Supporting Information

NIR-Sensitized Cationic and Hybrid Radical/Cationic Polymerization and Crosslinking

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Materials

NIR sensitizers 1a, 1d, 1g were received from FEW Chemicals GmbH (Bitterfeld-Wolfen, Germany) and 1'b was received from Spectrum Info Ltd. (Kiev, Ukraine). They were used without further purification. The iodonium salt 2a (CAS: 61358-25-6) was purchased from TCI. 2d was received from FEW Chemicals GmbH as S2617. Both of them were used without further purification. Other iodonium salts 2b, 2c, 2e, and 2f were synthesized by anion exchange according to a previous procedure\cite{1}. The (meth)acrylate monomers M1 (trimethylolpropane triacrylate, TMPTA) and M1b (lauryl methacrylate, LMA) were purchased from SigmaAldrich. The inhibitor was removed by running of them through basic Al\(_2\)O\(_3\) (Carl Roth GmbH) before it was transferred to the experiments. The oxetane monomers OXT-03 and OXT-04 were received as a from Gurun Technology (Hubei Jingmen, PR China) and used as received. Epikote 357 was available from Hexion and used as received. 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (ERL-4211) was purchased from IGM Resins as OMNILANE OC1005. All other chemicals and solvents mentioned were received from SigmaAldrich with the required purity. No further purification occurred.
Table SI1: Summary of NIR sensitizers, iodonium salts and monomers used, commercial trade name, and commercial source.

| Trade name | Source |
|------------|--------|
| 1a         | S2140  |
| 1d         | S2639  |
| 1g         | S2026  |
| 1' b       | S10761 |
| 2a         | IS-PF₆ |
| 2b         | IS-FAP |
| 2c         | IS-FAP(II) |
| 2d         | S2617  |
| 2e         | IS-Al(III) |
| 2f         | IS-CTf₃ |
| ITX        | i-propyl thioxanthone |
| M1         | trimethylolpropane triacrylate (TMPTA) |
| M1b        | lauryl methacrylate (LMA) |
| M2a        | OMNILANE OC1005 |
| M2b        | Epikote357 |
| M3         | HBVE   |
| M4a        | GR-OXT-03 |
| M4b        | GR-OXT-04 |
**Instrumentation**

New high-power NIR prototypes emitting at 395 nm, 805 nm and 870 nm were used for the investigations. The additional new NIR-LED prototype emitted at 805 nm with an exposure density of 1.2 W/cm² in a distance of 3 cm. It was gratefully received from Phoseon Ltd. It exhibited an exposure size 8 cm x 13 cm x 3 cm. The available exposure area covered 1.4 cm² in the aforementioned distance\(^2\).

The NIR-LED prototype emitting at 870nm with an exposure density of 1 W/cm² in a distance of 1 cm was gratefully received from EASYTEC GmbH and used for real-time FTIR experiments due to the smaller size. Figure S11 shows a general emission picture of all three NIR-LEDs. The available exposure area covered 1 cm² in the aforementioned distance\(^3\).

The UV-LED prototype emitting at 395 nm with an exposure density of 1.2 W/cm² in a distance of 3cm was gratefully received from EASYTEC GmbH. It exhibited a size 10cm x 20 cm x 5 cm. The available exposure area covers 3 cm² in the aforementioned distance.

![Emission spectra](image)

Figure S11: Emission spectra of 805nm NIR-LED(red), Emission spectra of 870nm High-power NIR-LED(blue), Emission spectra of 395nm NIR-LED(black). The measurement of emission spectra and photo intensity was carried out by a fiber optical spectrometer from Ocean Optics (USB4000).
UV-VIS-NIR Absorption Measurement

The UV-VIS-NIR absorption spectra of the sensitizers 1a, 1d, 1g and 1'b in OXT-03 were measured to study the influence of monomer on the absorption of the sensitizer. There was no significant change of absorption profile of the sensitizers in the oxetane monomer OXT-03 at the same concentration (6×10⁻³ mmol/g) indicating no significant hint on formation of aggregates applying a sensitizer concentration applied in the photopolymerization experiment. UV-VIS-NIR Spectra were measured with a Cary 5000 from Agilent with putting the sample in the middle of two pieces of the glasses.

![Absorption Spectra](image)

Figure SI2: the absorption spectra of the sensitizers 1a, 1d, 1g and 1'b in the OXT-03 ([Sens] = 6×10⁻³ mmol×g⁻¹).

Real Time FTIR

A regular real-time FTIR setup (Vertex 70 from Bruker) was used to measure the photopolymerization of the monomers with different sensitizers and iodonium salts. The samples were prepared by dissolving the NIR sensitizer (6×10⁻³ mmol/g) and iodonium salt (3.8×10⁻² mmol/g) in different monomers. Exposure occurred with the 805nm NIR-LED at 1.2W/cm² and in the case of the 870nm NIR-LED at 1W/cm². Spectra were taken in ATR mode. The films had a thickness of 20 μm. The peak area at 810 cm⁻¹ was used to determine the conversion of M1. The peak area at 975 cm⁻¹ was used to determine the conversion of M2a while 915 cm⁻¹ was used for monitoring the epoxide conversion of M2b. The peak area at 830 cm⁻¹ was used to determine the conversion of M4a and M4b. The peak area at 1650 cm⁻¹ was used to determine the conversion of M3.
Figure SI3: Real-time FTIR conversion degree-time profiles of NIR-sensitized photopolymerization pursued at 805 nm and 870nm investigated for different combinations of sensitizer (1/1’X and 2X’) in different cationic polymerizing monomers a): M2b, 805nm ; b): M2b, 870nm ; c): M3, 870nm; d): M4a, 870nm; e): M4b, 805nm , 870nm. Intensity of the 805 nm LED was 1.2W×cm⁻² and 870nm device was 1 W×cm⁻² ([Sens] = 6×10⁻³ mmol×g⁻¹, [2X’] = 3.8×10⁻² mmol×g⁻¹).
Figure SI4. Real-time FTIR conversion degree-time profiles of NIR-sensitized photopolymerization pursued at 805 nm of the reacting double bond of M1 and cationic polymerizing group of M2b investigated for the sensitizer combination 1d and 2d in the neat monomer following either radical or cationic polymerization protocol. Intensity of the 805 nm LED device was 1.2 W cm\(^{-2}\) ([1d] = 6 × 10\(^{-3}\) mmol g\(^{-1}\), [2d] = 3.8 × 10\(^{-2}\) mmol g\(^{-1}\)).

**Generation of Conjugate Acid**

The formation of conjugated acid was monitored with Rhodamine B lactone as an optrode after exposure with the 805 nm LED device (Phoseon) at 1.2 W cm\(^{-2}\), see reference\(^2\) for more details. The protonation of the Rhodamine B lactone results in a magenta colored solution with an absorption maximum located at 556 nm. The sensitizer (4.1 × 10\(^{-5}\) M) and iodonium salt (5.6 × 10\(^{-4}\) M) were dissolved in 10 mL Lauryl methacrylate (LMA) or n-Butyl acetate (BuAc) and exposed with LED light (1.2 W cm\(^{-2}\)) in a crystallization dish (diameter 3.0 cm). The solution was filled into a volumetric flask and the loss of the solvent was filled to 10 ml. The spectra were corrected by subtraction of the spectrum of the sensitizer and its photoproducts from the spectrum containing additionally the Rhodamine B lactone (1.0 × 10\(^{-4}\) M). The conjugate acid concentrations generated are given as \(a_{H^+}\) derived from the conversion of Rhodamine B lactone\(^2, 4\).
Figure SI5: Profiles for formation of conjugated acid as a function of exposure time at 805 nm (Intensity: 1.2 W×cm-2) according to a previous procedure using Rhodamine B lactone to probe quantitatively the amount on acidic species. a): 1a/2a in BuAc; b): 1b/2b in BuAc; c): 1b/2c in BuAc; d): 1d/2d in BuAc; e): 1d/2e in BuAc; f): 1d/2f in BuAc; g): 1d/2d in LMA; h): 1b/2b in LMA. Measurements were carried out in lauryl methacrylate (LMA) and butyl acetate (BuAc) ([1X-] = 4.1×10^{-5} M, [2X-] = 5.6×10^{-4} M).
Table SI1: Concentration of conjugated acid of the NIR initiator system (sensitizer: 4.1×10^{-5} M, [2X]: 5.6×10^{-4} M) in BuAc or LMA under NIR exposure using the 805nm LED device (photointensity: 1.2 W/cm², exposure time: 20 minutes)

| Time /min | a_{H^+} (1a / 2a) in BuAc/M | a_{H^+} (1'b / 2b) in BuAc/M | a_{H^+} (1'd / 2d) in BuAc/M | a_{H^+} (1'd / 2d) in LMA/M | a_{H^+} (1'b / 2b) in LMA/M |
|-----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 1         | 2.0×10^{-7}                 | 5.0×10^{-7}                 | 5.9×10^{-9}                 | 1.3×10^{-6}                 | 1.8×10^{-6}                 |
| 5         | 2.7×10^{-6}                 | 5.1×10^{-6}                 | 8.9×10^{-8}                 | 3.5×10^{-6}                 | 8.3×10^{-6}                 |
| 10        | 9.0×10^{-6}                 | 7.9×10^{-6}                 | 1.8×10^{-5}                 | 9.1×10^{-6}                 | 1.0×10^{-5}                 |
| 20        | 1.7×10^{-5}                 | 1.9×10^{-5}                 | 1.8×10^{-5}                 | 2.2×10^{-5}                 | 1.6×10^{-5}                 |

Temperature Measurement

The temperature generated by sensitizers were measured. The temperature was collected by NIR sensitive camera (test 0563 0885 V7) when the samples comprising 1d (6×10^{-3} mmol/g) and 2d (3.8×10^{-2} mmol/g) in different monomers were irradiated with the LED device from Phoseon at 805nm/1.2 W×cm^{-2} (Figure S16). The thickness of the film was 120µm and using glass covered. Irradiation time was 600s. 

Figure S16: The temperature (T/°C) generated by the samples (thickness is 120µm) in different monomers comprising 1d (6×10^{-3} mmol/g) and 2d (3.8×10^{-2} mmol/g).

Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of the films were characterized using DMA Q800 (TA Instruments, New Castle, USA) with a three-point bending clamp. The test temperature was varied from 50°C to 250 °C with a ramping rate of 3 °C min^{-1}, a frequency of 1 Hz, an amplitude of 1µm, and a preload of 0.01 N. The properties measured under this oscillating loading were storage modulus (E’) and tan δ. The ratio of the loss modulus (E”) to the storage modulus E’ is referred to as the
mechanical damping, or tan δ (i.e., tan δ = E″/E′). Data are available and could be provided upon request. The glass transition temperature (T_g) was determined at the position of the maximum on the tan δ graph.

The films were prepared from the samples which comprised the NIR sensitizer **1d** (6×10^{-3} mmol/g), iodonium salt **2d** (3.8×10^{-2} mmol/g) and different monomers, respectively. The sample was put on one piece of glass firstly, then another piece of glass was used to cover the sample on the first glass substrate to inhibit the influence of oxygen from the surrounding. Three pieces of tape with 40μm thickness was used to achieve a film thickness of about 120μm. Exposure occurred with the **805nm NIR-LED** (1.2 W×cm^{-2}, 10min) and **395nm UV-LED** (1.1 W×cm^{-2}, 2min).

Figure SI7. DMA data (tan δ) of films (thickness: 120 μm) exposed at 395 nm (1.1 W×cm^{-2}) and 805 nm (1.2 W×cm^{-2}) in the case of the monomers **M1** and **M4a** after 2 min and 10 min exposure at 395 nm (1.1 W×cm^{-2}) and 805 nm (1.1 W×cm^{-2}), respectively. The **i-propyl thioxanthone ITX** (0.1 wt%) and **2d** (3.8×10^{-2} mmol×g^{-1}) and the combination of **1d** (6.0×10^{-3} mmol×g^{-1}) and **2d** (3.8×10^{-2} mmol×g^{-1}) served as initiator combination for experiments at 395 nm and 805 nm, respectively.

Figure SI8 shows the DMA curves of the NIR systems investigated. They were exposed at 805 nm. The storage modulus showed no indication of crystallization in the case of the samples comprising oxetanes.
Figure SI8: DMA curves of films (thickness: 120 μm) exposed at 805 nm (1.2 W×cm\(^{-2}\)) comprising radical (M1) and cationic (M2a, M2b, M4a) cross-linkable monomers. a): M1/M4a/M1+M4a (1:1); b): M1/M2b/M1+M2b (1:1); c): M1/M2a/M1+M2a (1:1); d): M1+M2a(1:1)/M1+M4a (1:1)/M1+M2a+M4a (4:3:3); e): M1+M4a(1:1)/M1+M2b (1:1)/M1+M2b+M4a (4:3:3). The combination of 1d (6.0×10\(^{-3}\) mmol×g\(^{-1}\)) and 2d (3.8×10\(^{-2}\) mmol×g\(^{-1}\)) served as initiator combination.
Viscosity measurement

The viscosity measurements were carried out using a Stresstech rheometer from ATS Rheosystems (MCR 102 SN81432646 from Anton Paar) under atmospheric air conditions and 25°C with an oscillation frequency of 1.0 s\(^{-1}\) at constant stress of 200 Pa. M2a, M2b were measured with the measuring system of CP50-1 SN5236. M3, M4a, M4b were measured with the measuring system of CP25-1 SN49618. All of them were measured in the measuring cell P-PTD200+H-PTD200 SN82112134-82331887. The oscillation frequency of 1.0 s\(^{-1}\) was set at constant stress of 200 Pa.

Conductivity Measurement

Conductivity of the iodonium salts in different monomers was carried out with the 856 Conductivity Module comprising 900 Touch Control from Methrohm. The concentration of the iodonium salts keep the same with RTFTIR measurement, which is 3.8×10\(^{-2}\) mmol/g. The cell constant was determined using an KCl aq.\(^{[1b]}\)

Quantum Chemical Calculations

Spartan 16 was used for quantum chemical calculations using a MacPro with 8 cores as hardware. Geometry optimization showed no negative frequencies. The B3LYP function serves as functional applying the basis set 6-31G*.

Dark curing

The initiating system comprising heptamethine cyanine and iodonum salts could generate radicals and conjugate acid, both of which may add to olefin of the vinyl ether. Thereinto, the former trigger free radical polymerization, the later initiate cationic polymerization. Therefore, the dark curing of the M3 comprising heptamethine cyanine (1a) and iodonium salts (2a) was carried out to study its polymerization mechanism. A regular FTIR setup (Vertex 70 from Bruker\(^{[2]}\)) was used to measure the photopolymerization of the M3 upon irradiation 10s, and kept in the dark 20s, 60s, and 120s after irradiation 10s. Figure SI9 exhibits the FTIR spectra of M3 at around 1610\(\text{cm}^{-1}\) belonging to the stretching vibration absorption of the carbon carbon double bond (-C=C-) of the vinyl ether in different irradiation and dark time, where we can see the M3 occurred polymerization in the dark after 10s irradiation using 805nm NIR LED (1.2W/cm\(^2\)) because the absorbance of the peak becoming lower and lower with the dark time
increasing. The dark curing polymerization proved that the vinyl ether occurred the cationic polymerization.

Figure S19. The FTIR spectra of M3 at around 1610 cm\(^{-1}\) belonging to the stretching vibration absorption of the carbon carbon double bond (-C=C-) of the vinyl ether in different irradiation (0s, 10s) and dark time (20s, 60s, 120s). The combination of 1a (6.0×10\(^{-3}\) mmol×g\(^{-1}\)) and 2a (3.8×10\(^{-2}\) mmol×g\(^{-1}\)) served as initiator combination for experiments at 805 nm, 1.2 W/cm\(^2\).

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