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# Understanding the reactivity of photoinitiating systems for photopolymerization

**Summary** — The reactivity of photoinitiating systems (PIS) of polymerization reactions is the subject of many research works. Investigation of primary processes involved in PIS is largely based on time resolved laser spectroscopy techniques, mainly through the well known transient absorption spectroscopy (TRAS). Recently, transient infra-red spectroscopy, laser induced photoacoustic calorimetry, photoconductivity were introduced in order to collect useful information on the excited states which were not easily accessible by TRAS. By now, molecular modelling calculations performed at high level of theory are shown to provide unique thermodynamical data on the processes that govern the overall efficiency of PIS. A new approach that combines both experimental and theoretical aspects was found very promising for the understanding of the photochemical and chemical processes involved in photopolymerization reactions.
**Key words**: photoinitiator, photopolymerization, radicals, detection, reactivity.

WYJAŚNIENIE PODSTAW REAKTYWNOŚCI UKŁADÓW FOTOINICJUJĄCYCH FOTOPOLIMERYZACJĘ
**Streszczenie** — W artykule o charakterze monograficznym przedstawiono przegląd publikacji (w istotnym stopniu — prac własnych z ostatnich kilku lat) poświęconych metodom i wynikom badania mechanizmu reakcji elementarnych w procesie inicjowania fotopolimeryzacji przez układy fotoinicjujące (PIS). Omówiono wybrane wyniki uzyskiwane metodami TRAS (*Time-resolved absorption spectroscopy*), z uwzględnieniem nowej metody indukowanej laserem kalorymetrii fotoakustycznej (LIPAC). Sporo uwagi poświęcono zagadnieniu zależności reaktywności rodników od ich budowy oraz własnemu sposobowi bezpośredniej obserwacji rodników (na przykładzie rodników akrylanowych), a także ocenie ich reaktywności na podstawie metody TRAS (rys. 6—8).
**Słowa kluczowe**: fotoinicjator, fotopolimeryzacja, rodniki, wykrywanie, reaktywność.

The understanding of the reactivity of photoinitiating systems (PIS) used to induced structural modifications in photopolymers remains a fascinating topic [1—2]. For example, the radical polymerization of a monomer M in the presence of a photoinitiator (PI) upon light exposure is a largely encountered reaction in the radiation curing area. The PI efficiency is governed by i) the photophysical and photochemical processes involved in the excited states which affect the yield of the different primary reactions occurring before the initiating step, and ii) the reactivity of the photogenerated initiating species, such as initiating radicals $R^{\bullet}$. Additionally, in radical polymerization, the rate of polymerization is also strongly dependent on the rate constants of propagation ($k_p$) and termination ($k_t$) of the reaction.

Varied primary processes occur from the excited states. Cleavage reactions, electron-, energy- or hydrogen- transfer reactions, quenching of excited states by monomer, oxygen, light stabilizers, pigments or other additives are very often encountered and result in complicated overall mechanisms. It is therefore of prime importance to investigate these processes in order to propose some basic guidelines useful for the development of novel photoinitiating systems. Time-resolved laser absorption spectroscopies in the nanosecond and picosecond time-scale [3—5], time-resolved photothermal techniques [6], time-resolved photoconductivity [7], time-resolved FTIR vibrational spectroscopy [8], CIDNP [9] allow the investigation of the mechanisms involved. Apart from the mechanisms studied experimentally, molecular modelling calculations performed at high level of theory provide interesting thermodynamical data useful to propose final reaction schemes.

In the present paper, several examples are reviewed and show different aspects of such investigation. Examples are presented on excited state processes, sensitization reactions occurring in multi-component PIS, calculations of bond dissociation energies (BDE) of coinitiators, measurement of dissociation quantum yields, de-
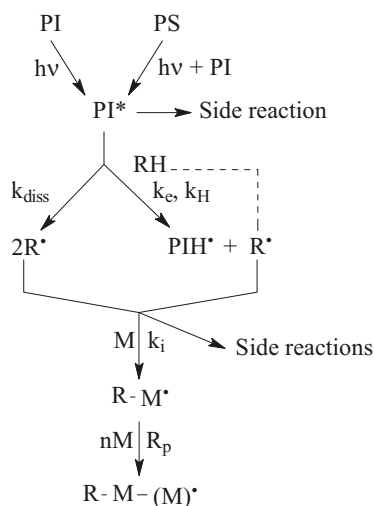
termination of thermodynamical data, and discussion of the addition reaction of initiating radicals to acrylate or methacrylate double bonds.

## THE OVERALL DIAGRAM OF EVOLUTION OF THE EXCITED STATES

Radical photopolymerization reactions are initiated by the conversion of light into reactive radicals. Different primary photoreactions can be used for the generation of radicals. Scheme A shows some of the processes that can be encountered from the absorption of light to the formation of the polymeric network [1—2]. Light can be directly absorbed by the photoinitiator PI or a photosensitizer PS. In the last case, the energy is transferred to the PI mainly through a triplet-triplet energy transfer mechanism. Most of the PIs react from their lowest triplet state to give radicals, mainly through two different ways: i) a direct cleavage from the triplet state, and ii) a hydrogen abstraction or electron/proton transfer from a coinitiator (RH). In the former case, the dissociation rate constant $k_{diss}$ governs the efficiency of the radical formation reaction. Two radicals are formed that can both react toward double bonds. In the latter case, the rate constant of hydrogen transfer $k_H$ or the rate constant of electron transfer $k_e$ is the main important parameter. Two radicals are also formed: the first one formed from the coinitiator ($R^\bullet$) being reactive toward double bond, and the second one, generally a ketyl radical, is considered as a terminating agent rather than an initiating one [1].

Although the processes involved can vary depending on the PIS used, time-resolved experiments allow to collect useful data that can help to describe, from a kinetic point of view, the overall diagram of evolution of the excited states and reactive intermediates of the PIS. Indeed, many parameters are by now accessible, such as: i) triplet state quantum yields and energy levels, ii) transient absorption spectra, excited state lifetimes and rate constants of interaction with oxygen, monomer or additives, iii) dissociation quantum yields of cleavable photoinitiators, iv) bond dissociation energies of coinitiators and formation enthalpies of the initiating radicals, v) addition rate constants between these radicals and the monomer double bonds. Other reactions such as direct evidence for ions or radical ions generation, direct investigation of absorbing and not absorbing radicals are also possible.

## THE CLEAVAGE PROCESS OF PHOTOINITIATORS FOLLOWED BY PICOSECOND SPECTROSCOPY

Since early times, photochemical processes leading to the generation of free radicals were studied by photochemists. These studies mainly based on steady-state photolysis and nanosecond laser flash photolysis have led to good description of the photocleavage [10—16]. However, most of the photocleavable PI react from their lowest triplet state within 100 ps to 10 ns time scale [17]. Therefore, a direct evidence for the cleavage of commercial photoinitiators was only possible through picosecond laser flash photolysis [3, 18, 19].

From example, 2,2-dimethoxy-2-phenylacetophenone [DMPA, "Irgacure 651", see (I)] is a very well known radical photoinitiator that efficiently cleaves from its triplet state.
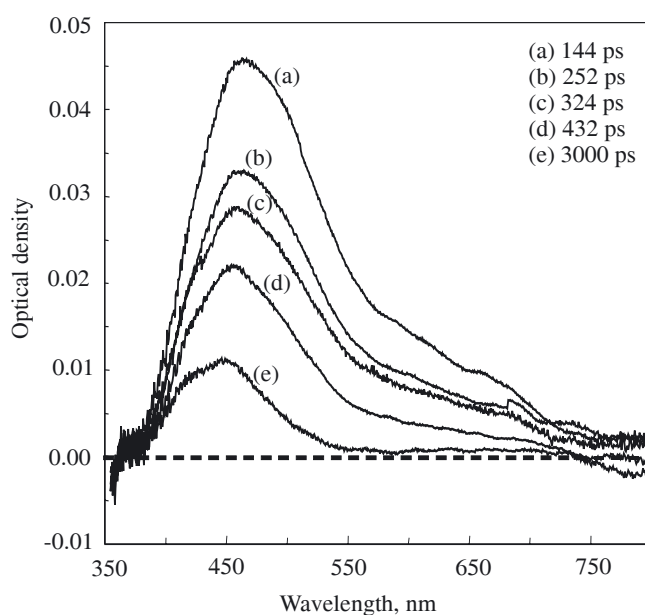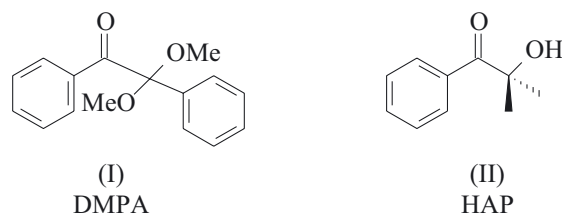
(I)
DMPA

(II)
HAP

*Fig. 1. Cleavage process of DMPA — transient absorption spectra in benzene (2 · 10⁻² M) as a function of time in picoseconds (ps)*

*Scheme A. Evolution of the excited states in radical photopolymerization reactions*
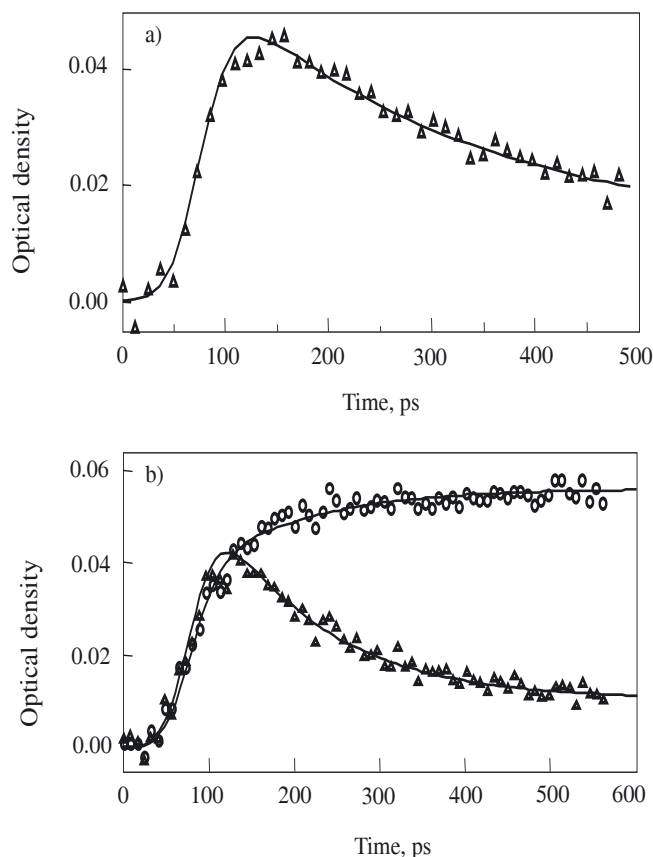
*Fig. 2. a) Triplet state decay of DMPA (triangle), b) quenching of the triplet state (triangle) at 475 nm by 0.5 M of naphthalene and formation of triplet state naphthalene at 420 nm (circles); solvent: benzene*

Time resolved laser spectroscopy [20] on the picosecond time scale shows the short lived transient absorptions observed upon light excitation (Figure 1). Intersystem crossing from the first excited singlet state ($S_1$) to the lowest triplet state ($T_1$) occurs within the response time of the apparatus, *i.e.* 15 ps. The triplet decays can be fitted with a first order law, giving a lifetime value of 250 ps in benzene (Figure 2a). The quenching by a triplet acceptor confirms the assignment of a triplet-triplet absorption: in the presence of naphthalene, a new long lived absorption due to the naphthalene triplet as well as the DMPA triplet state quenching are observed. The risetime of the naphthalene triplet state (formed during the energy transfer process from DMPA to naphthalene) corresponds to the triplet state decay of DMPA (Figure 2b).

The whole mechanism of creation of the radicals is depicted in reactions system 1a—1d where $k_{diss}$ represents the rate constant of dissociation from the triplet state and $k_{EnT}$ stands for the rate constant of energy transfer between the triplet state of DMPA and naphthalene (NAP).

Assuming that the triplet state decay in benzene is due to the cleavage reaction, the rate constant of dissociation can be estimated as $k_{diss} = 1/\tau_T = 4 \cdot 10^9$ s$^{-1}$.
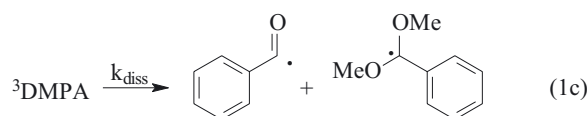


In the same way, time-resolved laser spectroscopy on the picosecond time scale allows the observation of the triplet-triplet absorption spectrum of 2-hydroxy-2-methyl-1-phenyl-1-propanone [HAP, "Irgacure 1173", see (II)] in benzene. The build up of the triplet state occurs in the 20 ps time scale *i.e.* close to the time resolution of the experimental setup. The analysis of the transient decay as a function of time gives a triplet state lifetime of 450 ps in benzene, resulting in an estimate of $2.2 \cdot 10^9$ s$^{-1}$ for $k_{diss}$ value. The quenching by naphthalene confirms the assignment of the triplet state.

## QUANTUM YIELD OF DISSOCIATION

Although it is of prime interest to confirm the fast cleavage of a PI with picosecond experiments, it is also very important to determine the efficiency of the process. Generally, quantum yields of photolysis have been measured by using steady-state photolysis [15]. More recently, a new method was introduced that gave the real dissociation quantum yield of a cleavable photoinitiator. Indeed, by using laser induced photoacoustic calorimetry (LIPAC) it is possible to determine the quantity $\phi_\alpha E_{rad}$, where $\phi_\alpha$ represents the quantum yield of dissociation and $E_{rad}$ the enthalpy of formation of the radical with respect to that of the PI ground state ($S_0$) (Figure 3). Actually, $E_{rad}$ represents the bond dissociation energy (BDE) of the photoinitiator and is written according to equation 2

$$S_F = h\nu - \phi_\alpha E_{rad} \qquad (2)$$

where: $S_F$ — *term is the fast signal normalized for the energy released and corresponds to the amplitude of the acoustic wave experimentally measurable.*
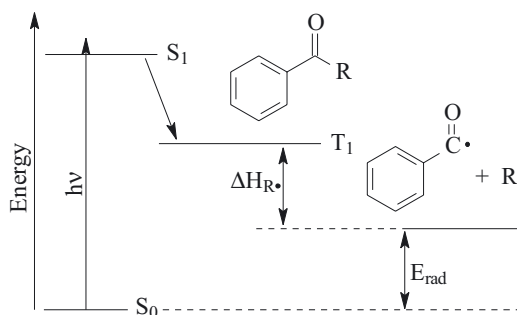


*Scheme B. LIPAC determination of quantum yield of discussion ($\phi_\alpha$)*

The BDE value is easily calculated by using molecular modelling; the value of $\phi_\alpha$ can thus be deduced. Such a procedure, applied to a large set of cleavable photoinitiators, gives values of 0.95 and 0.8 for DMPA and HAP respectively [21].

## MOLECULAR MODELLING OF A CLEAVAGE PROCESS

More information can be gained from molecular modelling at density functional theory (DFT) level. The theoretical investigation of the cleavage process of HAP has been recently described [19]. The triplet state $T_1$ is calculated to be of $n\pi^*$ nature with an energy of 75.7 kcal/mol, in very good agreement with the experimental value of 71.4 kcal/mol. This demonstrates the ability of the theoretical methods to accurately predict the photophysical properties of the photoinitiators.

By varying the C-C bond distance, the potential energy surface along the bond being broken can be calculated (Figure 3). After geometry optimization, the transition state is located 3.5 kcal/mol higher than the relaxed triplet state. As a consequence, the cleavage process of HAP is thermally activated. The BDE is computed to be
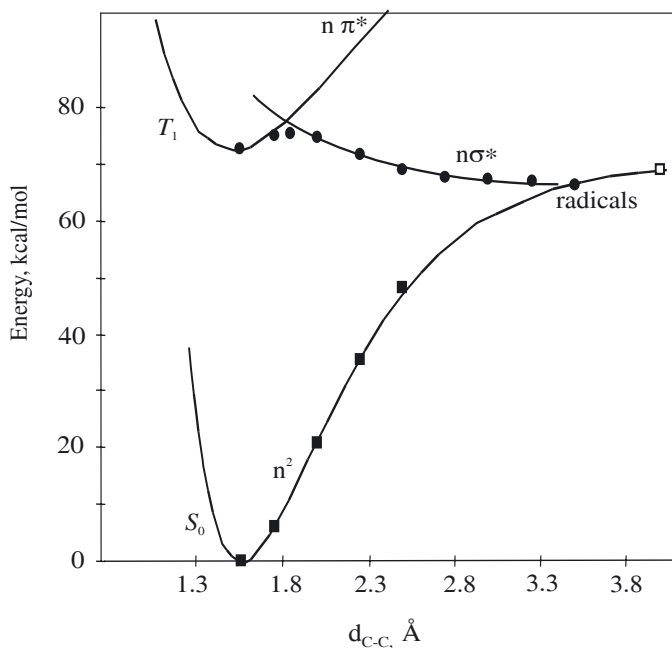


*Fig. 3. Potential energy surface along the bond being broken (C-C), showing the cleavage process of the typical photoinitiator HAP*

65.5 kcal/mol. The excitation of HAP quantitatively leads to the triplet state from which the dissociation can occur. The very low energy barrier explains the high value of the reported dissociation quantum yield (0.8) [21]. All these properties explain the high efficiency of HAP as a photoinitiator.

## THE $\beta$ DISSOCIATION OF A RADICAL PHOTOINITIATOR

Ketosulfone derivatives (such as bifunctional derivative registered as "Esacure 1001") exhibit a $\beta$ cleavage process in their triplet states [22] and are known as excellent photoinitiators (Scheme C). Triplet state lifetimes and energy levels as well as intersystem crossing quantum yields have been measured. Calculations of the
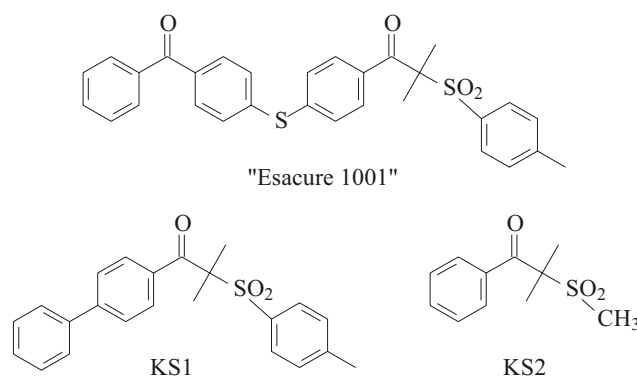


*Scheme C. The $\beta$ cleavage process of some photo initiators with ketosulfone group*

BDEs of the C-S bond show that bond breaking occurs when the triplet state is higher than the corresponding BDE. The evaluation of the enthalpy change demonstrates that the reaction is strongly exothermic although a slow cleavage process is observed in some cases; as a consequence, the enthalpy is not the driving factor for the cleavage process. Actually, the substituent on the benzophenone moiety increases the delocalisation of the
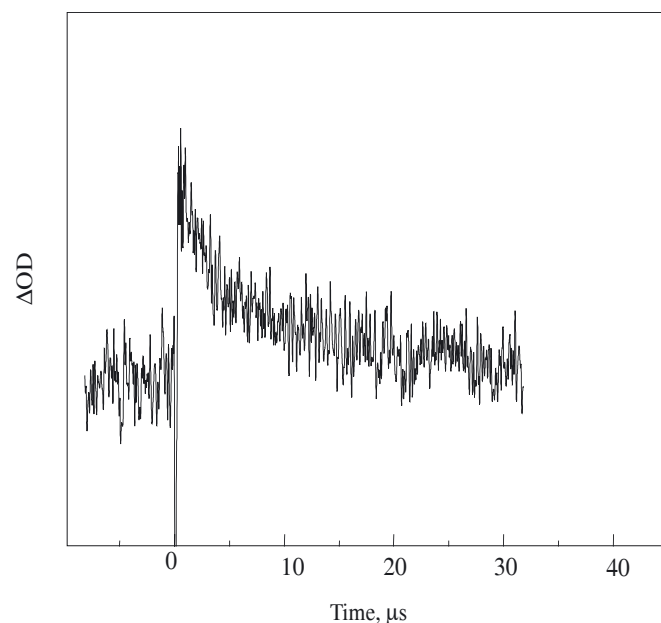


*Fig. 4. Transient absorption decay of a benzoyl radical at about 1825 cm$^{-1}$; OD — optical density*

triplet state; the energy should be localized near the bond to dissociate and the spin density at the $C_{C=O}$ carbon atom is expected to play a significant role.

The spin density directly controls the dissociation from the triplet state: the bond breaking can efficiently occur for values higher than 0.35. For example, the spin density of the two derivatives shown Scheme C are 0.01 and 0.54 for KS1 and KS2, respectively. Time-resolved absorption spectroscopy allows the determination of the corresponding triplet state lifetimes. The triplet state lifetime of KS1 is 6 μs and that of KS2 is 0.13 μs. This shows that the triplet state of KS2 cleaves much more efficiently than that of KS1, as a consequence of the highest spin density localized at the $C_{C=O}$ atom.

## DETECTION OF RADICALS THROUGH TIME-RESOLVED LASER SPECTROSCOPY IN THE INFRARED

Detection of photogenerated radicals allows the study of their reactivity toward the addition reaction to double bonds. Very often radicals are characterized by low extinction coefficient and absorption of light in the UV. Therefore, the study of the initiation process is quite difficult by time-resolved absorption spectroscopy (TRAS). Time resolved infrared spectroscopy (TRIS) can be a powerful alternative to TRAS in order to characterize the reactivity of transient intermediates exhibiting a weak absorption in the UV-visible region.

The most interesting example corresponds to the benzoyl radicals which are relatively difficult to observe by TRAS (weak and broad absorption band around 300—400 nm). Recently, the reactivity of photoinitiators was investigated by TRIS, and addition rate constants of benzoyl radicals to *n*-butylacrylate were determined [8]. In our Laboratory, a Nd:Yag laser is employed as the excitation source. The IR probe consists in a monochromator, a diode laser ("Mutek") having a maximum emission around 1820 cm$^{-1}$ and a IR detector (Vigo System S.A.). The kinetics associated with this radical, produced from the cleavage of phenyl-(2-hydroxy-2-propyl)ketone ("Irgacure 1173"), is observed at about 1825 cm$^{-1}$ in acetonitrile (Figure 4).

## REACTIVITY OF RADICALS

After formation of the radicals, the initiation process must occur between one initiating radical and one monomer unit. It is well known that the large variety of radicals that can be formed by light absorption behave in very different ways. For instance, aminoalkyl radicals are known to react at high rate constant and, by contrast, methyl radical is added to double bond at lower rate constants [23].

This addition reaction of a radical R$^\bullet$ to a monomer (M) double bond has been studied for many years, and generally, it is described by a state correlation diagram which involves the reactant ground state configuration

R$^\bullet$/M, the excited reactant configuration R$^\bullet$/$^3$M and two polar charge transfer configurations (CTC) R$^+$/M$^-$ and R$^-$/M$^+$ (Figure 5) [24]. The exothermicity of the reaction strongly affects the barrier height. The importance of the polar effects C increases as the configuration energy $\Delta E_{CT}$ decreases [$\Delta E_{CT}$ = IP(R$^\bullet$)-EA(M) or IP(M)--EA(R$^\bullet$)] for the R$^+$/M$^-$ and R$^-$/M$^+$ configurations, respectively, where IP — the ionization potential and EA — electron affinity of the reactants.
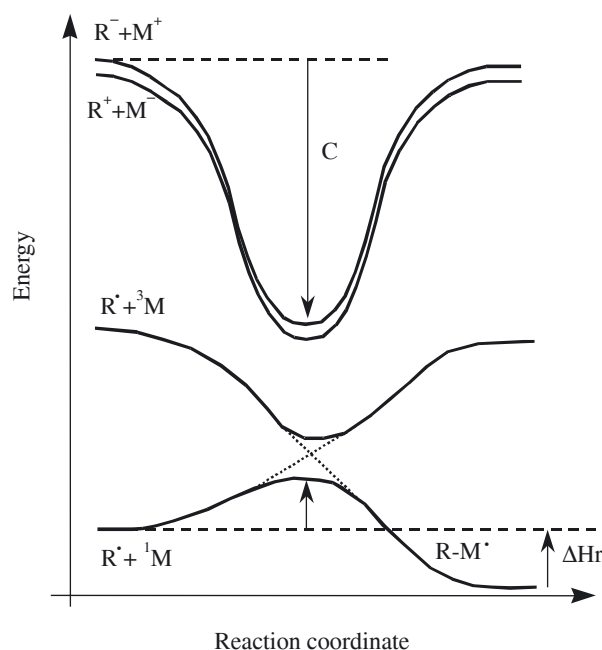


*Fig. 5. State Correlation Diagram for the radical addition reaction onto a double bond (see text)*

The different factors controlling the reactivity of a large series of carbon centered radicals towards the methyl acrylate monomer unit can be examined in detail by using molecular orbital calculations. In agreement with the state correlation diagram, the energy barrier is governed, for a large part, by the enthalpy term as supported by an increase of reactivity when increasing the exothermicity of the reaction. However, important polar effects were also highlighted: they dramatically enhance the reactivity of nucleophilic radicals (*e.g.* aminoalkyl or dialkylketyl radicals) as well as that of electrophilic radicals (*e.g.* malonyl radical) [25].

The reactivity of three selected carbon centered radicals (aminoalkyl, methyl and cyanomethyl) toward five double bonds exhibiting large differences in their nucleophilic/electrophilic characters and also representative of widespread monomers (vinylether, vinylacetate, acrylonitrile, methylacrylate and ethylene) was also examined [26].

The observed reactivity is still strongly influenced by the reaction exothermicity demonstrating that the energy barrier is largely governed by the enthalpy term. Polar effects drastically enhance the reactivity. In addition

to the effect of the charge transfer configurations on the barrier, a large influence on the transition state geometry is evidenced. A clear separation of the relative role of the polar and enthalpy effects was obtained [12, 26]. The separation of the relative contributions of the enthalpy and polar effect to the activation energies allows to explain the reactivity of the benzoyl and isopropyl radicals towards different monomers [27]. It thus appears that the proposed treatment adequately describes the reactivity trends and that the dominant factors giving rise to a high reactivity can be confidently used to predict the efficiency evolution for the addition of a given radical to different alkene structures.

The addition properties of $RS^{\bullet}$ radicals to a monomer double bond and the further back fragmentation reaction of the $RSM^{\bullet}$ radical remain both largely unknown. Therefore, the radical addition reaction of three particular sulfur centered radicals [derived from mercaptans (RSH) such as mercaptobenzoxazole (MBO), mercaptobenzimidazole (MBI) and mercaptobenzothiazole (MBT)] to double bonds has been investigated both experimentally and theoretically [28]. In that case, the polar effects appear as the major factor governing the addition reaction and play a spectacular unique role whereas the enthalpy effects govern the back fragmentation reaction. A general investigation of the reactivity of very different sulfur centered radicals certainly remains a fascinating task because a large panel of situations through a careful selection of RSH and double bond compounds could be expected.

### DIRECT DETECTION OF POLYMERIC RADICALS

The direct observation of radical species is rather difficult compared to the usual detection of transient states because of an absorption very often located in the UV part of the spectrum: few examples of a direct optical detection have been provided and indirect methods have been sometimes employed. In the past few years, LIPAC was shown as a powerful technique [6].

A new procedure was developed very recently [28] which allows to generate a given aminoalkyl radical $R^{\bullet}$ and to probe its reactivity through TRAS. Through the optical absorption of the transient, it is possible to form and to observe the first monomer radical $RM^{\bullet}$ due to the addition of $R^{\bullet}$ to the monomer double bond. Then, the recombination of two $RM^{\bullet}$ radicals, the addition of $RM^{\bullet}$ to a new monomer unit and the interaction of $RM^{\bullet}$ with various additives are easily followed. Whereas the absorption of alkyl-substituted acrylate radicals ranges between 300 nm and 350 nm, the addition of an amino-alkyl substituent shifts the absorption in the range 400—550 nm allowing a very easy monitoring. For example, the addition of the triethylamine-derived radical $TEA^{\bullet}$ to 2-(2-ethoxy-ethoxy) ethyl acrylate (DEEA) yields a new transient that is clearly observed in the visible range (Figure 6) and ascribed to the TEA-DEEA$^{\bullet}$
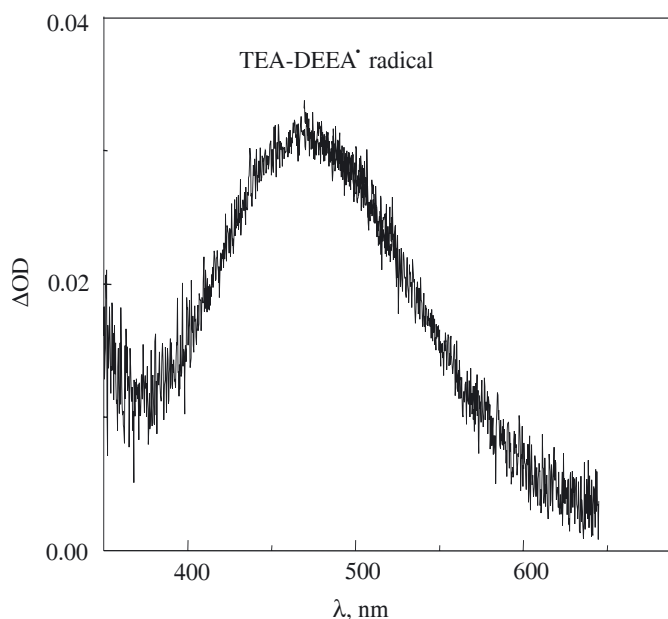


*Fig. 6. Transient absorption spectrum of TEA-DEEA$^{\bullet}$, taken 1 μs after the laser pulse*

adduct radical. Compared to the parent $M^{\bullet}$ acrylate radicals previously observed by pulsed radiolysis in the UV range, the radicals produced by the addition of $TEA^{\bullet}$ to an acrylate unit are characterized by an intense absorption band in the visible range. This behavior seems general and has been observed by us on a large variety of acrylate structures.

Interestingly, the absorption band experimentally observed in the UV is quite well reproduced by time-dependent computations. For TEA-DEEA$^{\bullet}$, in addition to this usual UV absorption band, the experimentally observed low energy transition between is also reproduced by molecular calculations and corresponds to the transi-
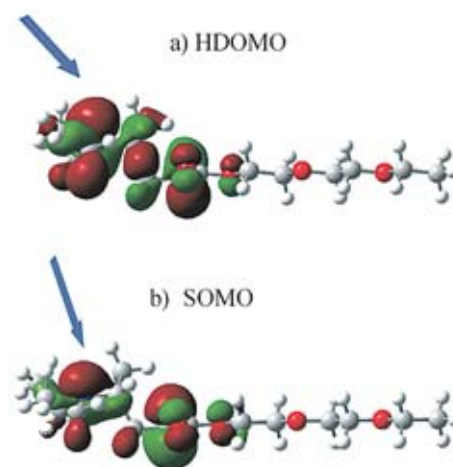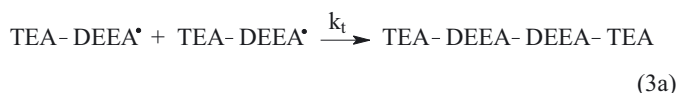


*Fig. 7. Orbitals involved in the transition experimentally observed at 470 nm for TEA-DEEA$^{\bullet}$. a) highest doubly occupied molecular orbital (HDOMO), b) singly occupied molecular orbital (SOMO). The fragment of the orbital representative of the nitrogen lone pair is indicated by an arrow*

tion between the highest doubly occupied molecular orbital (HDOMO) and the singly occupied one (SOMO), as shown in Figure 7. The contribution of the nitrogen lone pair to this transition is particularly important due to the hyperconjugation with the π orbitals of the radical center. The intensity of this transition is directly related to the number of monomer units and strongly decreases from TEA-M$^\bullet$ to TEA-M-M$^\bullet$.

Our direct observation of the acrylate radicals can be useful for the determination of the propagation $k_p$ and

$$\text{TEA-DEEA}^\bullet + \text{TEA-DEEA}^\bullet \xrightarrow{k_t} \text{TEA-DEEA-DEEA-TEA}$$

(3a)

$$\text{TEA-DEEA}^\bullet + \text{DEEA} \xrightarrow{k_p} \text{TEA-DEEA-DEEA}^\bullet$$  (3b)

recombination $k_t$ rate constants in polymerization reactions [equations (3a) and (3b), respectively] whose determination based on indirect methods remains a difficult task.

The method is based on the analysis of the reactions observed in solution at relatively low and high monomer concentrations. For a low acrylate concentration (~0.1M), the kinetics is experimentally fitted by a second order law allowing the determination of the recombination rate constant $k_t$ for two polymerization propagating radicals (TEA-DEEA$^\bullet$). At very high acrylate concentrations (2M to 4M), the addition of the TEA-DEEA$^\bullet$ radical with a second acrylate monomer unit (rate constant $k_p$) is easily fitted by a first order law (Figure 8). The recombination reaction is found almost diffusion controlled in solution ($k_t = 0.9 \cdot 10^9$ M$^{-1} \cdot$ s$^{-1}$) albeit slightly lower for DEEA than for MA. The $k_p$ value for DEEA is 1.5—2.3 $\cdot 10^4$ M$^{-1} \cdot$ s$^{-1}$, very similar to that determined pre-



*Fig. 8. Transient absorption decay traces for TEA-DEEA$^\bullet$ observed at 470 nm*

viously for methyl acrylate (MA) and corresponds to the usual values recently determined (*e.g.* for butylacrylate — BA) by Pulse Laser Polymerization.

This new approach appears as a very convenient way to gather a lot of experimental values of both $k_p$ and $k_t$ in solution: a forthcoming paper will detail this aspect and discuss the potential of our method. Furthermore, this study should be extended in bulk media for a better knowledge of the viscosity effect on $k_p$ and $k_t$ and the changes associated during the photopolymerization reaction. All this work might help in the design of new highly reactive acrylic systems.

### REACTIVITY OF RADICALS IN BULK

Radical photopolymerization experiments clearly show the huge effect of the viscosity of the oxygen free photopolymerizable medium on the relative efficiency of various cleavable photoinitiators. The increase of the efficiency when going from bulk to solution is mainly attributed to the fact that the initiation rate constants are very high in solution but are diffusion controlled in bulk, thereby decreasing the corresponding values by several orders of magnitude. In addition, the differences in the absorption properties of the photoinitiators have an important effect on the whole efficiency of the system. This is particularly true in usual industrial polymerization conditions under polychromatic light with a fixed photoinitiator concentration: the relative practical efficiency will be obviously different because of change of the amount of the light absorbed. For practical applications in aerated media, the role of the oxygen must be also taken into account.

An interesting point [29] is the evidence of a quite acceptable correlation of the relative efficiency $\phi_{rel}$ of a set of cleavable photoinitiators with their dissociation quantum yield in viscous media such as "Ebecryl 605". This correlation remains valid in less viscous (BA/PMMA) or fluid (BA or MA solutions) media providing that the monomer quenching of the photoinitiator triplet state is weak and the radical addition to the monomer is efficient: this is the case for i) most of photoinitiators since they have rather short lived triplet states and ii) most of the usual photoinitiating radicals toward acrylates and methacrylates, excepted the benzoyl radical. The dependence is more complicated in the case of methacrylates because of the high values for the quenching rate constants. This study shows that a deep knowledge of the photophysics and photochemistry of the photoinitiators in solution can thus serve as a good basis for the prediction of the polymerization efficiency in film experiments.

### CONCLUSIONS

Through some selected examples, this paper clearly shows that a considerable progress has been done for the
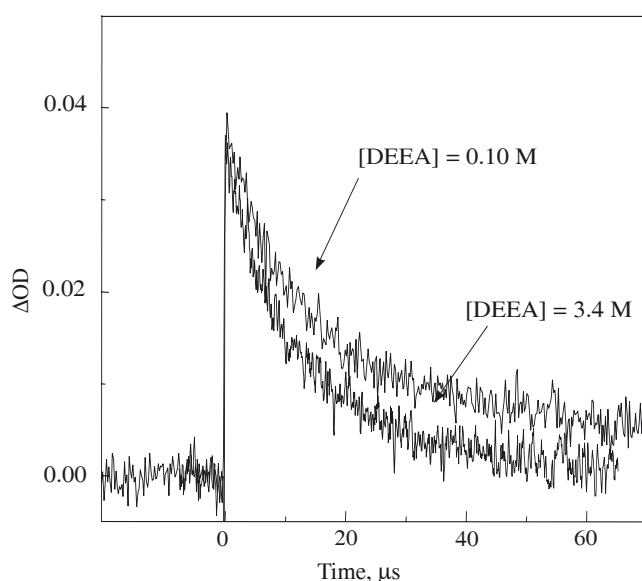
past few years in the experimental and theoretical investigation of radical photoinitiators: the large use of more powerful techniques and the availability of modelling calculations allow an access to inaccessible information up to now. This should help the design and the development of high performance systems [30].

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