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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[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_2O_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**	FEW Chemicals GmbH
1d	**S2639**	FEW Chemicals GmbH
1g	**S2026**	FEW Chemicals GmbH
1‘b	**S10761**	Spectrum Info
2a	**IS-PF$_6$**	TCI
2b	**IS-FAP**	Synthesized in the lab[1]
2c	**IS-FAP(II)**	Synthesized in the lab[1]
2d	**S2617**	FEW Chemicals GmbH
2e	**IS-Al(II)**	Synthesized in the lab[1]
2f	**IS-CTf$_3$**	Synthesized in the lab[1]
ITX	***i*-propyl thioxanthone**	TCI
M1	**trimethylolpropane triacrylate (TMPTA)**	SigmaAldrich
M1b	**lauryl methacrylate (LMA)**	SigmaAldrich
M2a	**OMNILANE OC1005**	IGM Resins
M2b	**Epikote357**	Hexion
M3	**HBVE**	SigmaAldrich
M4a	**GR-OXT-03**	Hubei Gurun Technology
M4b	**GR-OXT-04**	Hubei Gurun Technology

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/cm^2 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 cm^2 in the aforementioned distance[2].

The **NIR-LED** prototype emitting at **870nm** with an exposure density of 1 W/cm^2 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 SI1 shows a general emission picture of all three NIR-LEDs. The available exposure area covered 1 cm^2 in the aforementioned distance[3].

The **UV-LED** prototype emitting at **395 nm** with an exposure density of 1.2 W/cm^2 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 cm^2 in the aforementioned distance.

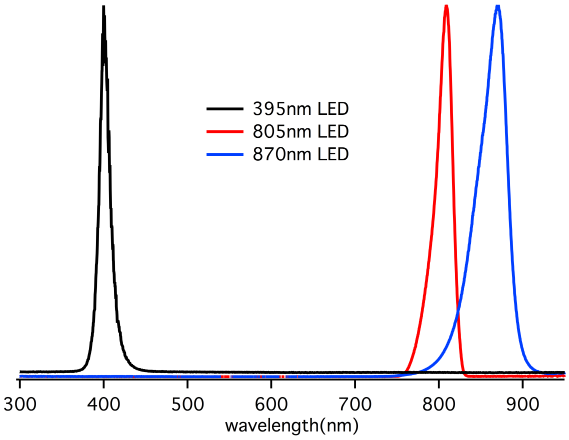


Figure SI1: Emission spectra of 805nm NIR-LED(red), Emission spectra of 870nm High-power NIR-LED(blue), Emission spectra of 395nm NIR-LED(black). The measurement of emission spectra and photo intensity was carried out by a fiber optical spectrometer from Ocean Optics (USB4000).

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.

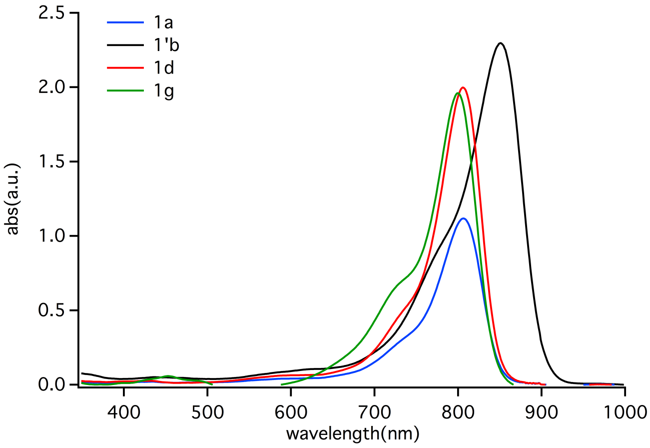


Figure SI2: the absorption spectra of the sensitizers **1a**, **1d**, **1g** and **1'b** in the **OXT-03** ([Sens] = 6×10^{-3} mmol$\times$g^{-1}).

Real Time FTIR

A regular real-time FTIR setup (Vertex 70 from Bruker)[2] 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/cm^2 and in the case of the **870nm NIR-LED** at 1W/cm^2. 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**.

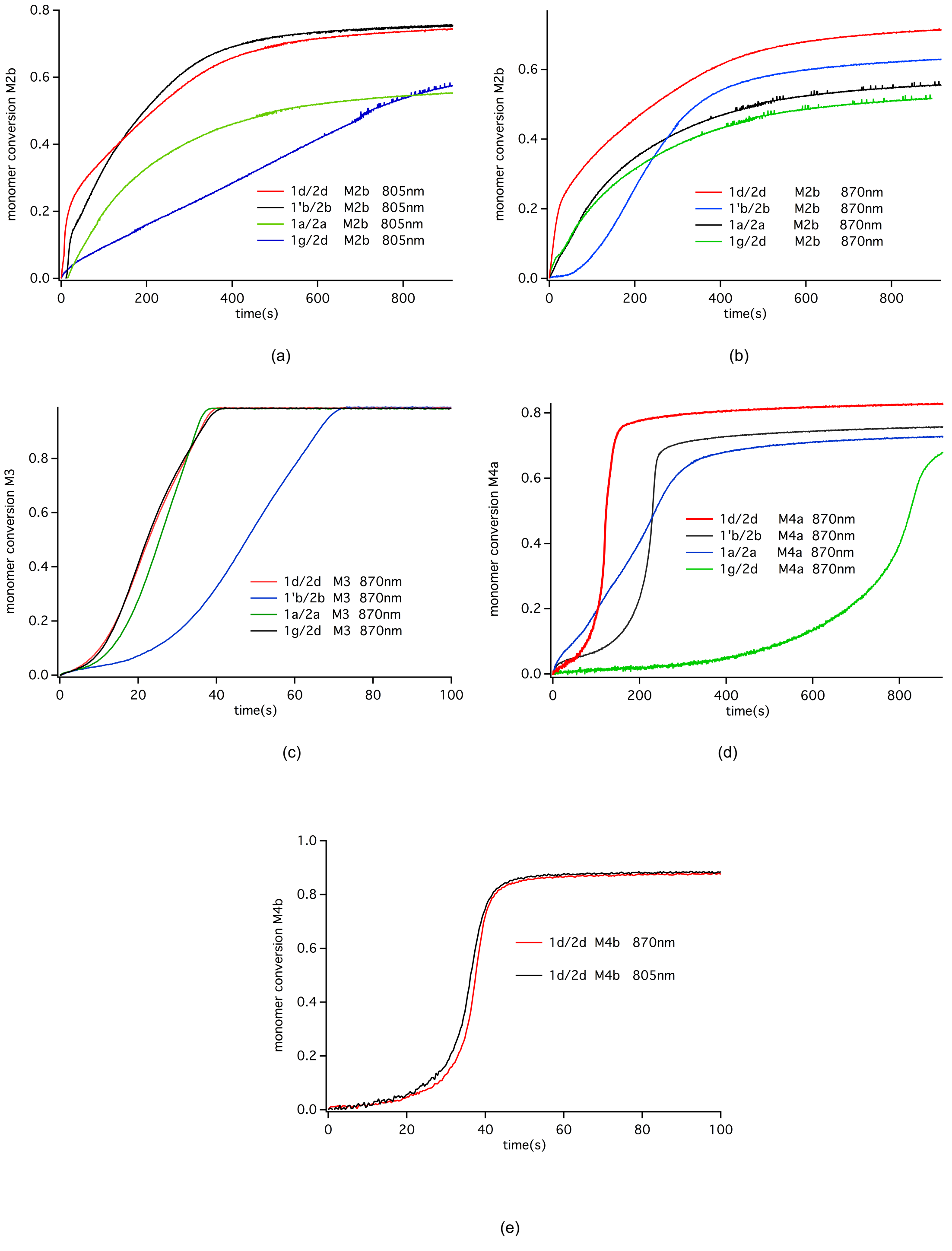


Figure SI3: Real-time FTIR conversion degree-time profiles of NIR-sensitized photopolymerization pursued at 805 nm and 870nm investigated for different combinations of sensitzer (**1**/**1'**X^- and **2**X^-) in different cationic polymerizing monomers a): **M2b**, 805nm ; b): **M2b**, 870nm ; c): **M3**, 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}).

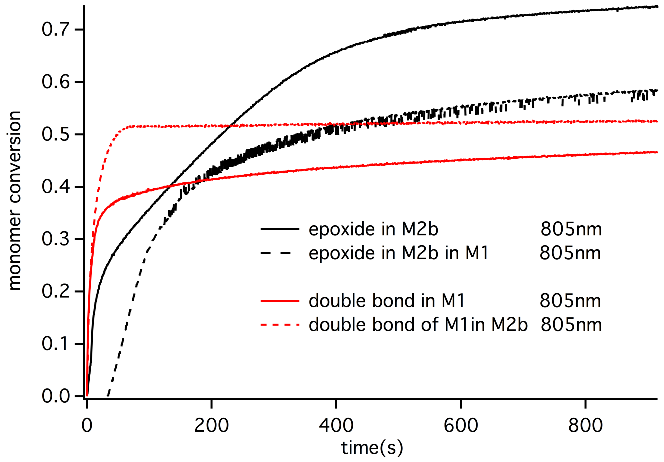
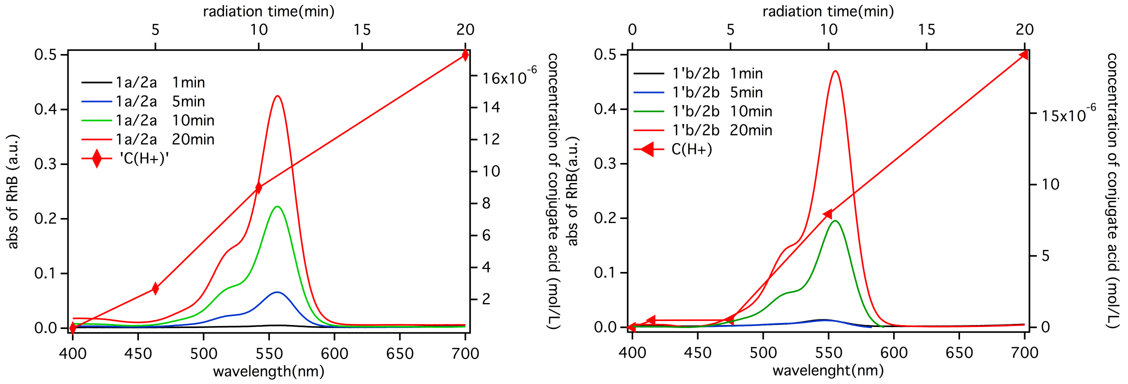


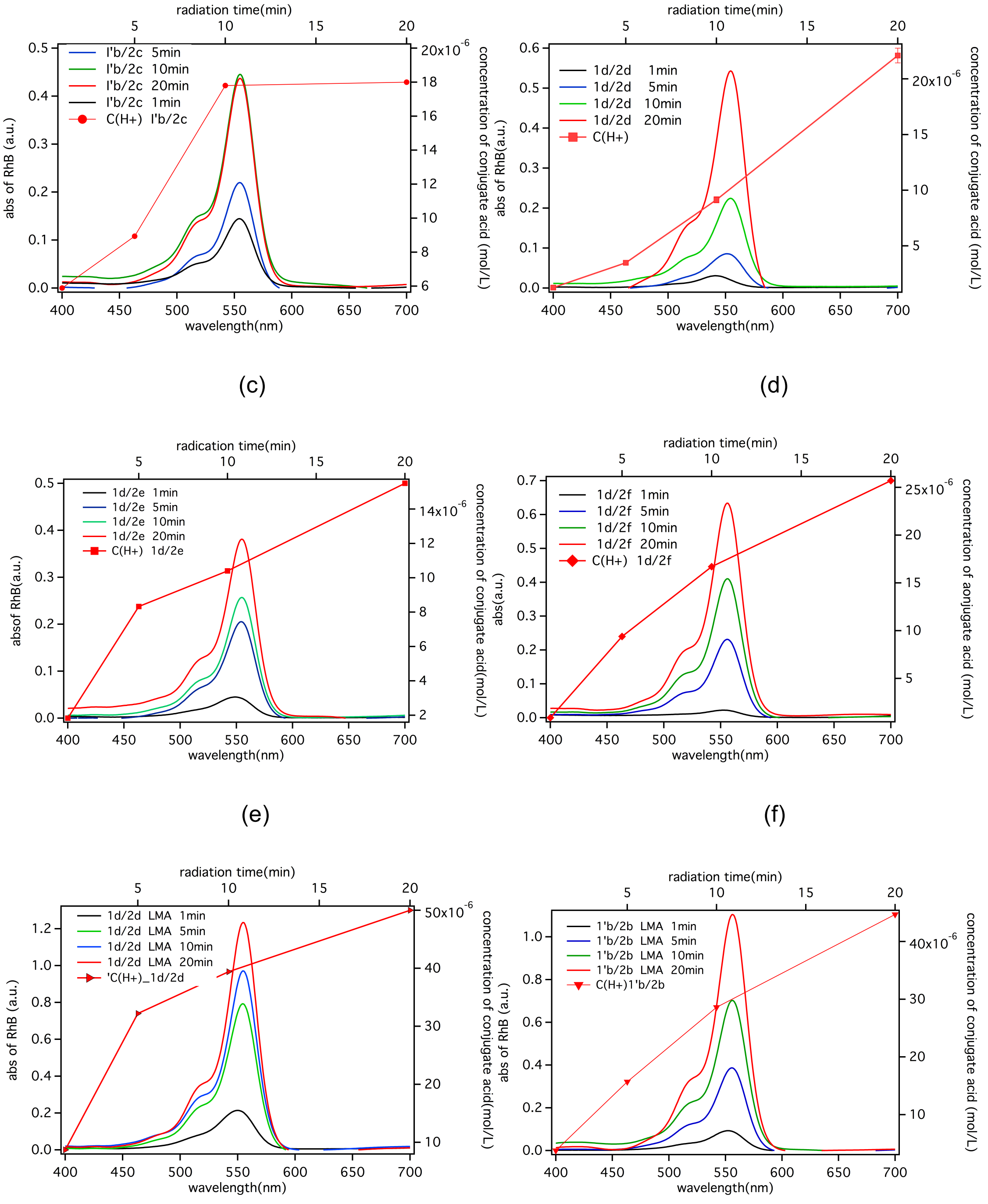
Figure SI4 . Real-time FTIR conversion degree-time profiles of NIR-sensitized photopolymerization pursued at **805 nm** of the reacting double bond of **M1** and cationic polymerizing group of **M2b** investigated for the sensitizer combination **1d** and **2d** in the neat monomer following either radical 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 **805nm 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].



(a) (b)



(c) (d)

(e) (f)

(g) (h)

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): **1'b/2b** in BuAc; c):**1'b/2c** in BuAc; d): **1d/2d** in BuAc; e): **1d/2e** in BuAc; f): 1d/2f in BuAc; g): 1d/2d in LMA; h) 1'b/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, [**2**X^-]: $5.6\cdot\times10^{-4}$ M) in **BuAc** or **LMA** under NIR exposure using the **805nm LED** device (photointensity:1.2 W×cm^{-2}, exposure time: 20 minutes)

Time /min	a_{H+} (**1a** / **2a**) in BuAc/M	a_{H+} (**1'b** / **2b**) in BuAc/M	a_{H+} (**1'b** / **2c**) in BuAc/M	a_{H+} (**1d** / **2d**) in BuAc/M	a_{H+} (**1d** / **2e**) in BuAc/M	a_{H+} (**1d** / **2f**) in BuAc/M	a_{H+} (**1d** / **2d**) in LMA/M	a_{H+} (**1'b** / **2b**) in LMA/M
1	$2.0\cdot10^{-7}$	$5.0\cdot10^{-7}$	$5.9\cdot10^{-6}$	$1.3\cdot10^{-6}$	$1.8\cdot10^{-6}$	$8.9\cdot10^{-7}$	$8.7\cdot10^{-6}$	$3.8\cdot10^{-6}$
5	$2.7\cdot10^{-6}$	$5.1\cdot10^{-7}$	$8.9\cdot10^{-6}$	$3.5\cdot10^{-6}$	$8.3\cdot10^{-6}$	$9.4\cdot10^{-6}$	$3.2\cdot10^{-5}$	$1.6\cdot10^{-5}$
10	$9.0\cdot10^{-6}$	$7.9\cdot10^{-6}$	$1.8\cdot10^{-5}$	$9.1\cdot10^{-6}$	$1.0\cdot10^{-5}$	$1.7\cdot10^{-5}$	$3.9\cdot10^{-5}$	$2.9\cdot10^{-5}$
20	$1.7\cdot10^{-5}$	$1.9\cdot10^{-5}$	$1.8\cdot10^{-5}$	$2.2\cdot10^{-5}$	$1.6\cdot10^{-5}$	$2.6\cdot10^{-5}$	$5.0\cdot10^{-5}$	$4.5\cdot10^{-5}$

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 SI6). The thickness of the film was 120μm and using glass covered. Irradiation time was 600s[3].

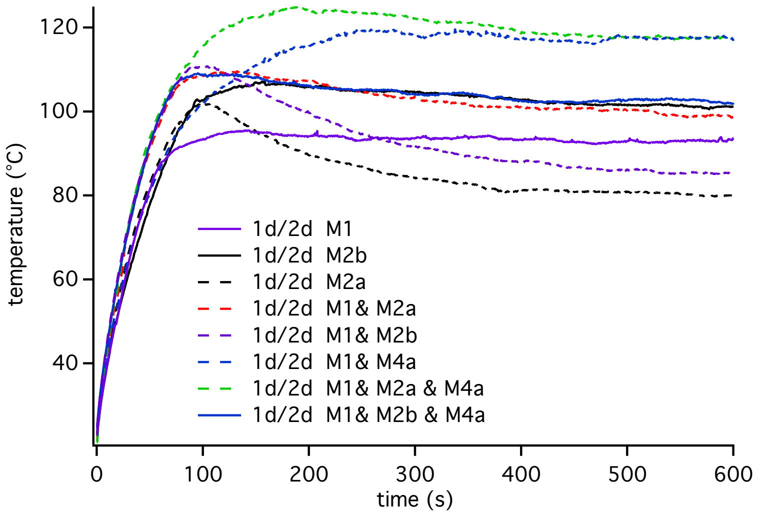


Figure SI6: The temperature (T/°C) generated by the samples (thickness is 120μm) in different monomers comprising **1d** (6×10^{-3} mmol/g) and **2d** (3.8×10^{-2} mmol/g).

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[5].

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).

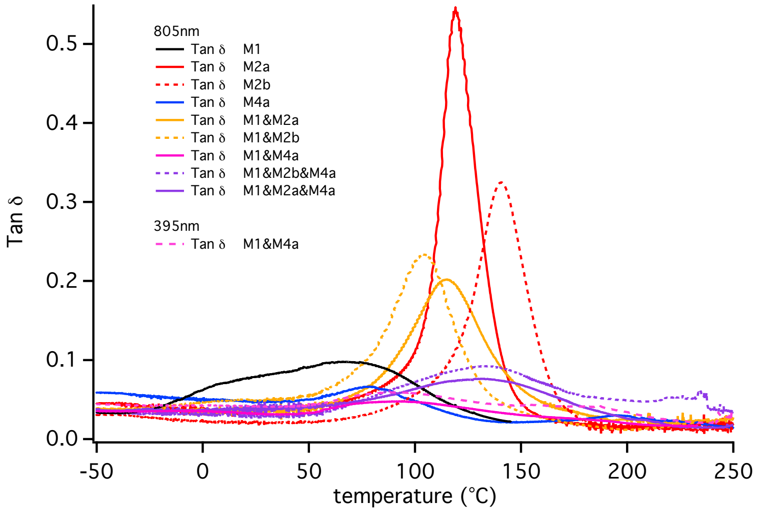
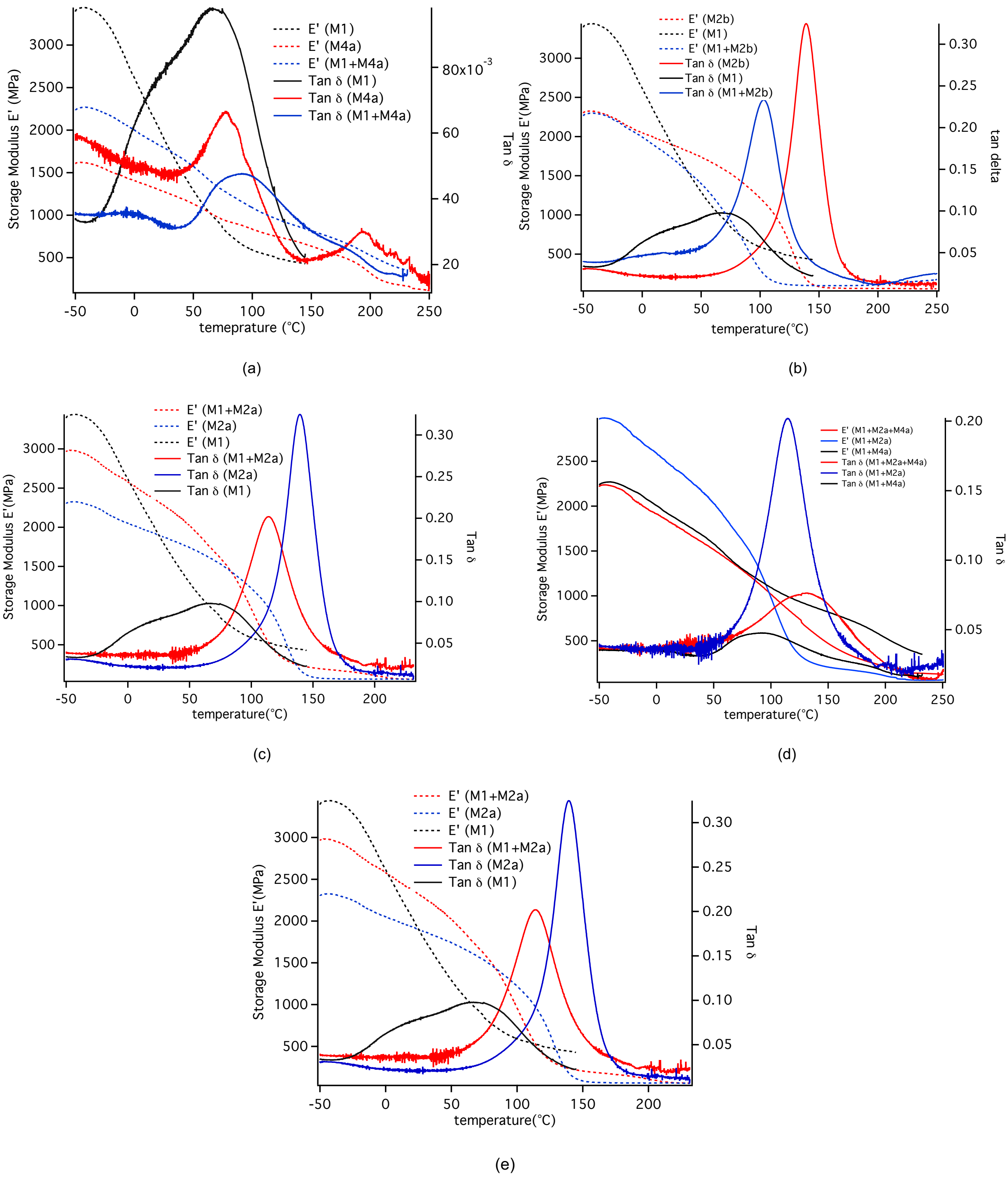


Figure SI7. DMA data (tan δ) of films (thickness: 120 μm) exposed at 395 nm (1.1 W×cm^{-2}) and 805 nm (1.2 W×cm-2) in the case of the monomers **M1** and M4a after 2 min and 10 min exposure at 395 nm (1.1 W×cm^{-2}) and 805 nm (1.1 W×cm^{-2}), respectively. The *i*-propyl thioxanthone **ITX** (0.1 wt%)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



(a)

(b)

(c)

(d)

(e)

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 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 1610cm^{-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.

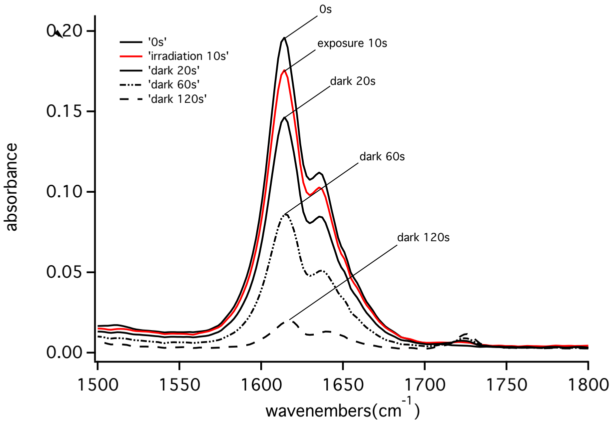


Figure SI9. The FTIR spectra of M3 at around1610cm^{-1} belonging to the stretching vibration absorption of the carbon carbon double bond (-C=C-) of the vinyl ether in different irradiation (0s,10s) and dark time(20s, 60s, 120s). the combination of 1a (6.0×10^{-3} mmol×g^{-1}) and 2a (3.8×10^{-2} mmol×g-1) served as initiator combination for experiments at 805 nm,1.2W/cm^{2}.

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