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Near-infrared light for polymer re-shaping and re-processing applications

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Abstract

The shaping and reprocessing of polymers are usually associated with strong energetic costs, strongly limiting their practical usage. In this paper, a new approach is proposed based on a NIR activation of the material in presence of a NIR heater for a highly efficient process upon ecofriendly NIR light emitting diodes irradiation. Markedly, due to this light-triggered process, a spatial control of the shaping/reprocessing behavior can be obtained *i.e.* only the needed parts are irradiated preventing a heating of all the sample. In this work, different thermoplastics are reshaped or reprocessed due to NIR activation in presence of an organic NIR dye used as heater. As other examples of photothermal treatment upon NIR light, the on-demand dehydration of polyethylene glycol (PEG)-based hydrogels are also provided. All the processes are followed in real time by thermal imaging camera.

1. Introduction

Free-radical polymerization (FRP) has been widely studied since its discovery one century ago.[1,2] However, the development of environmentally friendly processes has been at the core of debates with the awareness of the global warming some decades ago. In this context, the use of light to induce FRP, called photopolymerization, has been the first thought to overcome hard polymerization conditions. In fact, photopolymerization offers noteworthy benefits over conventional FRP approaches. From an environmental perspective, the energy consumption and the release of volatile compounds are highly reduced. Moreover, photopolymerizations are quite fast and require little space (e.g. use in dental materials). However, UV-light includes some severe drawbacks. In such cases, eyes and skin can be damaged and ozone is produced by wavelengths under 250 nm which is deleterious for both health and environment. For these reasons, photopolymerization induced by visible[3] and near-infrared light[4,5] has been more and more reported in the literature during the last years.[6]

In this context of safe and ecofriendly processes, Near-infrared (NIR) light possesses many strengths. First, NIR wavelengths are highly penetrating into polymers in comparison with shorter wavelengths.[7] Second, the light-to-heat conversion is known to be highly efficient in the NIR range (called a photothermal effect). Third, this photothermal effect can be spatially controlled in the irradiating areas.[8] Moreover, this latter effect can be activated on demand by turning on or off the light source. Finally, NIR wavelengths are less dangerous for health and these light sources are usually more efficient than the UV ones. For all of these strengths and with all of the actions taken tending towards greater safety and environment protection, NIR light will probably be used in more and more fields in the future. It is already used for a few years in some fields such as biology with bioimaging applications [9,10], chemistry through photocatalysis[11,12], medicine with photothermal therapy[13] and materials through self-healing applications using graphene oxide[14] or nanoparticles[15].

Especially, NIR light could be used for the shaping of polymers. Indeed, NIR light is used for polymer synthesis but not really for the reprocessing of polymers. However, the light-to-heat conversion provided by an efficient NIR system and the associated spatial control offer attractive perspectives. Indeed, the polymer reprocessing is mainly carried out over thermal treatments. Besides, smart materials with shape memory ability have granted

more and more attention in the past few years.[16,17] More specifically, the shape memory ability of hydrogels are particularly studied[18] due to their potential biomedical applications.[19] Indeed, the elasticity conferred by the partial rigidity and the non-toxicity of hydrogels are of great interest in such applications, notably for the controlled release of the active substance in the body. Some studies have already reported the interest of NIR light in hydrogels to achieve a thermal response but this latter is still not fully optimized.[20,21,22]

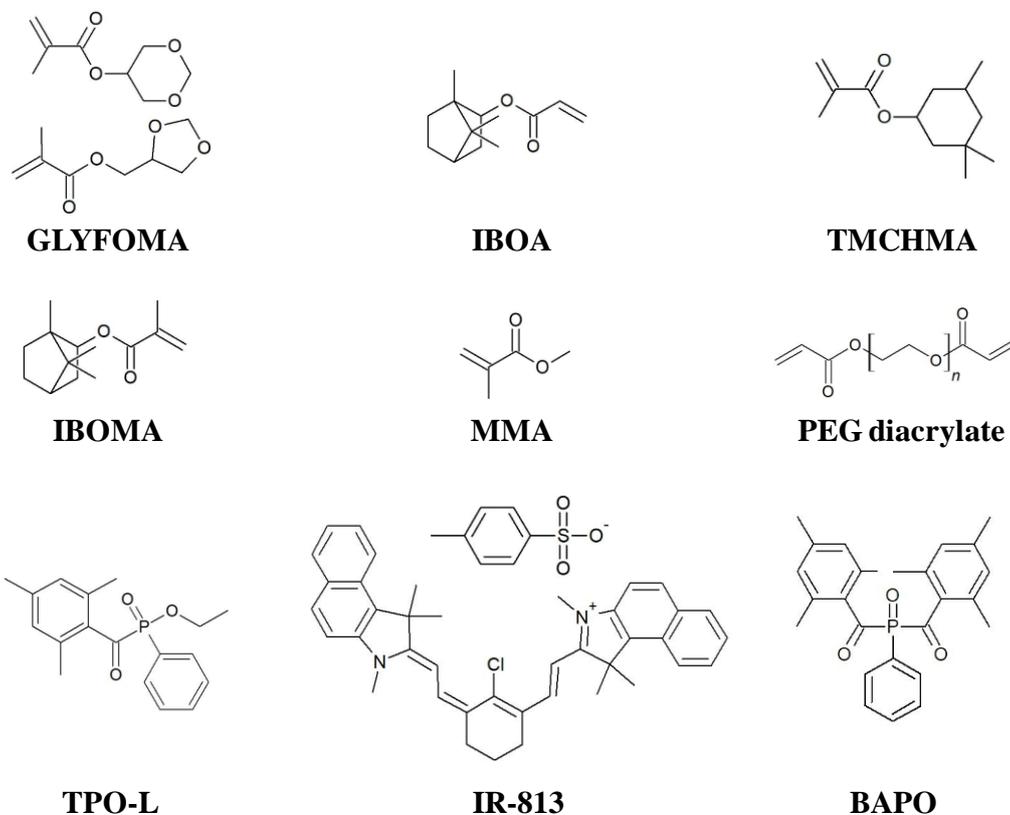
In a previous study, we proposed the use of NIR organic dyes (fully soluble in the polymers) to generate a strong photothermal effect.[8] Indeed, controllable temperatures could be reached by the polymer under NIR light compared to graphene oxide and nanoparticles often used to produce this photothermal effect.[14,15] In the present study, we used the photothermal effect produced by a NIR organic dye in-situ embedded in a thermoplastic polymer or a hydrogel for re-processing applications. Indeed, polymers could be shaped under a short irradiation period with a specific NIR light. This shaping was fully reversible on demand by re-irradiating upon NIR light. Furthermore, the NIR dye has been used in hydrogel for shape memory experiments. By converting light to heat in the hydrogels, high temperatures could be reached to quickly remove the water from samples by dehydration. Since hydrogels are swelled by water absorption, the dehydration led the samples to return their initial shapes.

2. Experimental section

2.1. Chemical compounds

Isobornyl methacrylate (IBOMA), 3,3,5-trimethyl cyclohexyl methacrylate (TMCHMA) and polyethylene glycol diacrylate (SR610) were obtained from Sartomer-Europe, *bis*(2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) and ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L) were purchased from Lambson Ltd (UK), IR-813 *p*-toluenesulfonate (IR-813) was supplied from Tokyo Chemical Industry (TCI-Europe), MMA and crayvallac SLT were provided from Arkema, glycerol formal methacrylate (Glyfoma) was obtained from Evonik and isobornyl acrylate (IBOA) came from Allnex.

Chemical structures of these molecules are presented in the Scheme 1, except that of the crayvallac SLT which was used as a thickener in Glyfoma formulations.



Scheme 1. Chemical structures of monomers (Glyfoma, IBOA, TMCHMA, IBOMA, MMA and PEG diacrylate), NIR heater (IR-813) and photoinitiators (TPO-L, BAPO) used in this study.

2.2. Preparation of polymers

For the preparation of thermoplastics, monofunctional monomers were selected and the thermoplastics were generated by a photopolymerization process. The photoinitiator and the NIR heater (IR-813) were added in the formulation and for Glyfoma, a thickener (crayvallac SLT) agent was used to increase the viscosity of the sample. Finally, the samples were irradiated 10 minutes upon LED @405 nm in a silicone mold covered by a polypropylene film to avoid the oxygen inhibition.

For hydrogels preparation, a PEG-diacrylate leading to a PEG based polymer was used. Then, the photoinitiator and the NIR heater (IR-813) were added in the formulation. Afterwards, a computer-controlled and programmed laser diode with a spot size of about 50 μm was used at 405 nm ($110 \text{ mW}\cdot\text{cm}^{-2}$) for a spatially controlled irradiation to produce

specific 3D patterns deposited on a homemade resin tank. The thickness of the final polymer was 1 mm.

For Glyfoma, IBOA, IBOMA, TMCHMA and PEG diacrylate, 1%_{wt} of BAPO as photoinitiator was used and the LED irradiance was 500 mW.cm⁻² whereas 5%_{wt} of TPO-L was used as photoinitiator for MMA and the LED irradiance was 1 W.cm⁻².

2.3. RT-FTIR Spectroscopy

In order to know the (meth)acrylate function conversion of the photosensitive formulations, photopolymerization experiments have been carried out in a mold at room temperature upon irradiation with a laser diode at 405 nm (450 mW.cm⁻²). The mold was covered by a polypropylene film to avoid the oxygen inhibition. A Jasco 6600 real-time Fourier transformed infrared spectrometer (RT-FTIR) was used to follow in real time the C=C acrylate double bond conversion between 6100 and 6200 cm⁻¹ during the irradiation time. Final polymers have a thickness of 2 mm.

2.4. Thermal imaging camera

The sample temperatures reached during the NIR irradiation experiments performed in this study have been followed by the Fluke TiX500 infrared thermal imaging camera. Irradiations with NIR light LEDs were done at a distance of 4 cm with the LED@810 nm and 6 cm with the LED@850 nm (NIR LEDs from Thorlabs).

2.5. Phoseon LEDs panel

For larger irradiations at 810 nm, a Phoseon LEDs panel prototype was used (Figure S1, Supporting Information). The light intensity of this prototype goes up to 9W. As shown Figure S1A, there are 6 cm between the LEDs panel and the sample (Figure S1B).

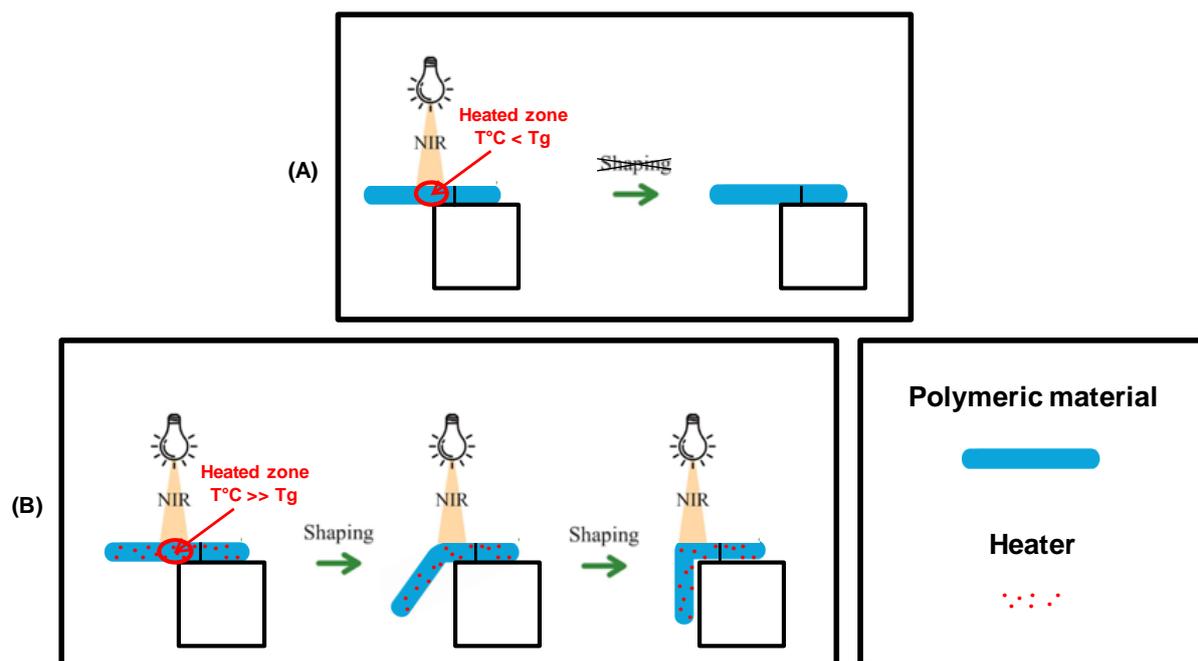
2.6. Differential Scanning Calorimetry (DSC)

To determine the glass transition temperature (T_g) of polymers, the DSC Mettler Toledo DSC1 and the Star software were used. A first run was performed out to erase their thermal background and a second one was carried out to determine the T_g with the tangent of the transition phase. DSC tests were performed from 0°C to 200°C under air with a rise of temperature of 10 K.min⁻¹.

3. Results and Discussion

3.1. The reprocessing of thermoplastics

Scheme 2 summarizes the idea of using a NIR heater in-situ embedded in a thermoplastic material. Since the NIR heater is not involved in the polymerization process, it can still be used to photothermally activate the generated polymers upon NIR light. The photopolymerization profiles of monomers used in this study are given in Supporting Information (Figure S2-S6). In absence of NIR heater, the polymeric material temperature should not exceed the glass transition temperature (T_g) upon NIR light (See Scheme 2A) whereas this T_g should be reached in the presence of heater (Scheme 2B). Therefore, we can expect the NIR activation of thermoplastics with in-situ embedded heater to allow an efficient shaping/reprocessing of the polymer.



Scheme 2. (A) Behavior of heater-free polymer upon NIR irradiation. (B) Shaping/reprocessing of a polymer containing a NIR heater upon NIR irradiation.

Irradiation of a Glyfoma-based polymer upon NIR light was recorded by thermal imaging camera without NIR-heater (See Figure 1A) and compared to the situation in

presence of NIR heater (Figure 1B). Videos from which the thermal imaging camera pictures were extracted are respectively given in Video 1 and Video 2 in Supporting Information. As expected, the shaping of the heater-free sample was not possible and a maximal temperature of 55°C could only be reached. Markedly, the shape could be easily modified in the presence of heater (See Figure 1B). These results are corroborated by temperature curves presented in Figure 1C. Indeed, the temperature reached by the NIR heater-free polymer is far below the T_g which makes the reshaping impossible. In contrast, the temperature reached by the polymer containing heater is much higher than the T_g so the shaping can theoretically be performed.

Then, this shaping/reprocessing behavior has been investigated for different thermoplastics based on other (meth)acrylate monomers (for IBOA, IBOMA, TMCHMA, MMA based polymers) and their behaviors upon NIR light are given in Figures S7-S10. In the absence of heater, the shaping of all of these polymers was impossible. Videos from which the thermal imaging camera pictures were extracted are respectively given in Video 3, Video 4, Video 5 and Video 6. As for Glyfoma-based polymers, IBOA, IBOMA, TMCHMA and MMA-based polymers could however be shaped under 1 minute of NIR irradiation in the presence of heater (Videos 7-9, Supporting Information). For MMA, a partial degradation was noticed. However, the LED irradiance can be smartly controlled to avoid this degradation and achieve the folding.

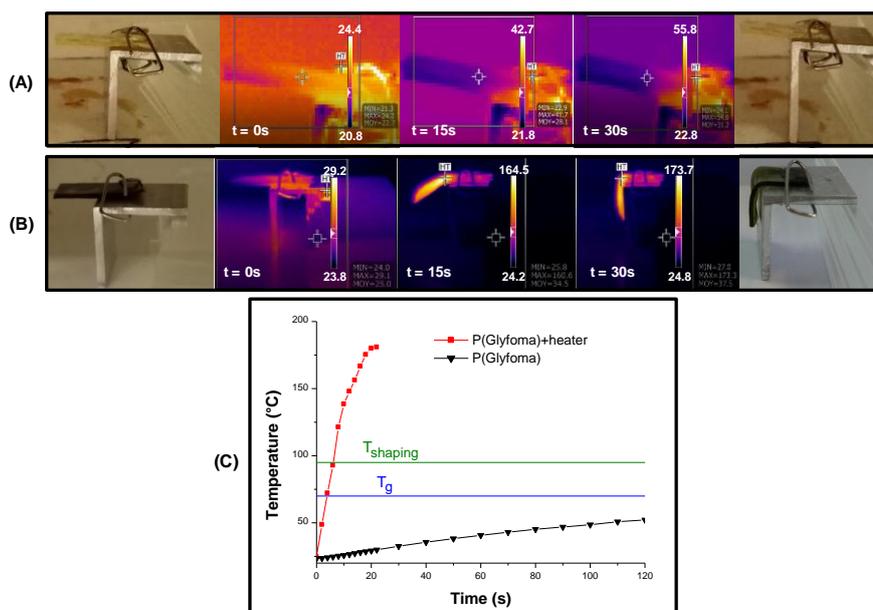


Figure 1. (A) Irradiation of Glyfoma-based polymer (NIR heater-free sample) upon LEDs panel at 810 nm (9 W.cm^{-2}). (B) Irradiation of Glyfoma-based polymer containing IR-813 (0.1%_w) upon LEDs panel at 810 nm (9 W.cm^{-2}). (C) Temperatures of Glyfoma-based polymers upon LEDs panel (with and without NIR heater) at 810 nm (9 W.cm^{-2}) in the irradiated area *versus* time. Irradiations start from $t = 0 \text{ s}$.

The different temperatures reached by all of these polymers in the presence as well as in the absence of NIR heater are depicted in the Figure 2. These results clearly show a huge temperature difference between NIR heater-free polymers and polymers containing NIR dye. The data extracted from this figure are also given in the Table 1. The T_g of these polymers were determined by DSC (Figure S11-15). The DSC of MMA-based polymer shows a degradation after 170°C . T_{shaping} represents the temperature from which the shaping of the polymer starts to be observed and T_{max} the maximum temperature reached by each polymer. Finally, t_{shaping} stands for the irradiation time required to observe the beginning of the shaping whereas t_{shaping} is the time required to entirely shape/reprocess the polymer. The most effective polymer is the Glyfoma-based one. Indeed, the outstanding photothermal effect compared to other polymers allows an almost instant shaping upon NIR light (7 s after the irradiation starts). Moreover, the shaping time to fold the polymer at 90° is really fast (29 s). However, the shaping times of the other polymers remain very fast (less than 1 min). If a longer shaping time is required, the intensity of the LED can simply be lowered since the heat generated by the heater is linear with the light intensity.

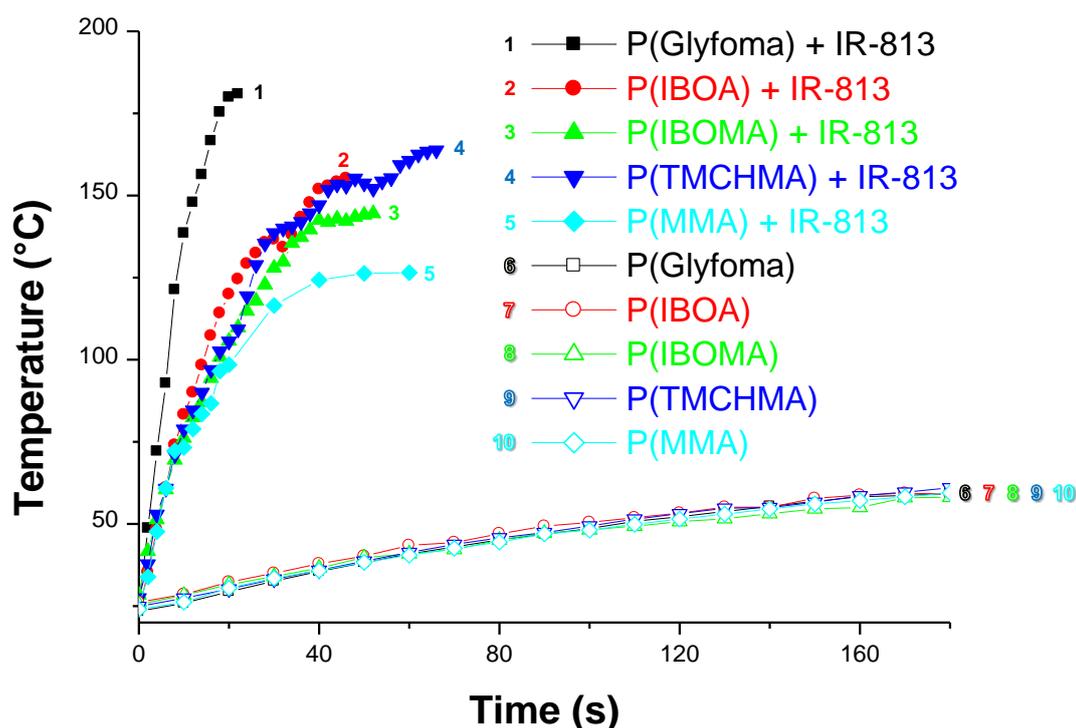


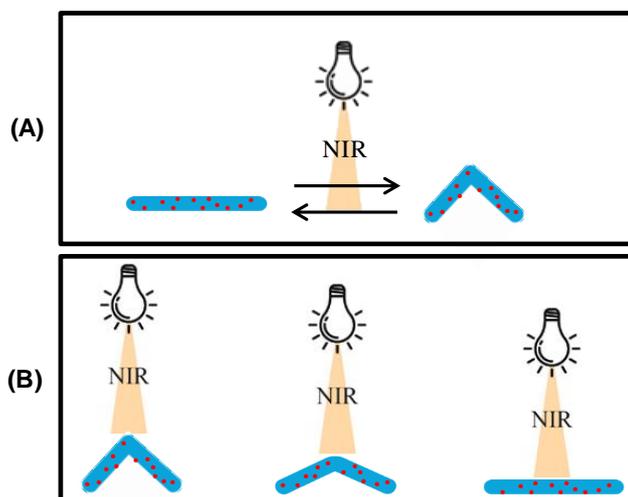
Figure 2. Temperature versus NIR irradiation time for (meth)acrylate-based polymers upon NIR light source at 810 nm ($9\text{W}\cdot\text{cm}^{-2}$). Irradiations start from $t = 0$ s. (1) Glyfoma-based polymer in presence of IR-813 (0.1% wt) ; (2) IBOA-based polymer in presence of IR-813 (0.1% wt) ; (3) IBOMA-based polymer in presence of IR-813 (0.1% wt) ; (4) TMCHMA-based polymer in presence of IR-813 (0.1% wt) ; (5) MMA-based polymer in presence of IR-813 (0.1% wt) ; (6) Glyfoma-based polymer ; (7) IBOA-based polymer ; (8) IBOMA-based polymer ; (9) TMCHMA-based polymer ; (10) MMA-based polymer. For (6)-(10): NIR heater-free samples.

Table 1. Temperatures and times related to the shaping/reprocessing of the different polymers

Polymers	P(Glyfoma)		P(IBOA)	P(IBOMA)	P(TMCHMA)	P(MMA)
T_g	84		92	74	79	79
T_{shaping}	95		108	113	85	84
T_{max}	181		156	149	164	127
$t_{\text{ishaping}} \text{ (s)}$	7		16	24	13	16
$t_{\text{shaping}} \text{ (s)}$	29		54	57	54	*

T_g : glass transition temperature
 T_{shaping} : temperature from which the shaping of the polymer starts to be observed.
 T_{max} : maximum temperature reached by the polymer.
 t_{ishaping} : irradiation time required to observe the beginning of the shaping.
 t_{shaping} : time required to entirely shape the polymer.
 *A small degradation is observed.

An experiment has been specifically designed to show the reversibility of the shaping process. Scheme 3A describes this cycle which can be separated in two parts. The first step consists in folding a polymer, as depicted in Scheme 2B. After this first step, Scheme 3B describes the way how to make the polymer back to its initial shape (defolding) to complete the cycle.



Scheme 3. (A) Shaping cycle of polymer containing NIR heater. (B) Shaping experiment to unfold polymer in order to make it back to its initial shape.

To this end, a folded Glyfoma-based polymer was placed upon irradiation with a LED@850 nm (1 W.cm^{-2}) and followed by thermal imaging camera (See Figure 3), the associated video is given in Video 10 in Supporting Information. Markedly, the NIR irradiation allows to restore the initial shape of the polymer without any additional external stimulus (See Figure 3).

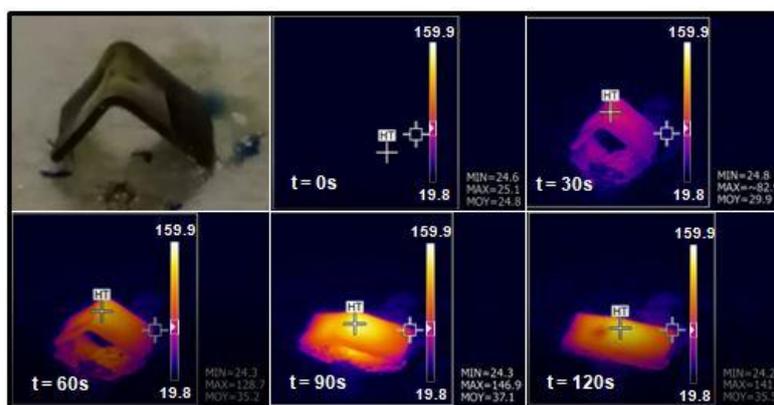
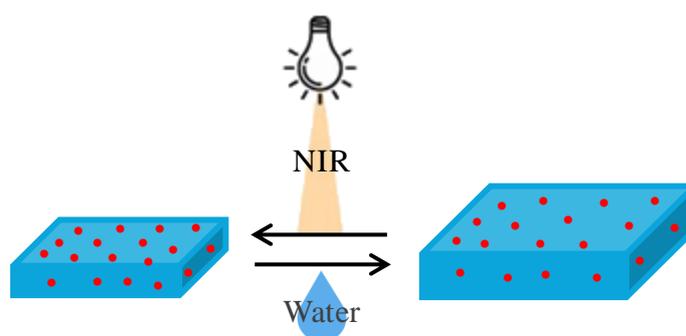


Figure 3. Irradiation of Glyfoma-based polymer containing NIR heater (0.1%_w) upon LEDs at 850 nm (1 W.cm⁻²). The irradiation starts from t = 0 s.

3.2. NIR dehydration of hydrogels

This second part focuses on the benefit of NIR heater on the shaping/reprocessing of hydrogels. When a hydrogel is placed under water, it swells due to the water absorption. This swelling is reversible by dehydration. In this way, the use of heater in-situ embedded is valuable considering that a high temperature can be efficiently reached upon NIR light irradiation. Scheme 4 describes the experiment designed to show this effect.



Scheme 1. Hydration of a hydrogel containing NIR heater in water and dehydration activated upon NIR light.

Accordingly, some PEG-based polymers have been prepared in the presence of heater and without heater. Afterwards, the swelling ratios of PEG-based polymers have been determined for systems with NIR heater (0.1%_w) and without heater at several hydration times (5 min, 10 min, 20 min, 30 min, 45 min, 1 h, 3 h, 6 h and 24 h) as shown in the Figure 4. A discoloration of PEG-based polymers has been observed when the sample was immersed in water. The more the PEG-based polymer is hydrated, the more it is decolorized due to

solvatochromic effect (Figure S16, Supporting Information). The first statement which can be learnt from this figure is the unchanged swelling ratio of prepared PEG-based polymers in the presence of heater. Second, the swelling of PEG-based polymers increases with the hydration time until around 3 hours to end with a swelling ratio of about 50%. After 3 hours of hydration, the swelling ratio remains stable.

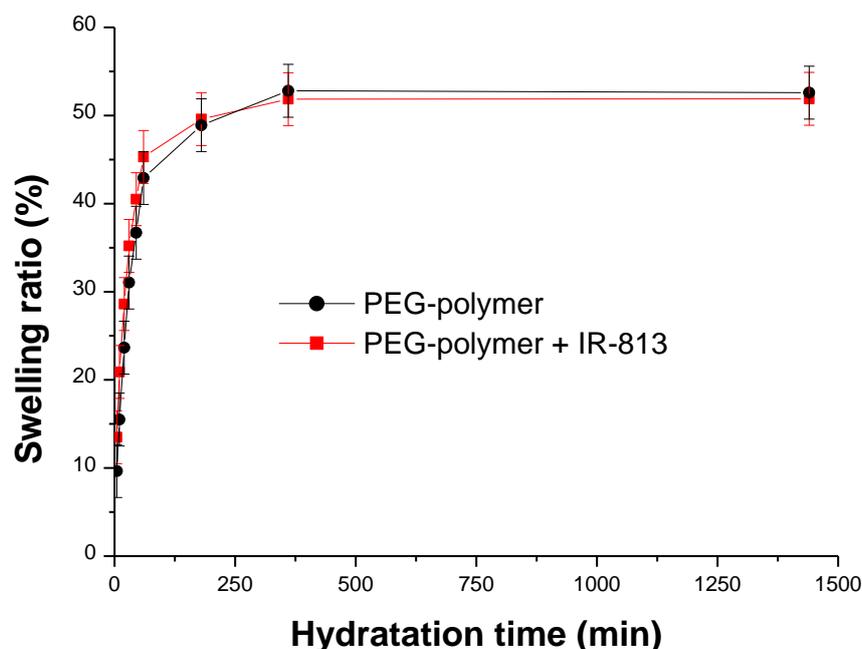


Figure 4. Swelling ratios in weight of PEG- polymers in the presence and in the absence of heater according to the hydration time.

Afterwards, reversibility of the swelling by dehydration triggered by NIR light has been studied. Thus, PEG-based samples have been irradiated 3 minutes upon NIR light at 810 nm (9 W.cm^{-2}) and the temperatures of PEG-based polymers hydrated from 5 to 60 min in the presence and in the absence of heater are presented in the Figure S17, Supporting Information. As expected, temperatures reached are much higher in the presence of NIR heater (from 120°C to more than 150°C) than without heater (between 40°C to 50°C) (Figure 5). Furthermore, the hydration time affects the temperatures reached by PEG-based polymers. Indeed, Figure S17 shows a decrease of temperature as the hydration time increases. Thus, the water absorbed by the hydrogel inhibits the heat transfer within the PEG-based polymer. These temperatures explain the huge dehydration difference between hydrogels containing NIR heater and samples without heater presented in the Figure S18. Indeed, an almost

complete dehydration is observed for samples with NIR heater. On the other hand, NIR heater-free hydrogels could not achieve high dehydration (<50%) in the same NIR irradiation conditions. Furthermore, the complete dehydration is reached in the presence of NIR heater after 5 min of hydration as shown in the Figure 5. Indeed, only 60 s of NIR light irradiation is required to achieve the complete dehydration with NIR heater whereas <50% is achieved after 3 min of NIR irradiation.

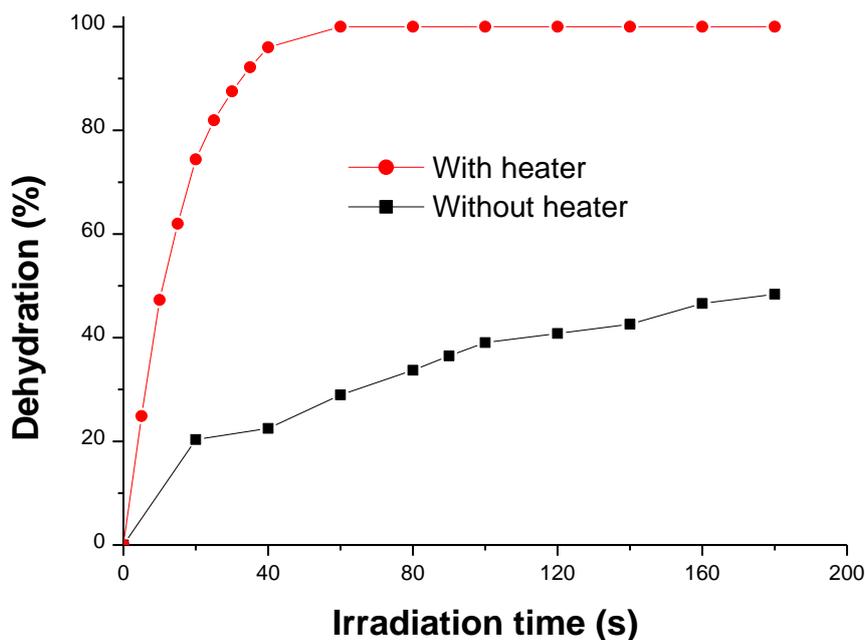


Figure 5. NIR activated dehydration of PEG-based polymers *versus* irradiation time (810 nm ; 9 W.cm⁻²) with NIR heater (0.1%_{wv}) and without heater (for a hydrogel after hydrating 5 min in deionized water).

Finally, Figure 6 shows the size modifications of the studied hydrogels without heater (See Figure 6A) and in the presence of IR-813 (Figure 6B) while hydrated in water or dehydrated upon NIR light. First, the size of hydrogels increases during the hydration. Second, these sizes decrease upon NIR irradiation. However, the NIR heater-free hydrogel does not return to its initial size due to the low temperature reached whereas the hydrogel containing heater returns to its initial size due to the high temperature reached.

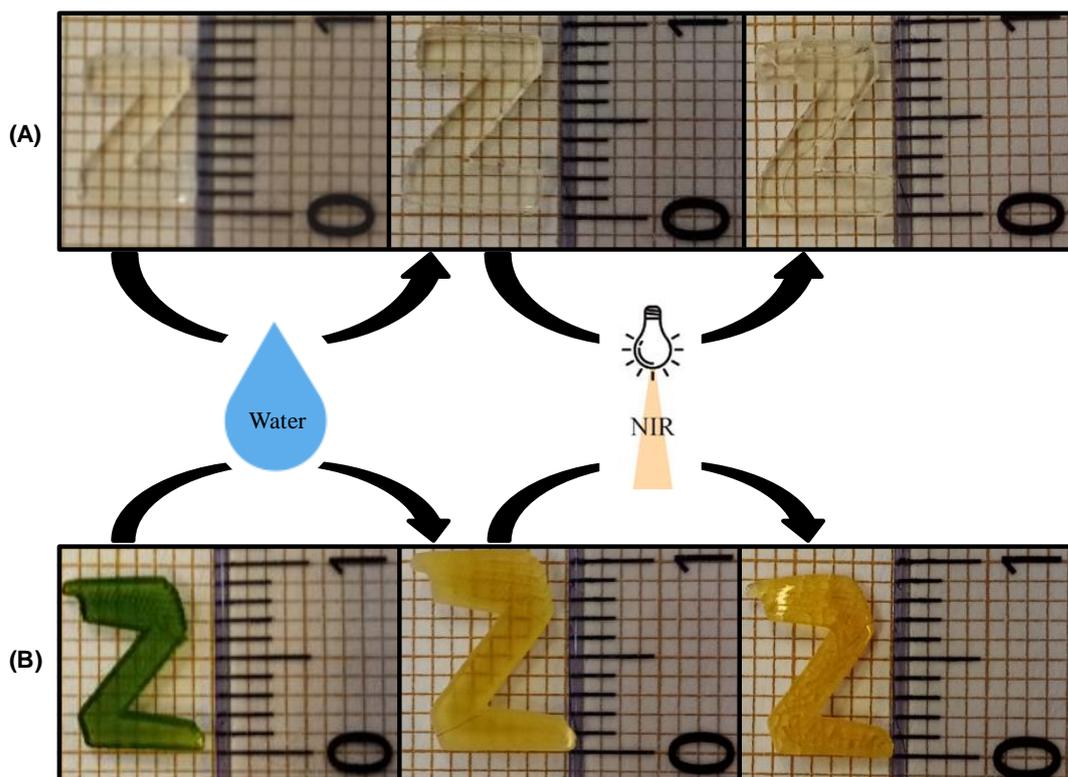


Figure 6. Hydration of a hydrogel 24 hours in deionized water and dehydration upon 3 minutes of NIR light at 810 nm (9 W.cm^{-2}). (A) Hydrogel without NIR heater; (B) Hydrogel with NIR heater ($0.1\%_{\text{wt}}$). The hydrogels were prepared in direct laser write experiments.

4. Conclusion

In conclusion, the shaping/reprocessing of polymers could be easily achieved upon NIR light in combination with a low NIR heater content ($<0.1\%_{\text{wt}}$). A high temperature could be reached thanks to the highly efficient photothermal effect of the organic NIR dye, allowing to exceed the T_g of the thermoplastics. Moreover, the shape was entirely reversible by re-irradiation upon NIR light. Then, the NIR heater properties were used in PEG-based hydrogels to provide an on-demand dehydration upon NIR light. Indeed, a total dehydration could be achieved by irradiating only 3 minutes upon NIR light whereas the reference heater-free PEG-based polymer dehydration was between 20% and 50% at room temperature. Shaping applications on 3D printed objects will be given in forthcoming papers.

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