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Fast curing of a biobased polyhydroxyurethane thermoset using near infra-red photothermal effect

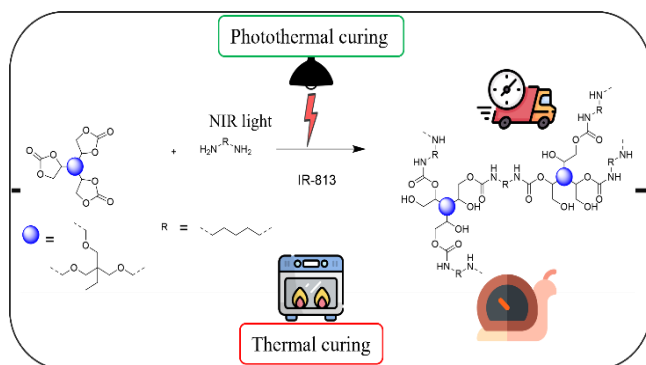
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Graphical abstract



Keywords: Photothermal polymerization, non-isocyanate polyurethane, polyhydroxyurethane, Near infra-red irradiation, photopolymerization.

Abstract Polyhydroxyurethanes (PHU), which are obtained by reaction of cyclocarbonates and amines, represent an eco-friendly alternative to conventional polyurethanes because their

synthesis relies on CO₂-based precursors, avoids the use of toxic isocyanates and allows introducing additional functionalities (“hydroxy”) in the polymer backbone. However, the low reactivity of the cyclocarbonates aminolysis to form polyhydroxyurethane represents a major drawback, particularly for industrialization. To overcome this lack of reactivity, we propose in this study to use the photothermal effect generated by the organic heater 2-chloro-3-[2-(1,1,3-trimethylbenz[e]indolin-2-ylidene)ethylidene]-1-[2-(1,1,3-trimethylbenz[e]indolium-2-yl)vinyl]cyclohexene p-toluenesulfonate (IR-813 p-toluene sulfonate) absorbing in the near-infra-red (NIR) region. IR-813 was chosen because of its commercial availability and, its good solubility in organic resins and REACH registered behavior. It was added to a formulation composed of trimethylolpropane tricarboxylate (TMPTC) and 1,5-pentanediamine, which curing under NIR light (850 nm) was subsequently studied. Various parameters were varied, such as the amount of IR-813 “heater” and the irradiance of the LED source, and their influence on gel time and maximum reached temperature were evaluated. The best system allowed reaching a temperature of 150 °C, a gel time of 3 minutes and a gel content of 94 %, using only light generated by the NIR light emitting diode (LED) as external energy source. Finally, energetic costs associated with LED curing were compared with those of conventional thermal curing. By providing energy savings of 36%, photothermal curing using LED proved to be a more sustainable alternative than conventional thermal curing using ovens.

Introduction

Over the last decade, polyhydroxyurethanes (PHUs)¹ have emerged as a promising alternative to polyurethanes (PU) conventionally obtained by the reaction of polyols with multifunctional isocyanates.² The main reason is that aminolysis of cyclic carbonates leading to PHUs allows access to the carbamate function while avoiding the use of toxic isocyanates and the

generation of any by-products (atom economy). More specifically, the synthesis of PHUs can be achieved using 5-membered cyclic carbonates (5CC) that can be obtained by reaction of carbon dioxide with the corresponding epoxides, making this pathway the least toxic and most eco-friendly route to PU.³⁻⁷ In particular, it has been recently demonstrated by Liang et al. that the emissions generated to produce one ton of PHU originating from biobased resources are between 16.1 % and 11.5 % lower than the emissions generated to produce one ton of fossil-based flexible and rigid PU foam, respectively.⁸ However, this reaction suffers from a lower percent completion of reaction compared to the isocyanate pathway, which has led several studies to be conducted in order to optimize the ring-opening reaction that is the elemental step of this polyaddition.⁹ Two phenomena accounts for this low reactivity: i) the inherent low reactivity of the 5CC itself and ii) the creation of numerous hydrogen bonds due to the formation of both urethane and hydroxyl groups during the reaction, which increases viscosity and thus limits the advancement of the step-growth polymerization. Accordingly, the influence of numerous parameters such as the addition of solvent, the increase of temperature, the addition of catalyst,^{10,11} the variation of cyclic carbonate substituents or amine structures was found crucial on the reaction rate and final advancement of the reaction. Despite these achievements, the synthesis of PHUs from 5CC in bulk and at room temperature still remains a challenge and only the production of PHU foams by using blowing agents has allowed full conversion of the cyclocarbonate functions at room temperature.¹² Other strategies have thus been established in order to overcome this reactivity problem, such as the use of larger cyclic carbonates (6CC, 7CC¹³ or 8CC¹⁴), addition of an hydroxy in beta position of the amine,⁹ employing exovinylene cyclic carbonates,¹⁵ or the combination of the cyclic carbonate/amine reaction with the polymerization of other functional groups like acrylates, methacrylates, epoxies, alkenes or siloxanes.¹⁶ However, one strategy that has not been considered yet is the photo-induced thermal polymerization of multi-5CC and multi-amines.

Photo-induced thermal polymerization, i.e the use of a photothermal conversion material or “heater” to transform light energy into thermal energy in order to activate a polymerization reaction, has recently appeared in the literature as a very effective strategy to increase the kinetics of well-known polymerization reactions.¹⁷⁻¹⁹ As a representative example, the rate of a step-growth polymerization between a diisocyanate and a polyol, performed in the presence of gold nanoparticles as heaters and dibutyl tin dilaurate as catalyst, was found 5 times faster under 532 nm irradiation than in the dark (room T).²⁰ Similarly, the crosslinking of polydimethylsiloxane (PDMS) by a photothermal process under 532 nm irradiation displayed reaction kinetics 150 times faster than those observed when using a conventional thermal process (T= 100 °C).²¹ Enhanced activity was also observed by Zhuo et al. for the copolymerization of epoxide and carbon dioxide in the presence of aluminum porphyrin complexes as photothermal agent under 635 nm irradiation as compared to regular thermal polymerization.²² Main reason for the enhanced reaction rate in photothermal processes can be found in the phenomena at the origin of heat generation with photothermal agents. **Indeed, after absorbing the electromagnetic radiation, photothermal agents first release energy from the vibrationally excited singlet states to the lowest vibrational state of S_1 through non-radiative relaxation (vibrational relaxation), according to Kasha's rule, inducing temperature released by colliding to the surrounding molecules. The photothermal agents go back from the relaxed S_1 to their ground state (S_0) through internal conversion due to the coupling of higher vibration of S_0 to vibrational ground state of S_1 . Intersystem crossing forming triplet state usually does not occur for cyanine dyes as shown by Wang *et al*²³ and Strehmel *et al*²⁴ and fluorescence quantum yields are extremely low leading to internal conversion as the main factor for the energy release to the surrounding matrix molecules through direct collision with them and these hot matrix molecules distribute it similarly to other matrix molecules. This**

corresponds to an increase of the average kinetic energy of the molecules corresponding to an increase of temperature.^{19,25}

In addition to induce faster kinetics, it has been demonstrated that for coating applications, photo-induced thermal polymerization using lasers or light emitting diodes (LEDs) would allow significant energy savings as compared to traditional curing using thermal ovens.²⁶ Since coating application represent 13% of PU global market, there is thus a very good opportunity to decrease the environmental impact of PU by producing PHU coatings through a photo-induced thermal process. In addition, the use of NIR light offers the advantage of better light penetration with very safe wavelengths.²⁷ Therefore, specific photothermal effect, created by a non-radiative relaxation process and vibrational relaxation of NIR heaters is attractive for PHU synthesis.²⁸

Accordingly, we propose herein to evaluate the potential of the photothermal effect for the fast curing of PHU obtained by aminolysis of 5CC. To this end, biobased liquid formulations composed of a trifunctional 5-membered cyclic carbonate, namely trimethylolpropane tricarboxylate (TMPTC), cadaverine as diamine, and 2-chloro-3-[2-(1,1,3-trimethylbenz[e]indolin-2-ylidene)ethylidene]-1-[2-(1,1,3-trimethylbenz[e]indolium-2-yl)vinyl]cyclohexene *p*-toluenesulfonate (IR-813) as heater were prepared. Trimethylolpropane tricarboxylate (TMPTC) was selected because it can be easily produced by carbonation of trimethylolpropane triglycidyl ether that may originate from biobased trimethylolpropane (Perstorp) and bio-based epichlorohydrin (several producers). On its side, cadaverine can be produced by decarboxylation of l-lysine catalyzed by l-lysine decarboxylase.²⁹ Both compounds being fully biobased they will allow the production of fully biobased PHUs. IR-813 was selected as heater since it was already proved to be effective for the photothermal polymerization of various monomers such as acrylate or epoxy amine systems^{27,30} and because it is soluble in both monomers (TMPTC and cadaverine, see

supporting information). As well described by Jung et al. and by Matter et al., organic dyes such as IR-813 generate heat under NIR irradiation through nonradiative relaxation pathways after absorbing photons.^{19,28} Then, the photothermal cross-linking of these formulations under irradiation was evaluated using different techniques such as thermal imaging, the determination of gel times by photorheology and the monitoring of monomer conversion with irradiation time by real-time NIR spectroscopy. Finally, the physico-chemical characteristics of the obtained PHU were assessed and compared to a PHU of the same composition cured using a traditional thermal oven.

Materials

Trimethylolpropane triglycidyl ether (TMPTGE, technical grade, Sigma Aldrich), tetrabutyl ammonium bromide (TBAB, 99%, Sigma Aldrich), magnesium sulfate (99%, Sigma Aldrich), 1,5-pentanediamine (99%, TCI EUROPE N.V), 2-chloro-3-[2-(1,1,3-trimethylbenz[e]indolin-2-ylidene)ethylidene]-1-[2-(1,1,3-trimethylbenz[e]indolium-2-yl)vinyl]cyclohexene *p*-toluenesulfonate (IR-813 *p*-toluene sulfonate) (99%, TCI EUROPE N.V), ethyl acetate (99%, VWR international S.A.S), dimethylformamide (DMF, 99%, VWR international S.A.S), deuterated chloroform (CDCl₃, 99.5%, Eurisotop) were employed as received.

Characterizations

NMR. ¹H NMR spectra were acquired on a Brüker Avance III 400 MHz NMR spectrometer at 25 °C using CDCl₃ as deuterated solvents. Spectra were analyzed using *mestrenova*.

Titration of the carbonate equivalent weight of TMPTC by ¹H-NMR. The Carbonate Equivalent Weight (CEW) represents the mass of product needed for one mole of reactive carbonate functions. It was determined according to Equation 1, using 1,3,5-trioxane as an internal standard during ¹H –NMR analysis. To this end, a known mass of TMPTC (~ 70 mg)

and 1,3,5-trioxane (~ 7 mg) were mixed with 500 μL of CDCl_3 and poured in an NMR tube. The CEW was calculated using Equation 1 by comparing the integral of the 1,3,5-trioxane signal (5.08 ppm, 6H) with the integral of the signal corresponding to the CH protons of the cyclocarbonate (4.77 ppm, 1H)

$$CEW = \frac{\int_{trioxane} \times H_{carbonate}}{\int_{carbonate} \times H_{trioxane}} \times \frac{m_{carbonate}}{m_{trioxane}} \times M_{trioxane} \quad (1)$$

With $\int_{trioxane}$: integral of the signal from trioxane protons ; $\int_{carbonate}$: integral of the signal from CH of the cyclocarbonate; $H_{carbonate}$: the number of protons in α position of the cyclocarbonate function; $H_{trioxane}$: the number of trioxane protons; $m_{carbonate}$: mass of cyclocarbonate; $m_{trioxane}$: mass of trioxane; $M_{trioxane}$: trioxane molar mass.

NIR Irradiation

For material synthesis in mold. Thorlabs Solis-850C High power LED was used for the irradiation of the formulation. This lamp irradiates at 850 nm (Figure 1) with an adjustable irradiance between 0 and 0.5 $\text{W}\cdot\text{cm}^{-2}$. The irradiance was measured with the optical power meter PM100D and the sensor S425C from Thorlabs.

Measurement of the temperature of the formulations subjected to NIR irradiation.

The change of the temperature due to the photothermal polymerization was followed using a thermal camera OPTRIS PI 400i and PIX connect software. The temperature was measured as the average value at the surface of the sample.

FTIR. Fourier transformed infrared (FTIR) spectra were recorded on a IS50 spectrometer from Thermo Fisher Scientific equipped with a golden gate diamond attenuated total reflection (ATR) heating plate from Specac. The data were analyzed using the software OMNIC 8.2 from Thermo Scientific. The characteristic IR bands of transmission mentioned in the text are reported in wavenumbers (cm^{-1}).

Real Time Conversion Measurements upon NIR Light. The first harmonic of the NH_2 vibration band ($6400\text{-}6600 \text{ cm}^{-1}$) is followed by real time Fourier transformed infrared (RT-

FTIR) spectroscopy using a JASCO4600 spectrometer. The photosensitive formulations were deposited on a polypropylene film in a mold (thickness of the sample = 1.4 mm) and polymerized under air by irradiation with a LED or a laser diode. The first overtones of C–H stretching band between 5300-6000 cm^{-1} was used as reference to normalize the FTIR spectra. The evolution of the absorbance allowed to follow the conversion using Equation 2.

$$\text{conv.}(\%) = \left(1 - \frac{A_t}{A_0}\right) \times 100 \quad (2)$$

Thermogravimetric analysis Thermogravimetric analyses (TGA) were performed using a TG 209F1 apparatus (Netzsch). Approximately 10 mg of product were placed in an aluminum crucible and heated from room temperature to 580 °C at a 20 °C.min⁻¹ heating rate under nitrogen atmosphere (60 mL.min⁻¹). The degradation temperature was measured at 2 % weight loss using proteus analysis software (Netzsch).

Differential scanning calorimetry Differential scanning calorimetry were carried out using a Sirius 3500 F3 apparatus (Netzsch), which was calibrated with indium, adamantane, tin and bismuth standards. Approximately 10 mg of product were placed in an aluminum pan (pierced lid) and the heat exchanges were recorded between -70 °C and 250 °C at 20 °C.min⁻¹ under nitrogen atmosphere, to observe exotherm ΔH and determine the glass transition temperature. The residual exotherm during the first heating ramp allowed to determine monomer conversion using Equation 3 and T_g after irradiation, the second heating ramp allowed to determine the T_g of the fully crosslinked thermoset.

$$\text{conv.}(\%) = \left(1 - \frac{\Delta H}{\Delta H_0}\right) \times 100 \quad (3)$$

ΔH_0 : enthalpy of reaction of the non-cured PHU system freshly prepared.

Gel time measurement. Gel times were measured with rheology experiments carried out on a ThermoScientific Haake Mars 60 rheometer equipped with photorheological system. The upper geometry is an 8 mm plane glass geometry allowing irradiation of the sample after the

light emitted by the CNI MDL-H-808 nm laser diode at 0.5 W.cm^{-2} has been directed with a guide and reflected by a mirror on top of the resin sample, Figure 1. The lower geometry consists of a flat Teflon plate and the resin-filled gap is 1 mm thick. The disk of PTFE was glued on the bottom geometry in order to obtain photothermal effect by separating the liquid resin from the Peltier plate (reduce the thermal loss), Figure 1. Due the necessary presence of the disk of PTFE, the temperature cannot be measured by peltier plate. The storage (G') and the lost (G'') moduli were measured in oscillation at frequency of 1 Hz and a 0.1 % shear strain applied on the samples before and during the irradiation. The gel time was determined at the crossover point of the two moduli. The gel time measured at 25 °C and 90 °C were measured using the same system without the laser and the PTFE disk.

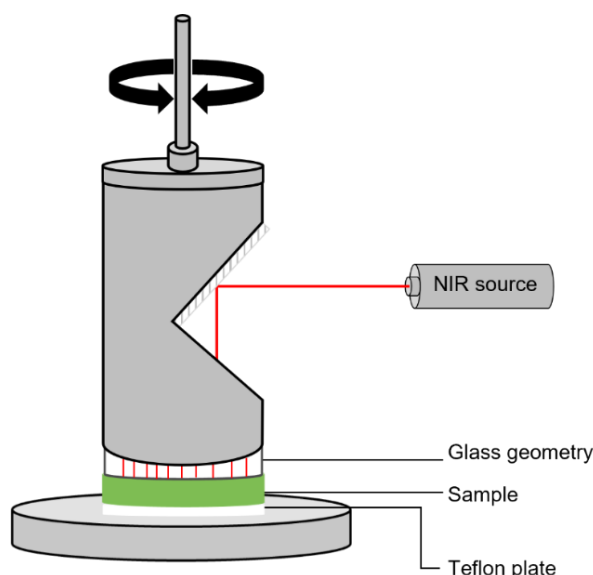


Figure 1. Photorheological system used during the study

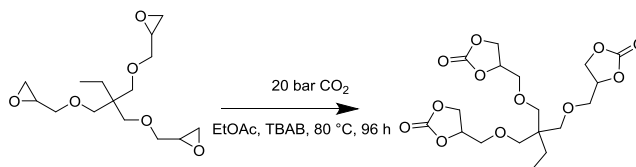
Swelling index. Three samples of known mass (around 35 mg) were immersed in 10 mL DMF for 24 h. The swelling index (SI) was calculated using Equation 4 where m_2 is the swelled mass of the sample and m_1 the mass of the sample before the immersion. The average value of three SI determined for one material is reported.

$$SI = \frac{m_2 - m_1}{m_1} \times 100 \quad (4)$$

Gel content. Three samples of known mass of about 35 mg of the same material were immersed in DMF for 24 h. After 24 h, the samples were recovered from the DMF and dried under vacuum in an oven at 100 °C for 24 h. The gel content (GC) was calculated using Equation 5 where m_3 is the mass of the sample dried under vacuum and m_1 the initial mass of the sample. The average value of three gel contents determined for the same material is reported.

$$GC = \frac{m_3}{m_1} \times 100 \quad (5)$$

Synthesis of trimethylolpropane tricarboxylate (TMPTC) (Scheme 1).



Scheme 1. Carbonation of TMPTGE at 80 °C under 20 bars of CO₂ in ethyl acetate catalyzed with tetrabutylammonium bromide.

Trimethylolpropane triglycidyl ether (TMPTGE; 300 g, 0.99 mol) and tetrabutylammonium bromide (TBAB; 14.5 g, 0.045 mol) were mixed with 150 mL of ethyl acetate in a 600 mL high pressure reactor with mechanical stirring. The reaction was carried out at 80 °C under 20 bars of CO₂ for 96 h. After reaction, the crude mixture was diluted in ethyl acetate then washed with water and brine in order to remove TBAB. The organic layer was then dried with magnesium sulfate and the solvent was removed under vacuum using a rotary evaporator at 40 °C. The yellowish viscous product was obtained with a 90 % yield. The 5-CC functionality was titrated by ¹H NMR, using Equation 1, to be CEW = 190 g.eq⁻¹.

¹H NMR (400 MHz, CDCl₃): δ/ppm = 0.78 (t, CH₃), 1.33 (m, CH₂), 3.1-3.96 (m, CH₂), 4.35 (m, CH), 4.45 (m, CH), 4.78 (m, CH).

General procedure of PHU synthesis under NIR irradiation. All PHU materials were synthesized by using a molar stoichiometric ratio of cyclocarbonate and amine functions. Example procedure for the synthesis of PHU in the presence of 2 wt.% (of the resin mass) of IR-813: IR-813 and 1,5-pentanediamine (0.423 g, 4.14 mmol, 8.3 mmol amine) were mixed using a vortex until the photothermal heater was fully dissolved. Then the mixture was added to TMPTC (1.577 g, 3.07 mmol, 8.3 mmol carbonate) and the formulation was stirred at 2500 round.min⁻¹ for 3 minutes with a SpeedMixer. The viscous formulation obtained was poured in a 21 mm diameter and 1 mm height PTFE mold and subjected to NIR irradiation for 20 minutes using the Thorlabs Solis-850C High power LED.

Results and discussion

The model PHU network studied in the present article was obtained by aminolysis of a tri-functional 5-CC monomer namely trimethylolpropane triglycidyl carbonate (TMPTC, obtained by epoxy carbonation with CO₂ as reported previously)³¹ with a biobased commercially available bifunctional primary amine, namely 1,5-pentane-diamine, commonly known as cadaverine (Figure 2). The near infra-red heater IR-813 was introduced in the formulation at different percentages from 0.25 to 4 wt.%. The heater was first solubilized in the amine leading to an orange solution more or less intense depending on the percentage of heater, which led to a green mixture after mixing with the cyclocarbonate. This easily reproducible protocol was used for all the experiments.

As reported previously, photothermal effect allows reaching high temperature in the core of the material much faster than conventional heating³² and is expected to drastically increase polymerization kinetics due to the presence of the near infra-red sensitive compound.²⁰ Since, to the best of our knowledge, the photothermal polymerization of the CC5-carbonate/amine system has never been reported so far, we optimized the heater content in the formulation by

following the temperature profile of the different formulations and the impact of the irradiance on the reached temperature.

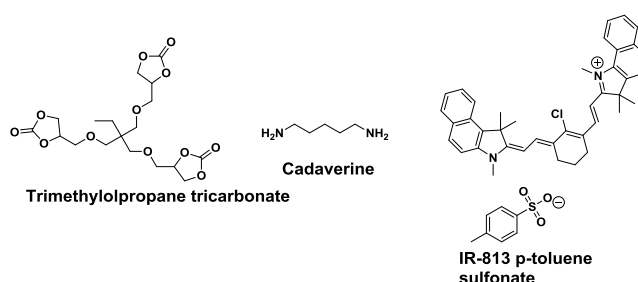
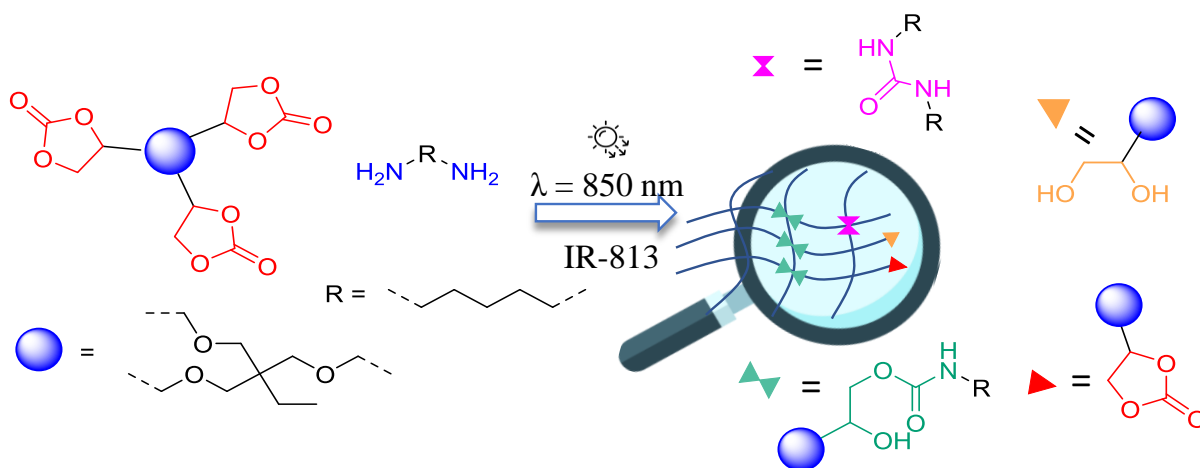


Figure 2. Chemical structures of the monomers employed for PHU thermosets synthesis and of the IR-813 *p*-toluene sulfonate.



Scheme 2. Reaction scheme of TMPTC with 1,5 diaminopentane under irradiation (850 nm) for the formation of thermoset polyhydroxyurethane in the presence of the near infrared heater.

Assessment of IR-813 as heater

Because polyurethanes found applications as coatings or adhesives, resulting in the production of thin layer of polymer³³, a first experiment was conducted by subjecting a thin film (120 μm) of a formulation comprising 2 wt% of IR-813 to NIR irradiation at 850 nm (0.5

$\text{W}\cdot\text{cm}^{-2}$). The aim was to produce a photothermally crosslinked PHU since PHU coatings have been found to provide better adhesion to substrates compared to PU, due to the presence of a higher number of hydrogen bonds.³⁴ However, only a small temperature increase was observed during the irradiation of the sample, as shown in Figure 3. Accordingly, incomplete cross-linking of the formulation was obtained as attested by the viscous and tacky nature of the coating. The same experiment was carried out on metal, glass and PTFE substrates, but the behavior of the formulation under irradiation remained the same, suggesting that the surface to volume ratio of the films was too high, leading to a high heat transfer to the substrates (heat sinks) and air and thus to thermal energy loss. This hypothesis was confirmed when irradiating a 1 mm thick film, since the temperature rose up in few seconds to 68 °C when the LED was turned on. Consequently, thickness of the samples was fixed at 1 mm for the remaining of the study in order to limit the heat loss during irradiation.

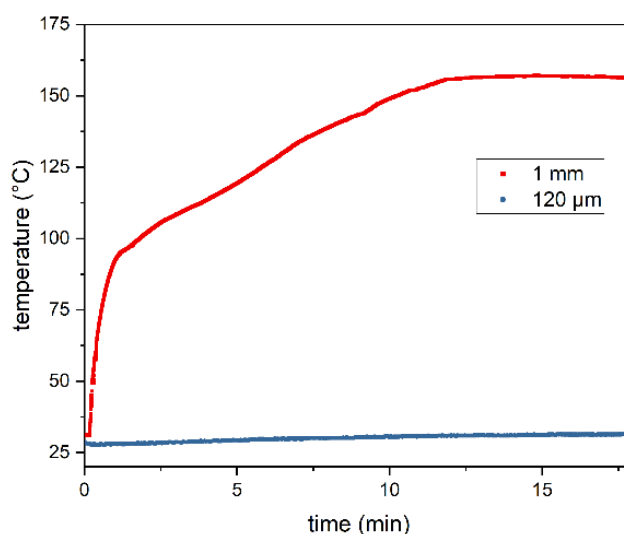


Figure 3. Influence of sample thickness (in red 1 mm, in blue 120 μm) on the photothermal profiles of TMPTC and cadaverine formulation with 2 wt.% of IR-813, irradiated at 850 nm and $0.5 \text{ W}\cdot\text{cm}^{-2}$, irradiation start at $t = 10 \text{ s}$.

Influence of NIR heater concentration

The influence of the heater content in the formulation was evaluated by following the temperature of the formulation with a thermal camera during irradiation. The photothermal profile of different formulations with IR-813 content ranging between 0 wt% and 4 wt% is presented in Figure 4A. As expected, when no heater was employed, the temperature recorded remained stable (around 30 °C) during irradiation. Therefore, irradiation itself is not able to heat the sample nor to activate the polymerization.

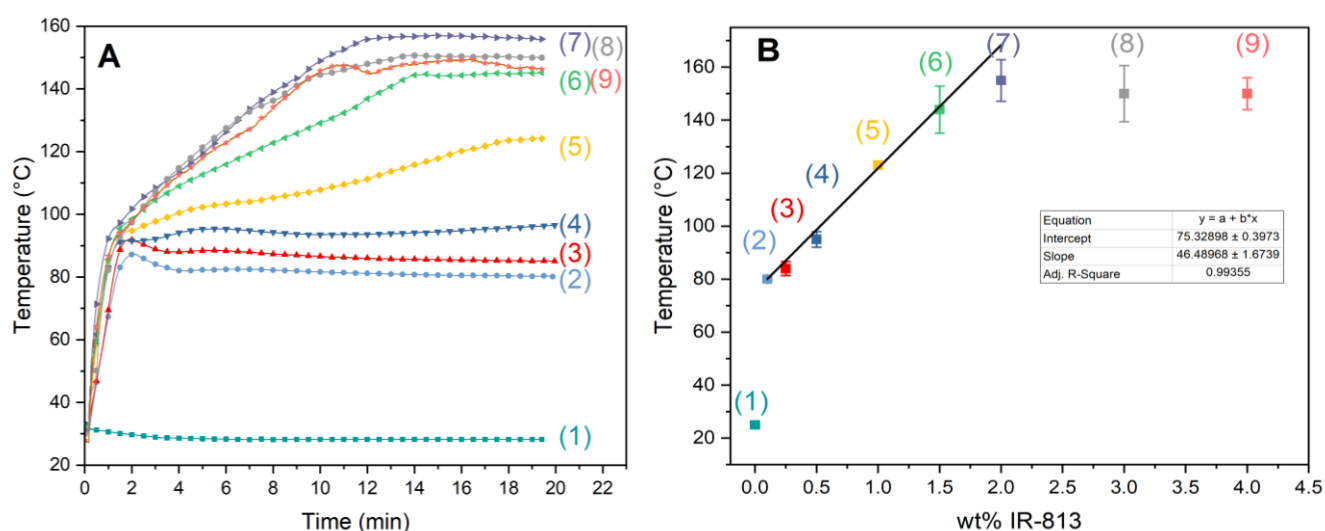


Figure 4. **A** Temperature versus time profiles during the photothermal polymerization of TMPTC and cadaverine with [IR-813] varying between (1) 0 wt.%, (2) 0.1 wt.%, (3) 0.25 wt.%, (4) 0.5 wt.%, (5) 1 wt.%, (6) 1.5 wt.%, (7) 2 wt.%, (8) 3 wt.%, (9) 4 wt.%; (20 minutes of irradiation with a LED at 850 nm and 0.5 W.cm^{-2}). The irradiation starts at $t = 10 \text{ s}$. **B** Mean value of the temperature measured after 20 min of irradiation for TMPTC and cadaverine thermoset with [IR-813] varying between 0 wt.% and 4 wt.% (irradiation with a LED emitting at 850 nm and 0.5 W.cm^{-2}). Error bars represent the standard deviation of the 3 maximum temperatures measured during 3 experiments.

In the presence of the heater, several stages in the temperature profile versus time can be distinguished once irradiation has been turned on. First, regardless of the heater concentration, a rapid increase of the temperature at the early stage (the first two minutes) of irradiation was

observed (runs 2-9) that can be attributed to the contribution of both photothermal effect and exothermal effect of the polymerization. All formulations reached temperatures ranging from 80 °C to 100 °C within a few minutes. Following this first temperature jump, two behaviors could be discerned. For formulations containing 0.5 wt.% or less of IR-813 (curves number 1 to 4, Figure 4A), a plateau was directly observed and the recorded temperature remained constant until the stop of irradiation. Alternatively, when the concentration of IR-813 ≥ 1 wt.%, a second temperature increase was observed prior to reach a new plateau after roughly 12 min of irradiation (runs 5-9). This behavior and the differences between formulations could be explained by the combination of two exothermal processes. Obviously, the photothermal effect participates in this rise of temperature but the exothermal polymerization induced by the ring-opening of 5-CC by the primary amine may be accounted for as well. For formulations prepared with an IR-813 content ≤ 0.5 wt.%, the temperature plateau can be attributed to the photothermal effect only. For formulations with a heater concentration above 1 wt.%, the second temperature increase is slower than the previous one, indicating that it can only be related to the photothermal effect. For these formulations, a temperature plateau was then reached, which temperature increased with the heater content up to 2 wt.%, as displayed in Figure 4B. Above this concentration threshold, the maximum temperature remained stable (Figure 4, 3 and 4 wt.%) and stabilized at 150 °C. Similar observation was made by Bonardi et al.³⁵ and can be explained by the occurrence of a light screening effect by the heater itself, thus decreasing the efficiency of the photothermal effect and consequently the reached temperature. Interestingly, the linear correlation of the reached temperature versus the heater concentration when the IR-813 content is below 2 wt.%, offers an elegant way to precisely tune the curing temperature of this system.

Influence of the irradiance on the photothermal effect

The NIR LED source used possessing a tunable irradiance from 0 to 0.5 W.cm^{-2} , the photothermal effect of the IR-813 was studied by varying the irradiance of the NIR emitting source with a 2 wt.% IR-813 formulation. The maximum temperature reached after 20 minutes of irradiation, corresponding to the final temperature plateau, is reported for each experiment in Figure 5. The temperature shows a linear dependency with the irradiance, thus giving another possibility to modulate the maximum temperature reached by the resin. Nevertheless, in order to obtain the fastest curing for the synthesis of PHU thermosets, the irradiance was fixed at 0.5 W.cm^{-2} (max. irradiance) for the remaining of the study.

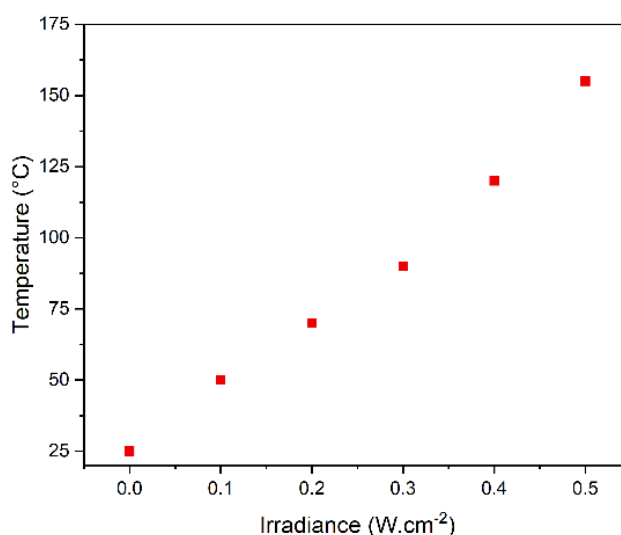


Figure 5. Temperature of the PHU resin reached after 20 minutes of irradiation at different irradiances in the presence of 2 wt.% [IR-813] using LED irradiating at 850 nm.

Having established that IR-813 exhibits a photothermal effect in the TMPTC/cadaverine formulation, we studied the influence of the heater concentration on the polymerization kinetics by determining the gel time for each formulation with the help of a photorheometer. This kinetic study was completed by following the conversion of the primary amine function in cadaverine through real-time NIR spectroscopy.

As mentioned earlier, one of the main drawbacks of the 5CC aminolysis is its relatively low reactivity that results in long gel times and the need to cure the formulation at high temperature for a long time before having a tack-free material.

Table 1. Gel times and conversions after 20 min reaction of a TMPTC/ cadaverine formulation containing different ratios of IR-813.

Ref	[IR-813] (wt.%)	Curing process	Gel time ^a	RT-FTIR conv. ^b (%)	DSC conv. ^c (%)
1	0.25	NIR irradiation	6 min 45 s	93	48
2	0.5	NIR irradiation	3 min 45 s	92	78
3	1	NIR irradiation	4 min 15 s	93	90
4	1.5	NIR irradiation	3 min 30 s	94	91
5	2	NIR irradiation	4 min 45 s	92	91
6	3	NIR irradiation	3 min	92	96
7	2	Thermal, 90 °C	9 min 50 s	//	77

a) Gel time was measured by time sweep rheology experiment under irradiation at 808 nm (0.5 W.cm^{-2}), b) conversion determined by RT-FTIR spectroscopy following the first harmonic of the NH_2 vibration band (see experimental section), using a NIR laser diode emitting @785 nm (0.5 W.cm^{-2}) as irradiation source (sample thickness = 1.4 mm), c) conversion determined by DSC after 20 minutes of (photo)curing.

Such a behavior is also observed with the TMPTC/cadaverine formulation employed in this study since in absence of irradiation, a 33 hours gel time at 25 °C was determined by

rheology. Figure 6A shows the typical photopolymerization profile of a TMPTC/cadaverine/IR-813 formulation under NIR irradiation, where the NIR laser was turned on at 1 minute. First, we can observe that once the sample was irradiated the moduli dropped instantaneously indicating a decrease of the viscosity due to the increase of temperature. Then, cross-linking of the system occurred as indicated by the crossover of G' and G'' . Gel times of the formulations cured under NIR irradiation are reported in Table 1 and vary between 3 and 5 min without dependence on the amount of heater added to the formulation, except for the formulation with a very low heater content of 0.25 wt% that possesses a gel time of 6 min 45s. As expected, the photo-induced thermal process allows much faster polymerization than the curing at room temperature with kinetics of gelation almost 500 times faster thanks to the photothermal effect. Nevertheless, this kinetics should also be compared to a curing process involving conventional thermal energy. Thus, we also determined the gel time of the formulation with 2 wt% of IR-813 cured at 90 °C. This temperature was selected because it matches the temperature reached by all formulations containing IR-813 after the first 2 min of irradiation.

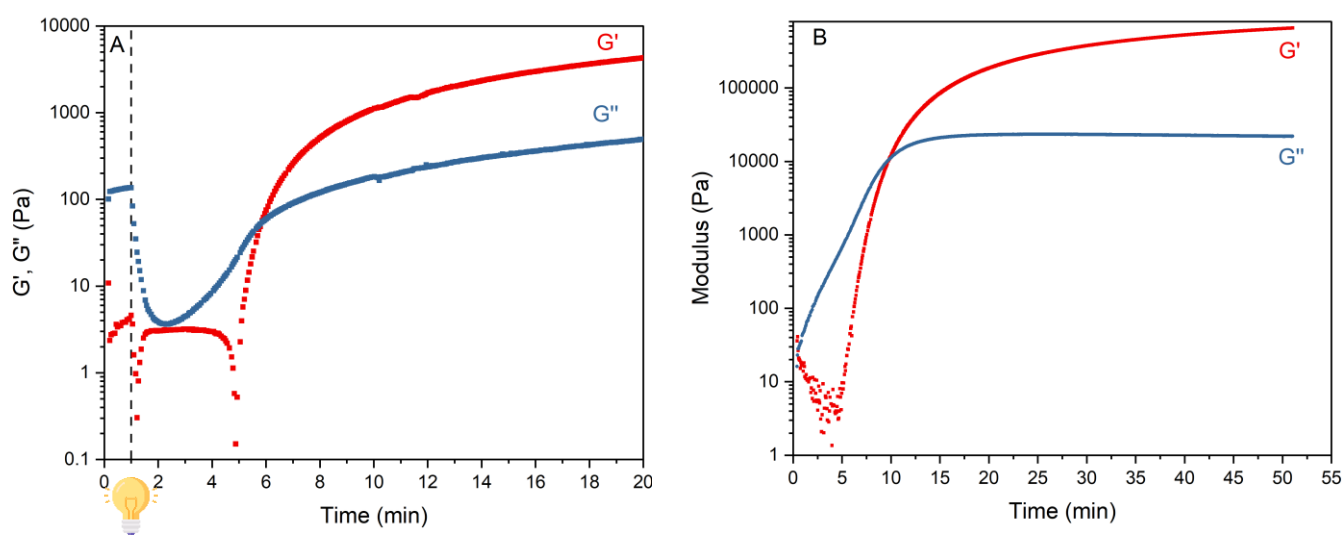


Figure 6. G' and G'' curves ($f = 1$ Hz, $\gamma = 0.1\%$) of a TMPTC/ cadaverine formulation containing 2 wt.% of IR-813 A Photothermal polymerization under irradiation using a laser

diode irradiating at 808 nm and 0.5 W.cm^{-2} . The irradiation starts at $t = 1 \text{ min}$ (the dashed line represents the start of irradiation), **B** Thermal polymerization, rheometer set up at $90 \text{ }^\circ\text{C}$

During thermal polymerization at $90 \text{ }^\circ\text{C}$, the gelation time of the PHU formulation was 9 min 48s (figure 6B) showing a great improvement due to the heating compared to the gelation time at room temperature (33 hours). This fast gelation time by thermal polymerization shows that the acceleration in the gelation kinetic is due to the increase of the temperature. The photorheological study confirmed that the photothermal effect accelerates the curing of the PHU's thermosets compared to the polymerization at room temperature and was faster than the thermal polymerization.

The gel times measured by photorheology were corroborated by the evolution of the amine conversion with irradiation time as followed by RT-FTIR (NIR) spectroscopy (Figure 7). The use of NIR detection allows measuring the absorbance over the entire thickness of the sample. Additionally, it allows measuring the evolution of the amine conversion in real time by simply following the disappearance of the first harmonic of the NH_2 vibration band between 6300 cm^{-1} and 6700 cm^{-1} (Figure 7A). For all formulations, 70% conversion was obtained in less than 5 min of irradiation, which reached 90% after 20 min of irradiation. For comparison, the non-irradiated PHU system raised only 20% conversion after 20 minutes at room temperature (Figure 7B). Interestingly, the photorheometry and NIR-spectroscopy experiments also revealed that the reaction almost ceases to evolve after 20 min of irradiation. Accordingly, PHU thermosets were synthesized through irradiation of the formulations for 20 min and its physico-chemical properties were assessed.

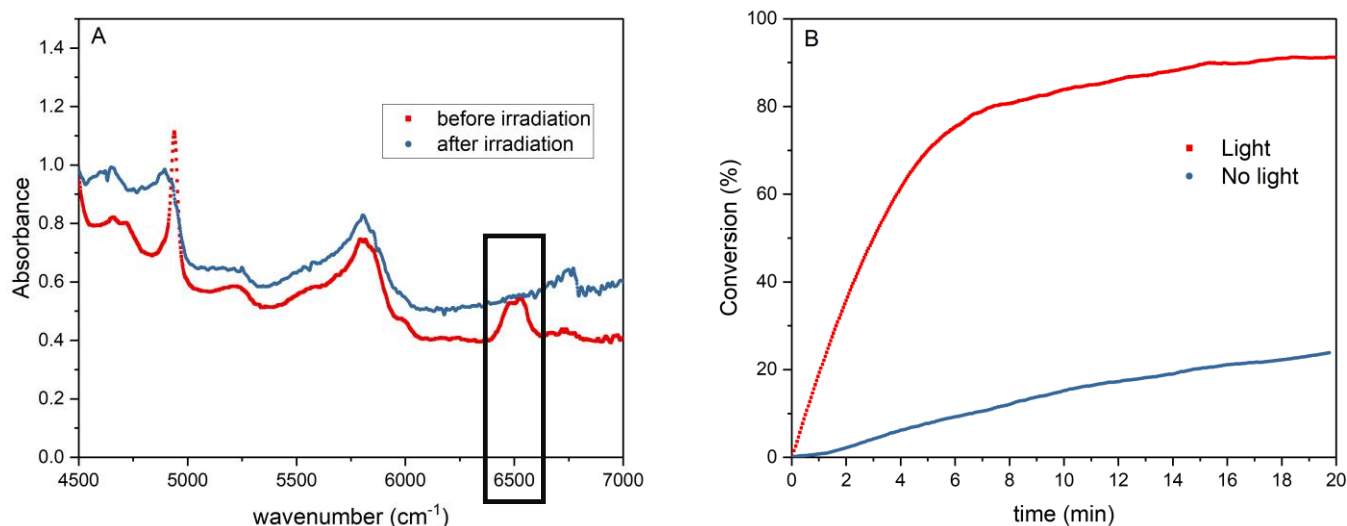


Figure 7. **A** NIR spectra of TMPTC and cadaverine with 2 wt.% of IR-813 before and after the irradiation; **B** Conversion of primary amine during irradiation at 785 nm measured by NIR spectroscopy in transmission for the TMPTC-cadaverine formulation with 2 wt.% IR-813.

Regarding the macroscopic properties of the obtained PHU thermosets after 20 minutes of irradiation, only the PHU containing 0.1 wt.% of IR-813 remained liquid while the other materials appeared cross-linked when touched. Indeed, as presented in Table 2, all PHU materials remained insoluble after several hours in DMF at 60 °C and displayed gel contents above 90%, confirming high cross-linking of the materials. The formulation containing 0.25 wt.% of IR-813 exhibited a slightly higher swelling ratio and lower insoluble content probably due to a lower conversion of the 5-membered ring cyclocarbonates.

Table 2. Thermal properties, swelling index and gel content of PHUs synthesized from TMPTC and 1,5-diaminopentane with [IR-813] varying between 0.25 wt.% and 3 wt.% and cured for 20 minutes.

Ref	[IR-813] In wt.%	Curing process	T_g^b (°C)	ΔH^b (J.g ⁻¹)	DSC conv. (%)	Swelling index ^c (wt.%)	Gel content ^c (wt.%)
1	0	No curing	//	112	//	//	//
2	0.25	NIR ^a	14	58	48	306 ± 23	82 ± 1

3	0.5	NIR ^a	21	24	78	264 ± 17	92 ± 1
4	1	NIR ^a	28	11	90	248 ± 9	93 ± 1
5	1.5	NIR ^a	28	10	91	230 ± 12	92 ± 1
6	2	NIR ^a	29	10	91	249 ± 20	91 ± 1
7	3	NIR ^a	31	5	96	275 ± 9	91 ± 1
8	2	oven 155 °C	22	26	77	254 ± 13	90 ± 1

a) LED sources $\lambda = 850 \text{ nm}$ $I = 0.5 \text{ W.cm}^{-2}$, b) determined from first ramp of DSC analysis, c) in DMF at 60 °C

In order to determine the final advancement of the reaction, DSC analysis of the PHU samples were also performed to measure the enthalpy of the remaining nonreacted monomers by comparison to that of an uncured mixture ($\Delta H_0 = 112 \text{ J.g}^{-1}$). Additionally, their glass transition temperature was determined and compared to the glass transition temperature of a fully cured material ($T_{g\text{max}} = 41 \text{ °C}$). Analysis of as obtained PHU thermosets, *i.e.* after 20 minutes of irradiation, by DSC (Figure 8) confirmed the high monomer conversion measured in RT-FTIR (conv. $\geq 90\%$) since materials obtained with 1 – 3.0 wt.% of IR-813 have similar glass transition temperatures ($28^\circ\text{C} \leq T_g \leq 31 \text{ °C}$). Nevertheless, this is lower than the 41°C obtained for a PHU with 100% monomer conversion.

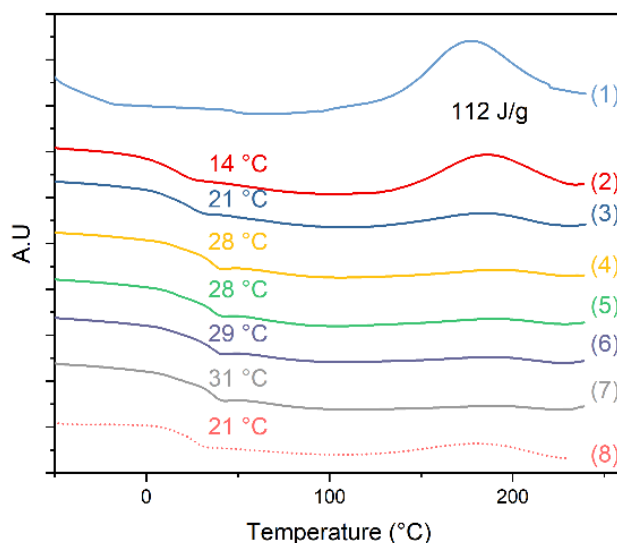


Figure 8. DSC thermograms of PHU thermoset cured with varying amount of IR-813 wt.% (1) crude formulation, (2) 0.25 wt.%, (3) 0.5 wt.%, (4) 1 wt.%, (5) 1.5 wt.%, (6) 2 wt.%, (7) 3 wt.% after 20 minutes of irradiation (850 nm , $0.5\text{ W}\cdot\text{cm}^{-2}$) and (8) resin with 2 wt.% IR-813 cured in an oven at $155\text{ }^{\circ}\text{C}$ for 20 minutes.

The lower T_g obtained by DSC analysis for PHU prepared with 0.25 wt.% of IR-813 also confirmed what was observed in swelling experiments as a lower conversion (78%) was measured in this case.

Through DSC analysis, the efficacy of the photothermal polymerization of PHU has been shown allowing higher conversion (91%) than the classic thermal curing (77%) in 20 minutes.

FTIR analysis

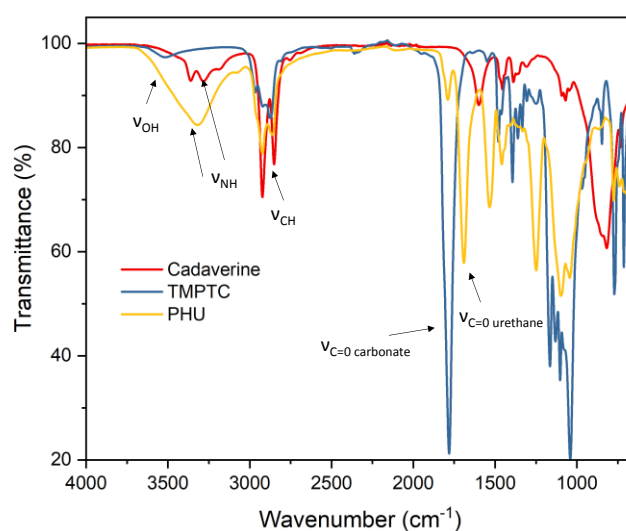


Figure 9. FTIR full spectra of cadaverine, TMPTC and PHU thermoset with [IR-813] of 2 wt.% cured under NIR at 850 nm and $0.5\text{ W}\cdot\text{cm}^{-2}$ for 20 minutes.

Thanks to the DSC curved, high conversion has been observed but without information on the chemical structure of the network. Thus, FTIR analysis of the sample were performed to confirm the formation of a polyhydroxyurethane network. The surface's ATR-IR analysis of the PHU showed the apparition of the stretching band of hydroxy group at 3300 cm^{-1} and of

the stretching band of the urethane at 1700 cm^{-1} with the disappearance of the cyclocarbonate stretching band at 1790 cm^{-1} (figure 9). The appearance of these two bands confirmed the formation of hydroxyurethane during the reaction. The two faces of the samples were analyzed and the face in contact with the air showed lower conversion of cyclocarbonate compared to the face in contact with the PTFE mold: the isolation effect of the PTFE allowed the mold to store heat and lead to less heat loss compared to the face in contact with air. Nevertheless, this inhomogeneity has not been observed on different spots of each side, confirming the homogeneity of the NIR-LED irradiation.

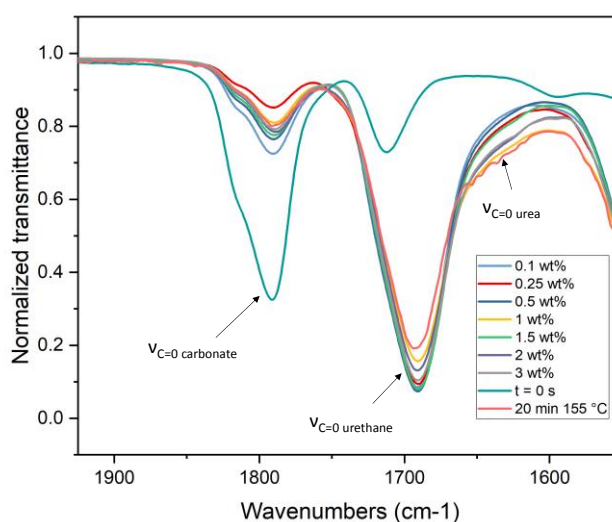
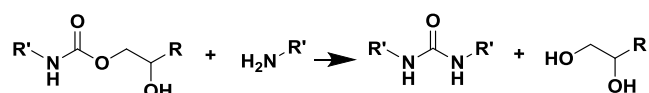


Figure 10. FTIR spectra of PHU thermoset of TMPTC and 1,5-diaminopentane with IR-813 0.1-3 wt.% after 20 minutes NIR irradiation (850 nm , $0.5\text{ W}\cdot\text{cm}^{-2}$) and resin with 2 wt.% IR-813 at $155\text{ }^{\circ}\text{C}$ in an oven for 20 minutes. (Normalized on the C-O vibration band at 1100 cm^{-1})

First of all, after 20 minutes of irradiation the stretching band at 1790 cm^{-1} drastically decreases (Figure 10), but some cyclocarbonate remained for all the analyzed samples. In addition, regardless of the IR-813 concentration, the ratios cyclocarbonate/urethane were similar, even for the sample cured at $155\text{ }^{\circ}\text{C}$ in an oven for 20 minutes.

Nevertheless, a shoulder at 1640 cm^{-1} was observed on the spectra, witnessing the formation of urea during the curing (Scheme 3). Indeed, it has been demonstrated that when temperature above $100\text{ }^{\circ}\text{C}$ were reached, urea started to form.³⁶ In the case of linear polymer this reaction limits the growth of the polymeric chain so the molecular weight¹⁶. In the case of crosslinked network, it decreased the crosslinking density leading to poorer properties (high swelling, low T_g ...).



Scheme 3. Reaction of amine with hydroxy urethane forming urea and diol

Surprisingly even if the reached temperatures were superior to $100\text{ }^{\circ}\text{C}$, the amount of urea remained lower when the photothermal effect was used compared to the PHU cured at $155\text{ }^{\circ}\text{C}$. This behavior could be explained by the very fast increase of temperature that allows the very fast cyclocarbonate aminolysis, thus consuming most of the primary amine and limiting the formation of urea. On the contrary, in the oven, the temperature increases slowly inside the resin and the proportion of free amine stays higher during the curing process, allowing the formation of urea by reaction with already formed hydroxyurethane groups.

Comparison of energy requirements between conventional thermal and photothermal curing

As mentioned in the introduction, photo-induced thermal polymerization using LEDs may result in significant energy savings for the production of coatings when compared to traditional curing using thermal ovens. In order to determine the energetic cost associated with both technologies, calculations of the energy input required to cure the proposed formulation either with the LED set-up or with an oven were performed (see supporting information). For a fair comparison of both systems, the energy required to cure the same

surface area was considered for both cases. Indeed, the LED set-up employed in this study allows to cure only 4.0 cm² of coating in 20 min, while the oven allows to cure 270 cm² in 8 h at 90 °C. Although both set-ups do not represent industrial processes, comparing the energy required per coating surface in both cases appears more relevant. Accordingly, for oven curing, we considered that 2 samples, with dimensions 34 cm x 40 cm, could be cured at the same time by placing them on the upper and lower positions in the oven. The oven was considered to heat at maximum power (1900 W) for 15 min to increase the temperature inside the oven from room temperature to 90 °C, and to use only 25% of the maximum power to maintain the temperature over the remaining 8 h required to complete the curing process. Using these parameters, 54.1 MJ/m² were found necessary to cure the formulation in the oven, while only 41.4 MJ/m² were required with the LED set-up. Consequently, the LED curing process allows for about 36% energy savings, making this technology more sustainable than conventional curing. It should be noted that these calculations were made without considering the low energy efficiency of thermal processes, which is of 65% with state of the art ovens.^{37,38} Higher energy savings, of 50% or more, are thus expected when using NIR LED set-ups combined with NIR “heaters” in place of conventional thermal ovens.

Conclusion

In this study, we demonstrate the efficiency of the NIR heater IR-813 to generate heat under NIR irradiation to cure a resin composed of the CO₂ based trifonctionnal-5-CC TMPTC and a biobased diamine, namely cadaverine. By varying the amount of heater or the irradiance, we were able to tune the reached temperature from 80 °C up to 155 °C. Markedly, the photothermal curing allows to drastically accelerate the kinetics of the aminolysis of the cyclocarbonate, compared to conventional thermal polymerization, allowing reaching a short gel time of 3 minutes under 808 nm irradiation (0.5 w.cm⁻²) in the presence of 2 wt% of NIR heater. In addition, high conversion (92%) was achieved in short times (20 minutes),

compared to thermal curing (77%). Although the reaction is fast and the reached temperature is high, the network structure appears to be similar between PHU thermosets prepared conventionally by thermal curing and PHU thermosets prepared using the photothermal effect. The fast photothermal polymerization reported in this article allows to consider PHUs as a substitute to PUs for coatings applications where fast and energy efficient curing are sought after. Moreover, calculations were performed to determine the energy input required to cure the PHU formulation either with the LED set-up or with an oven. If the energy required to cure the same surface area is considered, it appears that the LED curing process allows 36% energy savings (55.5 MJ/m² for the oven process vs 35.4 MJ/m² for the NIR LED process), making this process more sustainable than the conventional thermal process. Finally, the fast kinetics and the deep penetration of light allowed by NIR irradiation may also be of interest for the production of PHUs foams, which is currently under study in our laboratory.

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Authors contribution

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