Supporting Information

Azo-Containing Polymers with Degradation On-Demand Feature

Mathieu A. Ayer\textsuperscript{1}, Yoan C. Simon\textsuperscript{1,2}, Christoph Weder\textsuperscript{1}* 

\textsuperscript{1}Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

\textsuperscript{2}School of Polymers and High Performance Materials, The University of Southern Mississippi, 118 College Dr., Hattiesburg MS 39406, USA

To whom correspondence should be addressed, E-mail: christoph.weder@unifr.ch
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Pristine azo-PA

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![Image of NMR spectrum]
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Elemental analyses (EA) of pristine and heated azo-PA, ref-PA, azo-PU, and ref-PU

**Pristine azo-PA**

$$(\text{Jeff}_{0.802} \text{DAD}_{0.200} \text{SC}_{0.797} \text{J}_{0.202})_n$$

$$\left((C_2H_4O)_{39}(C_3H_6O)_6C_3H_8N_2)_{0.802}(C_{10}H_{22}N_2)_{0.200}(C_{10}H_{16}O_2)_{0.797}(C_{12}H_{14}N_4O_2)_{0.202}$$

Anal. Calcd: C, 57.03; H, 9.41; N, 2.04. Found: C, 56.5; H, 9.8; N, 2.0.

**Heated azo-PA (solid state, 140 °C for 5 min)**

$$(\text{Jeff}_{0.802} \text{DAD}_{0.200} \text{SC}_{0.797} \text{J}_{0.202})_n$$

$$\left((C_2H_4O)_{39}(C_3H_6O)_6C_3H_8N_2)_{0.802}(C_{10}H_{22}N_2)_{0.200}(C_{10}H_{16}O_2)_{0.797}(C_{12}H_{14}N_4O_2)_{0.202}$$

Anal. Calcd: C, 57.19; H, 9.45; N, 1.75. * Found: C, 56.0; H, 9.7; N, 1.8.

*Assuming dissociation of all azo groups, complete release of N$_2$, and quantitative recombination of the radicals produced.

**Pristine ref-PA**

$$(\text{Jeff}_{0.802} \text{DAD}_{0.200} \text{SC}_{1.031})_n$$

$$\left((C_2H_4O)_{39}(C_3H_6O)_6C_3H_8N_2)_{0.802}(C_{10}H_{22}N_2)_{0.209}(C_{10}H_{16}O_2)_{1.031}$$

Anal. Calcd: C, 57.30; H, 9.51; N, 1.47. Found: C, 56.2; H, 9.9; N, 1.4.

**Heated ref-PA (solid state, 140 °C for 5 min)**

$$(\text{Jeff}_{0.802} \text{DAD}_{0.200} \text{SC}_{1.031})_n$$

$$\left((C_2H_4O)_{39}(C_3H_6O)_6C_3H_8N_2)_{0.802}(C_{10}H_{22}N_2)_{0.209}(C_{10}H_{16}O_2)_{1.031}$$

Anal. Calcd: C, 57.30; H, 9.51; N, 1.47. Found: C, 56.7; H, 9.8; N 1.4.
Pristine azo-PU

$$(\text{MDI}_{7.957}\text{BDO}_{3.950} \text{PTHF}_{2.107}^2)_{2.100n}$$

$$(\text{C}_{15}\text{H}_{10}\text{N}_{2}\text{O}_{2})_{7.957}(\text{C}_{4}\text{H}_{10}\text{O}_{2})_{3.950}((\text{C}_{4}\text{H}_{8}\text{O})_{27.486}\text{H}_{2}\text{O})_{2.107}(\text{C}_{12}\text{H}_{24}\text{N}_{2}\text{O}_{4})_{1.200}$$


Heated azo-PU (solid state, 150 °C for 5 min)

$$(\text{MDI}_{7.957}\text{BDO}_{3.950} \text{PTHF}_{2.107}^2)_{2.400n}$$

$$(\text{C}_{15}\text{H}_{10}\text{N}_{2}\text{O}_{2})_{7.957}(\text{C}_{4}\text{H}_{10}\text{O}_{2})_{3.950}((\text{C}_{4}\text{H}_{8}\text{O})_{27.486}\text{H}_{2}\text{O})_{2.107}(\text{C}_{6}\text{H}_{13}\text{NO}_{2})_{2.400}$$


*Assuming dissociation of all azo groups, complete release of N$_2$, carbon-centered radicals formed and further reaction, i.e. proton abstraction or recombination.

Pristine ref-PU

$$(\text{MDI}_{15.765}\text{BDO}_{9.284} \text{PTHF}_{4.997})_{n}$$

$$(\text{C}_{15}\text{H}_{10}\text{N}_{2}\text{O}_{2})_{15.765}(\text{C}_{4}\text{H}_{10}\text{O}_{2})_{9.284}((\text{C}_{4}\text{H}_{8}\text{O})_{27.486}\text{H}_{2}\text{O})_{4.997}$$


Heated ref-PU (solid state, 150 °C for 5 min)

$$(\text{MDI}_{15.765}\text{BDO}_{9.284} \text{PTHF}_{4.997})_{n}$$

$$(\text{C}_{15}\text{H}_{10}\text{N}_{2}\text{O}_{2})_{15.765}(\text{C}_{4}\text{H}_{10}\text{O}_{2})_{9.284}((\text{C}_{4}\text{H}_{8}\text{O})_{27.486}\text{H}_{2}\text{O})_{4.997}$$

Thermogravimetric analyses (TGA)

Figure S19. TGA traces of the azo-containing polyamide \textit{azo-PA} (red) and the reference polymer \textit{ref-PA} (black) performed under N$_2$ at a heating rate of 10 °C/min. The samples were dried prior to measurement.
Figure S20. TGA traces of the azo-containing polyamide \textit{azo-PU} (red) and the reference polymer \textit{ref-PU} (black) performed under N$_2$ at a heating rate of 10 °C/min. The samples were dried prior to measurement.
Differential scanning calorimetry (DSC)

**Figure S21.** DSC thermograms of the azo-containing polyamide azo-PA recorded under N₂ at heating and cooling rates of 10 °C/min in the range from (a) -80 to 220 °C and (b) -80 to 60 °C. The samples (polymer film pieces) were dried prior to the measurements.
Figure S22. DSC thermograms of the reference polyamide **ref-PA** recorded under N₂ at heating and cooling rates of 10 °C/min in the range from (a) -80 to 220 °C and (b) -80 to 60 °C. The samples (polymer film pieces) were dried prior to measurement.
Figure S23. DSC thermograms of the azo-containing polyurethane azo-PU recorded under N₂ at heating and cooling rates of 10°C/min. The sample (polymer film piece) was dried prior to measurement.
Figure S24. DSC thermogram of the reference polyurethane ref-PU recorded under N₂ at heating and cooling rates of 10°C/min. The sample (polymer film piece) was dried prior to measurement.
Dynamic mechanical analyses (DMA)

<table>
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<tr>
<th></th>
<th>$E'$ at -70°C (MPa)</th>
<th>$E'$ at 25°C (MPa)</th>
<th>$T_g$ (°C)</th>
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<tr>
<td>Azo PA</td>
<td>3639 ± 47</td>
<td>234 ± 41</td>
<td>-15 ± 2</td>
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<tr>
<td>Ref- PA</td>
<td>3773 ± 189</td>
<td>264 ± 5</td>
<td>-21 ± 1</td>
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Figure S25. Representative dynamic mechanical analysis (DMA) traces of films of the azo-containing polyamide azo-PA (solid red line) and the reference polymer ref-PA (black line). The loss tangent (tan δ) traces of the azo-PA (dashed red line) and the reference polymer ref-PA (dashed black line) are also shown. The measurements were carried out at a heating rate of 3 °C/min and a frequency of 1 Hz under N$_2$. The storage moduli ($E'$) at -70 and 25 °C and the glass transition temperatures ($T_g$, determined from the maxima of the tan δ traces) are also reported. Values indicated in the table are averages of 3 samples.
Figure S26. Representative dynamic mechanical analysis (DMA) traces of films of the azo-containing polyurethane **azo-PU** (solid red line) and the reference polymer **ref-PU** (black line). The loss tangent (\(\tan \delta\)) traces of the **azo-PU** (dashed red line) and the reference polymer **ref-PU** (dashed black line) are also shown. The measurements were carried out at a heating rate of 3 °C/min and a frequency of 1 Hz under N\(_2\). The storage moduli (\(E'\)) at -70 and 25 °C and the glass transition temperatures (\(T_g\), determined from the maxima of the \(\tan \delta\) traces) are also reported. Values indicated in the table are averages of 3 samples.
Heating in solution (THF): size exclusion chromatography (SEC) traces of polyurethanes

Figure S27. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after heat treatment in solution (THF, microwave synthesizer), at 140 °C for 5 min (red line), 140 °C for 10 min (green line), 150 °C for 5 min (blue line) and 160 °C for 5 min (magenta line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).

<table>
<thead>
<tr>
<th></th>
<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
<th>$D$</th>
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</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>93,700</td>
<td>49,300</td>
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</tr>
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<td>140 °C, 5 min</td>
<td>57,500</td>
<td>27,500</td>
<td>2.09</td>
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<tr>
<td>140 °C, 10 min</td>
<td>56,100</td>
<td>24,600</td>
<td>2.28</td>
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<tr>
<td>150 °C, 5 min</td>
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<td>160 °C, 5 min</td>
<td>37,600</td>
<td>18,500</td>
<td>2.03</td>
</tr>
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</table>
Figure S28. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane ref-PU (black line) and samples of ref-PU after heat treatment in solution (THF, microwave synthesizer), at 140 °C for 5 min (red line), 150 °C for 5 min (green line) and 160 °C for 5 min (blue line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
Heating in the solid state: size exclusion chromatography (SEC) traces of polyurethanes

![Graph showing SEC traces of azo-PU](image)

<table>
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<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
<th>$D$</th>
</tr>
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<tbody>
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<td>Pristine</td>
<td>93,700</td>
<td>49,300</td>
<td>1.90</td>
</tr>
<tr>
<td>140 °C, 5 min</td>
<td>47,100</td>
<td>22,700</td>
<td>2.07</td>
</tr>
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<td>140 °C, 10 min</td>
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<td>18,500</td>
<td>2.12</td>
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<tr>
<td>150 °C, 5 min</td>
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<td>2.34</td>
</tr>
<tr>
<td>160 °C, 5 min</td>
<td>36,800</td>
<td>15,700</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Figure S29. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane azo-PU (black line) and samples of azo-PU after heat treatment in the solid state (pre-heated hot press), 140 °C for 5 min (red line), 140 °C for 10 min (green line), 150 °C for 5 min (blue line) and 160 °C for 5 min (magenta line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
**Figure S30.** Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane ref-PU (black line) and samples of ref-PU after heat treatment in the solid state (pre-heated hot press), 140 °C for 5 min (red line), 150 °C for 5 min (green line) and 160 °C for 5 min (blue line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
Figure S31. Size exclusion chromatography (SEC) traces of pristine samples of the azo-containing and reference polyurethanes azo-PU and ref-PU (red and black dashed lines) and samples of azo-PU and ref-PU after heat treatment in the solid state (pre-heated hot press) at 150 °C for 30 min (red and black solid lines). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
UV light irradiation in solution (THF): UV-Vis spectrum of the azo compound 2 and size exclusion chromatography (SEC) traces of polyurethanes

**Figure S32.** UV-Vis spectrum of the azo compound 2 in water (0.028 M). The extinction coefficient (371 nm) is 12.32 L·mol⁻¹·cm⁻¹.
**Figure S33.** Size exclusion chromatography (SEC) traces of a pristine sample of azo-containing polyurethane *azo-PU* (black line) and samples of *azo-PU* after exposure to UV light in solution (THF, 320-390 nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 15 sec with CCl₄ (blue line), for 30 sec (magenta line) and for 60 sec (cyan line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
**Figure S34.** Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after exposure to UV light in solution (THF, 320-390nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 15 sec with CCl₄ (blue line), for 30 sec (magenta line) and for 60 sec (cyan line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
UV light irradiation in the solid state of polyurethanes: UV-Vis spectra, set-up picture, size exclusion chromatography (SEC) traces and temperature vs. time diagrams

**Figure S35.** UV-Vis spectra of solid state samples of the azo-containing polyurethane *azo-PU* (red line) and the reference polymer *ref-PU* (black line).

**Figure S36.** Picture depicting the set-up used for the light irradiation processes. The sample (5x5 mm) deposited on a glass slide was irradiated from the top (15 mm distance) and its temperature was monitored with an IR camera from the left.
**Figure S37.** Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after exposure to UV light in the solid state (320-390 nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 30 sec (blue line) and for 60 sec (magenta line). The weight average ($M_w$) and number average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
Figure S38. Temperature vs. time curves of azo-containing polyurethane azo-PU samples irradiated with UV light in the solid state (320-390 nm, 600 mW/cm$^2$), for 7.5 sec (red line), for 15 sec (green line), for 30 sec (blue line) and for 60 sec (magenta line). The temperature was monitored with an IR camera.
**Figure S39.** Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after exposure to UV light in the solid state (320-390 nm, 600 mW/cm²), for 30 sec (red line) and for 60 sec (green line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
**Figure S40.** Temperature vs. time curves of reference polyurethane ref-PU samples irradiated with UV light in the solid state (320-390 nm, 600 mW/cm²), for 30 sec (red line) and 60 sec (green line). The temperature was monitored with an IR camera.
UV light irradiation in the solid state of polyamides: size exclusion chromatography (SEC) traces and temperature vs. time diagrams

![UV irradiation in the solid state of azo-PA](image)

<table>
<thead>
<tr>
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<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
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<tr>
<td>Pristine</td>
<td>33,000</td>
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</tr>
<tr>
<td>15 sec</td>
<td>34,000</td>
<td>23,300</td>
<td>1.46</td>
</tr>
<tr>
<td>30 sec</td>
<td>34,100</td>
<td>23,300</td>
<td>1.46</td>
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</table>

**Figure S41.** Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyamide azo-PA (black line) and samples of azo-PA after exposure to UV light in the solid state (320-390 nm, 600 mW/cm$^2$), for 15 sec (red line) and for 30 sec (green line). The weight average ($M_w$) and number average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
Figure S42. Temperature vs. time curves of azo-containing polyamide azo-PA samples irradiated with UV light in the solid state (320-390 nm, 600 mW/cm²), for 15 sec (red line) and for 30 sec (green line). The temperature was monitored with an IR camera.
UV light irradiation in the solid state of dogbone shaped specimens of polyurethanes: set-up pictures and temperature vs. time diagrams

Figure S43. Pictures depicting (a) the set-up used for the UV light irradiation of dogbone shaped specimens of azo-containing and reference polyurethanes azo-PU and ref-PU prior to the stress-strain measurements and (b) two azo-PU dogbone shaped specimens, the top one was irradiated while the bottom one is pristine. The scale is in cm.
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Temperature (°C)</th>
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<tbody>
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<td>10</td>
<td>22</td>
</tr>
<tr>
<td>20</td>
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</tr>
<tr>
<td>70</td>
<td>40</td>
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**Figure S44.** Representative temperature vs. time curve of a dogbone shaped specimen of the azo-containing polyurethane azo-PU irradiated with UV light (320-390 nm, 600 mW/cm², 30 sec). The temperature was monitored with an IR camera. The temperature elevation value indicated in the table is an average obtained of the 3 samples used for the stress-strain measurements.
Figure S45. Representative temperature vs. time curve of a dogbone shaped specimen of the reference polyurethane ref-PU irradiated with UV light (320-390 nm, 600 mW/cm², 30 sec). The temperature was monitored with an IR camera. The temperature elevation value indicated in the table is an average of the 3 samples used for the stress-strain measurements.
Stress-strain data for pristine, heated and irradiated polyurethanes

Table S46. Elongation and stress at break values, and Young’s modulus values derived from stress-strain measurements of pristine and samples exposed to heat or UV light.

<table>
<thead>
<tr>
<th></th>
<th>Elongation at break&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Stress at break&lt;sup&gt;c&lt;/sup&gt; (MPa)</th>
<th>Young’s modulus&lt;sup&gt;d&lt;/sup&gt; (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine azo-PU</td>
<td>556 ± 25</td>
<td>81 ± 9</td>
<td>41 ± 1</td>
</tr>
<tr>
<td>Heated&lt;sup&gt;a&lt;/sup&gt;</td>
<td>270 ± 35</td>
<td>9 ± 1</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>Irradiated&lt;sup&gt;b&lt;/sup&gt;</td>
<td>333 ± 6</td>
<td>13 ± 1</td>
<td>35 ± 2</td>
</tr>
<tr>
<td>Pristine ref-PU</td>
<td>574 ± 14</td>
<td>67 ± 2</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>Heated&lt;sup&gt;a&lt;/sup&gt;</td>
<td>606 ± 70</td>
<td>64 ± 19</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>Irradiated&lt;sup&gt;b&lt;/sup&gt;</td>
<td>563 ± 18</td>
<td>75 ± 5</td>
<td>24 ± 1</td>
</tr>
</tbody>
</table>

<sup>a</sup>The heat treatment (pre-heated hot press, 150 °C for 5 min) undergone by the samples was applied prior to cut them into a dogbone shape. 
<sup>b</sup>The UV irradiation (320-390 nm, 600 mW/cm<sup>2</sup>, 30 sec) was performed in the central area of the dogbone shaped specimens after cutting. 
<sup>c</sup>The elongation and stress at break values are averages from 3 samples. 
<sup>d</sup>The Young’s modulus values are averages from the same 3 samples and derived from the slope of the stress-strain curves between 0.5 and 1.0 %.
Visible light irradiation in the solid state: lamp emission spectrum, size exclusion chromatography (SEC) traces of polyurethanes and temperature vs. time diagrams.

Figure S47. Emission spectrum of the visible light emitting source used (Hönle UV lamp equipped with a 390-500 nm filter).
Visible light irradiation in the solid state of azo-PU

<table>
<thead>
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<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
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<td>Pristine</td>
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<td>30 sec</td>
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<td>60 sec</td>
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</table>

Figure S48. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane azo-PU (black line) and samples of azo-PU after exposure to visible light in the solid state (390-500 nm, 600 mW/cm$^2$), for 30 sec (red line) and for 60 sec (green line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersity value ($D$).
Figure S49. Temperature vs. time curves of azo-containing polyurethane azo-PU samples irradiated with visible light in the solid state (390-500 nm, 600 mW/cm²), for 30 sec (red line) and 60 sec (green line). The temperature was monitored with an IR camera.
Figure S50. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane ref-PU (black line) and samples of ref-PU after exposure to visible light in the solid state (390-500 nm, 600 mW/cm²) for 60 sec (red line). The weight-average ($M_w$) and number-average molecular weight ($M_n$) values are indicated in the table as well as the dispersionsity value ($D$).

<table>
<thead>
<tr>
<th></th>
<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>204,700</td>
<td>93,600</td>
<td>2.19</td>
</tr>
<tr>
<td>60 sec</td>
<td>199,500</td>
<td>92,500</td>
<td>2.16</td>
</tr>
</tbody>
</table>
**Figure S51.** Temperature vs. time curve of a reference polyurethane ref-PU sample irradiated with visible light in the solid state (390-500 nm, 600 mW/cm²) for 60 sec. The temperature was monitored with an IR camera.