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Article

Thermal Initiators as Additives for Photopolymerization of Methacrylates upon Blue Light

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Abstract: Free radical polymerization is often performed by thermal initiation but also more and more by light-assisted polymerization processes. This second approach allows the polymerization to be carried out under mild conditions (under air, upon blue light exposure, under low light intensity). The aim and the originality of the present paper is to perform photopolymerization in the presence of a thermal initiator, i.e., we can take advantage of the exothermicity of the photopolymerization process to decompose the thermal initiator, leading to enhanced polymerization rates. The performance of the photoinitiating system is discussed in the present study based on real-time Fourier-transform infrared spectroscopy measurements (following the C=C bond content evolution vs. time) and by thermal imaging experiments. Mechanisms of the new system proposed in this work are also fully detailed using cyclic voltammetry, electron spin resonance (ESR) spin trapping, and UV-visible absorption properties.

Keywords: free radical polymerization; heat generation; light-emitting diodes (LEDs); visible light; alkoxyamines

1. Introduction

Polymers are materials that surround us everywhere and constitute the building units of many materials. Their synthesis can involve several mechanisms and, particularly, a free radical polymerization (FRP) pathway, a chain-growth process in which the active site is a free radical. From an industrial point of view, this mechanism is interesting because it can be carried out with relatively undemanding conditions [1]. Thus, a large number of commercial polymers are produced with this type of mechanism for applications ranging from packaging to household plastics, electronics, paints, and coatings [2]. FRP requires three main steps to proceed: Initiation, propagation, and termination. The key step is the generation of the active species. It requires an initiator, for example, an azo-compound or a peroxide that can undergo a bond homolysis, to form free radicals. To perform the homolysis, the system requires energy, which is, most of the time, delivered by heat. However, generation of radicals can also be achieved through light irradiation, and various photoinitiation pathways have been developed [3]. This method of initiation offers several advantages compared to the other initiation strategies due to the properties of light and the light sources involved. First, it is a green method, releasing less solvent and producing polymers under mild conditions (no need to heat

the system, low pressure used). In addition, due to the easiness of turning the light on or off, a spatial and temporal control of the initiation step can be reached; such a behavior is not possible by heating. Thus, development of new initiating systems able to initiate polymerization in such conditions is at the center of numerous research [4].

Methacrylate polymerizations involve the transformation of a π -system (carbon–carbon double bond) into a σ -system (carbon–carbon simple bond) so that some energy is released under the form of heat in the system. Faced with these considerations, this phenomenon of heat production incited us to add a thermal initiator in the resin that could decompose during polymerization, leading to an additional source of initiating radicals and allowing higher final monomer conversions to be reached.

In the proposed system, the heat released during the photopolymerization process will generate additional active species by decomposition of the thermal photoinitiator, boosting the polymerization process. In the present paper, as an originality, a thermal initiator, i.e., an alkoxyamine, has been used in addition to a three-component photoinitiating system based on the dye/iodonium salt/phosphine combination. The three-component photoinitiating system examined in this study has already been proposed for a pure photochemical initiation, with a naphthalimide derivative used as the photoinitiator [5]. This system was capable of efficiently initiating the photopolymerization of methacrylates upon blue light irradiation, under air and with good-to-excellent monomer conversions. Especially, LEDs with low light intensities and with wavelengths greater than UV were used to photoactivate the three-component system, UV being known to be noxious both for humans and for the environment [6]. This approach is of particular interest for applications such as coatings, inks, paints, or 3D-printing, for which high polymerization rates and high monomer conversions should be obtained within a minimum of time.

BlocBuilder[®] MA (whose chemical structure is presented in Figure 1) is an alkoxyamine, which is extensively used as a thermal initiator for the polymerization of methacrylates. Considering its efficiency in FRP, this thermal initiator has been selected as the initiator to be added to our system. The choice of this photoinitiator is also motivated by the following criteria: (1) Homolysis of the C–ON bond by thermal pathways has been reported in precedent works for this compound [7]; (2) BlocBuilder[®] MA is an efficient initiator for the polymerization of our monomer; (3) an extension is possible to living radical polymerization. BlocBuilder[®] MA is a well-known initiator enabling us to initiate a controlled radical polymerization. This polymerization technique is even known as the nitroxide-mediated polymerization (NMP) [8]. (4) BlocBuilder[®] MA exhibits a low temperature of dissociation and (5) this benchmark initiator is easily available at the industrial scale. In this context, BlocBuilder[®] MA appeared to be ideal for our study. Use of BlocBuilder[®] MA in combination with a light-induced polymerization has already been reported in the literature but only in the context of a polymerization carried out upon near-infrared (NIR) light irradiation [9]. In that study, a NIR dye was specifically used as a heat generator, releasing heat upon photoexcitation. As a result of the elevation of temperature, the heat released by the heat generator in the resin could induce the decomposition of the thermal initiator, thus initiating the polymerization process. In the present paper, a completely different approach is used as it is the heat released during the photopolymerization initiated by the three-component system that is responsible for the homolysis of the thermal initiator, providing an additional source of radicals in the course of the polymerization reaction.

Several initiating systems combining a thermal initiating system and a photoinitiating system have already been reported in the literature. For example, a US patent by Muthiah et al. [10] published in 2000 describes a system with a UV initiator combined with a thermal initiator. This mixture formed a dual cure initiating system for powder coating. Traditionally, powder coatings are cured by heat treatment but, as reported in this patent, some substrates such as wood or plastic are heat sensitive. Incorporation of a photoinitiator in a thermic initiating system allowed a significant decrease in the temperature needed to initiate the polymerization process. In 2006, another dual initiating system was patented by Molock et al. [11] for an application in photochromic ophthalmic devices. These devices allow the blocking of UV radiation and protecting of consumers from the sun thanks to the presence of

photochromic dyes. However, these dyes also lead to an incomplete photopolymerization by absorbing the light of the irradiation source used to initiate the polymerization. Thus, the addition of a thermal initiator such as a peroxide could allow a full curing of the resin. However, the heat necessary to finish the polymerization process required a thermal curing time comprising between 1 min and 6 h. As a third example, a dual-cure free radical polymerization was proposed by Retailleau et al. in 2014 [12]. Notably, the authors described a thermal system enabling the polymerization of an acrylate resin to be initiated from the bottom of the sample to the surface. However, the surface being exposed to air, an uncured layer was observed on top due to the contact of the surface with dioxygen. To circumvent this problem, addition of a photoinitiator to cure this upper part of the layer through UV irradiation was proposed. As an advantage of this approach, UV-curing is a particularly fast process so that the polymerization of the surface offered a physical barrier to dioxygen, enhancing the thermal polymerization by limiting the dioxygen inhibition.

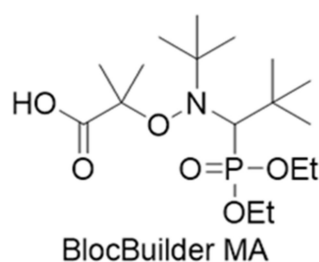


Figure 1. Chemical structure of Blocbuilder® MA.

In the present work, a different approach compared to the previous studies is proposed. Herein, we present the decomposition of a thermal initiator through the heat released by photopolymerization of a high-performance photoinitiating system upon irradiation with a blue LED. The heat produced during the photopolymerization process can enhance the free radical polymerization of acrylates, as depicted in Figure 2. Therefore, photo- and thermal-polymerization are coupled.

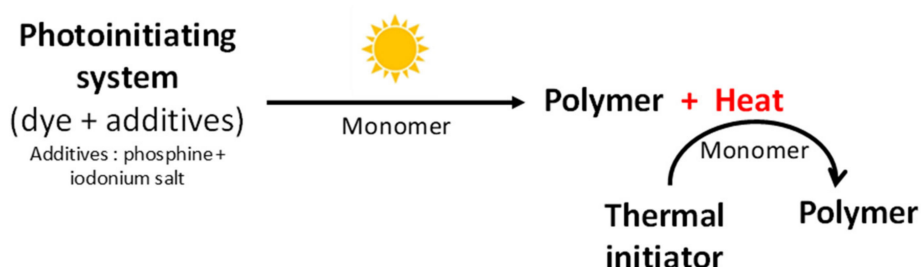


Figure 2. Orthogonal approach between thermal initiation vs. photoinitiation.

The kinetics of photopolymerization are presented and the associated chemical mechanisms are also proposed. To prove the mechanism of the abovementioned reaction, real-time Fourier-transform infrared spectroscopy measurements have been performed during the polymerization process. Heat has been measured thanks to thermal imaging experiments and the initiating system has been fully characterized by UV-visible spectroscopy measurements, differential scanning calorimetry (DSC), and electron spin resonance (ESR) measurements.

2. Materials and Methods

2.1. Chemical Compounds

2.1.1. Commercial Products

The different products used for this study have been used as received, without further purifications. Acetonitrile was purchased from Merck.

2.1.2. Monomer

Two different benchmarked resins have been used for the present study: Trimethylolpropane triacrylate (TMPTA) and Mix-MA (Figure 3). TMPTA has been obtained from Allnex with a viscosity at 25 °C between 0.080 and 0.135 Pa s. Mix-Ma, a resin used as a reference resin, is composed of a mixture of three monomers (33/33/33 wt.%/wt.%/wt.%), namely (2-hydroxypropyl)methacrylate (HPMA), 1,4-butanediol dimethacrylate (1,4-BDDMA), and a urethane dimethacrylate (UDMA). Mix-Ma exhibits a low viscosity of 0.053 Pa s. This resin has been prepared from monomers supplied by Merck. For all different formulations presented in the paper, all weight percentages are related to the resin.

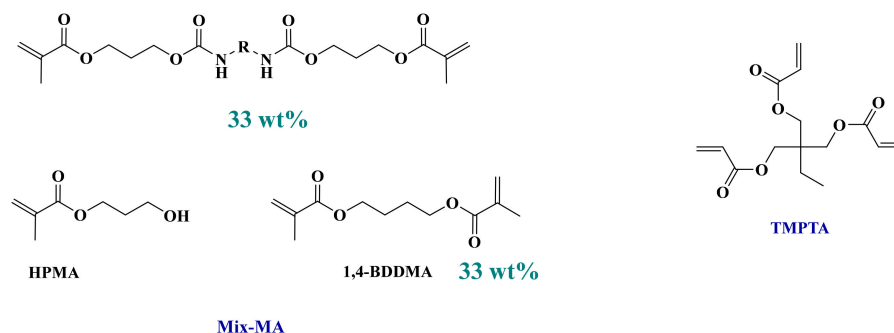


Figure 3. Compositions of the reference resins (Mix-MA and trimethylolpropane triacrylate (TMPTA)).

2.1.3. Additives

The photoinitiating system used in this work has been inspired from that reported in Reference [5] and comprises two additives. The iodonium salt, i.e., *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate ($\text{Ar}_2\text{I}^+/\text{PF}_6^-$ or also Speedcure 938), was obtained from Lambson Ltd., (Wetherby, UK), and a phosphine, 4-(diphenylphosphino)benzoic acid (4-dppba), has been supplied by Tokyo Chemical Industry Co., Ltd., (TCI) Japan. Both components are depicted in Figure 4.

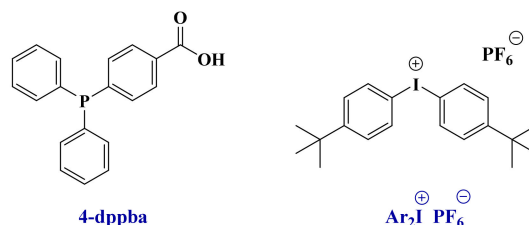


Figure 4. Chemical structures of the additives.

2.1.4. Thermal Initiator

An alkoxyamine, i.e., BlocBuilder[®] MA (Figure 1) was used as the thermal initiator.

2.1.5. Non-Commercial Products

A 1,8-naphthalimide derivative (Napht) has been chosen as the dye. This chromophore has been studied for its efficiency to initiate the free radical photopolymerization of a methacrylate resin in a previous study [5]. The chemical structure of this dye is presented in the Figure 5.

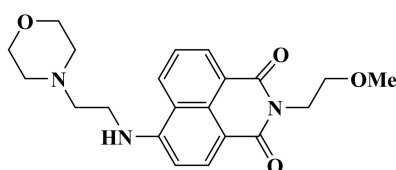


Figure 5. Chemical structure of Napht.

2.2. Irradiation Source

A light-emitting diode (LED) has been used with an irradiation at 405 nm and an incident light intensity at the surface of the sample, which is of 110 mW cm^{-2} . The light source was supplied by Thorlabs (Exeter, UK).

2.3. Free Radical Photopolymerization (FRP)

In order to estimate the initiation ability of the different systems described in the present work, kinetics of the consumption of the characteristic methacrylate C=C bond in the MIX-MA resin (observed at $6100\text{--}6220 \text{ cm}^{-1}$; see in [5]) has been monitored using a real-time Fourier-transform infrared device FTIR 4100 from JASCO (Tokyo, Japan).

The photoinitiating system, mixed in the monomer, is deposited in a 1.4 mm thick mold. The free radical polymerization was performed under air and at room temperature. For all the experiments, recording of the infrared spectra started 10 s before the light was switched on in order to have a baseline for the conversion calculation. Specific conditions for each experiment such as the concentrations of the different compounds in the initiating systems are given in the text and figure captions. More details about the procedure are reported in [13].

2.4. ESR Spin Trapping (ESR-ST) Experiments

The detection and characterization of the generated free radicals have been followed using an ESR-ST device (X-Band spectrometer) from Bruker EMX-Plus (Bruker, Rheinstetten, Germany). ESR-spin trapping of Napht in combination with BlocBuilder[®] MA, $\text{Ar}_2\text{I}^+\text{PF}_6^-$, and 4-dppba in Mix-MA have been carried out directly into the monomer, without use of any solvents and under air. Spectra were recorded after 15 s of the irradiation starting with the LED@405 nm ($I_0 = 110 \text{ mW cm}^{-2}$). More details about the experimental procedures and the spectra simulation with the PEST WINSIM program are given in [14,15].

2.5. Thermal Measurements

Thermal release of the system has been monitored using an infrared thermal imaging camera obtained by Fluke TiX500 (Wilmington, CA, USA). These measurements were analyzed using Fluke SmartView4.1 software and a script written in Python language enabling the extraction of the maximal temperature vs. time. Conversion of the C=C characteristic band recording and thermal measurement were performed simultaneously using an experimental set-up described in detail in [16].

2.6. Differential Scanning Calorimetric (DSC) Measurements

The thermal polymerization has been evaluated by DSC with a Mettler-Toledo DSC 1 differential scanning calorimeter (Viroflay, France). In addition, 10 mg of Mix-MA with thermal initiator (2 wt.%) formulations was inserted in an aluminum 100 μL pan. Thermal polymerization was performed from 0 to 200 °C at a heating rate of 10 °C/min under nitrogen flow (100 mL/min).

3. Results

3.1. Photopolymerization Results

In a recent work [5], we proposed a three-component photoinitiating system for the photopolymerization of methacrylates upon 405 nm LED irradiation. The system described was based on a three-component system comprising a 1,8-naphthalimide derivative (noted Napht-B1 in the reference work) as the photoinitiator, an iodonium salt, and a dioxygen scavenger (a phosphine) for a photopolymerization carried out under blue light. The kinetics of polymerization using this system was very good, showing its high performance to initiate polymerization under mild irradiation conditions [5].

To determine the ability of this remarkable photoinitiating system to decompose a thermal initiator, temperature measurements were carried out during the photopolymerization process. Variation in the reaction temperature vs. the polymerization time is presented in Figure 6. As anticipated, the photopolymerization involves the conversion of a π -system (carbon–carbon double bond) into a σ -system (carbon–carbon single bond) so that this reaction is particularly exothermic. The maximal temperature measured by thermal imaging was 90 °C. From this observation came the idea to add a thermal initiator, which can be homolyzed by the heat released through the photopolymerization process.

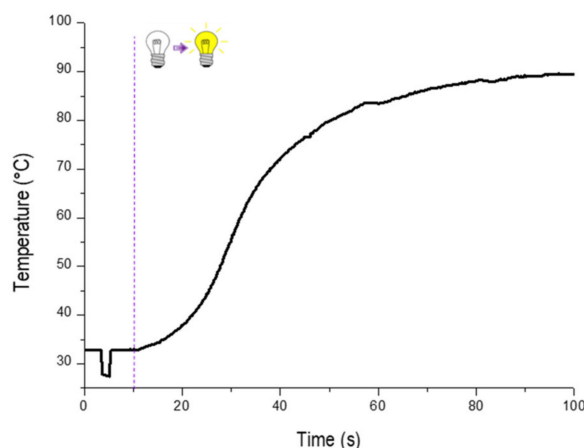


Figure 6. Thermal imaging photopolymerization follow-ups (temperature vs. irradiation time; 1.4 mm sample) under air upon LED@405 nm (110 mW cm^{-2}) irradiation for Mix-MA in the presence of Napht (0.1 wt.%), $\text{Ar}_2\text{I}^+\text{PF}_6^-$ (1.5 wt.%), and 4-dppba (0.5 wt.%); irradiation starts after 10 s.

The heat-activated initiator BlocBuilder[®]-MA has been chosen because of its low dissociation temperature. Its ability to initiate the free radical polymerization of methacrylates has been studied such as in [7]. With this initiator, the temperature needed for successful polymerization of methyl methacrylate is below 80 °C according to [17]. The set temperature necessary to perform the homolysis of the thermal initiator and, by consequence, the free radical polymerization depends on the resin chosen [2]. Consequently, DSC measurements were performed to evaluate the range of decomposition of BlocBuilder[®] in Mix-MA. Next, 2 wt.% of the thermal initiator was mixed with the Mix-MA resin and the resulting formulation was inserted in a pan of 100 μL . The temperature was made to rise under nitrogen flow. According to the results presented in Figure 7, the decomposition of BlocBuilder[®] MA was found to be between 50 and 70 °C. We concluded that the heat released during the photopolymerization process (Figure 6) was sufficient to perform the homolysis of the benchmark BlocBuilder[®] MA. The selected monomers/polymers are stable below 200 °C (from thermogravimetric analysis). Therefore, the proposed approach is fully possible without degradation of the polymer.

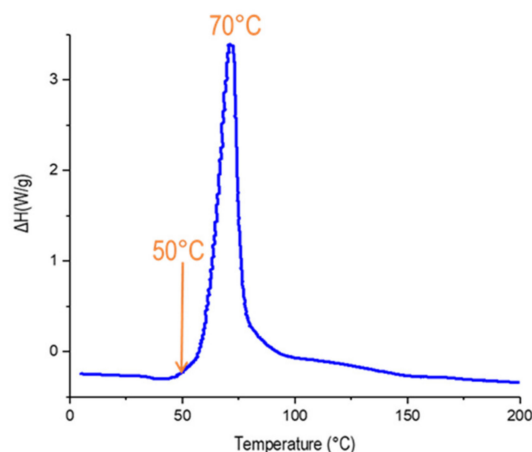


Figure 7. DCS evaluation of the thermal initiating ability of Blocbuilder[®] MA (2 wt.%) in Mix-MA; under N₂ (100 mL/min); 10 °C/min; 0–200 °C.

3.2. Simultaneous Thermal Imaging and Conversion Measurements

In the following section, experiments were done using the photoinitiating system presented in [5], i.e., the photosensitizer Napht (0.1 wt.%), the iodonium salt Ar₂I⁺/PF₆⁻ (1.5 wt.%), and the phosphine 4-dppba (0.5 wt.%) in combination with BlocBuilder[®] MA (2 wt.%) used as the thermal initiator. The photopolymerization experiments were performed at 405 nm ($I = 110 \text{ mW cm}^{-2}$). Specific conditions will be specified for each experiment.

First of all, simultaneous real-time Fourier transform infrared spectroscopy (RT-FTIR) and thermal imaging photopolymerization were performed on the four-component system (see Figure 8).

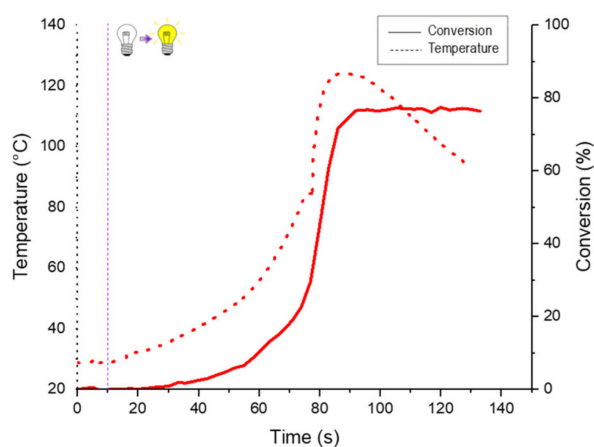


Figure 8. Simultaneous RT-FTIR (C=C conversion vs. irradiation time) and thermal imaging (temperature vs. irradiation time) photopolymerization follow-ups (1.4 mm sample) under air upon LED@405 nm irradiation for Mix-MA in the presence of Napht (0.1 wt.%), Ar₂I⁺PF₆⁻ (1.5 wt.%), 4-dppba (0.5 wt.%), and Blocbuilder[®] MA (2 wt.%); irradiation starts after 10 s.

First of all, the relation existing between the C=C conversion and the temperature of the sample is clearly evidenced. A good correlation between the conversion curve (plain curve) and the temperature rise (dot curve) was found. Interestingly, as soon as the decomposition temperature of BlocBuilder[®] MA is reached (50 °C; see Figure 7), a rapid increase in the kinetics of polymerization is observed. Thus, we proposed a two-step mechanism (illustrated in Figure 9) with (1) a photoinitiation step and (2) a thermal step with the release of additional initiating species in the resin due to the decomposition of the thermal initiator. The photoinitiation step is possible through blue light irradiation, as proposed in [5], which leads to an exothermic polymerization of the resin (Figure 6). The temperature rise thus allows the homolysis of BlocBuilder[®] MA. A higher final conversion is reached for the combined

photochemical and thermal processes (77%—Figure 8) compared to a pure photochemical process (without Blocbuilder) (64% of final acrylate function conversion), clearly showing that the additional initiating radicals are useful for obtaining better curing.

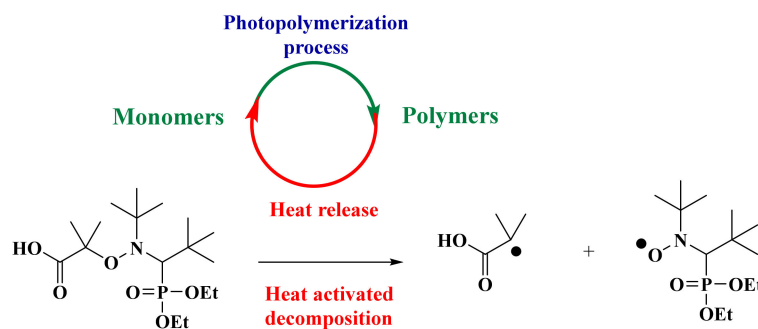


Figure 9. Photopolymerization mechanism.

3.3. Blank Experiments

The initiation step of the polymerization process proposed in Figure 9 is possible through light irradiation. For a pure photopolymerization process, a photoinitiator is required. As the alkoxyamine selected in this work does not absorb blue light, no polymerization is possible without the photoinitiator (here, Napht). This hypothesis has been fully confirmed by RT-FTIR measurements as reported in Figure 10.

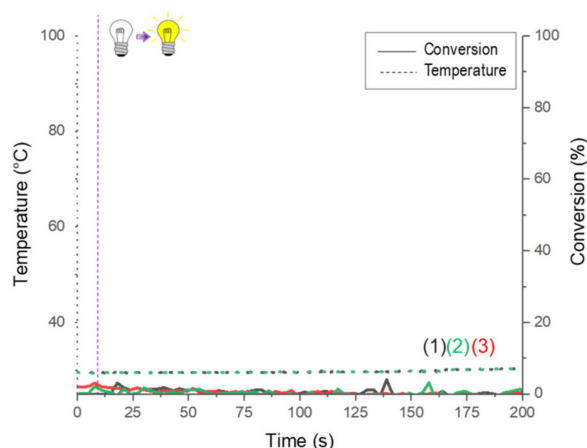


Figure 10. Simultaneous RT-FTIR/thermal imaging photopolymerization kinetics (C=C conversion vs. irradiation time and temperature vs. irradiation time; 1.4 mm sample) under air upon LED@405 nm irradiation for Mix-MA in the presence of (1) monomer alone, (2) Blocbuilder[®]-MA (2 wt.%), and (3) Ar₂I⁺PF₆⁻ (1.5 wt.%), 4-dppba (0.5 wt.%), and Blocbuilder[®]-MA (2 wt.%); the irradiation starts after 10 s.

Irradiation of the monomer alone (curve (1) in Figure 10) or of BlocBuilder[®]MA into the monomer (curve (2) in Figure 10) does not lead to polymerization. During the time of the recording (200 s), no polymerization is observed with the iodonium salt and the phosphine without Napht upon irradiation with blue light, as evidenced with the curve (3) in Figure 10. However, for longer irradiation times, a very slight polymerization process was observed due to the formation of a charge transfer complex (CTC). This latter CTC absorbs at 405 nm, as reported in [18]. However, this reaction is very slow compared to the polymerization initiated by the naphthalimide derivative.

The second step of the chemical mechanisms proposed in Figure 9 also releases initiating species in the system. In our set-up conditions, the generation of nitroxide radicals is only possible if the temperature of the sample is high enough. Similar conditions of photopolymerization in combination

with BlocBuilder[®] MA have been previously reported in Reference [19]. In this former work, the polymerization of Mix-MA by this thermal initiator was issued by the heat released by the NIR heater upon photoexcitation, and not from the heat released by the photoinitiated polymerization as in the present case. In order to prove that none of the components used in the present article could act as a light-to-heat converter upon blue light irradiation, temperature measurements upon irradiation at 405 nm and under air were performed with the different additives. These profiles are available in Supporting Information (Figure S1).

4. Discussion

To discuss the results obtained above, the chemical mechanisms must be established.

4.1. ESR-ST Experiments

The polymerization process of the system presented in this paper is based on the formation of additional free radicals in the presence of a thermal initiator. The detection and characterization of the free radical species generated during the polymerization process are possible by ESR-ST experiments. In [5], the formation of aryl radicals has been reported by irradiation of the three-component photoinitiating system comprising the naphthalimide derivative in combination with the iodonium salt and the phosphine, and the formation of aryl radicals has been proven in the aforementioned article by ESR-ST experiments (Figure 9).

The reaction presented in Figure 9 proposes the formation of carbon-centered radicals as the second initiating species. Concomitantly, nitroxide radicals are also generated, and these radicals are also observable by ESR experiments. To support the proposed mechanism, ESR-ST experiments of the photoinitiating system in combination with BlocBuilder[®] MA have been performed directly in the monomer. Indeed, the formation of these radicals is due to the thermal homolysis of the alkoxyamine. The heat comes from the polymerization process. Thus, it was not possible to perform the experiments in acetonitrile as it is usually done. Here, ESR-ST experiments and polymerization upon 405 nm were performed simultaneously. The ESR-ST experiment spectrum presented in Figure 11 corresponds to the observation after 15 s of irradiation. Two radical species are observed and their chemical structures have been simulated. The simulation presented in Figure 11b corresponds to the presence of both species simultaneously, and their respective ratios have been predicted with the PEST WINSIM program. The first radical observed (shown in Figure 11a) is a nitroxide radical and, more particularly, the acyclic β -phosphorylated nitroxide SG1 (N-tert-butyl-N-[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]-N-oxyl nitroxide) radical. This is in excellent agreement with the simulated spectra (e.g., $a_N = 13.7$ G; $a_P = 45.7$ G; Figure 11b [20]). These data can be linked to the lower bond dissociation energy (BDE) of the C–O bond than those of the N–O bond (BDE ~ 25.74 kcal/mol vs. ~ 39.37 kcal/mol calculated at UB3LYP/6-31G* level theory [21]). These results prove that the cleavage of the C–O bond is more favorable than the N–O. The second species observed correspond to peroxy radicals ROO• (not trapped by PBN) and are in agreement with the simulated spectra. This corresponds to 25% of radicals detected in the mixture. Without Blocbuilder, no nitroxide radicals are observed and only peroxy (ROO^o) is detected.

4.2. Conclusion about Mechanistic Aspects

In previous sections, the different experiments proposed confirmed the two first hypotheses:

- the polymerization is induced by light irradiation
- some heat is released by the polymerization process and this latter is capable of initiating the dissociation of a thermal initiator
- In the present section, a third hypothesis has been confirmed:
- the thermal initiator dissociation enhances the polymerization process by the creation of additional initiating species.

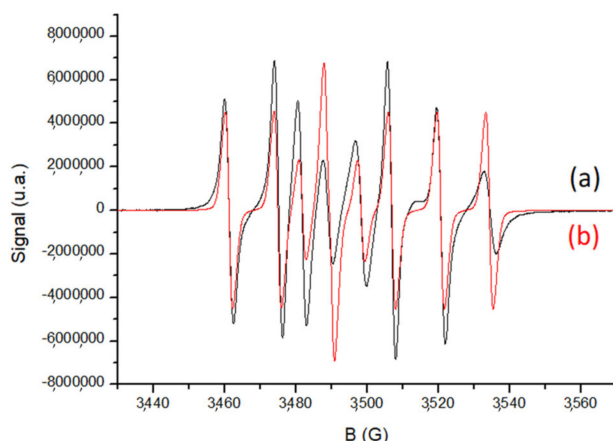
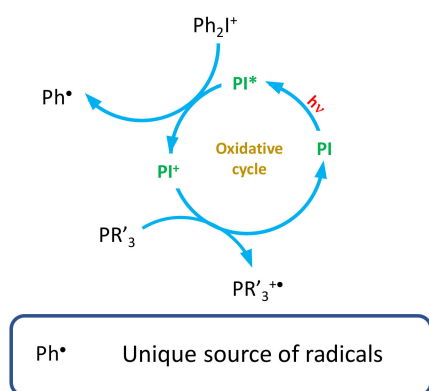


Figure 11. ESR-spin trapping spectrum of Napht in combination with Blocbuilder[®]MA Ar₂I⁺PF₆⁻ and 4-dppba in Mix-MA; under air after 15 s of irradiation with an LED@405 nm (110 mW cm⁻²) exposure: (a) Experimental; (b) Simulation of the ESR-spin trapping spectrum of 75% of SG1 radicals (*a*_N = 13.7 g; *a*_P = 45.7 g) and 25% of ROO• (*a*_H = 8.2 G; *G* = 2.011).

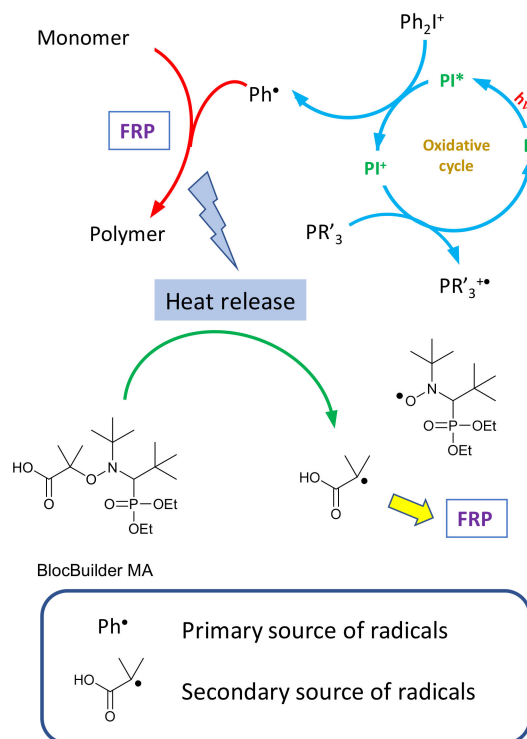
A global scheme to compare pure photochemical processes with photo- and thermal-combined processes is given in Figure 12.

Photochemical process



(a)

Photo and thermal combined process



(b)

Figure 12. Comparison of pure photochemical (a) and combined photochemical and photothermal processes (b).

4.3. Comparison with Other Monomers

All the previous experiments have been performed in the benchmarked resin (Mix-MA). To expand the scope of application, the polymerization performances have also been checked in TMPTA. The influence of the choice of monomer on heat release to the surroundings has already been discussed

in [20] but for the NIR heater approach. More particularly, in this latter paper, it has been proven that the viscosity of the monomer is a key factor for the diffusion of heat to its surroundings which has a strong influence on the dissociation of the thermal initiator. It has been observed that the increase in the viscosity of the monomer leads to higher polymerization temperatures. The values of the viscosities for the monomers used in the present study are 0.135 and 0.053 Pa s for TMPTA and Mix-MA, respectively. TMPTA is more viscous than Mix-MA, and temperatures measured in the same conditions are higher for TMPTA than for Mix-MA.

However, it should be noticed that in [20], the creation of initiating radicals only relied on the decomposition of the thermal initiator upon NIR excitation, similar to the reaction reported in Figure 9. Here, the mechanisms proposed for radical generation are totally different. Radicals are first generated by a pure photochemical mechanism (Figure 9), and a second source of radicals originate from the decomposition of the thermal initiator. The first observation in Figure 13 is that under the temperature of dissociation of BlocBuilder[®] MA (between 50 and 70 °C, in orange in the figure and in concordance with DSC experiments, Figure 7), the kinetics for the two monomers is the same. As soon as the dissociation temperature is reached, a faster polymerization in TMPTA than in Mix-MA was observed. There are two reasons for this: First, as observed in [19], the more viscous the monomer is, the less the heat is diffused and the faster the BlocBuilder[®] MA is dissociated. Secondly, acrylates are known to be more reactive than methacrylates, as reported in [22]. Thus, the final conversion is reached faster in TMPTA than in Mix-MA. However, the final reactive function conversion remains the same. Other interesting works on photopolymerization reactions can be found in, e.g., [23–25].

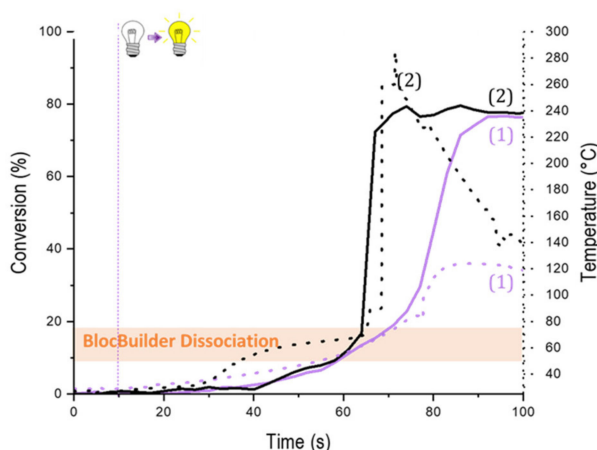


Figure 13. Simultaneous RT-FTIR/thermal imaging photopolymerization follow-ups (C=C conversion vs. irradiation time and temperature vs. irradiation time; 1.4 mm sample) under air upon LED@405 nm irradiation in the presence of Napht (0.1 wt.%), Ar₂I⁺PF₆⁻ (1.5 wt.%), 4-dppba (0.5 wt.%), and Blocbuilder[®]-MA (2 wt.%); in (1) Mix-MA; (2) TMPTA; the irradiation starts after 10 s.

5. Conclusions

To conclude, an original use of a thermal initiator for methacrylate photosensitive formulation is presented in this paper. BlocBuilder[®] MA was employed as an additive in the range of 2 wt.% for a photoinitiating system based on a 1,8-naphthalimide derivative, an iodonium salt, and a phosphine. Photopolymerization upon blue light irradiation was followed by RT-FTIR to prove the conversion of the C=C double bond of the monomer into a highly cross-linked polymer. Very good conversions and interesting kinetics are observed using this system compared to the system without the alkoxyamine. The heat released during the photopolymerization process will generate additional active species by decomposition of the thermal photoinitiator, boosting the polymerization process. As most of the polymerization processes are exothermic reactions, we could imagine that using a thermal initiator as an additive for the photopolymerization process can be used at different wavelengths of irradiation or for other exothermic polymerization mechanisms such as cationic polymerizations.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/10/5/478/s1>, Figure S1: Temperature profiles of Mix-MA under air (temperature of the sample vs. irradiation time) in the presence of (1) monomer alone (2 wt.%), (2) Napht (0.1 wt.%), (3) Ar₂I⁺/PF₆⁻ (1.5 wt.%), (4) BlocBuilder-MA (2 wt.%), (5) 4-dppba (0.5 wt.%); LED@405 nm (110 mW cm⁻²); thickness = 10 mm; under air.

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References

1. Information Resources Management Association. *Materials Science and Engineering: Concepts, Methodologies, Tools, and Applications: Concepts, Methodologies, Tools, and Applications*; IGI Global: Hershey, PA, USA, 2017.
2. Moad, G.; Solomon, D.H. *The Chemistry of Radical Polymerization*; Elsevier Science: Amsterdam, The Netherlands, 2005.
3. Fouassier, J.P.; Lalevée, J. *Photoinitiators for Polymer Synthesis: Scope, Reactivity, and Efficiency*; Wiley: Hoboken, NJ, USA, 2012.
4. Andrzejewska, E.; Grajek, K. Recent advances in photo-induced free-radical polymerization. *MOJ Polym. Sci.* **2017**, *1*, 58–60. [[CrossRef](#)]
5. Bonardi, A.-H.; Zahouily, S.; Dietlin, C.; Graff, B.; Morlet-Savary, F.; Ibrahim-Ouali, M.; Gignes, D.; Hoffmann, N.; Dumur, F.; Lalevée, J. New 1,8-naphthalimide derivatives as photoinitiators for free-radical polymerization upon visible light. *Catalysts* **2019**, *9*, 637. [[CrossRef](#)]
6. Moseley, H. Ultraviolet and laser radiation safety. *Phys. Med. Biol.* **1994**, *39*, 1765–1799. [[CrossRef](#)] [[PubMed](#)]
7. Gignes, D.; Dufils, P.-E.; Glé, D.; Bertin, D.; Lefay, C.; Guillauneuf, Y. Intermolecular radical 1,2-addition of the BlocBuilder MA alkoxyamine onto activated olefins: A versatile tool for the synthesis of complex macromolecular architecture. *Polym. Chem.* **2011**, *2*, 1624–1631. [[CrossRef](#)]
8. Grishin, D.F.; Grishin, I.D. Mechanisms of Polymer Polymerization. In *Polymeric Materials for Clean Water*; Das, R., Ed.; Springer Series on Polymer and Composite Materials; Springer International Publishing: Cham, Switzerland, 2019; pp. 7–58.
9. Bonardi, A.-H.; Bonardi, F.; Morlet-Savary, F.; Dietlin, C.; Noirbent, G.; Grant, T.M.; Fouassier, J.-P.; Dumur, F.; Lessard, B.H.; Gignes, D.; et al. Photoinduced thermal polymerization reactions. *Macromolecules* **2018**, *51*, 8808–8820. [[CrossRef](#)]
10. Muthiah, J.; Daly, A.T.; Haley, R.P.; Kozlowski, J.J. Dual Thermal and Ultraviolet Curable Powder Coatings. Patent US6017640A, 25 January 2000.
11. Molock, F.; Cullerton, G.; Mahadevan, S. Photochromic Ophthalmic Devices Made with Dual Initiator System. Patent US20060227287A1, 12 October 2006.
12. Retailleau, M.; Ibrahim, A.; Allonas, X. Dual-cure photochemical/thermal polymerization of acrylates: A photoassisted process at low light intensity. *Polym. Chem.* **2014**, *5*, 6503–6509. [[CrossRef](#)]
13. Lalevée, J.; Blanchard, N.; Tehfe, M.-A.; Peter, M.; Morlet-Savary, F.; Fouassier, J.P. A novel photopolymerization initiating system based on an iridium complex photocatalyst. *Macromol. Rapid Commun.* **2011**, *32*, 917–920. [[CrossRef](#)] [[PubMed](#)]
14. Tehfe, M.-A.; Lalevée, J.; Gignes, D.; Fouassier, J.P. Green chemistry: Sunlight-induced cationic polymerization of renewable epoxy monomers under air. *Macromolecules* **2010**, *43*, 1364–1370. [[CrossRef](#)]
15. Duling, D.R. Simulation of multiple isotropic spin-trap EPR spectra. *J. Magn. Reson. B* **1994**, *104*, 105–110. [[CrossRef](#)] [[PubMed](#)]
16. Garra, P.; Bonardi, A.-H.; Baralle, A.; Al Mousawi, A.; Bonardi, F.; Dietlin, C.; Morlet-Savary, F.; Fouassier, J.-P.; Lalevée, J. Monitoring photopolymerization reactions through thermal imaging: A unique tool for the real-time follow-up of thick samples, 3d printing, and composites. *J. Polym. Sci. Part A: Polym. Chem.* **2018**, *56*, 889–899. [[CrossRef](#)]

17. Nicolas, J.; Brusseau, S.; Charleux, B. A minimal amount of acrylonitrile turns the nitroxide-mediated polymerization of methyl methacrylate into an almost ideal controlled/living system. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *48*, 34–47. [[CrossRef](#)]
18. Garra, P.; Graff, B.; Morlet-Savary, F.; Dietlin, C.; Becht, J.-M.; Fouassier, J.-P.; Lalevée, J. Charge transfer complexes as pan-scaled photoinitiating systems: From 50 μm 3d printed polymers at 405 nm to extremely deep photopolymerization (31 cm). *Macromolecules* **2018**, *51*, 57–70. [[CrossRef](#)]
19. Bonardi, A.H.; Bonardi, F.; Dumur, F.; Gimes, D.; Fouassier, J.P.; Lalevee, J. Fillers as heaters for photothermal polymerization upon NIR light. *Macromol. Rapid Commun.* **2019**, *40*, 1900495. [[CrossRef](#)] [[PubMed](#)]
20. Guillaneuf, Y.; Bertin, D.; Gimes, D.; Versace, D.-L.; Lalevée, J.; Fouassier, J.-P. Toward nitroxide-mediated photopolymerization. *Macromolecules* **2010**, *43*, 2204–2212. [[CrossRef](#)]
21. Poole, C.P.J.; Farach, H.A. (Eds.) *Handbook of Electron Spin Resonance*; Springer: New York, NY, USA, 1999.
22. Bevington, J.C.; Harris, D.O. Reactivities of acrylates and methacrylates. *J. Polym. Sci. Part B: Polym. Lett.* **1967**, *5*, 799–802. [[CrossRef](#)]
23. Msaadi, R.; Yilmaz, G.; Allushi, A.; Hamadi, S.; Ammar, S.; Chehimi, M.M.; Yagci, Y. Highly selective copper ion imprinted clay/polymer nanocomposites prepared by visible light initiated radical photopolymerization. *Polymers* **2019**, *11*, 286. [[CrossRef](#)] [[PubMed](#)]
24. Li, Z.; Zou, X.; Shi, F.; Liu, R.; Yagci, Y. Highly efficient dandelion-like near-infrared light photoinitiator for free radical and thiol-ene photopolymerizations. *Nat. Commun.* **2019**, *10*, 3560. [[CrossRef](#)] [[PubMed](#)]
25. Cao, Q.; Heil, T.; Kumru, B.; Antonietti, M.; Schmidt, B.V.K. Visible-light induced emulsion photopolymerization with carbon nitride as a stabilizer and photoinitiator. *Polym. Chem.* **2019**, *10*, 5315–5323. [[CrossRef](#)]



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