NIR Sensitizer Operating under Long Wavelength (1064 nm) for Free Radical Photopolymerization Processes

Haifaa Mokbel^{1,2}, Bernadette Graff^{1,2}, Frédéric Dumur³, Jacques Lalevée^{1,2*}

¹Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

²Université de Strasbourg, France

³Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France

Corresponding author: jacques.lalevee@uha.fr

Free radical polymerization upon near-infrared (NIR) light is still the subject of intense research efforts and remains a huge challenge particularly for long wavelength (> 1000 nm). In this study, a NIR dye operating upon long wavelength (1064 nm) is proposed for an efficient polymerization of acrylate monomers. A new three-component photoinitiating system is developed comprising the NIR dye in combination with an Iodonium salt (Iod) and an amine. Remarkably, the NIR dye (IR 1064) absorbing strongly in all the near infrared region (700-1200 nm) offers the possibility to use a broad range of irradiation wavelengths i.e. examples are provided at 785 nm and 1064 nm. Such long wavelengths are characterized by many advantages such as a deeper penetration of light and therefore a better curing of the monomer but it is also much safer than UV light. Excellent performance is observed for the three-component IR 1064/Iod/Amine system under air: high conversion of acrylate functions associated with a fast polymerization time. Three different amines have been examined in this study. The use of IR 1064 as NIR dye with a broad NIR absorption is - to the best of our knowledge - never proposed in the literature. The photoinitiating performances were studied using Real-Time Fourier Transform Infrared Spectroscopy.

Keywords: NIR dye, NIR irradiation, long wavelength, Free radical polymerization.

Light induced polymerization reaction is the subject of intensive research efforts [1-4]. Photopolymerization displays many advantages over conventional thermal processes. Reactions are very fast and take place at room temperature, what decrease the energy demand and reduce thermal runaway hazards. In addition, a spatial and temporal control is easy to achieve with photopolymerization. Most of photopolymerizable formulations are solvent-free, considerably reducing the emission of volatile organic compounds. From this viewpoint, photopolymerization can be considered as an “eco-friendly” polymerization process. Free radical photopolymerization (FRP) upon UV light is now widely used in industry, [5] and FRP notably finds applications in different areas such as coatings, inks, paints, 3D printing, medicine etc ... [1].

At present, most of the photoinitiating systems (PISs) under use in industry are adapted for UV irradiation setups. These short wavelengths are well-known to be harmful and allow only the curing of thin samples [6]. Therefore, the

development of photosensitive systems operating under longer and safer wavelengths are actively researched [7-12]. When having a look into the photoinitiating systems currently proposed, most of them are capable to initiate a polymerization under visible light [13-16]. More precisely, if an increasing number of systems have been reported during the past 10 years for successful photopolymerizations upon visible light (400-700 nm) exposure, the use of near-infrared (NIR) light irradiation (>750 nm) still remains a challenge due to the low photon energy that decreases the potential photochemical reactivity. NIR photopolymerization strategy could however address the major toxicity and depth of cure issues associated with UV curing. The use of longer wavelengths above 750 nm, specifically, the near-infrared (NIR) wavelength is very convenient and advantageous. NIR light is an ideal spectral range for photopolymerization process as it exhibits several advantages: i) efficiency of the process with low energy consumption and a moderate device cost to proceed contrary to thermal solutions; ii) mild irradiation conditions: safer and cheaper light sources and iii) a deeper light penetration inside the sample allowing the polymerization of thick and highly filled samples [17-19].

Over the past decades, NIR dyes have found applications in various research fields such as in bioimaging, photothermal therapy, theranostic or non-linear optical applications [13-17,20-22], but also in the photographic industry [16]. Obviously, literature data on NIR dyes remains limited and the search for new dyes as good candidates for photopolymerization is a huge challenge [7,9, 23-25]. Most of the near infrared absorbing dyes are based on cyanine. Cyanine dyes have previously been used as photosensitizer for the curing of NIR photoinitiating systems [6,13,14,17,19]. From this point of view, cyanine dyes possess high molar extinction coefficients and absorb in the red to near-infrared region, but these dyes are also characterized by a good chemical and photochemical stability [26]. They can be used as heater (light to heat convertor) and they have attracted the interest of researchers due to their application in the medical fields [20-22].

The NIR dye can act as a photosensitizer; it absorbs the light emitted by the NIR light source and reacts with a combination of additives to generate reactive species. Recently, Bonardi et al. developed different photoinitiating systems based on NIR dyes absorbing at long wavelengths.[18] In this example, two NIR dyes (IR 1048: 1-Butyl-2-[2-[3-[(1-butyl-6-chlorobenzylidene)indol-2(1H)-

ylidene) ethylidene]-2-chloro-1-cyclohexen-1-yl]ethenyl]-6-chlorobenz[*cd*]indolium tetrafluoroborate and IR 1061: 4-[2-[2-Chloro-3-[(2,6-diphenyl-4*H*-thiopyran-4-ylidene) ethylidene]-1-cyclohexen-1-yl] ethenyl]-2,6-diphenylthiopyrylium tetrafluoroborate) with absorption maxima at 1048 and 1061 nm respectively, were used to develop a photothermal approach. The four-component photoinitiating system (PIS) containing the NIR dye/Iodonium salt (Iod)/phosphine/thermal initiator combination was able to initiate the FRP of a methacrylate monomer upon exposure to a LD@1064 nm [18]. Besides, this example still showed slow kinetics of polymerization with a high inhibition time (up to 100s) for polymerization under air. Therefore, the design of new PIS, especially for long wavelengths (1064 nm), remains a challenging task for mild irradiation conditions and under air.

In this context, we propose a NIR dye characterized by an original chemical structure and a good absorption in all the 700-1200 nm range for the FRP of acrylate monomers. Interestingly here, through a photochemical approach, the IR 1064/Iod/amine PIS is proposed as an efficient system for polymerization processes carried out at long wavelength (@1064 nm). IR 1064 presented here (Scheme 1) has an absorption maximum at 1064 nm, but the reactivity was also quite good upon exposure to a LD@785 nm. The frontier orbitals (highest occupied – HOMO – and lowest unoccupied molecular – LUMO – orbitals are depicted in Figure S1 in supporting information) show a clear charge transfer character for the lowest energy transition with HOMO and LUMO located on different moieties of the structure. From our best knowledge, IR 1064 has never been reported in the literature in NIR photosensitive systems. Originality of this work relies on the possibility to change the irradiation wavelength over a wide spectral range. A comparison of the reactivity of different amines is also provided (Scheme 2). Amine compounds are known to be cheaper and more stable than phosphines. To monitor the polymerization kinetics, Real-Time Fourier Transform (RT-FTIR) spectroscopy was used as an appropriate technique.

Scheme 1. Chemical structure of IR 1064 “*N*¹,*N*¹,*N*⁴,*N*⁴-tetrakis(4-(diethylamino)phenyl)benzene-1,4-diaminium hexafluoroantimonate” NIR dye purchased from Lotchem Ltd. (China).

Scheme 2. Chemical structures of additives investigated in this work.

Photoinitiating ability of IR 1064 for the FRP: Effect of the amine structure

IR 1064 has been used in this study to initiate the free radical polymerization of a benchmark acrylate monomer (PETIA) upon irradiation with a LD@1064 nm. The three-component photoinitiating system containing IR 1064 (IR 1064/Iod/Amine; Scheme 2) leads to high polymerization rates. High final acrylate function conversions (FC close to 90%) were obtained with the three amines proposed. Tack-free samples were obtained within 20-100 seconds of irradiation (Figure 1A). These results are in full agreement with the IR spectra recorded before and after light activation of the IR 1064 based PIS (Figure 1B), where the characteristic pic of the acrylate function at 6160 cm⁻¹ drastically decreased after irradiation. Without the dye, no polymerization is observed.

Figure 1. (A) Photopolymerization profiles of PETIA (Acrylate function conversion vs. irradiation time) using IR 1064/Iod/Amine (0.1/2/3 %wt) where amine is (1) MHPT, (2) NPG and (3) DABA; (B) RT-FTIR spectra of PETIA monomer using IR 1064/Iod/MHPT (0.1/2/3 %wt) recorded before and after irradiation, the peak representative of acrylate function is indicated, upon exposure to LD@1064 nm ($I=1.6 \text{ W/cm}^2$, thickness = 1.4 mm, under air conditions. The irradiation starts after 10 seconds.

However, as shown in the Figure 1A, major differences can be found concerning the efficiency of the different amines: obviously, the polymerization is delayed as a function of the amine used. The polymerization reactions were performed under air and the formed initiating radicals react more rapidly with oxygen than with the monomer. By taking into account the time necessary to reach high final conversions, the efficiency trend followed the order shown in Figure 1A: 3-(Dimethylamino)benzyl alcohol (DABA) > 2-(*N*-methyl-*p*-toluidino)ethanol (MHPT) > *N*-phenylglycine (NPG). The inhibition time is clearly longer in the case of NPG compared to the two other amines, evidencing the dramatic influence of the amine structure on the polymerization process. Therefore, the interaction existing

between the dye and the amine is an important parameter governing the formation of initiating radicals. The low reactivity of NPG vs. MHPT and DABA can be probably ascribed to the low production of initiating radicals in this case, rendering the associated PIS less efficient to overcome the oxygen inhibition. Tertiary amine (such as DABA and MHPT in this work) are more efficient than the secondary one (NPG in this work), as already mentioned in the literature [27]. In all cases, an excellent reactivity of the different amines examined in this work could be evidenced, suggesting that the NIR approach was an elegant strategy for fast curing of thick samples upon long wavelength irradiation, what is beneficial for numerous applications.

Monomer effect on the initiation of FRP using IR 1064

In the previous section, photopolymerization measurements were done in PETIA monomer. The efficiency of NIR dye has also been demonstrated in di(trimethylolpropane)tetraacrylate (TA) as a benchmark monomer (Scheme 3). It is important to note that both monomers have very different viscosity (1000 mPa.s for PETIA and 160 mPa.s for TA). Therefore, the viscosity of the monomers is expected to have a major impact on the oxygen inhibition: The higher the viscosity of the monomer is, the less the oxygen inhibition is. In other words, the polymerization of viscous monomers is faster under air than for the fluid ones.

As anticipated, Figure 2 clearly indicates that a fast polymerization process could be obtained using the PETIA monomer whereas a slower polymerization kinetic was observed in TA. Besides, in the two cases, a similar final monomer conversion could be determined in the two monomers. The time necessary to reach a high final conversion is 30 seconds in PETIA, whereas this value increased to 55 seconds in TA. However, the final acrylate conversion is roughly 85 – 90% for the two multifunctional monomers. Tack-free samples were obtained with the two monomers. These data show the high reactivity of IR 1064 in terms of efficiency in different acrylate monomers.

Figure 2. Photopolymerization profiles (Acrylate function conversion vs. irradiation time) using IR 1064/Iod/DABA (0.1/2/3 %wt) in (1) PETIA and (2) TA; upon exposure to LD@1064 nm ($I=1.6 \text{ W/cm}^2$), thickness = 1.4 mm, under air conditions. The irradiation starts after 10 seconds.

Effect of irradiation wavelengths

Influence of the irradiation wavelength on the polymerization rate and the final monomer conversion has been checked in this section. The NIR dye IR 1064 allowed a satisfying polymerization under very different irradiation conditions. At 785 nm, the polymers obtained were tack-free using different amines. However, the polymerization was slower compared to the results obtained upon exposure to a LD@1064 nm. Using the two irradiation wavelengths, FCs approaching 90% could be determined. Meanwhile, the time necessary to reach high final conversions was considerably higher using the LD@785 nm in the presence of different photoinitiating systems: from 150 seconds upon LD @785 nm vs. 30 seconds upon LD @1064 nm for the three-component system IR1064/Iod/DABA as shown in Figure 3A. Modification of the inhibition time is directly related to the absorption properties of IR 1064 at these two wavelengths. Indeed, IR 1064 exhibits a better absorption at 1064 nm than at 785 nm (Figure 3B). An improved photoactivation was thus evidenced upon irradiation at 1064 nm, even if good efficiencies were still obtained at 785 nm.

Scheme 3. Benchmark acrylate monomers used in this work.

Irradiation device

Two laser diodes (LD) with different wavelengths were used throughout the study: LD@785 nm with a tunable irradiance (from 0 to 2.55 W/cm²) and LD@1064 nm with a tunable irradiance (from 0 to 2.55 W/cm²), both from Changchun New Industries (CNI).

Photopolymerization experiments

Kinetics of polymerization of the photosensitive formulations were followed through the double bond C=C conversion of acrylate function vs. time. The peak followed by Real-Time Transform Infrared (RT-FTIR) Spectroscopy (JASCO 6600) is located in the near infrared region at 6100-6220 cm⁻¹. Photosensitive formulations were deposited on a polypropylene film in a mold (thickness of the sample = 1.4 mm) and polymerized under air upon irradiation with NIR laser diodes. The light was turned on 10 seconds after the first spectrum measurements. More details about the photopolymerization experiments are given in the figure captions. All the experiments are carried out at room temperature (RT) and under air.

UV-visible absorption spectroscopy

The UV-visible-NIR absorption spectrum of IR 1064 in acetonitrile were acquired using a Varian Cary 3 spectrometer.

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Figure 3. (A) Representative time necessary to reach high acrylate function conversion (FC = 90%) using IR 1064/Iod/Amine (0.1/2/3 %wt) upon exposure to LD@1064 nm (I=1.6 W/cm²) and LD@785 nm (I=0.9 W/cm²), thickness = 1.4 mm, under air conditions. The irradiation starts after 10 seconds; (B) UV-visible-NIR absorption spectrum of IR 1064 in ACN.

In all cases, IR 1064 can be assumed as a versatile NIR dye that can be activated in all the 700-1200 nm spectral range (Figure 3B) ensuring a fairly good overlap with the emission spectra of the many NIR LEDs or laser diodes of academic or industrial interest.

Conclusion:

In this paper, IR 1064 was proposed as an interesting NIR dye for the development of new high performance PIS upon near-infrared irradiation. Excellent efficiencies were found for the free radical polymerization of multifunctional acrylate monomers such as PETIA and TA (Scheme 3). The three-component photoinitiating systems IR 1064/Iod/Amine were very reactive: different amines can be excellent candidates. The most interesting aspect of this work is clearly the possibility to photoactivate our PIS at two different wavelengths separated from each other by almost 300 nm. A control of the polymerization time with the selected light source was also demonstrated, what is of crucial importance for practical applications. For the forthcoming studies, new photoinitiating systems offering a wider photoactivation window will be presented. More particularly, the development of other NIR dyes for absorption > 1000 nm will be presented in forthcoming papers.

Experimental part:

Chemical compounds

Chemical structures of the different additives used in this study are given in Scheme 2. *Bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) were obtained from Lambson Ltd. (UK). *N*-phenyl glycine (NPG) and 3-(dimethylamino)benzyl alcohol (DABA) were purchased from Sigma-Aldrich. 2-(*N*-methyl-*p*-toluidino)ethanol (MHPT) was obtained from Albemarle. All chemical compounds were selected with highest purity available and used as received.

Efficiency of the different PISs was checked with a benchmarked multifunctional monomer containing acrylate functions (See Scheme 3). Pentaerythritol triacrylate (PETIA) and Di(trimethylolpropane)tetraacrylate (TA) were received from Allnex.

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Graphical Abstract

Textual Information

A brief abstract
(required)

In this study, a NIR dye operating upon long wavelength (1064 nm) is proposed for an efficient polymerization of acrylate monomers. As unique originality, IR 1064 is used here in NIR photoinitiating systems. A new three-component photoinitiating system is developed comprising the NIR dye in combination with an Iodonium salt (Iod) and an amine. Remarkably, the NIR dye (IR 1064) absorbing strongly in all the near infrared region (700-1200 nm) offers the possibility to use a broad range of irradiation wavelengths i.e. examples are provided at 785 nm and 1064 nm.

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Authors' Names(required)

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Graphical Information

Supporting Information

Figure S1. Frontier orbitals HOMO and LUMO at UB3LYP/6-31G* level for IR 1064.