Near-Infrared induced photothermal decomposition of Charge Transfer Complexes: a new way to initiate thermal polymerization

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ABSTRACT: A new approach for the Near-Infrared induced free radical photopolymerisation (FRP) of (meth)acrylate-based polymers through the use of Charge Transfer Complex (CTC) is proposed. This challenging strategy is based on Near-Infrared sensitizers (e.g. cyanines) which act as very efficient heat generator (heater) upon NIR irradiation, allowing the activation of CTC in-situ formed between an electron rich *N*-aromatic amine and an iodonium salt used as an electron acceptor. The thermal ability of the different systems to initiate a polymerization upon thermal activation has been investigated by Differential Scanning Calorimetry (DSC) and their behaviors upon NIR irradiation have been examined by thermal imaging experiments. The role of cyanines has also been highlighted by spectrophotometry as well as Fourier Transform Infrared (FTIR) spectrometry. Finally, to highlight the huge potential of the proposed approach, these systems have been tested on glass and carbon fibres prepreps to the composite's development.

Polymers can be found almost in every material used in our daily life so that the development of safer, environmentally friendly and more efficient initiating systems are actively researched. In this field, Charge Transfer Complexes (CTC) between *N*-aromatic amines (donors) and iodonium/sulfonium salts (acceptor) constitute an efficient strategy to design thermal-, photo- or duals initiators i.e. activable under both thermal and photochemical stimuli (Scheme 1).¹⁻³ Their high stabilities, their lower hazards and their in-situ formations establish them as ideal alternatives to the classical free radical polymerisation (FRP) initiators. Indeed, FRP initiators usually contain peroxides (O-O) or azo (N=N) compounds, which are well-known for being unstable and to present a poor stability in resins. CTCs also constitute a versatile approach for the design of photoinitiating systems as a careful selection of both the donor and the acceptor allow to efficiently tune the absorption maximum as well as the molar extinction coefficient. Lastly, Near-infrared wavelengths have been regarded as an appropriate spectral range for initiating a polymerization process^{4,5} as these long wavelengths offer a deeper light penetration than UV light. As a result of this, the scope of application of photopolymerization has been revolutionized, giving access to the unprecedented polymerization of thick samples⁶. Parallel to this, NIR light is also safer than UV light for manipulators, addressing the safety concerns that have come to the forefront about the use of UV light sources.

Nevertheless, considering the NIR light is less energetic than UV light, initiating systems that are activated in this

spectral range have also to be extremely reactive in order to overcome the low energy provided by the system. At present, two distinct strategies have been developed in the literature concerning the use of NIR light for photoinitiation. First, by combining a NIR photosensitizer with the appropriate additives, the FRP of acrylates could be efficiently promoted⁴. Second, due to the heat released by excitation of a NIR dye, the decomposition of a thermal initiator could be controlled, inducing the polymerization⁵. Aim of this study is therefore to conjugate the beneficial effects of a NIR irradiation, enabling to use NIR sensitizer as heaters with those of the CTCs which can be highly reactive initiating systems (See Scheme 1). Especially, the challenge in this work consisted in the initiation of a polymerization process while providing a minimum of energy to the system, what can be achieved while selecting NIR light sources for irradiation. The two cyanines selected for this work have been chosen for their ability to act as NIR heaters. Notably, their capacities to reach elevated temperature upon photoexcitation and thus to induce a thermal polymerization have been demonstrated in previous works.^{5,7-9}

Based on these requirements, two NIR sensitizers were selected, namely S2025 and S0507. To form the Charge Transfer Complexes, 1,3-phenylenediamine (**PDA**), *N,N*-dimethyl-*p*-toluidine (**DMPT**) and *N,N*,3,5-tetramethylaniline (**TMA**) were selected as representative amines and *bis*-(4-*tert*-butylphenyl)-iodonium hexafluorophosphate (**Iod**) as the electron acceptor. Chemical structures of the different compounds used in this study are presented in the Chart 1.

Scheme 1. Previous [Phosphines/ Amines/ Indole/ Pyrrole - Iodonium/Sulfonium Salt] CTC proposed as dual initiators and newly approach for the thermal initiator through a NIR irradiation

Chart 1. Main Chemical Compounds used in this study

The first step of this study consisted in comparing the polymerization results obtained with different CTC-based systems containing or not a NIR sensitizer. Different characterization methods were combined to have a full picture. Notable, the monomer conversion was monitored by FTIR measurements. The FTIR spectra collected before and after irradiation with a laser diode at 785 nm ($I_0 = 2.5\text{ W/cm}^2$) are presented in the Figure 1A and 1B and illustrate the crucial role of S2025 in the polymerization initiated by the [PDA – Iod] $_{\text{CTC}}$ in TMPTA. Indeed, a huge difference of the absorption intensity can be noted for the acrylate peak at 6160 cm^{-1} for the system containing the NIR sensitizer whereas only a weak difference could be found before and after irradiation for the resins without NIR sensitizer. A final acrylate function conversion of 72% could be calculated for the system containing the NIR sensitizer, against only 28% without it.

A similar calculation could be made for a second initiating system presented in the Figure S1 (S2025 – TMA – Iod in TMPTA) and that differs from the former one by the choice of the amine (TMA instead of PDA). Even if the conversion obtained with this second initiating system still comprising S2025 as the NIR dye was only of 35% for the reactive function, no conversion could be observed for the CTC system alone in TMPTA. This conclusion is reinforced by the physical state and the aspect of the samples after irradiation: while the TMPTA resin containing the [PDA–Iod] $_{\text{CTC}}$ system remained liquid after irradiation, the same resin containing

S2025 was totally cured (See Figure 1C) due to an efficient polymerization process.

Figure 1. A, B: FTIR Spectra measured before (1) and after (2) 5 min of irradiation with a laser diode at 785 nm, 2.5 W/cm^2 , RT, laminate. A: 0,005 % $_{\text{mol}}$. S2025 + 2 % $_{\text{wt}}$. PDA + 2 % $_{\text{wt}}$. Iod in TMPTA; B: 2 % $_{\text{wt}}$. PDA + 2 % $_{\text{wt}}$. Iod in TMPTA. C: Pictures of formulation containing 0,005 % $_{\text{mol}}$. S2025 + 2 % $_{\text{wt}}$. PDA + 2 % $_{\text{wt}}$. Iod in TMPTA after irradiation. D: Visible to NIR absorption spectra (in PMMA optic cuvette of 10 x 10 mm) of 2 % $_{\text{wt}}$. PDA + 2 % $_{\text{wt}}$. Iod in TMPTA without (1) and with 0,005 % $_{\text{mol}}$. S2025 (2)

Comparison of the visible to NIR absorption spectra of the S2025/PDA/Iod and PDA/Iod systems definitely established that the cyanine S2025 was the only compound capable to absorb and generate heat upon excitation with an incident NIR light at 785 nm (See Figure 1D). Similar conclusions in terms of absorption can be formulated when the second *N*-aromatic amine (TMA) was used to form the CTC. Besides, with this second CTC, lower acrylate function conversions were determined. The different results are presented in Supplementary Information (Figure S1).

In a second step, the thermal initiation properties of the charge transfer complexes have been explored by Differential Scanning Calorimetry (DSC) and the main data of these measurements are gathered in the Table 1A (the DSC traces are available in Supporting Information; Figure S2). As interesting finding, it can be noted that two CTC systems, namely [DMPT – Iod]_{CTC} and [TMA – Iod]_{CTC} have to be heated at least at 80°C to activate the CTC and at 105°C to properly initiate the polymerization.

The conversions in reactive functions have been calculated, based on the theoretical enthalpy value for a complete conversion of the acrylate's double bonds ($\Delta H_{\text{theor}}=78.2$ kJ/mol). Conversions of 63, 70 and 80 % could be respectively determined for the PDA, TMA and DMPT-based systems. These conversions are relatively high, considering that a trifunctional monomer has been used in this work. Indeed, due to the multifunctionality of TMPTA, a complete monomer conversion is not possible, reactive acrylate functions remaining inaccessible in the polymer network or isolated without partners to react.

Table 1. (A). Integrated Enthalpies and corresponding Peak Temperature for the CTCs used as Thermal Initiating Systems in TMPTA (DSC acquisition in Supporting Information); **(B)** Maximum temperatures reached by the different systems in TMPTA during irradiation with a diode laser at 785 nm, 2.5 W/cm² and recorded by Thermal Imaging Camera

A	System	ΔH (J/g)	T _{beginning} (°C) peak	T _{max} (°C) peak
	[PDA – Iod] _{CTC}	499	95	128
	[TMA – Iod] _{CTC}	556	75	105
	[DMPT – Iod] _{CTC}	635	72	105

B	System	T _{max} (°C)
	S2025 - [PDA – Iod] _{CTC}	126
	[PDA – Iod] _{CTC}	32
	S2025 - [TMA – Iod] _{CTC}	184
	[TMA – Iod] _{CTC}	25

To determine the exact temperature reached by the considered systems during NIR irradiation, an infrared thermal

imaging camera has been used. An example of the temperature profile reached at the surface of a formulation is proposed in Figure 2. As shown in this Figure, only the irradiated area is heated upon NIR light exposure offering a possibility a spatial control for the photothermal reaction. The temperatures reached by the different systems are summarized in the Table 1B. Two conclusions emerge from these different experiments: (i) the NIR sensitizer generate a great amount of heat as differences of almost 100°C for [PDA–Iod]_{CTC} and more than 150°C for [TMA–Iod]_{CTC} can be noticed between the systems with and without NIR sensitizer, and (ii) the heat reached by the system upon photoexcitation is sufficient to exceed the CTC's activation temperature so that the polymerization could be efficiently initiated. Finally, to evidence the versatility of our system, a methyl methacrylate-based (MMA-based) system was also used instead of the acrylate monomer (TMPTA).

To attest the broadness of applicability of our CTC-based systems, all of them have also been tested on glass and carbon fibres preregs. Actually, composite materials present strengthened mechanical properties as well as an extended durability compared to the pure polymer^{10,11}. These new initiating systems composed of NIR sensitizer dispersed into a CTC-based resin offer the great advantage of being present in a unique formulation, reducing the preparation time and making it easier to apply on the wanted surface compared to systems based on classical thermal initiator (e.g. peroxides) which are not stable in the monomer.

Figure 2. Example of thermal imaging experiment during irradiation of formulation (S2025 – [PDA – Iod]_{CTC} in TMPTA) placed in a 5 mL cork

A previous work has demonstrated that it was possible to use CTC on preregs with a 405 nm irradiation² but the present work is, to the best of our knowledge, the first attempt that a CTC is activated with a NIR light source. Few millilitres of formulation were dropped off on preregs, previously sliced. The different irradiation times and results to cure the composites for two types of CTCs are gathered in the Table 2. Remarkably, fast curing of the preregs are always obtained with the proposed approach (in less than 240s; Table 2).

Table 2. Maximum temperatures reached by the different systems during irradiation with a laser diode at 785 nm, 2.5W/cm² on two types of support and recorded by Thermal Imaging Experiments.

System	Irradiation time (s)	Result on pre-pregs
0.005 %mol. S2025 + 1 %wt. [PDA-Iod] _{CTC} in MMA-based system on glass fibres pre-pregs	206
0.005 %mol. S2025 + 1 %wt. [PDA-Iod] _{CTC} in MMA-based system on carbon pre-pregs	240
0.005 %mol. S2025 + 1 %wt. [TMA-Iod] _{CTC} in MMA-based system on glass fibres pre-pregs	180
0.005 %mol. S2025 + 1 %wt. [TMA-Iod] _{CTC} in MMA-based system on carbon fibres pre-pregs	180

Different experiments done for the three CTC systems in TMPTA based pre-pregs can be found in the following Table 3; in all case efficient curing were observed upon NIR light. Systems composed of a CTC formed with DMPT and the different CTC-based systems in which S2025 has been replaced by S0507 have been added to show the versatility of the proposed approach. Several conclusions can be drawn: first of all, MMA monomer can be used as a benchmarked resin to obtain tack free composites. Secondly, the irradiation time do not change in function of the pre-pregs, which can entail that the NIR wavelength efficacy is not strongly affected by material's absorbances (glass vs. carbon fibres – Table 2). Moreover, the temperature reached for the different fibers tested are rather similar for MMA based systems (Table 2). Finally, the system containing PDA needed a longer irradiation time than TMA system to decompose and initiate a polymerization. This can be assigned to the higher decomposition temperature of [PDA – Iod]_{CTC}, requiring more time for the appropriate temperature to be reached.

Table 3. Maximum temperatures reached by the different systems in TMPTA based glass fibers pre-pregs during irradiation with a laser diode at 785 nm, 2.5 W/cm²; recorded by Thermal Imaging Camera (cyanine introduced in 0.005 %mol. and CTC in 2 %wt).

System	T _{max} (°C) on glass fibres pre-pregs
S2025 – [TMA – Iod] _{CTC}	119
S2025 – [PDA – Iod] _{CTC}	152
S2025 – [DMPT] – Iod] _{CTC}	142
S0507 – [TMA – Iod] _{CTC}	102

Conclusion:

The results obtained with S2025 and S0507, combined with Charge Transfer Complexes between Iod and TMA/PDA/DMPT suggest that a Near-Infrared induced thermal polymerization of both acrylate and methacrylate monomers can be achieved. A new way to polymerize in depth opaque sample without peroxide is proposed here through the photothermal activation of in-situ stable CTCs. The role of S2025/S0507 has been highlighted as no polymerization is observed when the system does not contain cyanines. Complementary work will be performed in order to completely control the amount of heat released by the system, avoiding monomers and polymers degradation. For bigger samples, irradiation sources should be adapted in a way to increase the spot area. But the results obtained on glass and carbon fibres pre-pregs are promising for industrial applications, especially for composites. The use of this concept is 3D printing can also be examined in forthcoming works.

Experimental part:

All commercial chemicals were selected with the highest purity available and used as received. 1-Butyl-2-(2-[3-(2-(1-butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-diphenylamino-cyclopent-1-enyl)-vinyl]-3,3-dimethyl-3H-indolium tetrafluoroborate (**S2025**) and 2-[2-[3-(2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene)-2-(1-phenyl-1H-tetrazol-5-ylsulfanyl)-1-cyclohexen-1-yl]-eth-enyl]-1,3,3-trimethyl-3H-indolium chloride (**S0507**), purchased from Few Chemicals, were used as NIR sensitizers. CTCs systems were composed of an iodonium salt, *bis*-(4-*tert*-butylphenyl)iodonium hexafluorophosphate (**Iod**) from Lambson Ltd, and *N*-aromatic amines. For those latter and based on previous works, 1,3-phenylenediamine (**PDA**), *N,N*-dimethyl-*p*-toluidine (**DMPT**) were received from TCI and *N,N*,3,5-tetramethylaniline (**TMA**) was purchased from Alfa Aesar. Two monomers have been tested as benchmarked polymerizable systems: trimethylolpropane triacrylate (TMPTA) and a methyl methacrylate (MMA-based) monomer received from Sigma Aldrich.

The percentages of the different chemicals involved in the charge transfer complexes were calculated from the monomer content (in weight). The percentage of NIR sensitizers were calculated from the monomer content (in molar).

For the polymerization experiments, a Thorlabs laser diode was used to irradiate the sample placed in a 5mL cork at 785 nm, 2.5 W.cm⁻² during 5 min, at room temperature (RT) and under air. The temperature reached by the samples has been recorded during the irradiation time thanks to an infrared thermal imaging camera Fluke TiX500. Infrared absorption spectra have been acquired before and after irradiation using a Jasco 6600 Fourier Transform Infrared spectrometer (FTIR). The acrylate bands of interest (6100 – 6250 cm⁻¹) were compared before and after irradiation to confirm the polymerization. A Jasco V730 spectrophotometer has been used to measure the absorption of the formulation (placed in plastic cell) in the visible – NIR region (between approximatively 400 and 1100 nm) with a scan speed of 400 nm/min.

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