Supporting Information for

Sunlight-induced Crosslinking of 1,2-Polybutadienes: Access to Fluorescent Polymer Networks

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Materials. Formyl-benzoic acid (96 %, Acros Organics), *p*-toluenesulfonyl hydrazide (98 %, Alfa Aesar), pyridine (99 %, ABCR), anisidine (99 %, ABCR), HCl (37 %, Roth), sodium nitrite ($NaNO_2$, 98 %, Alfa Aesar) thionyl chloride ($SOCl_2$, 99.5 %, Acros Organics), polybutadiene predominantly 1,2-addition (**PBD-1**, approx. 90% 1,2-vinyl, Sigma-Aldrich), and tetrahydrofuran (THF, 99.5 % extra dry, Acros Organics) were used as received. 1,2-polybutadiene (JSR RB_820, **PBD-2**) was kindly provided by NRC (Nordmann, Rassmann).

Characterization. *Size exclusion chromatography (SEC)*. To determine molecular weight distributions (MWD) a SEC system (Polymer Laboratories PL-GPC 50 Plus) comprised of an auto injector, a guard column (PLgel Mixed C, 50 × 7.5 mm) followed by three linear columns (PLgel Mixed C, 300 × 7.5 mm, 5 µm bead-size) and a differential refractive index detector was employed. THF was used as the eluent at 35 °C, with a flow rate of 1 $mL \cdot min^{-1}$. The SEC system was calibrated using narrow poly(methyl methacrylate) standards ranging from 600 to 6×105 g mol^{-1} (Polymer Standards Service (PSS), Mainz, Germany). The resulting molecular weight distributions were determined by universal calibration using Mark-Houwink parameters for polystyrene ($K = 14.1 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.7$).

NMR spectroscopy. Bruker AM 250 (250 MHz) and Bruker AM 400 (400 MHz) spectrometers were used for the ^{1}H-NMR and ^{13}C-NMR spectroscopy, respectively. Samples were characterized using $CDCl_3$ as the solvent. The δ-scale is referenced to the internal standard trimethylsilane (TMS, $\delta = 0.00$ ppm).

Electrospray ionization - mass spectrometry (ESI-MS). ESI-MS spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode.

The instrument was calibrated in the *m*/*z* range of 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 4.5 kV was used. Nitrogen was applied at a dimensionless sweep gas flow-rate of 2 (approx. 3 L min^{-1}) and a dimensionless sheath gas flow-rate of 12 (approx. 1 L min^{-1}) were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature were set to 60 V, 110 V, and 275 °C respectively.

Fluorescence and UV-Vis spectroscopy. Fluorescence emission spectra were recorded for samples in quartz cuvettes loaded with a sample volume of 230 μL on a Varian Cary Eclipse Fluorescence Spectrometer. UV-Visible spectroscopy was performed using a Varian Cary 300 Bio spectrophotometer featuring a thermostatted sample cell holder. Absorption spectra were measured for 1.0×10^{-4} mol L^{-1} samples in acetonitrile solution from 200 to 800 nm with a resolution of 1 nm and slit width of 2 nm in a 1 cm UV cuvette.

Spectroscopic data of di-linker.

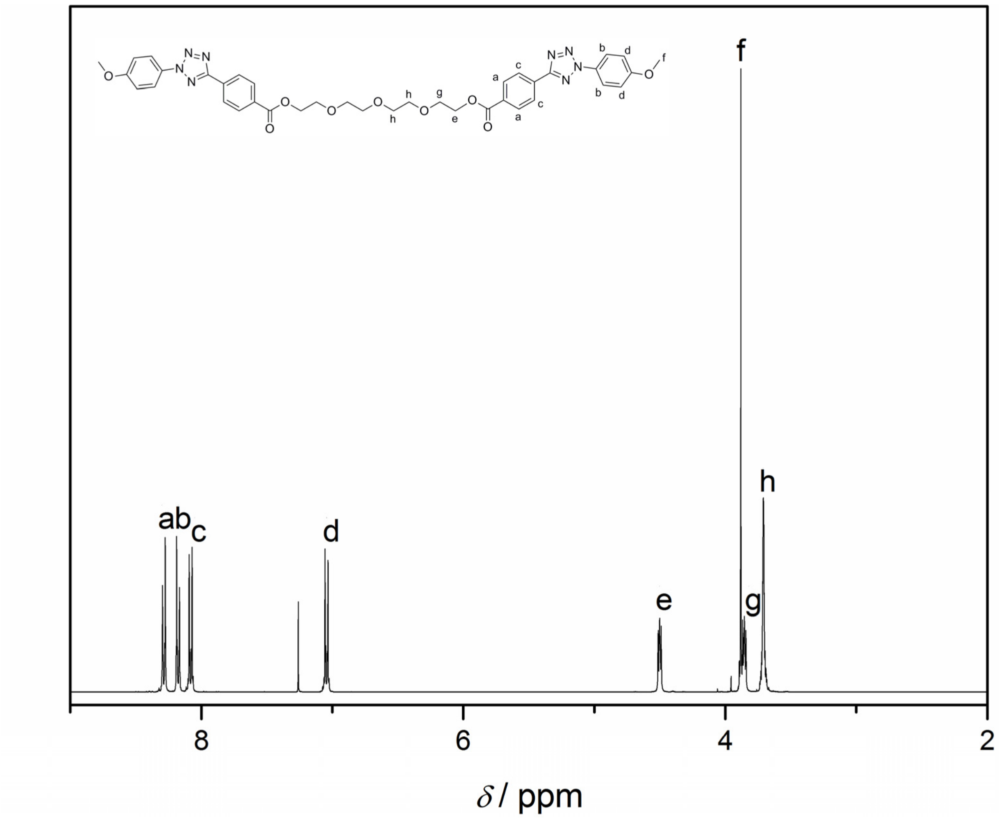

Figure S1. ^{1}H-NMR spectrum of **di-linker** in $CDCl_3$.

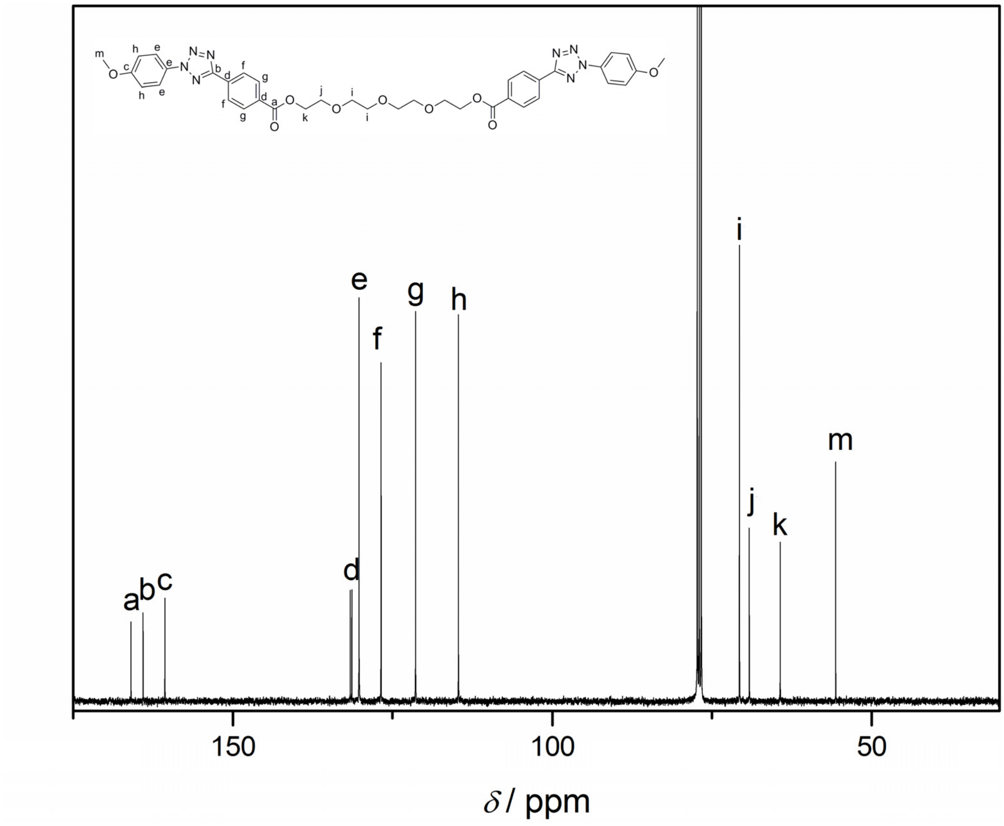

Figure S2. ^{13}C-NMR spectrum of **di-linker** in $CDCl_3$.

UV-lamp specifications.

- *Arimed B6*, Cosmedico GmBH, Stuttgart, Germany. Compact low-pressure fluorescent lamp, 36 W, λ_{max} = 320 nm (±30 nm).
- *Philips Cleo PL-L*, Philips Deutschland GmBH. Compact low-pressure fluorescent lamp, 36 W, λ_{max} = 355 nm (±50 nm).
- *Philips TL01,* Philips Deutschland GmBH. Philips Medical Therapy UV-B Narrow Band/01, 36W λ_{max} = 312 nm (±5 nm).

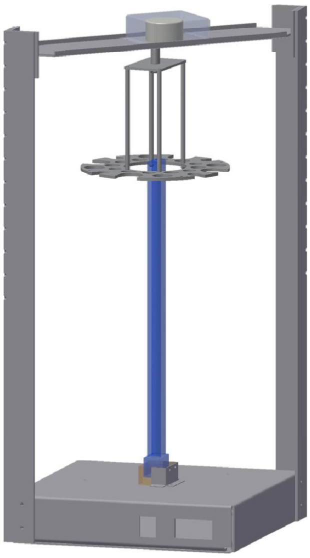

Figure S3. Illustration of the custom-built photoreactor employed in the current study.

Additional mass spectra concerning the small molecule model study.

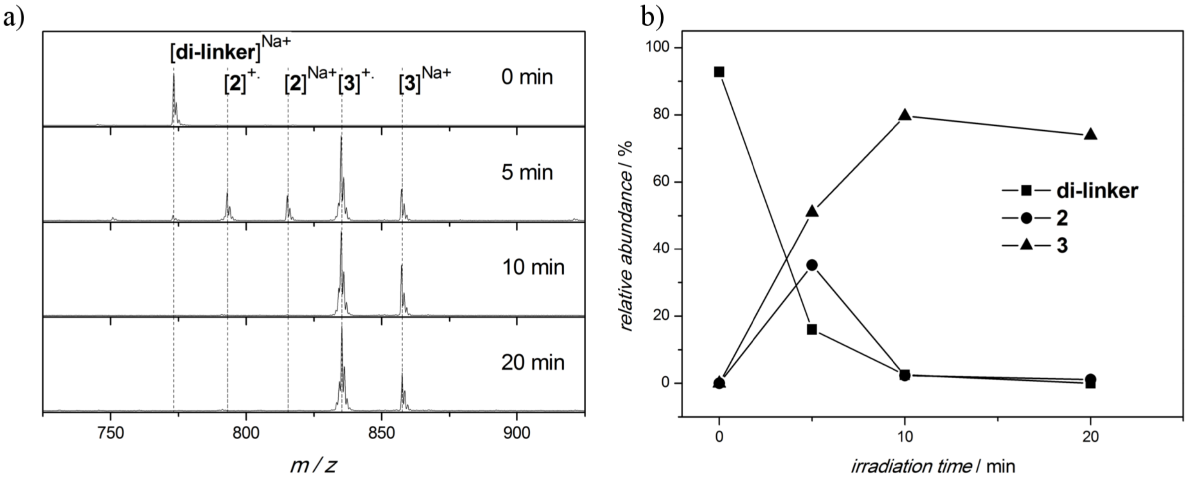

Figure S4. Kinetic investigation of the small molecule model reaction between 1-pentene and the **di-linker** employing the *Philips TL01* UV-lamp. a) ESI-MS spectra after 0, 5, 10, and 20 min of reaction time. b) graph of the relative abundance of di-linker, mono-functionalized intermediate (**2**) and di-functionalized product (**3**) as a function of irradiation time determined from integration of the corresponding ESI-MS spectra.

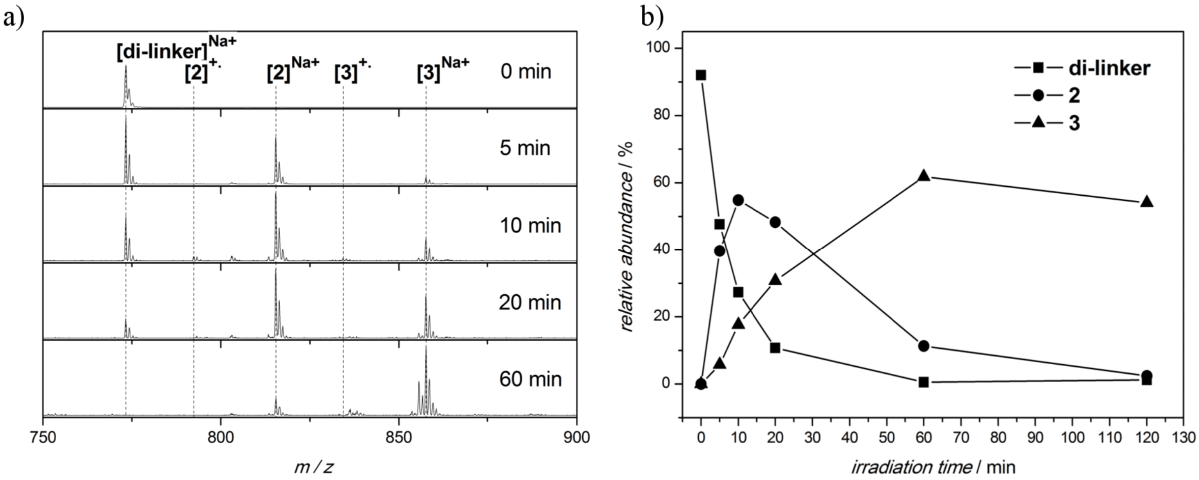

Figure S5. Kinetic investigation of the small molecule model reaction between 1-pentene and the **di-linker** employing the *Philips Cleo PL-L* UV-lamp. a) ESI-MS spectra after 0, 5, 10, 20, and 60 min of reaction time. b) graph of the relative abundance of di-linker, mono-functionalized intermediate (**2**) and di-functionalized product (**3**) as a function of irradiation time determined via integration of the corresponding ESI-MS spectra.

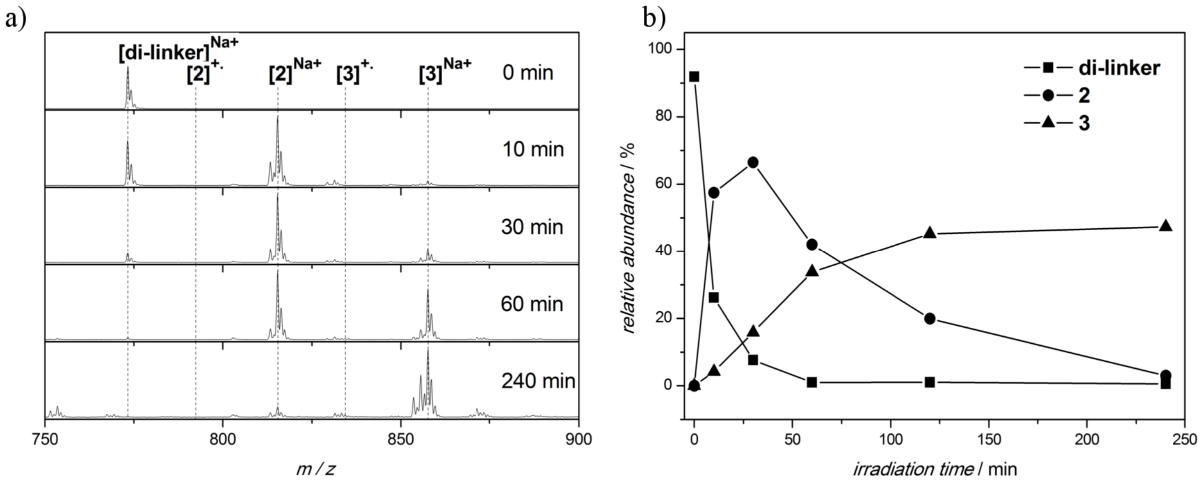

Figure S6. Kinetic investigation of the small molecule model reaction between 1-pentene and the **di-linker** in sunlight. a) ESI-MS spectra after 0, 10, 30, 120 and 240 min of reaction time. b) graph of the relative abundance of di-linker, mono-functionalized intermediate (**2**) and di-functionalized product (**3**) as a function of irradiation time determined from integration of the corresponding ESI-MS spectra.

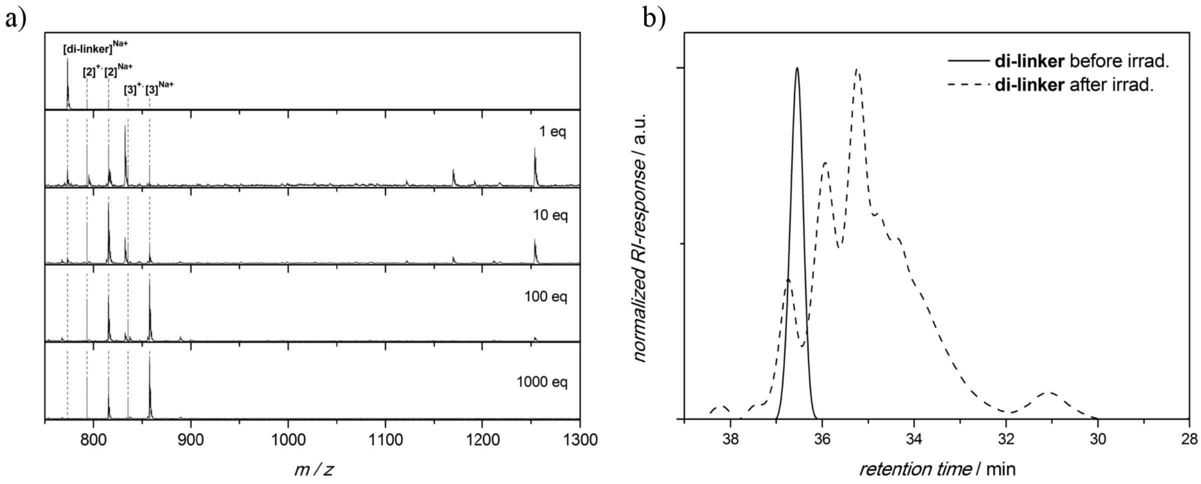

Figure S7. a) ESI-MS spectra of the reaction mixtures of the **di-linker** and 1-pentene with varying equivalents of the dipolarophile (1-pentene). b) SEC elugram of the dimerization reaction of the **di-linker** in THF. The reactions were performed at a **di-linker** concentration of 0.1 mg mL^{-1} under irradiation with the *Arimed B6* UV-lamp for 1 h.

Spectroscopic data of product 3.

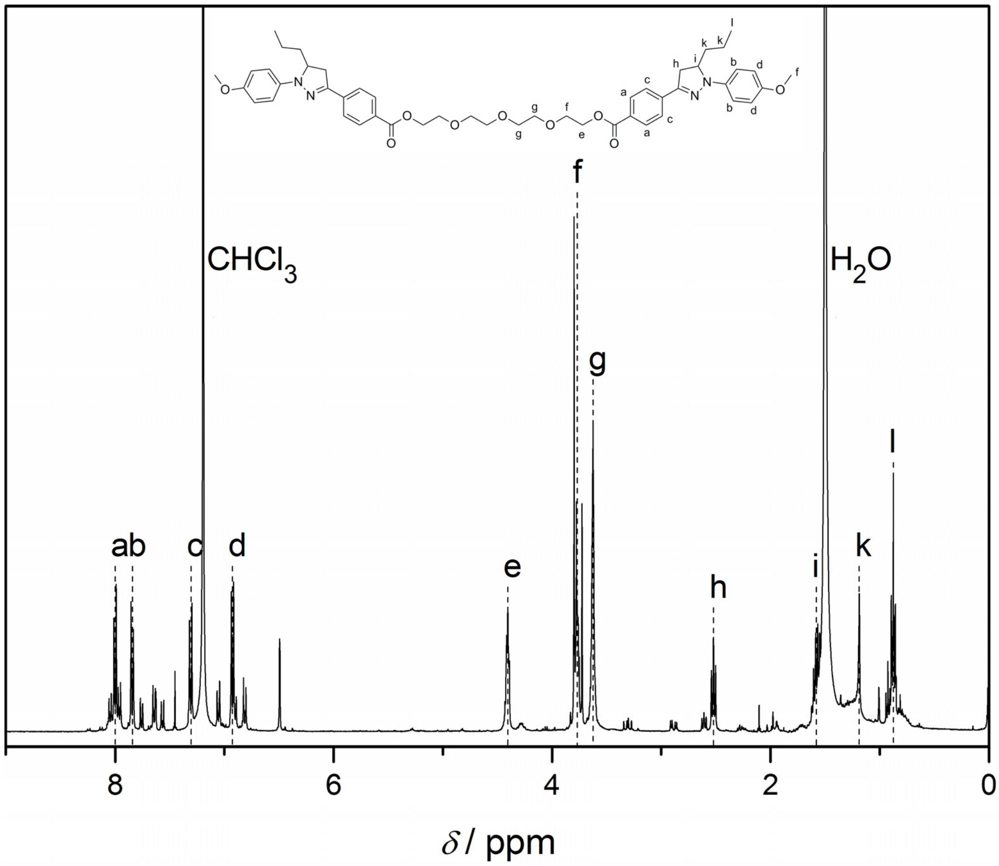

Figure S8: ^{1}H-NMR spectrum of **3** in $CDCl_3$. The signals referring to the main isomer are labeled in the depicted structure.