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 CH_2Cl_2 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): d 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).

SI. 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 SI.1.3.a. MAL(OH) is replaced by 9-methanol anthracene and a yellow solid is obtained [3^{'''}](7.84 g, 78 %). ¹H-NMR, (CDCl₃): 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).

SI. 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 %). ¹H-NMR, (CDCl₃): 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).

SI. 1.4.b. Synthesis of FUR(OH)₂ **[4''].** The same procedure described in section SI 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 %). ¹H-NMR, (CDCl₃): 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).

SI. 1.4.c. Synthesis of ANT(OH)₂ **[4'''].** The same procedure described in section SI 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 %). ¹H-NMR, (CDCl₃): 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).

SI. 2. 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 twonecked 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 μ l) 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 ¹H-NMR in DMSO-d6 (**Fig. SI.2.** here for the composition PU2).



¹H-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

Polyme	%mol of	%mol of	%mol of	Molar ratio	%wt of	%wt of	
r	thermoresponsive	maleimide furan		furan/maleimide	MAL(OH) ₂ ^(a)	FUR(OH) ₂ ^(a)	
	moieties (maleimide or furan)	(exp.) ^(b)	(exp.) ^(b)				
	(theo.) ^(a)						
PU1	18.7	16.4	15.3	0.93	14	9	
PU2	22.5	19.5	18.3	0.94	24	15	
PU3	22.5	18.5	17.7	0.96	29	18	

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

(a) As calculated from the feed composition; (b) as determined by ¹H-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.



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.

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

 Table SI. 5.
 Swelling tests of polyurethane networks

(a) Wdried after swelling 1/Wbefore swelling 1; (b) (Wafter swelling 2 – Wdried after swelling 2)/Wdried 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 Sl.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)

SI. 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

	Undamaged			After healing				
	Young modulus (MPa)	Breaking stress (MPa)	Breaking strain (%)	Young modulus (MPa)	Breaking stress (MPa)	Breaking strain (%)	Breaking strain recovery (%)	Tensile strength recovery (%)
PU2	239 ± 5	25 ± 2	138 ± 25	228 ± 10	17 ± 3	50 ± 4	40	68

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

- 1. M. Tonga, N. Cengiz, M. M. Kose, T. Dede and A. Sanyal, *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, 48, 410-416.
- 2. L. Billiet, O. Gok, A. P. Dove, A. Sanyal, L.-T. T. Nguyen and F. E. Du Prez, *Macromolecules*, 2011, 44, 7874-7878.