

# Acrylate monomer reactivity studied through time resolved laser spectroscopy

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## Abstract

The acrylate radicals produced by addition of aminoalkyl radicals to an acrylate unit were directly observed by transient absorption spectroscopy. These acrylate radicals are characterized by a strong absorption in the visible region of the spectrum allowing an easy study of their chemical reactivity. Therefore, a new method for the determination of both the addition and recombination rate constants is proposed. These radicals being particularly important as possible representative of polymerization propagating radicals, this approach appears powerful and promising to study the reactivity of different monomers and to determine both propagation and termination rate constants of radical polymerization.

## Introduction.

It is very well known that the photoinitiator (PI) plays a crucial role in photopolymerization reactions. The use of time resolved experimental techniques as well as, in the last years, the development of molecular modeling techniques offers new opportunities for the investigation of the reactivity of PIs. We have been interested for many years with this problem.<sup>1-5</sup> The addition reaction of a free radical  $R'$  to a monomer double bond  $M$  is one of the most important steps in the radical polymerization reaction. However, this reaction generally competes with other processes (such as hydrogen transfer or oxygen interaction) which decrease the whole efficiency of the photoinitiated polymerization process. In order to improve the initiation reaction efficiency, it is of prime importance to understand the factors governing the reactivity of initiating radicals towards double bonds. The interpretation of the  $R'/M$  and  $RM'/additive$  reactivity represents a fascinating field of research both from a theoretical and an experimental point of view. Although this reaction remains the subject of large debates,<sup>6-11</sup> different studies have unambiguously confirmed that two main factors govern the addition rate constant  $k_i$ : i) the reaction exothermicity ( $\Delta H_r$ ) of the  $R'/M$  addition and ii) the polar effects ascribed to the involvement of the charge transfer configurations  $R^+/M^-$  or  $R^-/M^+$  to the transition state (TS) structure.<sup>4,6,8-9,12-13</sup> Despite the great interest for the investigation of radicals reactivity, relatively few

experimental  $k_i$  values were obtained through direct detection or even through indirect methods: such experiments involve a complex set of reactions and are rather difficult to carry out.

We will show here how it is possible to monitor the absorption of a set of  $RM^\bullet$  acrylate radicals. The interaction of  $RM^\bullet$  with various radical inhibitors (such as oxygen, spin traps and phenolic derivatives) and the addition of  $RM^\bullet$  to an other double bond  $M$  are readily followed. To the best of our knowledge, this has never been done. Molecular modeling calculations will shed more light on the reactivity of these acrylate radicals.

## The addition reaction of a radical onto a monomer

This addition reaction of a radical  $R^\bullet$  to a monomer  $M$  is usually described by a state correlation diagram which involves the reactant ground state configuration  $R^\bullet/M$ , the excited reactant configuration  $R^\bullet/M^*$  and two polar charge transfer configurations (CTC)  $R^+/M^-$  and  $R^-/M^+$ . In this scheme, the exothermicity of the reaction strongly affects the barrier height. The importance of the polar effects 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 and EA stand for the ionization potential and the electron affinity of the reactants).<sup>6, 12-14</sup>

## The reactivity of radicals as studied by molecular modeling

The different factors controlling the reactivity of a large series of carbon centered radicals toward the methyl acrylate monomer unit was examined in detail by using molecular orbital calculations.<sup>12-14</sup> 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, as evidenced by molecular calculations on the transition states, are 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).<sup>12</sup> The reactivity of three selected carbon centered radicals (aminoalkyl, methyl and cyanomethyl) toward several double bonds exhibiting large differences in their nucleophilic/electrophilic characters and also representative of widespread monomers (vinylether, vinylacetate, acrylonitrile, methylacrylate) was also examined.<sup>13</sup> 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 recently obtained.<sup>12-13</sup> 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.<sup>14</sup> 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 direct detection of radicals

The direct observation of radical species is rather difficult compared to the usual detection of other transient states because of an absorption located in the UV range: few examples of a direct optical detection have been provided and indirect methods sometimes employed. In the past few years, Laser Induced PhotoAcoustic Calorimetry (LIPAC) was shown as a powerful technique.<sup>5</sup>

We propose here a new procedure. A recently revisited<sup>15</sup> method allows to:

i) generate a particular radical  $R^\bullet$  by laser flash photolysis. This two step process first consists in photolysing tert-butylperoxide. then, the produced tert-butoxyl radical reacts with a suitable compound X and leads to  $X^\bullet$  through hydrogen abstraction.

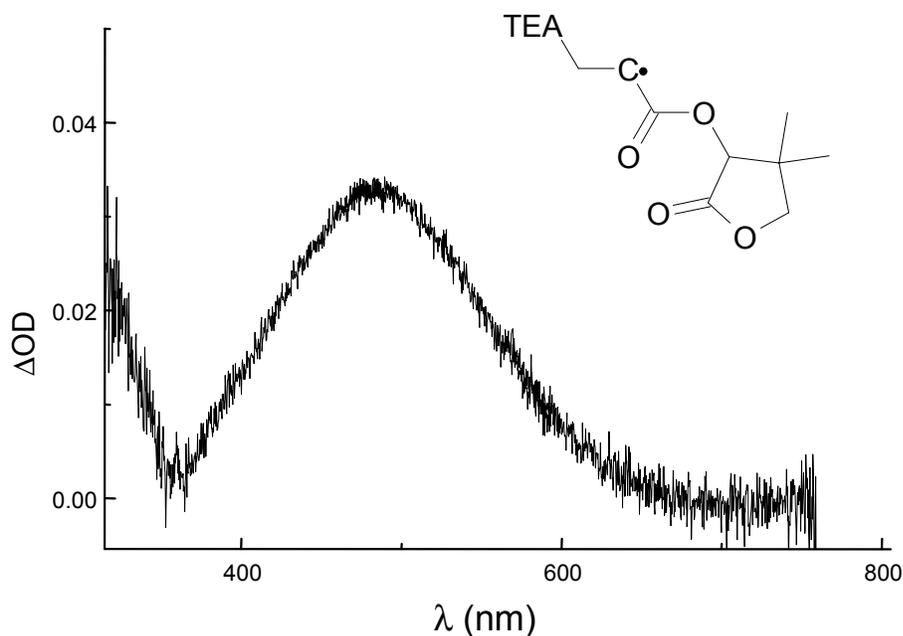
ii) get the optical absorption of  $X^\bullet$

iii) investigate the subsequent reactions of  $X^\bullet$

This procedure was successfully applied to the detection of thiyl radicals. The addition properties of  $RS^\bullet$  radicals to a monomer double bond M as well as the further back fragmentation reaction of the  $RSM^\bullet$  radical remain 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.<sup>16</sup> The polar effects appear as the major factor governing the addition reaction; they play a spectacular unique role whereas the enthalpy effects govern the back fragmentation reaction. A general investigation of the reactivity of very different sulfur radicals appears as a fascinating task because a large panel of situations through a careful selection of RSH and double bonds compounds is expected: a first account will be published soon.

## The direct detection of monomer/polymer radicals through their absorption in the visible wavelength range

The idea consists in the observation of the first monomer radical  $RM^\bullet$  due to the addition of  $R^\bullet$  to the monomer double bond M. 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. For example, using triethylamine as X, the  $TEA^\bullet$  radical is formed; upon addition of a monomer (such as Lactone derived acrylate - Acryloxy- $\beta$ ,  $\beta$ ,dimethyl- $\gamma$ -butyrolactone or LacA) to  $TEA^\bullet$ , a new transient (Figure 1) is clearly observed in the visible range: it is ascribed to the  $TEA$ -LacA $^\bullet$  adduct radical. Compared to the parent LacA $^\bullet$  acrylate radicals which absorb in the UV range, the radicals produced by the addition of  $TEA^\bullet$  to an acrylate unit are characterized by a new intense absorption band in the visible region. This behavior seems general and has been observed by us on a large variety of acrylate structures.



**Figure 1.** Transient absorption spectrum of TEA-LacA $\cdot$ , taken 1  $\mu$ s after the laser pulse.

The absorption properties of the parent acrylate radicals M $\cdot$  (corresponding to the addition of H $\cdot$  to M) and TEA-M $\cdot$  were calculated. Both the absorption band of M $\cdot$  observed in the UV, and that of TEA-M $\cdot$  detected as a low energy transition in the visible, are reproduced by molecular calculations. The intensity of this transition is directly related to the number of monomer units and strongly decreases from TEA-M $\cdot$  to TEA-M-M $\cdot$  or TEA-M-M-M $\cdot$ .<sup>15</sup>

### **The recombination of monomer/polymer radicals and their addition to a monomer unit**

Our direct observation of the acrylate radicals can be useful for the determination of the interaction rate constants ( $k_1$  for the recombination and  $k_2$  for the addition to another monomer unit) which can represent the propagation  $k_p$  and termination  $k_t$  rate constants in polymerization reactions whose the determination, based on indirect methods, still remains a difficult task.

Our method is based on the analysis of the reactions observed in solution at relatively low and high monomer concentrations.<sup>17</sup> For a low acrylate concentration, the kinetics are experimentally fitted by a second order law allowing the determination of the recombination rate constant  $k_1$  for two polymerization propagating radicals TEA-M $\cdot$ . At high concentration, the decay obeys to a first order law and yields the rate constant  $k_2$  value.

The recombination reaction is found almost diffusion controlled in solution (value close to  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The  $k_2$  value for LacA is very similar to that determined previously for MA and corresponds to the usual values recently determined (e.g. for butylacrylate) by Pulsed Laser Polymerization. The propagation rate constant is relatively insensitive to the acrylate structures (even for some investigated industrial mono- and di- functional monomers): the values are always found between  $1-3 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . In contrast, the recombination rate constants of two polymerization propagating acrylate radicals in solution strongly vary with the acrylate substituent.

Values of  $k_t$  found in the literature are in agreement with ours when the comparison is possible: e.g.  $k_t$  values in the  $10^9-10^8 \text{ M}^{-1} \text{ s}^{-1}$  magnitude were obtained for MA and AN. In fluid media or in monomer at very low conversion, the termination process is found nearly diffusion controlled (value close to  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). This suggests that in bulk the reaction should be governed by the diffusion process, even at very low double bond conversion in full agreement with the now well accepted statement for the first stages of the polymerization reaction.

Concerning the termination reaction in solution, a noticeable influence of the double bond substituent can be noted. This result can be probably ascribed to the steric effect i.e. bulky substituent reduces the efficiency of the recombination process. For MMA or MA, this reaction is highly efficient. The monomer structure can have a strong influence on  $k_t$  as exemplified by the  $\sim 7$  fold decrease when going from MA to LacA, possibly through steric or dipolar effects...

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, our 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.

The interest of our approach is also exemplified by the following point. The higher reactivity of LacA relatively to classical acrylate structures in photopolymerization experiments has been recently ascribed (by using the dark polymerization indirect method) to a reduced efficiency of the termination process.<sup>18</sup> In addition to the fact that  $k_t$  is effectively lower for this monomer, our work shows that  $k_p$  is also lower. As a consequence, the ratio  $k_p/k_t^{0.5} = 2.4$  for LacA compared to 2 for 2-(2-Ethoxy-ethoxy) ethyl acrylate (DEEA) cannot explain alone the difference in  $R_p$  (8 fold increase) when going from LacA to DEEA: the reason must be searched elsewhere e.g. in the initiation rate constant of the  $\text{TEA}^+/\text{M}$  reaction or in the photoinitiator excited states or radical species/ LacA or DEEA interactions.

To our opinion, the first direct observation of acrylate monomer derived radicals in the visible range by time resolved transient absorption spectroscopy can offer new opportunities to investigate both the propagation and termination steps of radical polymerization reactions. The obtained  $k_p$  values in a lot of systems appear as quite reliable and in good agreement with the best recently accepted PLP values. The interest of our approach lies on the relative easiness of the measurements: they allow the possibility of an access to  $k_p$  and  $k_t$  in a large series of compounds. As a consequence, they can be easily used to follow the evolution of a monomer radical addition to a monomer and a monomer radical recombination as a function of the monomer structure.

Using this method, the access to  $k_p$  is obviously limited by the efficiency of the addition reaction since rate constants lower than  $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  cannot be measured (such as in MMA and AN monomers). On the other hand, the present method which uses the nucleophilic alpha-amino initiating radical is obviously well adapted to acrylates because the addition reaction is fast. Other monomers can be likely studied by carefully selecting other initiating radicals which would allow to study for example acrylamide, styrene, vinylpyrrolidone, vinylcarbazole, vinyl ether, allyl ether... Although the method is

primarily suited to self propagation, cross polymerization might be also investigated, e.g. the addition of TEA-M' to vinyl ether since TEA' does not react with the vinyl ether.

The results obtained with this procedure can be also extended to the behavior of different acrylate structures in photopolymerization experiments carried out in bulk. The combination of this new approach with RT-FTIR experiments appears as promising for a more complete discussion of the different factors which affect  $R_p$  and for the design of new highly reactive monomer structures. All these aspects will be discussed in forthcoming papers.

## Direct detection of radicals through their absorption in the infra red region

Time resolved infrared spectroscopy can also be a powerful tool to characterize the reactivity of transient intermediates exhibiting a weak absorption in the UV-visible region and being relatively difficult to detect. In our Laboratory, a Nd:Yag laser is employed as the excitation source. The IR probe consists in a monochromator, a diode laser having a maximum emission around  $1820\text{ cm}^{-1}$  and a IR detector (Vigo System S.A.). As an example, the kinetics associated with the benzoyl radical, produced from the cleavage of Irgacure 1173, is observed at about  $1825\text{ cm}^{-1}$  in acetonitrile (Figure 2).

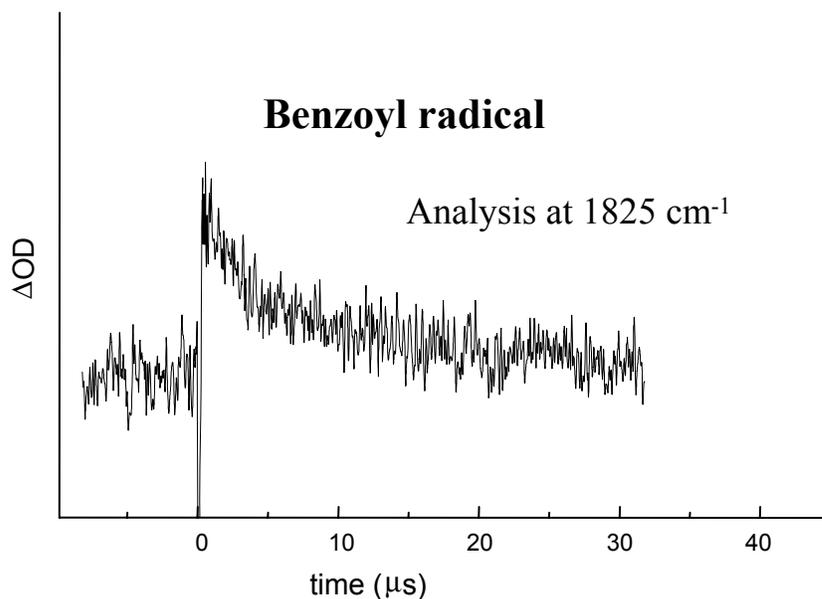


Figure 2. Typical decay trace of a transient observed through its infrared absorption.

## Conclusion

Through our 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 excited state processes in photoinitiators of polymerization: the large use of more powerful techniques and the availability of

modeling calculations allow an access to information inaccessible up to now. This should help the design and the development of high performance systems.

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