydispersity index PDI of PMMA have been determined; the transient absorption spectra and the interaction rate constants of the radicals have been measured. Both the (alkyloxythiocarbonyl)thiyl and (benzylcarbonyl)thiyl radicals are found very efficient to control a photopolymerization process. For 40% of the monomer conversion obtained in a few minutes, the  $M_n$  are ranging from 6000 to 14000 and the PDI can reach 1.6. A five fold decrease of the light intensity increases  $M_n$  by 25% and decreases PDI by 5%.

## Sulfur centered radical in Barton's esters

Different photoinitiators based on Barton thiohydroxamic esters - O-acyl-N-hydroxypyridine-2(1H)-thione and O-acyl-N-hydroxy-thiazole-2(3H)-thione derivatives - were tested in photopolymerization reactions through RT-FTIR experiments. Good rates of polymerization and final monomer conversions were obtained for some compounds. The excited state processes, investigated by time resolved absorption spectroscopy, lie on a fast singlet state cleavage leading to a N-O bond breaking presumably followed by a fast decarboxylation and the generation of a R radical. Through a rearrangement of the derived pyridinyl radical, a sulfur centered radical is formed. A triplet state is observed for some derivatives. The thiyl and alkyl radicals are able to initiate a polymerization. Computational studies helped to describe the excited state properties and show a strong difference in the spin localization in the formed thiyl initiating radicals [14-15]. The spin density of the pyridine-thiyl radical formed after cleavage in the triplet state is clearly localized on the sulfur atom whereas it is delocalized on the five-ring moiety in the thiazole thione derivatives (Figure 2).



**Figure 2.** Spin densities on the thiyl radical formed in barton esters (computed at a B3LYP/6-31G\* level)

The modification of the chromophoric group (which plays a crucial role in the excited state processes), the structure of the thiyl radical and the R leaving group (leading to a competition between initiation and degradation of the starting compound due to chain reactions) presumably have a strong influence on the balance between the different processes. This work could serve as a starting point to design more efficient systems.

### Conclusion:

This paper outlines the specific reactivity of sulfur centered radicals derived from various structures usable in radical photopolymerization reactions. Many interesting comparisons with other kinds of radicals can be drawn.

### References:

1. J.P. Fouassier, "Photoinitiation Photopolymerization and Photocuring", Hanser Publishers Munich, 1995; "Photochemistry and UV curing: new trends", JP. Fouassier Ed., Research Signpost, Trivandrum, 2006.
- 2 J. Lalevée, X. Allonas, S. Genet, J.P. Fouassier, J. Am. Chem. Soc., 125, 9377 (2003).
- 3 J. Lalevée, X. Allonas, J.P. Fouassier, Chem. Phys. Letters, 429, 282 (2006)
- 4 J. Lalevée, X. Allonas, J.P. Fouassier, Chem. Phys. Letters, 415, 287 (2005).
- 5 J. Lalevée, X. Allonas, J.P. Fouassier, J. Polym. Sci. Part. A: Polym. Chem., 44, 3577 (2006).
- 6 J. Lalevée, X. Allonas, J.P. Fouassier, J. Phys. Chem. A, 108, 4326 (2004).
- 7 J. Lalevée, X. Allonas, J.P. Fouassier, J. Org. Chem., 70, 814 (2005).

- 8 J. Lalevée, X. Allonas, J.P. Fouassier, *Macromolecules*, 38, 4521 (2005).
- 9 J. Lalevée, X. Allonas, F. Morlet-Savary, J.P. Fouassier *J. Phys. Chem. A*, 110, 11605 (2006).
- 10 J. Lalevée, L. Zadoina, X. Allonas, J.P. Fouassier *J. Polym. Sci. Part. A: Polym. Chem.*, 45, 2494  
(2007).
- 11 J. Lalevée, X. Allonas, J.P. Fouassier, *J. Org. Chem.*, 71, 9723 (2006).
- 12 J. Lalevée, X. Allonas, J.P. Fouassier, *Macromolecules*, 39, 8216 (2006).
- 13 J. Lalevée, M. El-Roz, X. Allonas, J.P. Fouassier, *J. Polym. Sci. Part. A: Polym. Chem.*, 45, 2436  
(2007).
- 14 J. Lalevée, X. Allonas, J.P. Fouassier, *J. Photochem. Photobiol., A : Chem.*, 159, 127 (2003).
- 15 X. Allonas, J. Lalevée, F. Morlet-Savary, J.P. Fouassier, *Photochem. and Photobiol.*, 82, 88 (2006).