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# FREE-RADICAL POLYMERIZATION UPON NEAR- INFRARED LIGHT IRRADIATION, MERGING PHOTOCHEMICAL AND PHOTOTHERMAL INITIATING METHODS

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## ABSTRACT

Polymerization of (meth)acrylate resins upon Near-Infrared (NIR) light remains a huge challenge. In this study, a new photo-induced method of polymerization of methacrylic monomers is presented, originally merging a photochemical and a photothermal pathway. A four-component system is proposed comprising a NIR dye combined with an iodonium salt, a phosphine and a thermal initiator. A selection of dyes is suggested regarding electron transfer properties and/or light-to-heat conversion abilities. Several thermal initiators are studied: an alkoxyamine (BlocBuilder<sup>®</sup> MA), an azo derivative and a peroxide. For the first time, a NIR absorbing dye is used in photopolymerization using both its capacities of light-to-heat conversion and its ability to initiate an electron transfer reaction. Three wavelengths of irradiation will be presented here: 785 nm, 940 nm and 1064 nm. These long wavelengths are challenging because the energy of photons is extremely low but these wavelengths offer significant advantages in term of light penetration (e.g. for the access to composites through photopolymerization processes). The different systems presented here exhibit high and rapid conversions of methacrylate functions. The underlying chemical mechanism will be fully depicted by Real-Time Fourier Transform Infrared Spectroscopy and Thermal Imaging measurements.

## 1. INTRODUCTION:

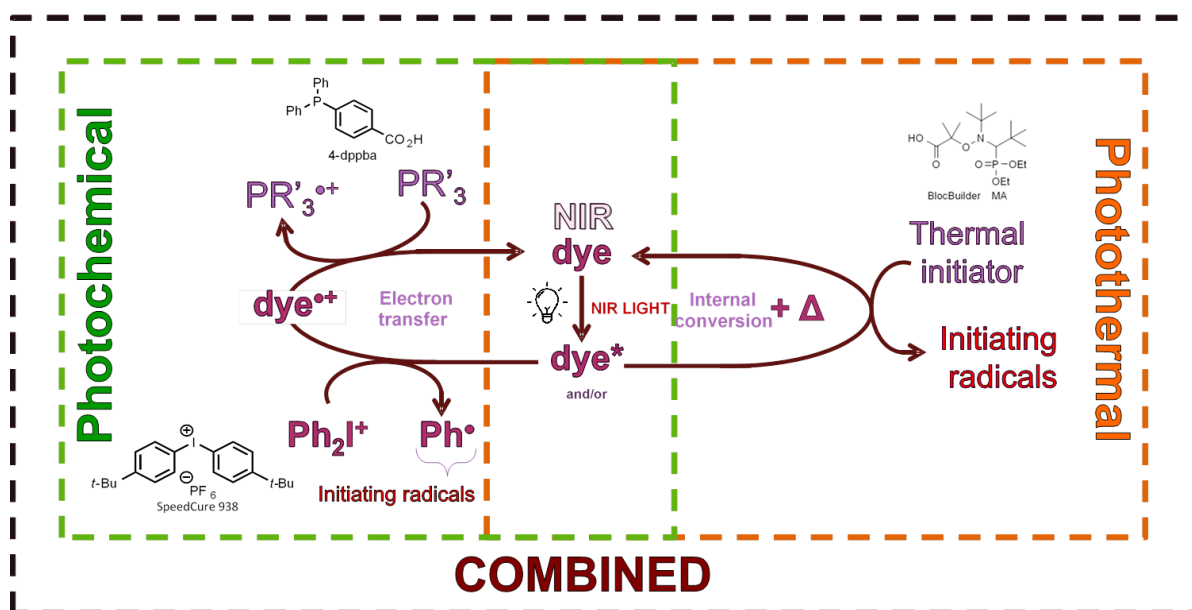
Free radical polymerization (FRP) has been the subject of many researches since the apparition of the first free radically synthesized polymers.[1] This particular type of polymerization offers a high compatibility with a wide range of monomers; the polymerization of highly specific monomers is now possible with this type of polymerization.[2] More particularly, it is possible to cure (meth)acrylate resins. Methacrylates are less reactive than the more commonly used acrylates,[3] but they are less susceptible to undergo a hydrolysis and this monomer is also less toxic.[4] The polymerization of these monomers is already largely encountered in the dental field or as surgical sealant.[5,6] Knowing that the initiation step is the most challenging part of the polymerization process in free radical polymerization, new initiating methods are always welcomed. The idea is to find an initiating method more adequate with today's preoccupations (safety and environmental impact). In such context, development of photopolymerization, i.e. polymerization induced by light, has been a first answer for milder initiation conditions. Indeed, the use of light instead of heat to initiate the polymerization offers significant advantages such as a reduced energy consumption, no or very few release of volatile organic compounds, high productivity (it is easier to perform on-demand pieces with such methods) and space saver (in term of manufacturing machinery).[7]

For these reasons, photoinitiated polymerization have attracted increasing attention during the last decades. The well-established systems developed are able to polymerize under UV-light and are now used for coatings, inks, paints for example.[8] Because of the high energy photons delivered by such light sources, polymerization is possible as soon as the light is turned on. However, these short wavelengths are less and less used in favor of longer wavelengths. A main reason justifying this choice is that the UV light is dangerous for the user (it can cause skin and eye damages [9]) and the environment (ozone release [10]). This leads to a democratization of the polymerization process carried out under blue light but polymerization under Near-Infrared Light (NIR-light) still remains challenging.[11-14] However, these longer wavelengths are enticing in terms of light penetration. In-depth polymerizations, for thick and/or highly filled samples are now possible upon NIR light. A severe limitation of these types of NIR systems is the low energy of the photons.[15] Thus, it is impossible to perform the homolysis of a bond of a Type I photoinitiator with a NIR light (a mechanism commonly used for UV-photoinitiators). That's why development of such photoinitiating systems remains challenging. Another non-negligible advantage of the polymerization done under NIR light is the possibility to use cheap irradiation devices (e.g. Light Emitting Diodes LEDs) contrarily to the UV irradiation requiring the use of expensive setups.

Herein, we propose new photoinitiating system (PIS) for photoinitiation under NIR light. Recently, a three-component photoinitiating system using a dye, a phosphine and an iodonium salt has been proposed for methacrylate polymerization under low light intensity at 785 nm.[14] Through this photochemical approach, radicals able to initiate the FRP are generated by an electron transfer reaction between the excited state of the NIR dye and the iodonium salt. In parallel, a NIR absorbing dye is also used to perform the photopolymerization of a methacrylate resin, this time in combination with a thermal initiator through a photothermal mechanism. The NIR absorbing dye used in this second pathway has the property of light-to-heat conversion, particularly observed with cyanine dyes.[16] Heat generated is sufficient to initiate a thermal polymerization. Thus, it is probably possible to merge thermal curing and photocuring and in particular, to combine the advantages of both methods. As the light can be switched on/off on demand, the polymerization can be started and stopped whenever the user wants. On the contrary, with the conventional thermal process, preheating and cooling down are necessary and the temporal control is not possible. Moreover, the thermal polymerization is already widely used with a long history, particularly in the industrial field, therefore, the thermal initiators are easily accessible and cheap.

In the present article, we propose to merge both photoinitiating systems efficient in photochemical redox processes and photothermal NIR heater. Herein, a four-component initiating system comprising a NIR absorbing dye, an iodonium salt, a phosphine (these three-component being used for redox photoinitiation) and a thermal initiator (for photothermal initiation) is proposed for the polymerization of methacrylate resins with light emitting between 785 nm and 1064 nm. The principle of polymerization is presented in Scheme 1. A selection of NIR dyes will be presented and sorted regarding their behavior under light irradiation: if they are more susceptible to act through a photochemical approach, a thermal approach or if they need a combination of both approaches to be good candidates in a photoinitiating system. Kinetics of polymerization and temperature of the sample versus time will illustrate this ability.

**Scheme 1. Principle of the combined (photochemical+photothermal) approach**

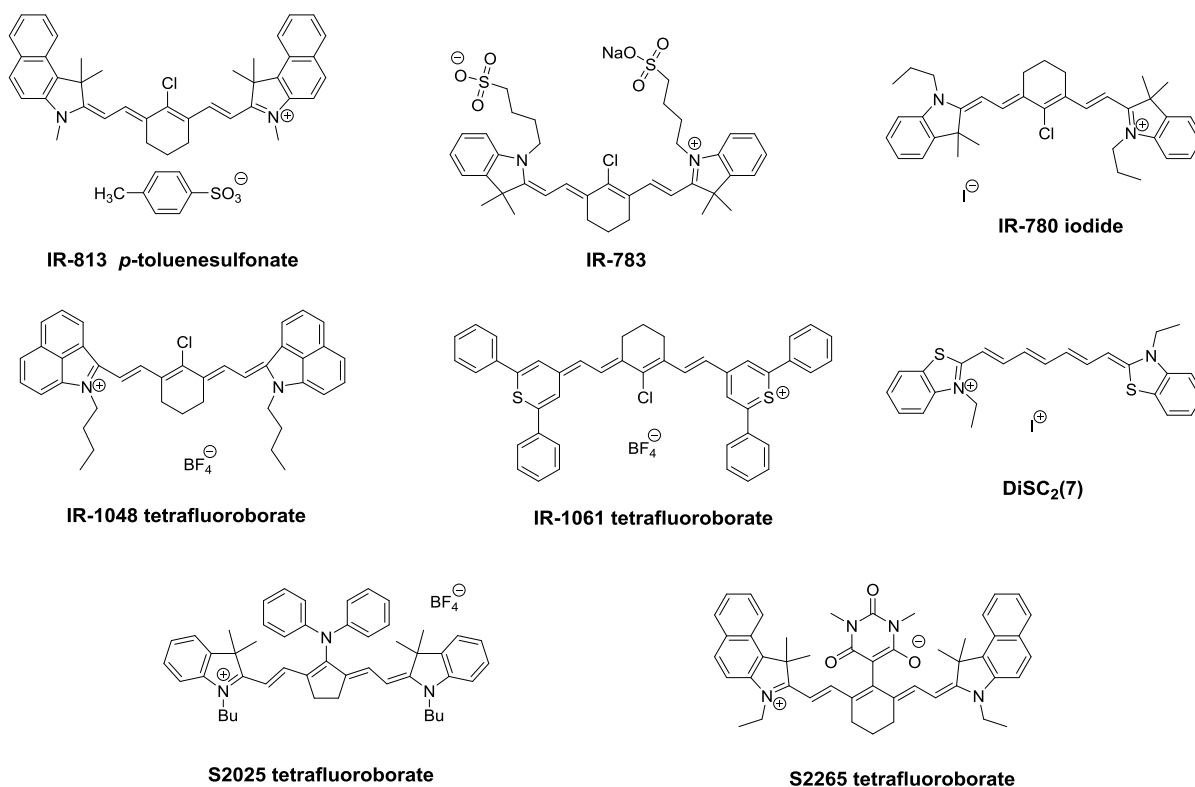


## 2. EXPERIMENTAL SECTION

### 2.1. NIR DYES

IR-780 iodide, IR-783, IR-813 *p*-toluenesulfonate, IR-1048 and IR-1061 (Scheme 2) were purchased from Sigma-Aldrich. DiSC<sub>2</sub>(7) (Scheme 2) was purchased from Alfa Aesar and S2265 and S2025 (Scheme 2) were obtained from Few Chemicals.

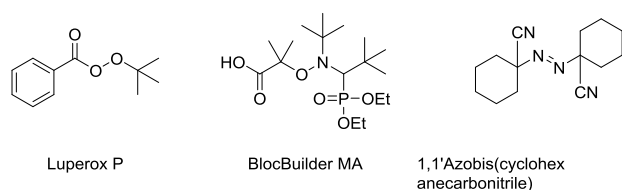
**Scheme 2. Structure of NIR dyes**



## 2.2 THERMAL FREE RADICAL INITIATORS

Luperox P and 1,1'-azobis(cyclohexane-carbonitrile) (Scheme 3) were obtained from Sigma Aldrich. **BlocBuilder<sup>®</sup>MA** is obtained from Arkema.

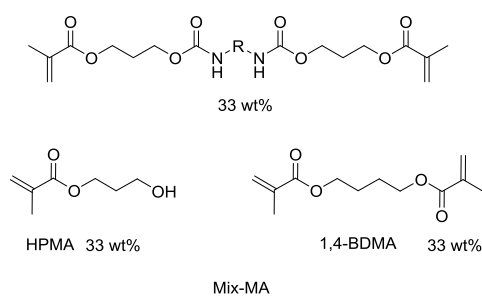
### Scheme 3. Chemical structures of thermal free radical initiators



## 2.3 MONOMERS

As a benchmarked resin, "Mix-MA" has been chosen for the present work. This blend has been prepared with 33.3wt% of (hydroxypropyl)methacrylate (HPMA), 33.3wt% of 1,4-butanediol dimethacrylate (1,4-BDMA) and 33.3wt% of a urethane dimethacrylate monomer (UDMA), obtained from Sigma Aldrich and the composition of the mixture is presented in Scheme 4.

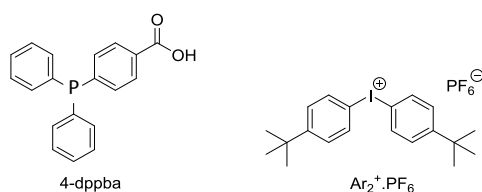
### Scheme 4. Mix-MA resin mix



## 2.4 ADDITIVES

The iodonium salt *bis(4-tert-butylphenyl)iodonium hexafluorophosphate* ( $\text{Ar}_2\text{I}^+/\text{PF}_6^-$ ; Scheme 5) was obtained from Lambson Ltd (UK). 4-(Diphenylphosphino)benzoic acid (4-dppba, Scheme 5) was purchased from Sigma-Aldrich.

### Scheme 5. Chemical structures of additives



## 2.5 IRRADIATION SOURCES

Several NIR laser diodes purchased from Changchun New Industries (CNI) were used: Laser diode@785nm with selectable irradiance from 0W to 2.55W/cm<sup>2</sup>, Laser diode@940nm with selectable irradiance from 0W to 4W/cm<sup>2</sup> and Laser diode@1064nm with selectable irradiance from 0W to 1W/cm<sup>2</sup>.

## 2.6 REAL-TIME CONVERSION MEASUREMENTS UPON NIR LIGHT

Kinetics of polymerization of the photosensitive formulations were followed through the double bond C=C conversion vs. time. The peak followed by Real Time Fourier Transform Infrared (RT-FTIR) spectroscopy (a Jasco 4600) is located at 6100-6220 cm<sup>-1</sup>. The concerned peak is represented before and after polymerization in Supporting information. Polymerization is performed in a mold (thickness = 1.4 mm), under air by irradiation with a laser diode. Light is turned on 17

seconds after the first spectrum measurements. Details for each experiment are given in the figures caption of the concerned experiment. The procedure has been described more in details in [17].

## 2.7 Simultaneous conversion and thermal imaging experiments

Temperature evaluation of the sample during photopolymerization is performed in the RT-FTIR spectrometer cavity during irradiation using an infrared thermal imaging camera (Fluke TiX500). Thermal resolution is about 1°C and maximum temperature of the sample during the polymerization is extracted with a Fluke SmartView 4.1. data software. Data and software parameters were extracted using a script written in Python. More details about the procedure are reported in [18]. The temperature is measured at the surface of the sample whereas the conversion is measured on the total thickness of the sample.

# 3. RESULT AND DISCUSSION

## 3.1 CONCEPT

As mentioned above, a four-component initiating system will be used for the free radical polymerization of a benchmarked methacrylate resin (Mix-MA) upon NIR light by merging two existing photoinitiating systems (Scheme 1). The NIR dye (0.1w%) is mixed into the resin in combination with  $\text{Ar}_2\text{I}^+/\text{PF}_6^-$  (3 w%) and 4-dppba (2 w%) and **BlocBuilder®MA** (2w%).

For the NIR dye/ $\text{Ar}_2\text{I}^+/\text{PF}_6^-$ /4-dppba combination, the photopolymerization is performed by a photochemical pathway and more particularly by an electron transfer between the dye and the iodonium salt, used as a co-initiator. The phosphine is used as an oxygen scavenger and participates to the photocatalytical cycle.[14] For the photothermal pathway, the initiation step is different.[16] The NIR dye is also excited by the NIR light irradiation but the energy is released by an internal conversion inside the system (transitions between the vibrational levels). This leads to a heating of the surroundings, and in our case of the resin. The temperature reached is then sufficient to initiate the homolysis of a bond of some selected thermal initiators for the free radical polymerization.

In both cases, it was possible to find dyes which give high degrees of conversion and the kinetics of polymerization are satisfying, even under low light intensity (400 mW/cm<sup>2</sup> is reported as being sufficient to perform the polymerization). However, it was not the case for all the investigated



dyes. Indeed, for some dyes, long inhibition times are observed and degrees of conversion could be enhanced. It is noticeable that among the selected dyes some of them are good candidates for an initiation through a photochemical pathway whereas other dyes are better candidates for an initiation by mean of a photothermal pathway. It is also possible to find some structures which have shown good initiation properties through both approaches. This is the reason why, herein, we propose to merge both systems in a four-components initiating system comprising the dye (0.1w%), the iodonium salt (3w%), the phosphine (2w%) and the thermal initiator (2w%).

In order to characterize which pathway is privileged by a dye, photopolymerization of Mix-MA with the three photoinitiating systems upon irradiation at 785 nm has been tested:

- photochemical PIS: dye/iodonium salt/phosphine (0.1w%/3w%/2w%)
- photothermal PIS: dye/thermal initiator (0.1w%/2w%)
- combined PIS: dye/iodonium salt/phosphine/thermal initiator (0.1w%/3w%/2w%/2w%)

Three typical behaviors have been observed for the different systems studied in this work and the results are summarized in the Table 1.

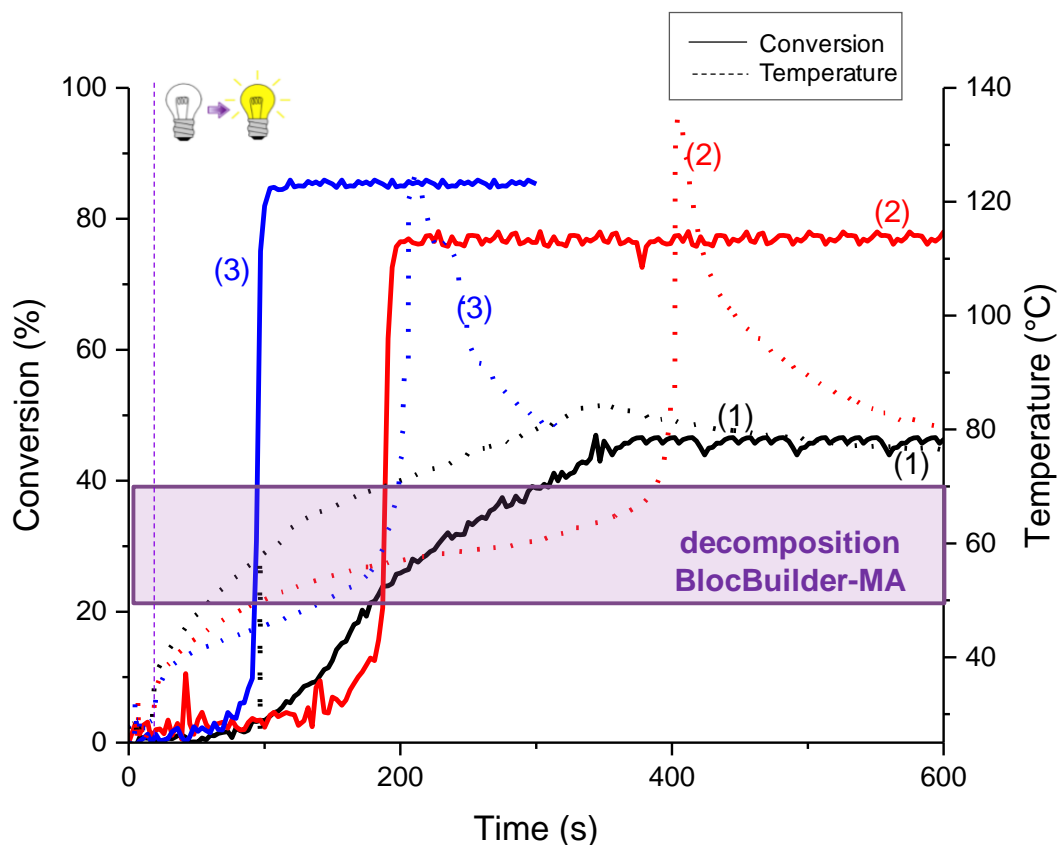
**Table 1. Behaviors observed with the 4-component initiating system (Good for rapid initiation and high final conversion of monomer, Bad if not)**

|            | Photochemical system | Photothermal system | Combined Mode |
|------------|----------------------|---------------------|---------------|
| Behavior 1 | Bad                  | Good                | Good          |
| Behavior 2 | Good                 | Bad                 | Good          |
| Behavior 3 | Bad                  | Bad                 | Good          |

### **BEHAVIOR 1**

The first behavior observed is a dye that is a good candidate for an initiation through a thermal pathway but which is not efficient for photochemical polymerizations; In this case, the NIR dye mainly acts as a heater. In the combined mode, the final C=C conversion is reached faster than with the photothermal mode alone and with higher values of conversion. S2025, a cyanine dye, is a representative example of NIR dyes with this behavior. Simultaneous follow-up of the kinetics and the temperature of polymerization vs. time are reported in Figure 1.

Figure 1. Simultaneous RT-FTIR/thermal imaging photopolymerization follow-ups (C=C conversion vs. irradiation time and temperature vs. irradiation time; 1.4 mm sample) under air upon exposure to a Laser Diode@785nm; 400mW/cm<sup>2</sup>; for Mix-MA in the presence of S2025 (0.1w%) and (1) 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%); (2) **BlocBuilder<sup>®</sup>MA** (2w%), and (3) 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%) and **BlocBuilder<sup>®</sup>MA** (2w%); the irradiation starts after 17s



Upon irradiation, temperature of the sample is increasing in the three cases. That corresponds to the excitation of the dye by mean of a NIR light and to a release of the energy under the form of heat. Heat is sufficient to promote the homolysis of a thermal initiator such as **BlocBuilder<sup>®</sup>MA**. Indeed, the range of temperatures for the decomposition of **BlocBuilder<sup>®</sup>MA** is depicted in the Figure 1 (from 50°C to 70°C). This temperature has been determined by DSC measurements in our specific resin, as reported in [17]. The homolysis of **BlocBuilder<sup>®</sup>MA** allows the initiation of the polymerization process. The temperature rising and the conversion of C=C are not observed at the same time. This delay is not due to the polymerization process but to the set-up used: the conversion is measured in all the sample depth whereas the temperature is measured only at the surface. Polymerization of methacrylate is very sensitive to oxygen and in particularly to oxygen in

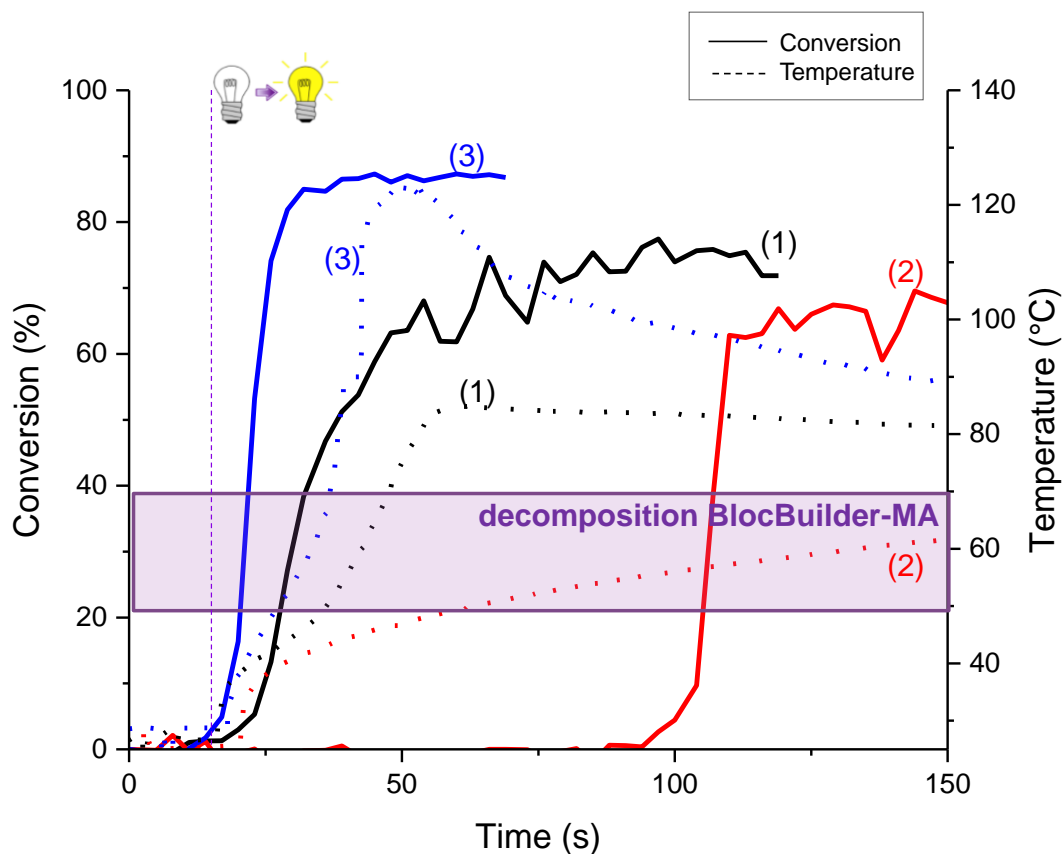
the air. Here, we proposed the photopolymerization to be carried out under air. We supposed that the photopolymerization began at the bottom of the sample (not exposed to oxygen) and finished at the surface. This explains the delay observed between the conversion and the temperature. This is true for all figures presented in this article.

However, we observed only a slight initiation during the time of the experiment using the photochemical system (Figure 1, curves 1). It is also observed that the polymerization is enhanced using the combined mode compared to the thermal initiation pathway (curve 3 being better than curve 2). This was predictable: in the combined mode, more initiating radicals are generated (from both redox and thermal processes). Moreover, the presence of the phosphine is essential as it acts as an oxygen scavenger [19]. Indeed, polymerizations are performed under air and the formed initiating radicals react more rapidly with oxygen than with the monomer. Thus, an inhibition time is observed before the beginning of the polymerization. The addition of an oxygen scavenger into the monomer blend allows a faster consumption of the oxygen and thus, to a lower inhibition time. This phenomenon has already been reported in [14] and [16].

## **BEHAVIOR 2**

Using the combined mode, a second behavior is also observed, consisting in a good photochemical initiation, a bad thermal initiation and a good behavior of the combined mode. This is particularly observed with S2265 for which the kinetics of polymerization and the temperature reached during irradiation are reported in Figure 2. For the NIR dye characterized by the behavior 2, they are mainly active in redox photochemical processes and less as a heater for the photothermal approach.

**Figure 2. Simultaneous RT-FTIR/thermal imaging photopolymerization follow-ups (C=C conversion vs. irradiation time and temperature vs. irradiation time; 1.4 mm sample) under air upon exposure to a Laser Diode@785nm; 400mW/cm<sup>2</sup>; for Mix-MA in the presence of S2265 (0.1w%) and (1) 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%); (2) **BlocBuilder<sup>®</sup>MA** (2w%), and (3) 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%) and **BlocBuilder<sup>®</sup>MA** (2w%); the irradiation starts after 17s**



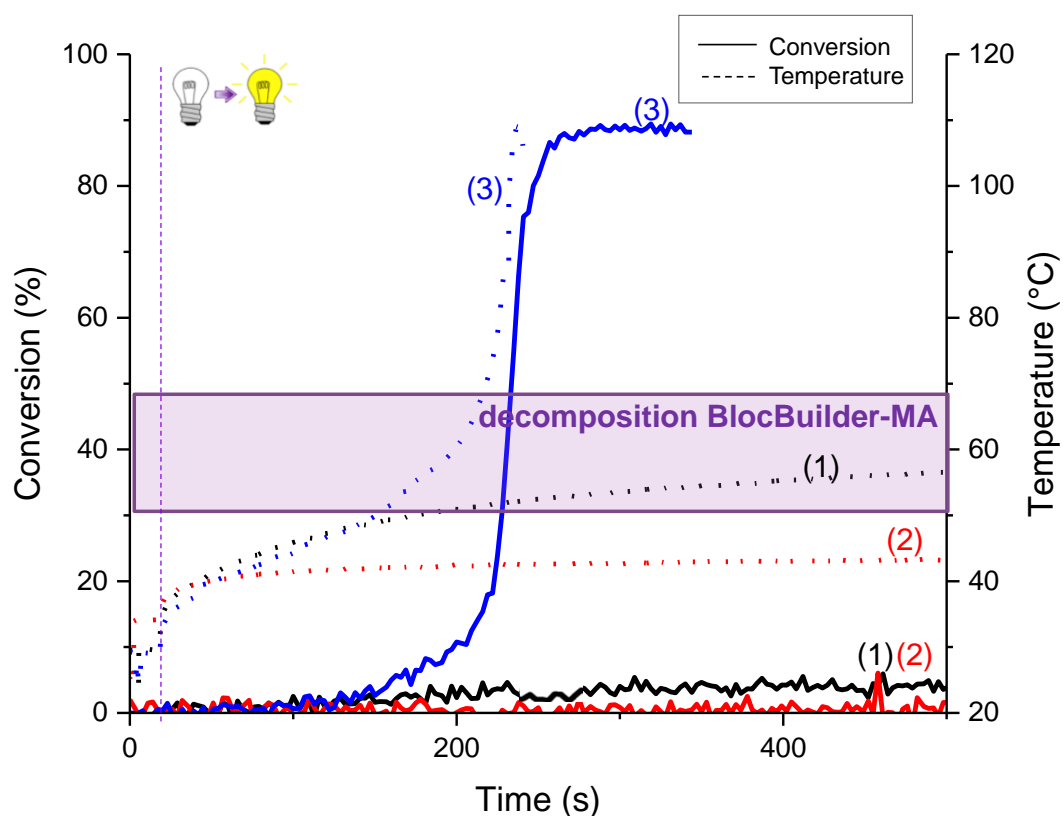
In the three cases, the temperature of the surroundings increases during irradiation. The photochemical mechanism is privileged using this dye: a rapid high conversion of C=C is observed. As observed for the first behavior, the combined mode leads to the fastest conversion of the methacrylate groups. This is predictable too. Indeed, the polymerization of methacrylate resins is exothermic due to the conversion of  $\pi$ -bonds into  $\sigma$ -bonds. The thermal energy released during the polymerization process and the heat resulting from the relaxation of the dye (heater behavior) is at this point sufficient to perform the homolysis of **BlocBuilder<sup>®</sup>MA**, which enhances the polymerization rate by the formation of additional initiating radicals. With this specific dye (S2265), the polymerization through a photothermal mode is possible but the time necessary for the polymerization to begin is much longer than using a photochemical system. We observed the same delay between conversion and temperature, as already discussed for behavior 1.

### **BEHAVIOR 3**

A third and interesting case is observed, namely, the dyes have rather poor initiation properties into both the photochemical and the photothermal pathways but exhibit good initiation

properties using the combined mode. This is particularly true with IR-813 *p*-toluenesulfonate, whose polymerization characteristics are represented in the Figure 3.

**Figure 3. Simultaneous RT-FTIR/thermal imaging photopolymerization follow-ups (C=C conversion vs. irradiation time and temperature vs. irradiation time; 1.4 mm sample) under air upon exposure to a Laser Diode@785nm; 400mW/cm<sup>2</sup>; for Mix-MA in the presence of IR-813 *p*-toluenesulfonate (0.1w%) and (1) 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%); (2) **BlocBuilder<sup>®</sup>MA** (2w%), and (3) 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%) and **BlocBuilder<sup>®</sup>MA** (2w%); the irradiation starts after 17s.**



In the three cases, the dye is excited by the NIR light and two mechanisms are competing: the photochemical mechanism where the excited dye reacts with the iodonium salt by an electron transfer to produce reactive aryl radicals and the relaxation of the dye through heat release. Formation of aryl radicals by electron transfer is not sufficient to initiate the polymerization under air using the photochemical system and the temperature reached by the blend is not sufficient to induce the homolysis of **BlocBuilder<sup>®</sup>MA** using only the photothermal system. However, by combination of both mechanisms, it is possible to obtain a polymerization in less than 300 seconds

of irradiation. Thus, we conclude that for this type of dyes, both mechanisms merge to give enough initiating radicals to overcome the oxygen inhibition.

### 3.2 POLYMERIZATION RESULTS

#### 3.2.1. WITH DIFFERENT DYES

In the precedent section, three different behaviors have been reported. These 4-component initiating systems are also very efficient for different dyes and upon different light irradiations. IR-780 iodide, IR-783, IR-813, DiSC<sub>2</sub>(7), S2265 and S2025 have been selected for their ability to initiate a polymerization with a Laser Diode @785 nm and a Laser Diode at @940 nm. They are classified regarding their behavior upon exposure to a light emitting @785 nm (Table 2) and their behavior upon exposure to a light emitting at @940 nm (Table 3). Kinetics measurements associated with these classifications are reported in Supporting Information.

**Table 2. Classification of dyes regarding their main behavior upon exposure to a light @785 nm**

|   | <b>Behavior 1</b> | <b>Behavior 2</b> | <b>Behavior 3</b> |
|---|-------------------|-------------------|-------------------|
| <b>IR-780 iodide</b>                    | X                 |                   |                   |
| <b>IR-783</b>                           |                   |                   | X                 |
| <b>IR-813 <i>p</i>-toluenesulfonate</b> |                   |                   | X                 |
| <b>DiSC<sub>2</sub>(7)</b>              |                   | X                 |                   |
| <b>S2265</b>                            |                   | X                 |                   |
| <b>S2025</b>                            | X                 |                   |                   |

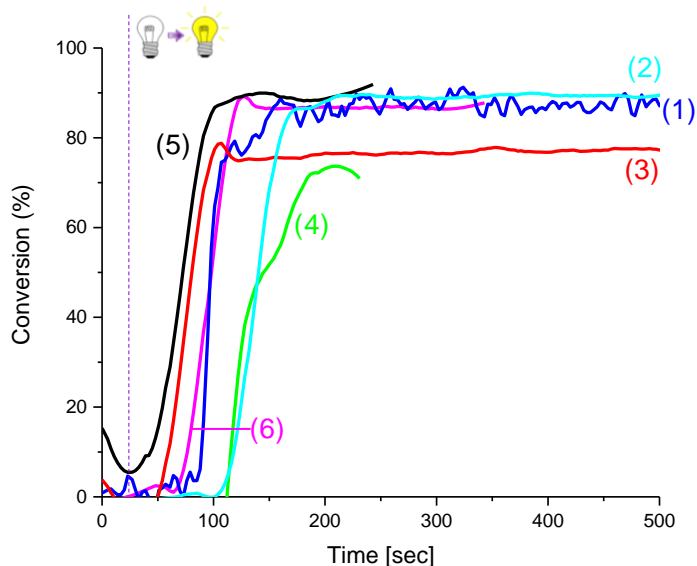
**Table 3. Classification of the different dyes regarding their behavior upon exposure to a light @ 940 nm**

|                                  | <b>Behavior 1</b>         | <b>Behavior 2</b> | <b>Behavior 3</b> |
|----------------------------------|---------------------------|-------------------|-------------------|
| <b>IR-780 iodide</b>             | Not efficient in any case |                   |                   |
| <b>IR-783</b>                    | X                         |                   |                   |
| <b>IR-813 p-toluenesulfonate</b> | X                         |                   |                   |
| <b>DiSC<sub>2</sub>(7)</b>       | X                         |                   |                   |
| <b>S2265</b>                     |                           | X                 |                   |
| <b>S2025</b>                     |                           |                   | X                 |

As evidenced by the results reported in the Table 2 and the Table 3, benefits of using the four-component systems are clearly shown. Thus, upon irradiation of IR-783 and IR-813 at 785 nm and S2025 at 940 nm, the three dyes exhibit the same behavior i.e. the behavior 3. In these conditions, a satisfying polymerization is observed only with the four-component initiating systems. With the dyes having the behavior 1 or the behavior 2, it is observed that the polymerization is always better using the combined mode: the polymerization is always faster and/or with higher final conversion. With the combined mode, polymers produced are tack-free (this is not always the case with only the photothermal or the photochemical mode). The only exception is DiSC<sub>2</sub>(7) when irradiated at 785 nm for which the polymerization kinetics in the photochemical mode and the combined mode are similar. In this case, we supposed that DiSC<sub>2</sub>(7) has no photothermal activity at all.

Examples of kinetics of photopolymerization using these dyes in the 4-component initiating systems are reported in the Figure 4 upon exposure to a Laser Diode@785 nm and in the Figure 5 upon exposure to a Laser Diode@940 nm.

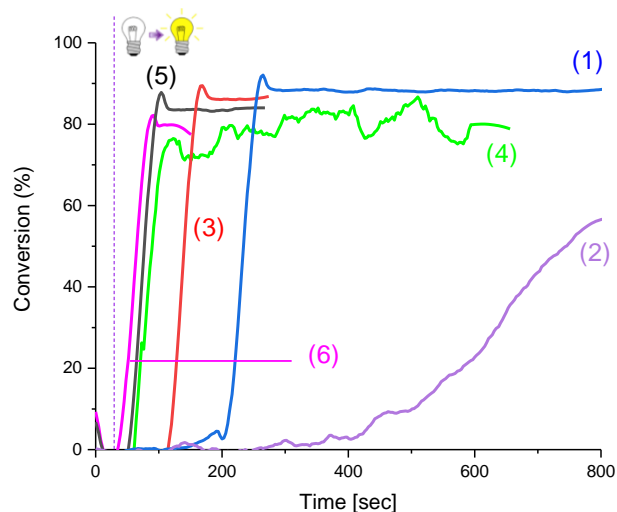
**Figure 4. Photopolymerization of Mix-MA under air (methacrylates function conversion vs. irradiation time) in the presence of  $\text{Ar}_2\text{I}^+/\text{PF}_6^-$  (3w%), 4-dppba (2w%), Blocbuilder<sup>®</sup>MA (2w%) and (1) S2025 (0.1w%), (2) IR-780 iodide (0.1w%), (3) DiSC<sub>2</sub> (7) (0.1w%), (4) IR-813 (0.1w%), (5) IR-783 (0.1w%) and (6) S2265 (0.1w%), LaserDiode@785nm, thickness=1.4mm, the irradiation starts after 17s**



The different dyes presented above are mainly cyanines with good absorption properties at 785 nm.[15][17] When used in the four-component initiating system, photopolymerization of methacrylate with these dyes is very efficient: Final conversions ranging between 70% and 90% are obtained within 130 seconds of irradiation. There are slight differences observed between the different dyes. The highest methacrylate final conversion (85%) is observed using S2025, IR-780, IR-783 and S2265. These dyes have similar behaviors in terms of polymerization rate, oxygen inhibition and final conversions.

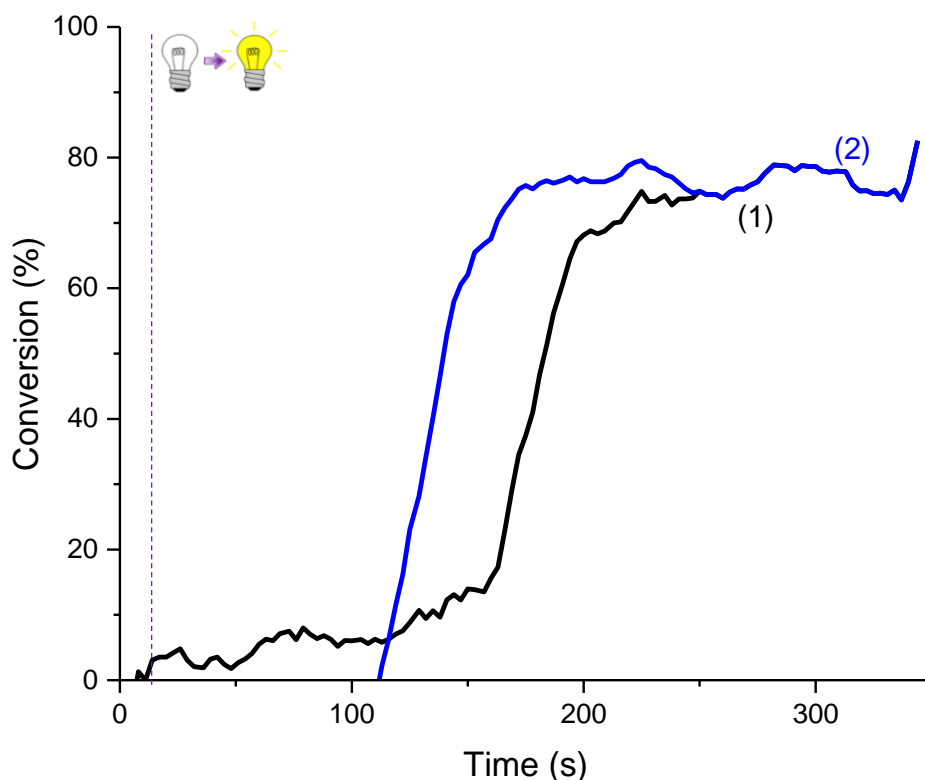
**Figure 5. Photopolymerization of Mix-MA under air (methacrylates function conversion vs. irradiation time) in the presence of  $\text{Ar}_2\text{I}^+/\text{PF}_6^-$  (3w%), 4-dppba (2w%), Blocbuilder<sup>®</sup>MA (2w%) and (1) DiSC<sub>2</sub> (7) (0.1w%), (2) IR-780 iodide (0.1w%), (3) IR-813 *p*-toluenesulfonate (0.1w%), (4) S2425(0.1w%), (5) IR-783 (0.1w%) and (6) S2265 (0.1w%), LaserDiode@940nm, thickness=1.4mm; the irradiation starts after 17s.**





For an irradiation @940 nm, very good polymerization profiles are observed. As shown in the Figure 5, only IR-780 gives poor results: it is predictable, the absorption of this dye is very low at 940 nm, as already reported in [20]. IR-1048 and IR-1061 are two other cyanines with absorption maxima at 1048 nm and 1061 nm, respectively. Good initiating abilities for the free radical polymerization of our benchmarked methacrylate resin in the 4-component initiating system has been observed with these two molecules upon exposure to a Laser Diode@1064 nm (Figure 6).

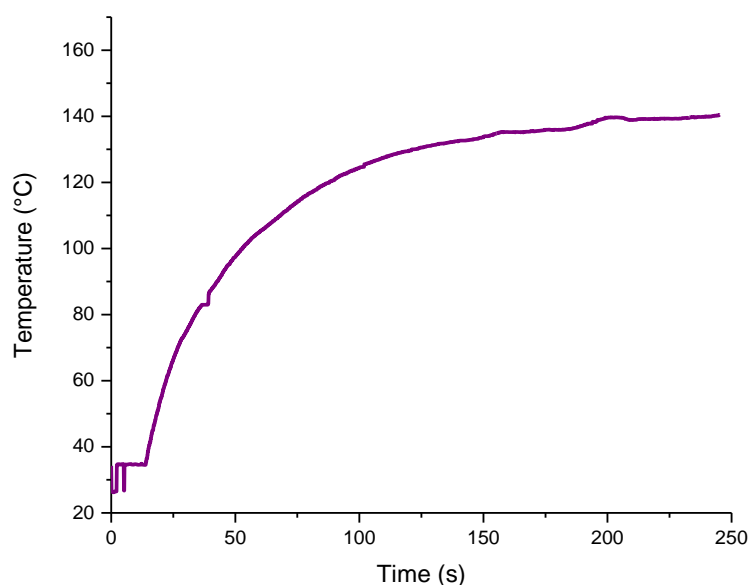
**Figure 6. Photopolymerization of Mix-MA under air (methacrylates function conversion vs. irradiation time) in the presence of  $Ar_2/PF_6^-$  (3w%), 4-dppba (2w%), Blocbuilder<sup>®</sup>MA (2w%) and (1) IR-1048 (0.1w%) and (2) IR-1061 (0.1w%) LaserDiode@1064nm, thickness=1.4mm; the irradiation starts after 17s.**



### 3.2.2 WITH DIFFERENT THERMAL INITIATORS

Previously, **BlocBuilder<sup>®</sup>MA** has been used as a thermal initiator for polymerization upon NIR light (photothermal effect). **BlocBuilder<sup>®</sup>MA** is an interesting thermal initiator because it forms simultaneously initiating and controlling radicals. Thus, a control of the free radical polymerization is possible playing on the concentration used. This has already been reported in the literature in (21) and the use of **BlocBuilder<sup>®</sup>MA** for the Nitroxide Mediated Polymerization (NMP) has been detailed. However, it is fully possible to use more "regular" thermal initiators in our combined photochemical/photothermal approach. Herein, we proposed to compare this combined mode using IR-780. Heat generated upon irradiation @785 nm by IR-780 is represented in Figure 7.

**Figure 7. Temperature profile of Mix-MA under air (temperature max of the sample vs. irradiation time) in the presence of IR-780 iodide (0.1w%); Laser@785nm; thickness=10 mm; the irradiation starts after 17s.**



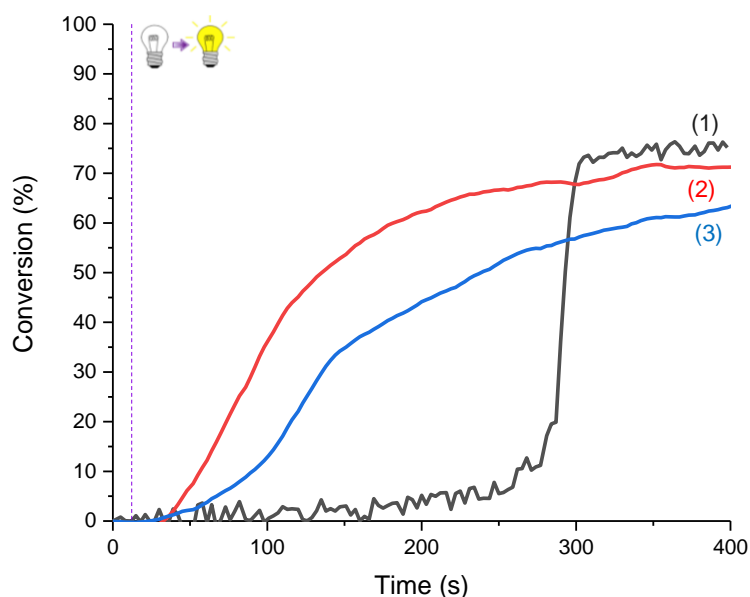
Therefore, two other thermal initiators are proposed: Luperox P which is a peroxide and 1,1'-azobis(cyclohexane-carbonitrile) which is a derivative from azobisisobutyronitrile (AIBN), commonly used in free radical polymerization. Thermal initiators were chosen on the basis of their decomposition temperature (Table 4). As the maximal temperature reached using IR-780 iodide upon irradiation is around 140°C (Figure 7), homolysis of these thermal initiators should be possible. The polymerization kinetics (Conversion of methacrylate functions vs. time of irradiation upon laser diode at 785 nm under air) are reported in Figure 8.

**Table 4. Temperature at which the half-life ( $t_{1/2}$ ) of the thermal initiator is 10h in a methacrylate monomer from (22).**

| Thermal initiator                     | Temperature (°C) for $t_{1/2} = 10\text{h}$ |
|---------------------------------------|---|
| Luperox P                             | 100-130°C                                   |
| BlocBuilder®MA                        | 60°C  |
| 1,1'-Azobis(cyclohexane-carbonitrile) | 80°C  |

**Figure 8. Photopolymerization of Mix-MA under air (methacrylate function conversion vs. irradiation time); Laser Diode@785nm, thickness=1.4mm, under air, with IR-780 (0.1w%), 4-dppba (2w%), Ar<sub>2</sub>I<sup>+</sup>/PF<sub>6</sub><sup>-</sup> (3w%)**

and (1) **BlocBuilder<sup>®</sup>MA** (2w%); (2) **1,1'-Azobis(cyclohexane-carbonitrile)** (2w%); (3) **Luperox P** (2w%); the irradiation starts after 17s.



As observed in Figure 8, with the three thermal initiators, good polymerization profiles are observed. As predicted, **BlocBuilder<sup>®</sup>MA** leads to a different shape of the curve. Indeed, as there is formation of both initiating and controller radicals, the inhibition time is expected to be longer. However, the polymerization is more brutal: as soon as the polymerization is initiated, higher conversion rate is observed. With the two other initiators (Luperox P and 1,1'-azobis(cyclohexane-carbonitrile)), the final conversion is reached more progressively. Using the azo initiator and Luperox, the polymerization process is more progressive (curve (2) and curve (3) in Figure 8). We also observed that the polymerization is faster using the azo derivative compare to the Luperox one, this is predictable: the temperature necessary for the dissociation of the dye is lower for the azo than for the Luperox.

#### 4. Conclusion:

In this study, a combined approach (photochemical and photothermal) for the NIR polymerization of methacrylate monomers is proposed. The first process is a photochemical polymerization i.e. formation of initiating species by electron transfer between a dye and an iodonium salt whereas the second process is a photothermal polymerization i.e. dissociation of a

thermal initiator with the heat released by the NIR heater. Several dyes, and more particularly cyanine dyes, are proposed with good behavior through NIR light excitation (785 nm, 940 nm and 1064 nm). These dyes allow photopolymerization of methacrylate resin under low light intensity (for example at 785 nm with only 400 mW/cm<sup>2</sup> are necessary to reach high C=C conversion). Thanks to thermal imaging measurements and follow-ups of conversion of C=C, the good synergy between the photochemical NIR system and the photothermal NIR system is presented. Final conversion and polymerization rates are, in most cases, enhanced using the combined system rather than the photochemical or the photothermal one alone. This combined mode will be investigated for the access to highly filled composites in forthcoming papers.

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## TOC GRAPHIC:

### Free Radical polymerization upon Near-Infrared Light, merging photochemical and photothermal initiating methods

