Supporting Information for One-component Diels-Alder based polyurethanes: a unique way to self-heal

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The electronic supporting information contains details of all synthesis of thermo-responsive diols and polyurethanes (SI 1-2), TGA curves (SI 3), FTIR analysis (SI 4 and 9), swelling tests (SI 5), DMA (SI 6 and 7), mechanical recovery (SI 8) and scratch recovery tests (SI 10 and 11).

SI. 1. Synthesis of thermo-responsive diols

The synthesis of monomers maleimide, furfuryl and anthracene diols (respectively named MAL(OH)₂, FUR(OH)₂ and ANT(OH)₂ hereafter) were inspired by the four-step synthesis strategy proposed by Tonga et al.¹. The general reaction pathway is summarized on Fig. SI. 1. and synthesis conditions are described in details in the following section.

Fig. SI. 1. Four-step synthesis of the thermo-responsive diols bearing furfuryl, anthracene and furan-protected maleimide groups.
SI. 1.1. Synthesis of 2,2′-Bis(hydroxymethyl) propionic acid acetonide [1]. 50 g of 2,2′-Bis(hydroxymethyl) propionic acid (bis-MPA) (0.372 mol), 3.55 g of p-toluenesulfonic acid monohydrate (0.018 mol) and 69 ml of 2,2-dimethoxypropane (0.559 mol) were dissolved in 250 ml of acetone. The reaction mixture was stirred 3 h at room temperature. After neutralization of the catalyst with 5 ml of a solution of 25% NH₃ in MeOH (7 N), the solvent was evaporated. The residue was dissolved in 1 l of CH₂Cl₂ and extracted with two portions of water (2*100 ml). The organic phase was dried with MgSO₄ and evaporated to give a white crystal [1] (59.34 g, 91%). ¹H-NMR (CDCl₃): δ 1.21 (s, 3H), 1.42 (s, 3H), 1.45 (s, 3H), 3.69 (d, 2H), 4.17 (d, 2H).

SI. 1.2. Synthesis of Acetonide 2,2′-Bis(hydroxymethyl) propionic anhydride [2]. 50 g of [1] (0.286 mol) was stirred in CH₂Cl₂ (200 ml). DCC (29.6 g, 0.144 mol) was added to the mixture and stirring was continued for 48 h at room temperature. The DCC-urea was filtered off and the solvent evaporated. The viscous residue was poured in 1 l of hexane at -78°C and stirred until a white solid formed. Thereafter, the solution was filtered through a glass filter and dried under vacuum to afford a white solid [2] (15.74 g, 74%). ¹H-NMR, (CDCl₃): 1.24 (s, 6H), 1.40 (s, 6H), 1.44 (s, 6H), 3.70 (d, 4H), 4.20 (d, 4H).

SI. 1.3.a. Synthesis of MAL Acetonide [3']. To a solution of 3.5 g of MAL(OH) (15.6 mmol) in 50 ml of CH₂Cl₂, 7.77 g of [2] (23.4 mmol), 1.68 g of DMAP (13.7 mmol) and 10.89 ml of pyridine (135.1 mmol) were added. The mixture was stirred at ambient temperature for 12 h followed by quenching of excess anhydride with (1:1) mixture of pyridine and water (12 ml). The reaction mixture was extracted with 1 M NaHSO₄ (3*20 ml), 10 % Na₂CO₃ (3*20 ml) and brine (1*20 ml). Then the combined organic layers were dried over anhydrous MgSO₄. The residue was concentrated in vacuo to afford a white solid [3'] (5.03 g, 85%). ¹H-NMR, (CDCl₃): 1.23 (s, 3H), 1.40 (s, 6H), 1.42 (s, 6H), 1.94 (m, 2H), 2.83 (s, 2H), 3.58 (t, 2H), 3.66 (d, 2H), 4.09 (t, 2H), 4.21 (d, 2H), 5.26 (s, 2H), 6.50 (s, 2H).

SI. 1.3.b. Synthesis of FUR Acetonide [3'’]. The procedure for the synthesis of FUR Acetonide is the same as the one described in section SI.1.3.a. MAL(OH) is replaced by furfuryl alcohol and a brown solid is obtained [3’’] (2.82 g, 71%). ¹H-NMR, (CDCl₃): 1.18 (s, 3H), 1.36 (s, 3H), 1.41 (s, 3H), 3.63 (d, 2H), 4.16 (d, 2H), 5.12 (s, 2H), 6.35 (d, 1H), 6.40 (d, 1H), 7.40 (d, 1H).
**Sl. 1.3.c. Synthesis of ANT Acetonide [3’’’]** The procedure for the synthesis of FUR Acetonide is the same as the one described in section Sl.1.3.a. MAL(OH) is replaced by 9-methanol anthracene and a yellow solid is obtained [3’’’](7.84 g, 78 %). $^1$H-NMR, (CDCl$_3$): 1.11 (s, 3H), 1.37 (s, 3H), 1.39 (s, 3H), 3.60 (d, 2H), 4.15 (d, 2H), 6.21 (s, 2H), 7.50 (t, 2H), 7.57 (t, 2H), 8.04 (d, 2H), 8.33 (d, 2H), 8.51 (s, 1H).

**Sl. 1.4.a. Synthesis of MAL(OH)$_2$ [4’].** 5 g of [3’] were dissolved in 90 ml of MeOH. To this solution were added two teaspoons of DOWEX H+ acidic resin. The resulting mixture was stirred at ambient temperature until the consumption of [3’] (observed via TLC, typically 24 h). The resin was then filtered off and washed with MeOH. The filtrate was concentrated in vacuo to afford a white solid [4’](4.37 g, 98 %). $^1$H-NMR, (CDCl$_3$): 1.11 (s, 3H), 1.96 (m, 2H), 2.85 (s, 2H), 3.13 (s, 2H), 3.61 (t, 2H), 3.78 (d, 2H), 3.87 (d, 2H), 4.08 (d, 2H), 5.26 (s, 2H). 6.51 (s, 2H).

**Sl. 1.4.b. Synthesis of FUR(OH)$_2$ [4’’].** The same procedure described in section Sl 1.4.a. was used for the synthesis of FUR(OH)$_2$ (starting with [3’’’]) and a brown solid was obtained [4’’](1.63 g, 97 %). $^1$H-NMR, (CDCl$_3$): 1.07 (s, 3H), 2.75 (s, 2H), 3.73 (d, 2H), 3.88 (d, 2H), 5.16 (s, 2H), 6.36 (d, 1H), 6.42 (d, 1H), 7.43 (d, 1H).

**Sl. 1.4.c. Synthesis of ANT(OH)$_2$ [4’’’].** The same procedure described in section Sl 1.4.a. was used for the synthesis of ANT(OH)$_2$ (starting with [3’’’]) and a yellow solid was obtained [4’’’](4.31 g, 97 %). $^1$H-NMR, (CDCl$_3$): 0.98 (s, 3H), 2.80 (s, 2H), 3.74 (d, 2H), 3.89 (d, 2H), 6.22 (s, 2H), 7.50 (t, 2H), 7.57 (t, 2H), 8.03 (d, 2H), 8.32 (d, 2H), 8.52(s, 1H).
Synthesis of single-component self-healing polyurethanes

The synthesis of the single-component protected polyurethane is sketched on Fig. 1 of the manuscript. The investigated compositions are summarized in Table 1 of the manuscript.

Typically, polypropylene glycol, MAL(OH)$_2$ and FUR(OH)$_2$ were introduced in a 100 ml two-necked round bottom flask under inert atmosphere and solubilized in 20 ml of anhydrous DMF. Hexamethylene diisocyanate (HMDI) was then introduced and the solution was stirred for 5 min. Finally, dibutyltin dilaurate (DBTDL) was added (100 µl) and the reactive mixture was stirred for 6 h at 70°C. Finally, the solution was poured in petri-dishes and placed in a ventilated oven to remove solvent till constant weight.

Note that the synthesis of irreversible polyurethane networks was similar as the aforementioned procedure, replacing FUR(OH)$_2$ by ANT(OH)$_2$.

The structure of the single-component protected polyurethane was attested by $^1$H-NMR in DMSO-d$_6$ (Fig. SI.2. here for the composition PU2).
$^1$H-NMR spectroscopy was used to quantify the content of thermos-responsive moieties (furan and maleimide) in the synthesized polyurethanes as previously reported (Table SI.2).\(^2\)

**Table. SI.2. Quantification of thermos-responsive moieties in the three polyurethanes**

<table>
<thead>
<tr>
<th>Polyme</th>
<th>%mol of thermoresponsive moieties (maleimide or furan) (theo.)(^a)</th>
<th>%mol of maleimide (exp.)(^b)</th>
<th>%mol of furan (exp.)(^b)</th>
<th>Molar ratio furan/maleimide</th>
<th>%wt of MAL(OH)(_2)(^a)</th>
<th>%wt of FUR(OH)(_2)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1</td>
<td>18.7</td>
<td>16.4</td>
<td>15.3</td>
<td>0.93</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>PU2</td>
<td>22.5</td>
<td>19.5</td>
<td>18.3</td>
<td>0.94</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>PU3</td>
<td>22.5</td>
<td>18.5</td>
<td>17.7</td>
<td>0.96</td>
<td>29</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\) As calculated from the feed composition; \(^b\) as determined by $^1$H-NMR in DMSO-d6
SI. 3. Thermo-gravimetric analysis of furan-protected and deprotected polyurethanes

TGA curves of furan-protected and deprotected polyurethanes are presented on Fig. SI. 3 (for composition PU2). A clear additional weight loss (8 wt%) was observed at 137°C for furan-protected PU2, corresponding to furan removal.

Fig. SI. 3. TGA curves of furan-protected and deprotected PU2
SI. 4. ATR-FTIR of furan-protected and deprotected polyurethanes

FTIR spectra of furan-protected and deprotected polyurethane are presented on Fig. SI. 4. (for composition PU2). Appearance of maleimide characteristic bands centered at 695 and 830 cm\(^{-1}\) for deprotected polyurethane are observed.

![ATR-FTIR spectra of furan-protected and deprotected PU2](image)

*Fig. SI. 4. ATR-FTIR spectra of furan-protected and deprotected PU2*
SI. 5. Swelling tests of the polyurethane networks

The results of the swelling tests of the polyurethane networks are summarized in **Table SI.5**. Samples were swelled in DMF at 25°C for 24 h and the swelling tests were replicated to get the insoluble fraction and the degree of swelling.

**Table SI. 5. Swelling tests of polyurethane networks**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Before swelling 1 (mg)</th>
<th>After swelling 1 (mg)</th>
<th>Dried after swelling 1 (mg)</th>
<th>Fraction of insoluble (a) (%)</th>
<th>After swelling 2 (mg)</th>
<th>Dried after swelling 2 (mg)</th>
<th>Degree of swelling (b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1</td>
<td>63</td>
<td>193</td>
<td>56</td>
<td>88</td>
<td>195</td>
<td>56</td>
<td>248</td>
</tr>
<tr>
<td>PU2</td>
<td>68</td>
<td>156</td>
<td>62</td>
<td>91</td>
<td>152</td>
<td>58</td>
<td>145</td>
</tr>
<tr>
<td>PU3</td>
<td>47</td>
<td>100</td>
<td>47</td>
<td>100</td>
<td>101</td>
<td>47</td>
<td>114</td>
</tr>
</tbody>
</table>

(a) \( \text{W}_{\text{dried after swelling 1}} / \text{W}_{\text{before swelling 1}} \); (b) \( (\text{W}_{\text{after swelling 2}} - \text{W}_{\text{dried after swelling 2}}) / \text{W}_{\text{dried after swelling 2}} \)
Si. 6. DMA analysis of PU2 at slow cooling rate

DMA analysis of PU2 at slow cooling rate (2°C.min⁻¹) is presented on Fig SI.6. After the retro-Diels-Alder transition at 140°C [1], two transitions are observed during the cooling ramp [2] and are respectively attributed to the recrosslinking of the Diels-Alder adduct and of the PUR network.

Fig. SI. 6. DMA of PU2 at slow cooling rate (2°C.min⁻¹)
Sl. 7. DMA analysis of PU1 and PU3

DMA analysis of PU1 and PU3 are presented respectively on Fig. SI. 7a and Fig. SI. 7b.

*Fig. SI. 7a. DMA curve of PU1*

*Fig. SI. 7b. DMA curve of PU3*
**Si. 8. Stress-strain curves of PU2 prior and after healing**

The stress-strain curves of PU2 before and after healing treatment are presented on Figure Si.8.

**Fig. Si.8. Stress-strain curves of PU2 prior and after healing**

Mechanical properties of PU2 are summarized on Table Si.8.

**Table. Si.8. Mechanical properties of PU2 prior and after healing**

<table>
<thead>
<tr>
<th></th>
<th>Undamaged</th>
<th></th>
<th>After healing</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young modulus (MPa)</td>
<td>Breaking stress (MPa)</td>
<td>Breaking strain (%)</td>
<td>Young modulus (MPa)</td>
<td>Breaking stress (MPa)</td>
<td>Breaking strain (%)</td>
</tr>
<tr>
<td>PU2</td>
<td>239 ± 5</td>
<td>25 ± 2</td>
<td>138 ± 25</td>
<td>228 ± 10</td>
<td>17 ± 3</td>
<td>50 ± 4</td>
</tr>
</tbody>
</table>


SI. 9. ATR-FTIR spectra of irreversible PU2 network

The chemical irreversibility of PU2 anthracene/maleimide network was attested by FTIR spectroscopy (Fig. SI. 9). The absence of reappearance of maleimide bands after heating treatment (130°C, 2 h) confirms the absence of reversibility at the investigated temperatures.

Fig. SI. 9. FTIR spectra of irreversible PU2 based on anthracene/maleimide couple
SI. 10. Scratch recovery of irreversible PU2

The scratch recovery of irreversible PU2 was attested by optical microscopy after heating treatment (20 min, 130°C) (Fig. SI. 10).

Fig. SI. 10. Scratch recovery of irreversible PU2 prior (a) and after heating treatment (b) (20 min, 130°C)
SI. 11. Scratch recovery of PU2 containing additional hydrogen bonds

The scratch recovery of PU2 containing additional hydrogen bonds is presented on Fig. SI. 11.

**Fig. SI.11.** Scratch recovery of PU2 containing hydrogen bonds prior (a) and after heating treatment (b) (20 min, 130°C)
Reference
