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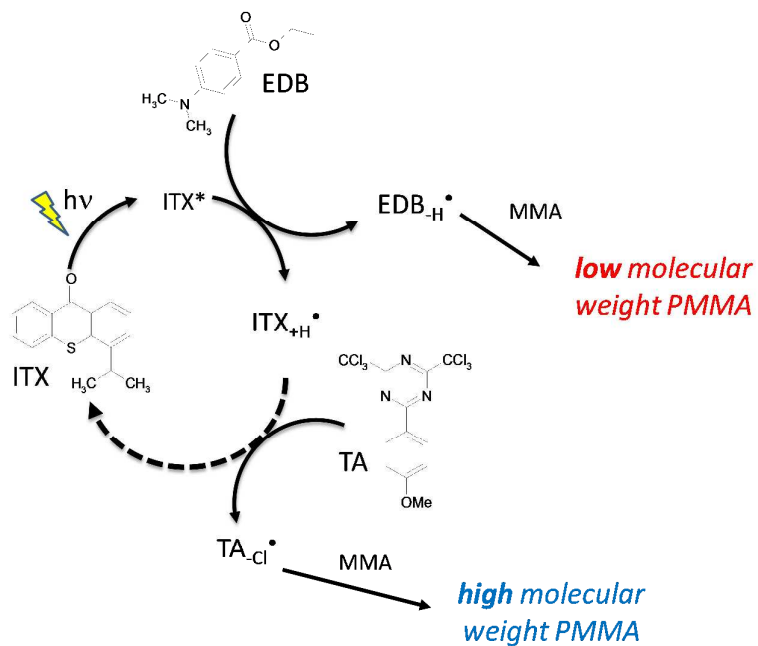
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Photopolymerization of methyl methacrylate: Effects of photochemical and photonic parameters on the chain length



## Photopolymerization of methyl methacrylate: Effects of photochemical and photonic parameters on the chain length.

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The effect of photochemical and photonic parameters are investigated on the chain length of poly(methylmethacrylate) (PMMA) as forms by free radical photopolymerization process. Different photoinitiators were tested for the photopolymerization of PMMA. The Type II system based on isopropyl thioxanthone (ITX)/ ethyl 4-(dimethylamino)benzoate (EDB) gives the best result. The conversion reaches 80% in 20 min contrary to type I photoinitiators. The decrease of the ITX concentrations from 3 wt % to 0.05 wt % allows the formation of higher chains of PMMA with  $M_w=170000$  g/mol, thanks to the decrease in photogenerated radicals. However, there is almost no influence of the light intensity on the polymer chains. To optimize the chain length of photopolymerized PMMA, Triazine A (TA) was added to reduce the formation of ketyl radicals arising from the reaction of ITX with EDB. The mechanism of the reaction of this three-component photoinitiating system studied by LFP confirmed the creation of ketyl radical and its oxidation by TA. Then, use of this three-component system increases both the kinetic of polymerization and the final conversion by virtue of the decrease in ketyl radicals, which act as terminating agents and concomitant increase of initiating radicals as formed from the reduced TA. Moreover, thanks to these new sources of initiating radicals, photopolymerization can take place at lower intensity of light. With TA, it was found possible to photopolymerize in very soft conditions and to allow the formation of longer polymer chains with  $M_w=200000$  g/mol at 1 mW/cm<sup>2</sup>.

### Introduction

The free radical polymerization of methyl methacrylate (MMA) to polymethylmethacrylate (PMMA) is usually performed under thermal conditions at moderate temperature (typically 40°C) through the use of peroxide initiators.<sup>1</sup> At lower temperature, the reaction time can exceed 10 hours.<sup>2</sup> Moreover at temperature higher than 50°C, the polymerization can be hazardous due to the exergonicity of the reaction. Then, an accurate control of the polymerization conditions is necessary to produce PMMA, a fact of matter when considering the huge industrial use of this thermoplastic. It could be of interest to polymerize MMA in a faster time scale through a photopolymerization process by exposure to ultraviolet or visible irradiation. Indeed, photopolymerization has recently gained prominence as an attractive alternative to traditional polymerization processes due to variety of advantages and benefits.<sup>3-7</sup> These profits can be attributed to the use of the

energy provided by light to induce polymerization reactions, rather than thermal energy. Photopolymerization also allows spatial and temporal control of the reaction.<sup>8-9</sup> For industrial process, the advantages of “cure on demand” eliminate premature reaction which can occur with thermally initiated reactions. Finally, photocuring is particularly well adapted for heat sensitive substrates without risk of thermal deformation.<sup>10-11</sup>

Traditionally, photopolymerization involves the use of multifunctional monomers and oligomers leading thus to the formation of tridimensional networks.<sup>8-12</sup> This reaction was rarely applied to the photopolymerization of monofunctional monomers to form linear polymer chains. The challenge in such case is the achievement of a polymer with molecular weight high enough to reach the properties required in industry. Indeed, increased molecular weight and narrowed weight distribution of macromolecular chains enhance the mechanical properties of the final polymer. Moreover, the brittleness can be

connected to the weight-average molecular weight while the hardness is linked to the number-average molecular weight.<sup>13-16</sup> Generally, the properties of polymers are better when the molecular weight is high. But, from a certain molecular weight which depend on the nature of the polymer, properties become independent of this molecular weight.<sup>13</sup>

In photopolymerization reaction, experimental conditions as temperature processing or light intensity can influence the structure of the polymer and therefore mechanical properties.<sup>17-19</sup> Consequently, the photopolymerization of MMA films at ambient temperature and the study of molecular weight as a function of experimental parameters is limited to a few papers. Then, the development of photopolymerized PMMA appears to be possible provided that the final molecular weight could be improved.

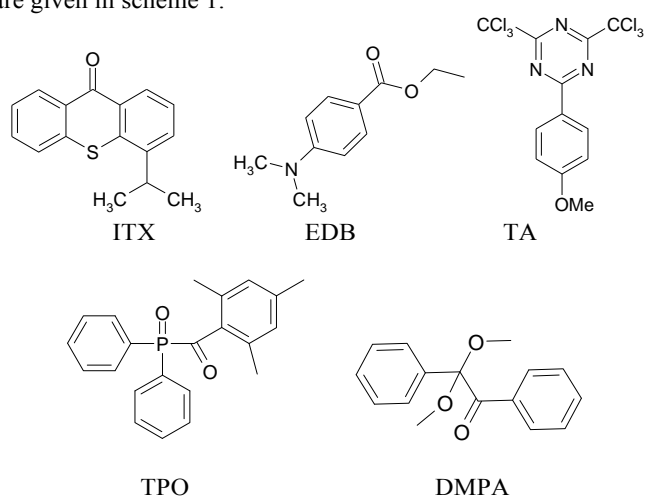
In this study, the photopolymerization of MMA is performed under UV light and the influence of the photonic and photochemical parameters on the chain length of polymers was studied. The photoinitiating system was optimized in order to reduce the detrimental effect of ketyl radicals that act as terminating agents. It is shown that high molecular PMMA can be obtained under well controlled conditions.

## Experimental

### Materials and samples preparation

Methyl methacrylate (MMA) and polymethylmethacrylate ( $M_w = 120000$  g/mol, MFCD00134349) were purchased from Sigma-Aldrich and used without any purification. Different photoinitiating systems were investigated throughout this study: diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, Sigma-Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, BASF) and a mixture of isopropyl thioxanthone (ITX, Sigma-Aldrich), ethyl 4-(dimethylamino)benzoate (EDB, Sigma-Aldrich) and triazine A (TA, PCAS) were added to the MMA /PMMA mixture at different ratios.

The corresponding absorption spectra are shown in Figure 1 and the different structures of photoinitiators and co-initiators are given in scheme 1.



Scheme 1

### Techniques

Photopolymerization kinetics and monomer conversions were followed by real-time FTIR<sup>20</sup> using a Vertex 70 from Bruker Optics operating in a rapid scan mode and equipped with a MCT detector. Time resolution was 0.1 s. The irradiation was provided by a high pressure mercury-xenon lamp (Hamamatsu LC10852) equipped with a reflector at 365 nm and a calorific filter which limits the transmission within a narrow range from 315 nm to 400 nm. As the infrared radiations are not transmitted, the sample is not heated by lamp during the experiment. The intensity of the lamp is measured using a calibrated fiber optic spectrometer (Ocean Optics, USB4000). From the emission spectrum of the lamp given in Figure 1, one can see that 93% of the energy is emitted at 366 nm and 7% at 334 nm. The output of the optical guide was placed at a distance of 4 cm from the sample with an incident angle of 90°. The photopolymerization reaction was carried out in laminated conditions using polypropylene film. The conversion of the monomer during the photopolymerization was determined by the decrease of the area of the C=C stretching vibration band of MMA at 1636 cm<sup>-1</sup>. The conversion of monomer  $C$  at time  $t$  is calculated from:

$$C (\%) = \frac{(A_0 - A_t)}{A_0} \times 100$$

where  $A_0$  is the initial absorption band area before exposure and  $A_t$  is the absorption area of the double bonds at time  $t$ .<sup>20,21</sup> The final conversion is evaluated as the mean value of three experiments to ensure a good reproducibility ( $\pm 5\%$  on the final conversion).

$R_{p,max}$  is defined as the maximum rate of polymerization during the first seconds of the polymerization and is calculated from:

$$Rp = [M_0] \frac{d(C (\%))}{dt}$$

where  $M_0$  is the initial concentration of the monomer and  $C$  the conversion of the monomer at time  $t$ .

$t_{2w}$  is defined as the time to reach the second polymerization wave.<sup>22</sup> It corresponds to the second maximum of the conversion curve derivative and is calculated from the same equation of  $R_p$ .

Molecular weight ( $M_w$ ) and polydispersity index (PDI) of the UV-polymerized thermoplastic were determined using size exclusion chromatography (SEC) analyses performed on a Shimadzu LC-20AD liquid chromatograph equipped with two Varian PL gel 5 $\mu$ m MIXED-C columns (column, injection and refractometer temperature: 30 °C; injection volume: 30  $\mu$ m) and a refractive index detector (Shimadzu RID-10A). THF was used as eluent at a flow rate of 1.0 mL/min. The molecular characteristics were determined relative to linear polystyrene calibration standards. Thus, experimental molecular weights were given as polystyrene equivalent.<sup>23</sup> Two different experiments were performed for each run to ensure a good reproducibility ( $\pm 200$ g/mol on  $M_w$ ).

UV-visible absorption spectrophotometer (Cary 4000, Varian) was used to determine the absorption spectra of photoinitiators in acetonitrile by using a quartz cell of 1 cm length.

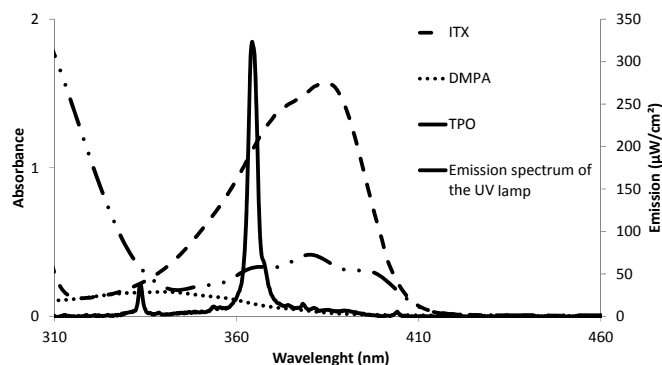


Figure 1: Absorption spectra of photoinitiators TPO, ITX and DMPA in acetonitrile,  $[PI]=0.5 \cdot 10^{-3} M$  and emission spectrum of the high pressure mercury-xenon lamp.

For the laser flash photolysis (LFP) experiments, the third harmonic (355 nm) of a nanosecond Nd-YAG laser (Surelite, Continuum) operating at 10 Hz was employed as the pump source and a pulsed 150 W xenon lamp as monitoring source. The energy of each pulse was fixed around 5-7 mJ with a pulse width about 10 ns. The photomultiplier (Applied Photophysics) output was monitored by a digital oscilloscope.<sup>24</sup> As LFP was used to determine the reaction mechanism occurring within the photoinitiating system, there is no need to match the same experimental conditions as for photopolymerization reactions. Then, experiments were performed in acetonitrile and all solutions were routinely degassed with argon. No degradation of the samples was observed during the experiment.

The triplet state quenching rate constants  ${}^3k_q$ , were measured by monitoring the decay of the triplet-triplet absorption of ITX ( $8 \cdot 10^{-5} M$ ) at 640 nm in acetonitrile.<sup>25</sup> The  ${}^3k_q$  values were determined according to the Stern-Volmer equation where the reciprocal lifetime  $\tau^{-1}$  is plotted versus the quencher concentration:

$$\tau^{-1} = \tau_0^{-1} + {}^3k_q[Q]$$

where  $[Q]$  is the molar concentration of quencher and  $\tau_0$  is the triplet lifetime in the absence of quencher.

## Results and discussion

### Photopolymerization of MMA with different radical photoinitiators

In order to monitor by RT FTIR MMA photopolymerization (initial viscosity of 0.6 mPa.s at 20°C) in films and limit flowing issues and high volume contraction (ca. 15 % for pure MMA),<sup>26</sup> it was necessary to increase the viscosity of the formulation by adding a PMMA pre-polymer ( $M_w = 120\,000$  g/mol). All the experiments were performed at a ratio of 30 wt% of PMMA dissolved in 70 wt% of MMA.

Photopolymerization experiments of the MMA/PMMA mixture were performed using either TPO or DMPA as Type I photoinitiators (5 wt%), and the combination of ITX with EDB as Type II photoinitiating system (1 wt% of ITX and 3 wt% of EDB). It can be seen from Figure 2 that the three different photoinitiating systems behave differently. The light intensity was set at 147 mW/cm<sup>2</sup>. The different characteristic parameters (maximal polymerization rate of the first wave of

polymerization  $R_{p,max}$  and final conversion ratio) are presented in Table 1.

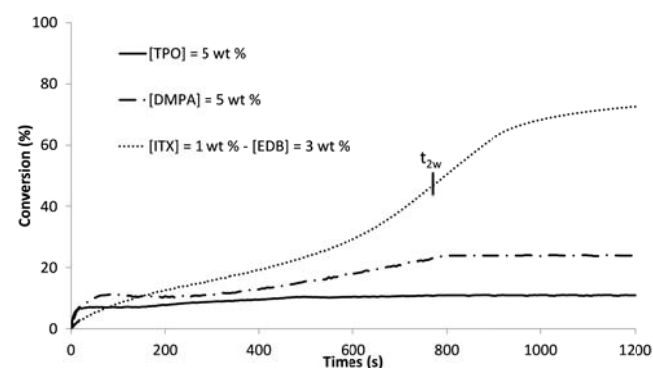


Figure 2: MMA conversion in MMA/PMMA systems with different photoinitiators: (•) ITX-EDB, (-•) DMPA, (-) TPO. Light intensity : 147 mW/cm<sup>2</sup>.

Table 1. Effect of the photoinitiator on the photopolymerization of MMA/PMMA system. Light intensity : 147 mW/cm<sup>2</sup>.

Photoinitiators	$R_{p,max}$ (mol.L <sup>-1</sup> .s <sup>-1</sup> )	Conversion (%)
TPO	0.13	10
DMPA	0.12	24
ITX/EDB	$8 \cdot 10^{-3}$	76.1

The photopolymerization of MMA/PMMA system with TPO reaches only 10% of conversion, albeit at fast rate ( $R_p = 0.13$  mol.L<sup>-1</sup>.s<sup>-1</sup>). DMPA exhibits a lower polymerization rate ( $R_p = 0.12$  mol.L<sup>-1</sup>.s<sup>-1</sup>), but leads to a higher final conversion of about 20%. The highest final conversion (80 %) was obtained for ITX/EDB. In that case, the photopolymerization process occurs in two steps, the first one exhibiting a low polymerization rate of  $8 \times 10^{-3}$  mol.L<sup>-1</sup>.s<sup>-1</sup>, followed after ca 600 s by a second wave of polymerization. This latter is attributed to the Trommsdorff-Norrish effect or autoacceleration, which is well-known for the polymerization of methyl methacrylate in bulk and described in publications.<sup>27</sup> This effect is based on a decrease of the termination rate caused by the raised viscosity of the polymerization region when the concentration of formed PMMA increases. It turns out from these experiments that ITX/EDB is the most suitable photoinitiating system to perform the photopolymerization of MMA.

### Effect of the photoinitiator concentration [ITX].

As mentioned in the introduction, it is well-known that the chain length of photopolymerized MMA strongly affects the properties of the polymer, especially mechanical properties. It is therefore of prime importance to study the influence of photochemical and photonic parameters on the chain length of photopolymerized PMMA. A series of experiments (Table 2) were performed to determine the effect of ITX concentration on the photopolymerization kinetics and on the resulting polymers molecular weights. Samples were prepared by photopolymerization of the MMA/PMMA mixture at a thickness of 100 μm between two polypropylene films during 25 min at the light intensity of 147 mW/cm<sup>2</sup>.

The decrease of ITX concentration induces a slowing down of the polymerization process and only a slight decrease of the final conversion. The time to reach the second wave of polymerization is increased by a factor of 2 when the concentration of ITX drops from 3 wt % to 0.05 wt % whereas the final conversion decreased from 75 % to 68%. During irradiation, the sample bleaches, allowing the light to penetrate in depth

Table 2. Effect of the photoinitiator concentration on the final conversion and the time to reach the second polymerization wave ( $t_{2w}$ ). EDB concentration : 3 wt%. Light intensity : 147mW/cm<sup>2</sup>.

[ITX] (wt%)	Final conversion (%)	$t_{2w}$ (s)
0.05	68	1065
0.2	72	1039
0.6	72	906
1	76	772
3	75	540

Figure 3 shows the influence of the photoinitiator concentration on the resulting polymers molecular weights. The decrease of ITX concentration induces an important increase of the Mw of the photopolymerized MMA. The Mw obtained with 3 wt% of ITX is around 56000g/mol while it reaches a value of 170000 g/mol with 0.05 wt% of ITX.

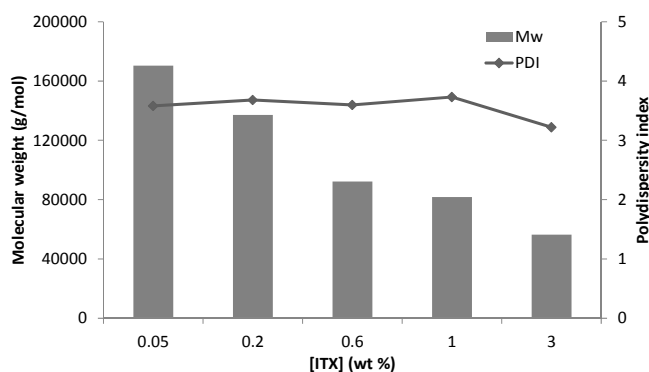


Figure 3: Effect of the photoinitiator concentration on the molecular weight of the photopolymer at 147mW/cm<sup>2</sup>. EDB concentration: 3 wt%.

The decrease in ITX concentration results in the formation of a lower steady-state concentration of initiating radicals and a depressed concentration of growing chains and lower conversion rates. Therefore, the probability of termination reactions is greatly reduced favouring high molecular weights.

Moreover, the polydispersity index is high (at around 3.5) but relatively constant showing a large diversity of chain lengths, as usual for free radical photopolymerization reactions. New active centers are created during the whole time of

polymerization, leading to the formation of chains with different lengths.

Figure 4 presents the SEC curves of the PMMA pre-polymer and the photopolymerized PMMA obtained at with different ITX concentrations. Because of the presence of the PMMA pre-polymer, the polydispersity indices and the Mw of the photopolymerized PMMA are skewed. The chromatogram shows that with 3 wt% of ITX, the SEC curve is shifted to the high retention times corresponding to the low Mw and consequently to the formation of short PMMA macromolecules, whereas, with 0.05 wt% of ITX, the SEC curve is shifted to lower retention time that indicated the formation of longer polymer chains.

Moreover, due to the use of linear polystyrene calibration standards, the reported molecular weights of the formed PMMA, as expressed in polystyrene equivalent, are lower than the actual values. Indeed, the PMMA pre-polymer has a Mw of 120000g/mol (according to commercial data) and the SEC data gives a Mw of only 84000g/mol.

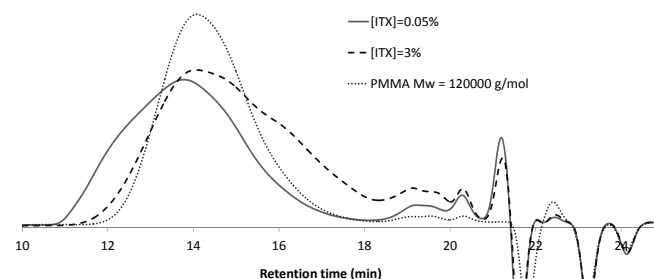


Figure 4: SEC curves of PMMA pre-polymer and photopolymerized PMMA obtained with different ITX photoinitiator concentrations (0.05 wt% and 3 wt%).

#### Effect of the light intensity

A series of experiments was performed to determine the effect of the light intensity on the photopolymerization kinetics and the resulting polymer molecular weights. In this part, the concentration of ITX/EDB was fixed at 1 and 3 wt%, respectively.

Table 3 shows the effect of the light intensity on the final conversion and polymerization kinetics. A sharp increase of light intensity from 5 mW/cm<sup>2</sup> to 147 mW/cm<sup>2</sup> only induces a slight increase of the final conversion, which is still around 71%. By contrast, an important acceleration of the polymerization kinetics is noticed: the time to reach the second wave of polymerization is decreased by 1.6.



Table 3. Effect of the light intensity on the conversion and the kinetic of polymerization. (ITX/EDB=1/3 wt/wt %)

Light Intensity (mW/cm <sup>2</sup> )	Final conversion (%)	t <sub>2w</sub> (s)
5	70	1248
14	68	1004
55	69	854
87	73	803
147	76	772

Finally, as shown in Figure 5 the light intensity marginally affects both the molecular weight of photopolymerized MMA and the polydispersity index.

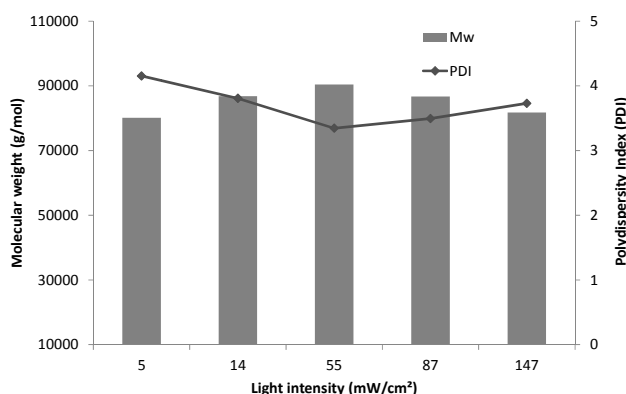


Figure 3: Effect of the light intensity on the molecular weight of the MMA photopolymer. [ITX]=1 wt% [EDB]=3 wt%

#### Optimization of the chain length by modification of photoinitiating system

With the ITX/EDB photoinitiating system, two different radicals are formed: an aminoalkyl radical, which is responsible for the initiation of the polymerization reaction and a ketyl radical, which is known to act as a terminating agent.<sup>28</sup> This latter can be responsible of the low molecular weight of the final polymer by favouring the termination reactions. It was recently shown that the reduced form of a photoinitiator can react with an electron acceptor, leading to the recovery of the initial photoinitiator and an additional initiating radical. This generally yields to higher rates of polymerization and higher final conversions.<sup>29-35</sup> Therefore, the addition of such a redox additive (triazine derivative) to the photoinitiating system was investigated with the aim of oxidizing the ketyl radical and consequently increasing the chain length of photopolymers by suppression of the terminating agent. The results given in Table 4 and Figure 6 show that the addition of TA in the formulation increases the final conversion of about 10%, reaching 83-84%. Additionally, the use of TA shortens the photopolymerization time: the time needed to reach the second wave of

polymerization is reduced by a factor of 5. This effect deserves a mechanistic study.

Table 4. Effect of the concentration of TA on the conversion and the polymerization kinetics of MMA/PMMA system. [ITX]=1 wt%. [EDB]=3 wt%. Light intensity =147mW/cm<sup>2</sup>

[TA] (wt%)	Conversion (%)	t <sub>2w</sub> (s)
0	76	772
0.5	83	170
1	84	140

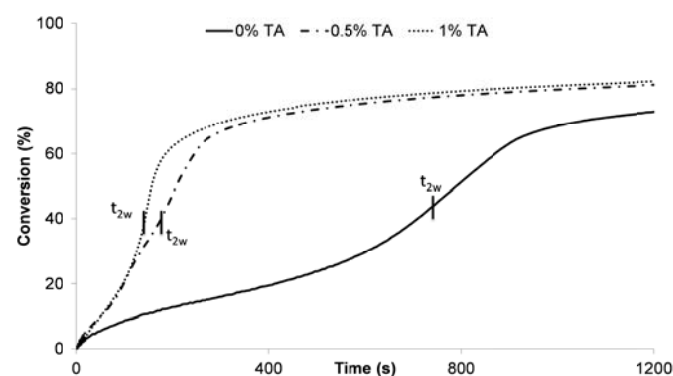
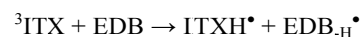


Figure 4: Effect of TA on the conversion profiles of MMA. Intensity =147mW/cm<sup>2</sup>

#### Investigation of the initiation mechanism

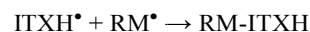
Following the laser excitation of ITX at 355 nm in acetonitrile, a transient absorption spectrum was observed with a peak at 640 nm which is attributed to the triplet-triplet absorption of ITX.<sup>25,36,37</sup> In the presence of EDB as hydrogen donor, ITX triplet state is rapidly quenched (Figure 5) with a quenching rate constant of  $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This reaction yields the formation of an aminoalkyl radical EDB-H<sup>•</sup> and a ketyl radical ITXH<sup>•</sup> which is observed at 420 nm (Figure 6) according to:<sup>36-37</sup>



It is known that the rate constants of addition of aminoalkyl radicals to double bonds are quite high ( $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for EDB-H<sup>•</sup> on methyl acrylate<sup>38</sup>). This leads to the initiation of the reaction and the formation of growing chains RM<sup>•</sup> that further propagate the polymerization reaction:



The addition rate constant of ITXH<sup>•</sup> onto MMA being  $40 \text{ M}^{-1} \text{ s}^{-1}$ , this radical cannot be considered as initiating radical.<sup>28</sup> On the contrary, the diffusion controlled recombination with growing chains will be favored:



This explains the role of ketyl radical as terminating agent. It should be underlined that as aminoalkyl and ketyl radicals are stoichiometric formed, an increase in the rate of initiation will also favor the rate of bimolecular termination reaction. Then, a

ketone/amine type II photoinitiating system produced under light both an initiating radical and a terminating agent.

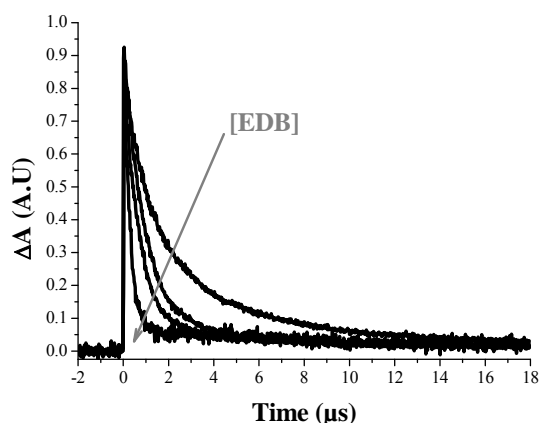


Figure 5:  $^3\text{ITX}$  transient absorption ( $\Delta A$ ) recorded in acetonitrile at 640 nm with an increasing concentration of EDB (from  $9.5 \times 10^{-5} \text{ mol.L}^{-1}$  to  $7.5 \times 10^{-4} \text{ mol.L}^{-1}$ ).

In the presence of TA as redox additive, a decrease of the ketyl radical transient was observed (Figure 6). This indicates that the triazine reacts with the ketyl radical yielding to the recovery of ITX ground state and the formation of the corresponding triazine radical.

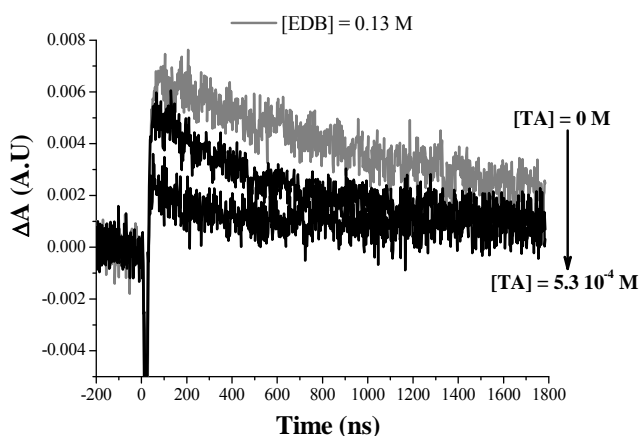
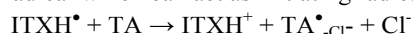


Figure 6: Ketyl radical  $\text{ITXH}^\bullet$  absorbance ( $\Delta A$ ) measured at 420 nm in argon saturated acetonitrile solution in the presence of TA.

TA is known to be a good electron acceptor which leads to fast heterolytic C-Cl cleavage after dissociative electron transfer.<sup>33-39</sup> Therefore, it is proposed that the reaction involves an electron transfer reaction from the ketyl radical to TA leading to triazynyl radical which can act as initiating radical:

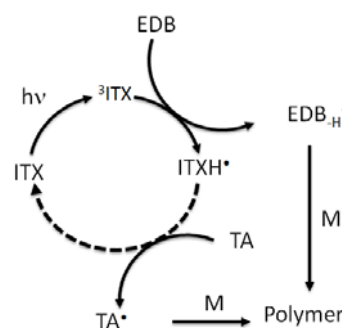


The starting photoinitiator ITX is recovered after deprotonation of  $\text{ITXH}^\bullet$ . As  $\text{ITXH}^\bullet$  is trapped during this process, the

termination reactions are expected to be considerably reduced, leading to higher probably of propagation reaction.

It should be mentioned that ITX triplet state is quenched in the presence of TA, with a rate constant of  $3.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , i.e. quite similar to that of EDB. Taking into account that the molar content of EDB is 13 times higher than that of TA, no specific interaction between ITX triplet state and TA is expected.

Then, the proposed mechanism for the three components ITX/EDB/TA photoinitiating system is depicted in Scheme 2. After excitation of ITX and formation of the triplet state, a photoreduction reaction occurs with EDB. This leads to the formation of an aminoalkyl radical ( $\text{EDB}_{\text{H}}^\bullet$ ) and a ketyl radical ( $\text{ITXH}^\bullet$ ). Then, a redox reaction occurs between the ketyl radical and TA which forms a new initiating radical and regenerates ITX. The disappearance of the ketyl radical and the formation of a new initiating radical account for the increasing photopolymerization efficiency of the ITX/EDB system in the presence of TA.



Scheme 2

**Towards very low intensity and low photoinitiator concentration.** It was shown that the decrease of the photoinitiator concentration can increase the molecular weight of the polymer chains formed by photopolymerization. Addition of TA has allowed an increase in both the polymerization kinetics and the final conversion. Therefore, it was interesting to study the influence of TA on the molecular weight of photopolymerized PMMA. The photopolymerization of a PMMA / MMA formulation (30/70 wt%) was performed for two low light intensities (1 and 5 mW/cm<sup>2</sup>) and at reduced concentration of the 3-component photoinitiating system (figure 7 and Table 5). At first, it can be seen that in presence of TA, it is possible to photopolymerize at very low intensities, as low as 1 mW/cm<sup>2</sup>, which is impossible with ITX / EDB photoinitiating system. An increase up to 5 mW/cm<sup>2</sup> does not have a great influence on the final conversion: 73% at 1 mW/cm<sup>2</sup> and 69% at 5mW/cm<sup>2</sup>. Similarly polymerization profiles are quite similar for the two intensities.

Table 5. Effect of the combination of low light intensity and low photoinitiator concentration on the conversion of PMMA/MMA formulations. [ITX] = 0.05 wt% [EDB]=3 wt%. [TA]=0.5wt%



Light intensity (mW/cm <sup>2</sup> )	Conversion (%)	t <sub>2w</sub> (s)
1	73	356
5	69	451

Interestingly, SEC experiments show that significant decrease of the light intensity combined with depressed concentration of PI system strongly affects the polymer chain length (Figure 7). The molecular weight of the chains is around 137000 g/mol and 200000 g/mol at 5mW/cm<sup>2</sup> and 1mW/cm<sup>2</sup>, respectively. The use of TA also increases the polydispersity of the chains since the PDI is around 5 for light intensity of 1 mW/cm<sup>2</sup>. The disappearance of the radical ketyl as terminating agent increases the departure from the control of the polymerization. Thanks to use of TA, it is possible to photopolymerize in mild conditions (low intensity and photoinitiator concentrations) and it allows the formation of longer polymer chains.

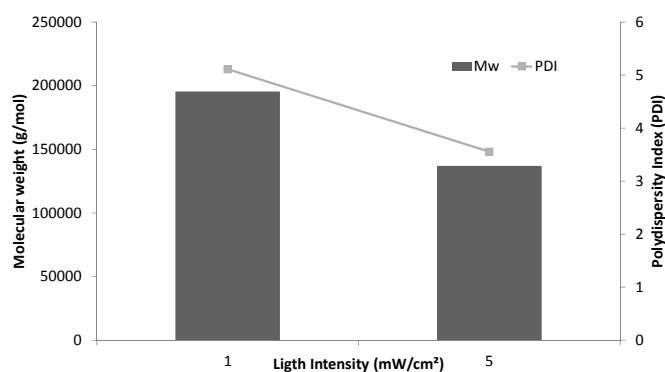


Figure 7: Effect of the light intensity on the molecular weight of the PMMA/MMA photopolymer. [ITX]=0.05% - [EDB]=3 wt% - [TA]=0.5%.

## Conclusion

In this study, the photopolymerization of MMA was performed using different photoinitiators. It was found that a photoinitiating system based on ITX/EDB leads to almost full conversion. After a mechanistic investigation of the photoinitiating process and identification of the reactive species, it was shown that the molecular weight of the photopolymerized PMMA can be modulated. The addition of a triazine derivative leads to the vanishing of the ITX ketyl radicals that acts as terminating agent. As a consequence, the molecular weight of the final polymer increases. This opens new opportunities to perform efficient photopolymerization of thermoplastics like MMA.

## Notes and references

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