Advances of Near Infrared Sensitized Radical and Cationic Photopolymerization: from Graphic Industry to Traditional Coatings

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This contribution summarizes recent progress in the field of near-infrared (NIR) initiated photopolymerization. The photoinitiator system consists of a cyanine as sensitizer (\textit{Sens}) and an iodonium salt with distinct structural pattern of both the cation and anion as radical initiator. Both, photonic and thermal events are discussed as the main source for formation of initiating species. Electron transfer between the excited state of \textit{Sens} (\textit{Sens}\textsuperscript{*}) and the iodonium salt can be seen as the main source for formation of initiating species such as radicals and protons/electrophiles. Furthermore, the ion mobility as probed by the electric conductivity possesses a major function to tune the reactivity of the photopolymer system. The reactivity of these systems was studied in different applications such as Computer to Plate (CtP), LED curing, photonic baking, and curing of powder coatings with NIR lasers exhibiting line shape focus.

Keywords: near infrared, photosensitizer, iodonium, crosslinking, laser, LED

1. Introduction

This contribution summarizes the use of NIR radiation to initiate polymerization processes according to a photonic and thermal mechanism. This type of chemistry was born in the graphic industry [1] using the Computer to Plate (CtP) technology for digital patterning of lithographic substrates. The first public report appeared in 1993 [2]. CtP uses NIR lasers to image lithographic patterns without the need of intermediate information carrier (film mask) [1,2]. Highly light sensitive materials are needed for such procedures because the time frame to expose one pixel covers only several $\mu$s/pixel. Nowadays, some feasibility studies successfully showed the working principle of NIR initiated photopolymerization for coatings [3-7]. The majority of radiation curing relies on the well established UV-curing [8].

Imaging systems based on CtP and photopolymerization consist of a cyanine as photosensitizer (\textit{Sens}) with absorption in the NIR and an acceptor that generates initiating radicals upon photoinduced electron transfer [1c]. The latter has been often called radical initiator (\textit{RI}).

Moreover, there exist only a few reports about NIR sensitized cationic crosslinking [6,9]. Thermal decomposition of diazo compounds by NIR absorbers upon excitation by NIR lasers has been applied in some commercialized imaging systems [1b,9]. This resulted in formation of protons according to a thermal process needed to crosslink resite resins.

The question often arises why a NIR initiated system has not reached the necessary attention in the photopolymerization community. One reason can be seen in insufficient solubility of the initiator components \textit{Sens} and \textit{RI} in the high viscous resins. Many NIR absorbers based on cyanines and radical initiators based on iodonium salts possess an insufficient solubility in common industrial coatings [3-6]. There is a need for materials exhibiting an improved solubility in such surroundings either.

In addition, it has been accepted that depending on molecular structure the excited singlet state mostly deactivates radiationless (>85%) while only
a small fraction fluoresces [5]. The function of heat generated by thermal deactivation has not been clear until today. Thus, it would be interesting to check whether the generation of radicals completely follows a photonic mechanism or the heat released carries an additional function in NIR photopolymers resulting in thermal decomposition of the radical initiator.

NIR initiated photopolymerization also requires the use of appropriate light sources. While NIR lasers with emission at either 808 nm or 830 nm have been successfully applied for imaging of large areas, the curing of classical coating would require the exposure with radiation sources comprising less expensive technical components. From this point of view, NIR LEDs would be an alternative to expose large area coatings according to a photonic mechanism. Several LED-arrays of lab size with emission at 750 nm, 790 nm, 850 nm, and 940 nm were selected to cure coatings comprising a cyanine as sensitizer and a RI. Furthermore, the structure of Sens was varied to obtain an optimal overlap between LED emission and the absorption of Sens. This required to change the substitution pattern of the absorber to adjust its absorption and to obtain an acceptable solubility in industrial coatings.

In addition, we focused our selection of RIs to iodonium salts because their general function in photopolymers has been well disclosed [1b-c]. Iodonium salts comprising different anions of low coordination capability were preferentially chosen for the investigations; that is the [BPh4]--anion, the [B(CN)4]--anion, the [B(C6F5)4]--anion, the [(CF3SO2)2N]--anion, and the PF6-- anion [4]. Borates have been used for a long time in cationic photopolymerization prefer to use the [B(C6F5)4]-- anion [11].

Furthermore, formation of protons should be also possible according to a mechanism based on photoinduced electron transfer. Donation of an electron by Sens* to RI results in a cation radical Sens++. This reacts in a consecutive step to photoproducts and protons. Further details about the reaction mechanism can be found elsewhere [5, 6,12].

Moreover, the development of modern lasers has led to systems generating a continuous line shaped focus. The line length can exceed up to several meters depending on the power while the width in the focus is between a few micrometers and a millimeter. This was already successfully tested for physical drying of offset printing inks using a NIR absorber that selectively uptakes radiation [13]. These NIR absorbers possess a high quantum yield of non-radiative deactivation while the efficiency to release fluorescence remains relatively low. In other words, non-radiative deactivation results in selective release of heat in the laser focus of the coating while a heat sensitive substrate (paper) can be used without causing any damages for example by burning. In general, this could be applicable for many coating systems as well requiring in nowadays thermal curing techniques the use of energy wasting oven processes for drying. This contribution demonstrates with some examples that line shaped focused lasers could be applicable to post-bake processed printing plates. This is called “Photonic Baking” because it still relies on absorption and radiationless deactivation processes of Sens.

In addition, line shaped focused laser systems can be applied to cure powder coatings [7]. This occurred in a short time frame where heat release of the absorber starts first the melting of the powder while in a consecutive step photonic crosslinking of the melt occurs based on electron transfer. Such thermal curing would open the opportunity to replace big and energy consuming ovens by lasers resulting in saving of energy.

The use of photonic technologies tremendously reduces energy consumption. Main benefits can be seen in (i) the saving of time to obtain the necessary processing temperature (immediate start of the process), (ii) the possibility to stop the process by turning off the system (no additional time for cooling down), and (iii) the possibility to transport the energy directly to the object. On the other hand, thermal systems require to generate huge amounts of energy in which the target consumes only a small fraction.

2. Photosensitive Materials and Their Function

2.1. NIR Sensitizers [5,6]

Scheme 1 shows the structure of the NIR-sensitizers used to initiate radical photopolymerization. S1-S6 derive from cyanines absorbing in the NIR between 750-850 nm depending on their substitution pattern. A barbituryl group at the meso-position in S1-S6 is necessary to obtain a sufficient sensitivity of the NIR-photopolymer system.
Previous investigations summarize their oxidation potentials and dissolution behavior of S1-S6 in acrylate monomers such as 1,6-hexanediol diacrylate (M1), tripropyleneglycol diacrylate (M2), poly(ethylene glycol) diacylate 600 (M3), and trimethylolpropane triacrylate (M4) [6]. Interestingly, sensitizers bearing a cyclohexene moiety (S3-S6) in the center dissolve better in these monomers compared to S1 and S2. The latter bear a cyclopentene moiety in the molecule center resulting in an almost flat geometry [12]. This presumably diminishes the dissolution behavior. S1, S2, S3, S4, S5, and S6 possess a solubility of 0.6 g·L⁻¹, 1.0 g·L⁻¹, 10.6 g·L⁻¹, 8.9 g·L⁻¹, 0.3 g·L⁻¹, and 0.9 g·L⁻¹ in M4, respectively [6]. The distorted geometries of S3-S6 explain their improved solubility in the monomers chosen [12]. Sensitizer S7 was included in this study. It exhibits an absorption maximum at 980 nm and sufficient solubility of in the monomers used in this study (λₘₐₓ: 992 nm, εₘₐₓ: 2.23 × 10⁻⁵ M⁻¹ · cm⁻¹; taken in MeOH) [6]. This absorber was used for exposure experiments using a line shape focused laser with emission at 980 nm.

2.2. Radical initiators [4,5]

Iodonium salts were used as radical initiators. They exhibit a different pattern of the cation. Anions were selected from borates (a-c, o, p), organic acids (d, e), inorganic acids (f-h), sulfonic acids (i-l), and imides (m, n). Scheme 2 summarizes the different structures combined in the iodonium salts. Interestingly, the best performance was obtained if the anion exhibits a low coordination capability; that is for example the anion n. There was no correlation observed between oxidation capability of the anion and reactivity (Eₒₓ (V): a = 0.99 V, b = no oxidation, c = no oxidation V, o = no oxidation, p = 1.22 V) [5]. Surprisingly, iodonium salts bearing the anion n exhibit a huge solubility in the monomers M1-M4. This is at least several 100 g · L⁻¹. Moreover, iodonium cations with large steric requirements (5n and 6n) result in solubilities larger than 2000 g · L⁻¹. Both of these iodonium salts are liquid at room temperature. Thus, such iodonium salts can be considered as ionic liquids. This giant solubility of iodonium salts comprising the anion n helps to introduce such materials in highly viscous industrial coatings.

Scheme 2. Summary of structures combined in the iodonium salts.
mechanism as long as the free energy of electron transfer $\Delta G_{el}$ between the excited state of an excited donor/sensitizer (Sens) and an acceptor/radical initiator (RI) is negative \[1c\].

Equations 1-7 describe the sensitized formation of radicals and protons using NIR radiation. Excitation leads to the first excited singlet state (Eq. 1), which deactivates non-radiatively (Eq. 2) or radiative by fluorescence (Eq. 3). Non-radiative deactivation represents the major pathway with an efficiency of $\approx 85\%$ \[5\]. Eq. 4 depicts the electron transfer between $^1$Sens* and the acceptor (RI) resulting in formation of the oxidized species Sens** and reduced species RI−. Both, Sens** and RI− appear as singlet radical pair, which can easily transfer back the electron resulting in back formation of Sens and RI without formation of any initiating radicals, Eq. 5. On the other hand, fast consecutive decomposition of Sens** in photoproducts and protons H+(solv) makes the system irreversible, Eq. 6. This results in a reduction of the electron back transfer efficiency (Eq. 5) and favors formation of initiation radicals In• by decomposition of RI− (Eq. 7).

\[
\begin{align*}
Sens & \xrightarrow{hv} ^1\text{Sens}* \quad (1) \\
^1\text{Sens}* & \rightarrow \text{Sens} + \Delta \quad (2) \\
^1\text{Sens}* & \rightarrow \text{Sens} + hv' \quad (3) \\
^1\text{Sens}* + \text{RI} & \rightarrow \text{Sens}^{**} + \text{RI}^{-} \quad (4) \\
\text{Sens}^{**} + \text{RI}^{-} & \rightarrow \text{Sens} + \text{RI} \quad (5) \\
\text{Sens}^{**} & \rightarrow \ldots \rightarrow \text{fast decomposition} \rightarrow \ldots \rightarrow \text{H}^+ + \text{products} \quad (6) \\
\text{RI}^{-} & \rightarrow \text{In}• + \text{products} \quad (7)
\end{align*}
\]

4. Influence of Heat

Intrinsic thermal initiated polymerization of olefinic monomers (Mi) starts at higher temperatures (Eq. 8) whose onset can be determined by DSC \[6\]. Interestingly, the addition of Sens (Eq. 9), RI (Eq. 10) and a mixture of both (Eq. 11) results in a decrease of the onset temperature of radical polymerization. Particular a mixture of Sens and RI led to the strongest decrease of the onset temperature \[6\].

As an example, the monomer M2 intrinsically starts to polymerize at 190 °C. Addition of 2 wt% 1n as RI reduces the onset temperature to 169 °C. An onset temperature of 89 °C was observed upon addition of a mixture comprising 0.1 wt% S4 and 2 wt% 1n to M2. This temperature can be easily reached in CTP systems upon excitation with diode lasers emitting at 830 nm. More details can be found in reference \[6\]. However, the addition of only 0.1 wt% S4 did not change the onset temperature of thermal initiation.

In addition, such a system can be seen as a thermal initiator system whose thermal instability may explain such thermal effects. Based on these considerations, such systems may be seen as hybrid systems requiring photons and heat to generate initiating radicals. The formation of acids can be seen as an additional benefit, which enables these systems to bivalent crosslinking pathways based on radicals and protons.

5. Relation between Sensitivity and Structure of Initiator Components

5.1. Relation between Reactivity and Structure of the Iodonium Salts in the Monomers M1-M4 \[4\]

Photopolymerization was studied by photo-DSC. The maximum of the polymerization rate $R_p^{max}$ was taken as a parameter to describe reactivity. Figure 1 shows a typical photopolymerization curve comprising S4 as sensitizer and 1n as RI.

![Figure 1](image-url)

Figure 1. Exothermal heat flow obtained upon exposure of a photopolymer composition with S4 (c = 0.83 mM) and the iodonium salt 1n (c = 15 mM) in M1 using a photo-DSC in combination with a NIR LED array (LED790-66-60 from Roithner). Reference \[4\] contains further experimental details.
This was measured for different iodonium salts shown in Scheme 2 in the monomers M1-M4. Our results showed no clear correlation between solubility and $R_p^{\text{max}}$. This was an unexpected finding, as we initially expected that a good solubility always causes a high reactivity as well.

![Graph](image)

**Figure 2.** Comparison between $R_p^{\text{max}}$ (NIR LED array emitting at 790 nm) and molar solubility of iodonium salts comprising cation I and different anions in the monomers M1 (a), and M2 (b), S3 concentration: 0.83 mM in M1, and 0.85 mM in M2; iodonium salt concentration: 15 mM in M1, and 15.4 mM in M2. Reference [4] contains further experimental details.

Aggregation can be partially followed by conductivity measurements because only separated solvated ions (⊕ and ⊖) contribute to conductivity. Figure 3 shows the dependence between $R_p^{\text{max}}$ and the conductivity of the iodonium salt in the monomer M1. A complete dissociation into the individual ions (⊕ and ⊖) causes a high conductivity of the surrounding. Thus, complete dissociation of the iodonium salt forms a prerequisite to obtain a high reactivity. Nevertheless, incomplete dissociation may explain the differences of reactivity. Conductivity relates to ion mobility, which also inversely depends on the radius of the ion. The larger the ion appears, the lower is the reactivity.

![Graph](image)

**Figure 3.** Relation between reactivity ($R_p^{\text{max}}$) of a photopolymer composition comprising S4 (0.83 mM) and different iodonium salts (15 mM) in 1,6-hexanediol diacrylate using a photo-DSC in combination with a NIR LED array (LED790-66-60 from Roithner). Conductivity of iodonium salts was taken in 10 mM monomer solution. Reference [4] contains further experimental details.

Different dissociation steps of the iodonium salt can explain the discrepancy between reactivity and solubility [4]. These are reactive separated solvated ions (⊕ and ⊖), non-dissociated ion pairs (⊕⊕), dimers (⊕⊕⊕), trimers (⊕⊕⊕⊕⊕) or higher molecular aggregates.

![Graph](image)

**Figure 4.** Relation between reactivity ($R_p^{\text{max}}$) of a photopolymer composition with S4 (0.83 mM) and different iodonium salts (15.4 mM) in tripropylene glycol diacrylate. Caption of Figure 3 summarizes further experimental details [4].

A similar pattern was obtained for the monomer
M2 (tripropylene glycol diacrylate), in Figure 4. In general, results confirm those shown in Figure 3. Iodonium salts with good conductivity exhibit a high reactivity. On the other hand, there exists no correlation according to Kohlrausch’s square root low for strong electrolytes or Ostwald’s dilution law for weak electrolytes. Nevertheless, the dissociation of electrolytes in organic surroundings has not been well understood until today. Thus, one cannot easily transfer the relations derived for the Debye-Hückel-theory to those systems.

5.2. Influence of the Sensitizer on the Reactivity of the Photopolymer Composition [6]

The sensitizers S1-S6 were investigated in the monomers M1-M4. Figure 5 depicts their different reactivities. No clear recognizable correlation is observed between sensitizer reactivity and its solubility in the monomers. Interestingly, the barbiturate based sensitizers exhibit the highest fluorescence quantum yield (10-15%) reported for cyanines with absorption in the NIR [5]. Therefore they possess a longer lifetime [5], which increases the probability of the excited state to react with the iodonium salt, Eq. 5. An acceptable fluorescence should consequently result in a photoinitiator system with higher reactivity but it is not mandatory. The reactivity differences observed in the monomers may be attributed to different solvation steps necessary to obtain a high reactivity [6].

![Figure 5](image)

**Figure 5.** $R_p^{\text{max}}$ obtained with different sensitizers (Sens = 0.06 wt%; $I_n$ = 2.0 wt%). Light source: 790 nm LED. The LED was adjusted to 40 mW·cm$^{-2}$ for all sensitizer samples.

5.3. Iodonium Salts in CtP Systems [1c,5]

Based on photophysical data, electrochemical properties (oxidation) and dissolution in organic coatings [6], S4 was chosen for further experiments. Sensitivity was first evaluated with iodonium salts comprising the cation 1 while the anion was changed. Exposure of the lithographic plates with different exposure energies resulted in the sigmoid curve shown in Figure 6. The sensitivity was defined as the energy where $dOD_{\text{plate}}/dE$ is largest. The lower the sensitivity, the higher the reactivity of the coating because the least exposure energy would be required to generate an acceptable image [5].

![Figure 6](image)

**Figure 6.** Optical density of the plate ($OD_{\text{plate}}$, full line) of a NIR photopolymer comprising S4 (2.21 wt%), and the iodonium salt Ia (6.51 wt%) as radical initiator. The photosensitive layer comprised a polymeric binder, monomers, and colorants. This layer was overcoated with PVA as oxygen barrier. Exposure was carried out using a Kodak Trendsetter 800 applying different exposure energy density ($E$) resulting in the markers (●) after processing in the Kodak developer SP500. $OD_{\text{plate}}$ was measured in reflection mode using the SpectroPlate from TechKon. The dashed line exhibits the first derivative of the plate’s optical density with respect to the exposure energy density ($dOD_{\text{plate}}/dE$). Reference [5] summarizes further details.

Change of the iodonium salt resulted in reactivities summarized in Figure 7. Surprisingly, the redox-inactive bis(trifluoromethyl sulfonyl) imide anion n and the tetracyanoborate c resulted in similar sensitivities compared to the oxidizable tetraphenylborate a. The different dissociation steps of the iodonium salt, (compare chapter 5.2) may explain these reactivities obtained in thin films.

In the next step, the cation structure was changed while the anion remained unchanged. This resulted in the salts 1n-6n. Figure 8 summarizes the data obtained. The picture shows a similar reactivity of the salts 1n-6n in comparison to the the oxidizable anion a. The sensitivity of these systems comprising the non-oxidizable anion.
n is even better compared to the commercially available iodonium salt 7g; that is OPPI.

6. Photopolymerization with Line Shape Focused Lasers

6.1. Photonic Baking [5]

NIR lasers with line focus were applied to post-treat the exposed and processed lithographic materials. Figure 9 shows a general setup of such a laser where a line-width of 2 cm and several µm thickness shines with almost similar intensity on the substrate [5].

The processed lithographic materials still contained some amounts of NIR sensitizer. The available sensitizer concentration should be sufficient to absorb light at 808 nm, which could be converted either to heat (Eq. 2) or to initiating radicals (Eq. 7). Thus, heat formation and photonic reaction between Sens and RI (Eq. 4) result in generation of reactive intermediates. This post-crosslinks available residual double bonds of both monomers and binder. Therefore, such treatment could be an alternative for thermal baking. This increases the stability of such coatings upon mechanic abrasion in the printing process and against the attack of aggressive printing chemicals.

From this point of view, the test developed with the 231 Negative Deletion Fluid allows to draw conclusions whether the thermal treatment was successful or not. This is an aggressive liquid, which easily removes crosslinked coating of exposed unbaked photopolymer printing plates from the substrate. On the other hand, it does not remove a successful baked coating. Figure 10 shows the successful treatment of processed lithographic materials. The arrow demonstrates the direction in which the laser line traversed the material. The black lines on the left hand side mark the width of the laser line. Furthermore, the ellipse depicts the area where the processed lithographic plate was treated with the aggressive fluid.

The use of a thermo-sensitive camera indicated a temperature increase >200°C depended on available energy density. Thus, Figure 10a demonstrates successful baking with photons as shown by the continuous blue stripe, which remained on the substrate after treatment with the aggressive processing liquid. This stripe also shows the erase of coating in regions where no laser line illuminated the material. Further increase of energy density led to the scenario in which heat migrated into the areas where the laser did not expose the material directly. This can be seen by the fuzzy edges between exposed and non-exposed parts in Figure 10b. Additional increase of the excitation energy leads to much more energy...
migration into non-exposed areas. This makes it more difficult to remove coating from these parts, Figure 10c. Significant higher temperature conditions resulted in deformation of the plate substrate that is made of aluminum having in top a small amount of Al$_2$O$_3$. This can be particular seen in Figure 10d where the laser energy was so high that bleaching of some pigments occurred. Treatment with the correction fluid erased coating particular in those parts with extreme excitation energy density due to the lower adhesion of the coating under strong exposure conditions.

Figure 9. Setup of a laser with line shape focus (laserline: 1.5 cm length, 0.8 mm width). An emitting phosphor was used to visualize the NIR light.

Figure 10. Exposed and processed photopolymer plates treated with different laser energies using S4 and In in the photoinitiator system. a: 41 W; b: 79 W; c: 107 W; d: 188 W. Sample speed: 40 cm min$^{-1}$. The ellipse indicates the area of correction fluid treatment.

6.2. Crosslinking of Powder Coatings with Line Shape NIR Lasers [7]

Powder coatings are commonly applied on suitable substrates with a corona discharge. They first melt by application of heat resulting in a high viscous liquid film which consecutively crosslinks at temperatures between 130-180 °C. This procedure requires to operate in long ovens needing a certain residence time also at high temperatures [14]. Some attempts reported the decrease of the operating temperature using UV-radiation for chemical solidification of the molten films [8,14]. Nevertheless, the use of UV radiation for crosslinking excludes the use of additives with UV absorption, such as a UV stabilizer. Moreover, both thermal and UV-curing systems need a separate melting process. Melting in UV powder coatings starts at 90-100°C. As a result, there exists a certain demand to have a system that melts and crosslinks in nearly one step. For the first time we demonstrated the feasibility to melt and chemically cure powder coatings in nearly one step by NIR lasers with line shaped focus emitting simultaneously at 808 nm and 980 nm [7].

Our NIR-photoinitiator system comprises the cyanines S4 and S7 absorbing at 808 and 980 nm, respectively, and as radical initiator the iodonium salt 1n. Excitation of S7 results in almost quantitative radiationless deactivation of its excited state as shown by the low fluorescence quantum yield [6] and the release of heat ($\Delta$). It functions therefore as a radiation absorber with no direct association to a chemical process. This requires a large absorption coefficient of S7 to ensure an almost complete absorption of the laser energy in the coating to avoid burning effects of the temperature sensitive substrate. A consecutive endothermic step, which can be either melting of the semi-crystalline powder coating or a thermal decomposition of an initiator component, consumes the heat released in the coating ensuring that it remains in the coating while no thermal destruction of the substrate occurs.

S4 operates as chemical sensitizer for photoinitiated radical polymerization according to the reactions shown in the Eqs. 1-7. Powder coatings based on an unsaturated polyester resin (UVECOAT3003) and vinyl ether urethane (Uracross P3307) comprising the NIR-photoinitiator system of S4, S7 and 1n were applied on an aluminium substrate by corona electrostatic application using the mobile Mini
Start powder coating cabin (Figs. 11a-b). This allows to apply the powder coating under technical conditions with low material consumption. Simultaneous laser exposure at 808nm and 980nm indicated fast conversion of the powder into a transparent film when the line-shaped laser swept over the coating (Fig. 11c). This result surprised because it has been believed that a longer time of residence would be necessary to first melt the powder and then crosslink the molten film [14]. It furthermore demonstrates the need to rethink the curing mechanism of powder coatings in such a new curing technique [7].

![Image of powder coating cabin and laser exposure](image)

**Figure 11.** Application of the powder coating using a MiniSTart cabin (a+b) and exposure with the line shape focused laser at 808 nm and 980 nm. The laser line went over the substrate with a speed of 10 mm·s⁻¹; [S7] = 0.06 wt%, [S4] = 0.06 wt%, [1n] = 2.0 wt%; Laser power: 808 nm = 107 W, 980 nm = 106 W. Reference [7] summarizes further experimental details.

Moreover, a thermal sensitive camera indicated a sudden and short temperature increase up to 120-400 °C depending on laser parameters used. This huge energy entry into the coating using S7 and S4 helps to melt the powder coating at the same time crosslinking occurs in the molten film by photonic initiation. Furthermore, both cyanines S7 and S4 are necessary for efficient melting and crosslinking. The use of only S4 results in less efficient melting but crosslinking was observed as well.

### 7. Formation of Protons/Electrophiles [7]

Protons should be formed according to the mechanism shown in Eqs. 1-7. Particular, the instability of the cation radical Sens⁺ responsibly tunes the formation of protons in the organic surroundings, Eq. 6. Our work focused on Rhodamine B lactone (RBL) to monitor proton formation. The latter opens the lactone ring of RBL resulting in formation of intensive red colored Rhodamine B [6, and cited references therein]. This procedure probes even small quantities of protons formed upon exposure because it detects the growth of a signal. The proton activity aH⁺ quantifies the protons formed in such organic surroundings.

Exposure of the different absorbers with 1f as initiator results in Figure 12. The value of aH⁺ differs two orders of magnitudes using a constant exposure time and a LED emitting at 790 nm. S1 results in the generation of the highest aH⁺ followed by S5. Furthermore, S2 and S4 show in a medium proton activity aH⁺. Nevertheless, there exists no clear relation between the NIR absorber structure and aH⁺ formed. The reactivity of Sens in the presence of 1f follows in acetone the following order:

\[
S1 > S5 > S2 ≈ S4 > S3 >> S6.
\]

![Graph showing proton activity](image)

**Figure 12.** Quantified cation activity (aH⁺) generated by NIR exposure (790 LED; P = 100 mW·cm⁻²) using different sensitizers (0.3 wt%) and 1f (3 wt%) as coinitiator; solvent: acetone. Data were taken after 10 min exposure to avoid an extremely long radiation for the less reactive samples comprising S6, and S3. Reference [7] summarizes further experimental details.
Again, the different protonation of the formed photoproducts may explain this distinct behavior considering an$^+\text{H}$-formation. Future studies will also focus on cationic polymerization of appropriate monomers. Aziridines would be favored because these monomers build a polymer in which chain growth occurs over the ammonium ion and not the carbocation [15]. Thus, these monomers tolerate a certain amount on nucleophiles, which can be photoproducts and the NIR sensitizer as well. First lab trials showed successful polymerization of aziridines and polycondensation of functionalized siloxanes/silanes.

8. Conclusion
NIR sensitized radical and cationic photopolymerization opens new technical opportunities to solidify and modify coatings on different substrates. This can be achieved either with NIR LEDs or NIR lasers. This technology does not compete but extends the established UV technology. It also opens up new opportunities in coating sciences.

Future work should focus on an improvement of reactivity, which appears in nowadays feasibility studies of NIR-photopolymerization significantly lower compared to UV systems. This could be accomplished with structural improvements of both the NIR sensitizer and radical initiator. Big potential would be seen to use anions with low coordinating properties because these components contribute to a significant improvement of compatibility.

One of the largest benefits of NIR initiation can be seen in the possibility to cure coatings with a thickness of more than 1 cm and to embed additives and fillers with significant UV absorption. UV systems exhibit substantial lack in this point. Thus, such systems will have potential in application fields wherever UV systems approach to their limits.

Furthermore, future studies will show if the curing of powder coatings with NIR lasers exhibiting line shape focus will lead to further technological developments in the coating technology. This will have a certain potential since it would offer the opportunity to replace energy and space consuming ovens by such modern exposure techniques.

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