# **Supporting Information of**

# Self-healing systems based on disulfide-thiol exchange reactions

Mark Pepels,<sup>1</sup> Ivo Filot,<sup>2</sup> Bert Klumperman<sup>\*1,3</sup> and Han Goossens<sup>\*1</sup>

Laboratory of Polymer Materials, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands. Tel: 31 40 2473899; Fax: 31 40 2436999; E-mail: J.G.P.Goossens@tue.nl <sup>1</sup>Inorganic Materials Chemistry Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands

<sup>1</sup>Stellenbosch University, Department of Chemistry and Polymer Science, Private Bag X1, Matieland 7602, South Africa, E-mail: bklump@sun.ac.za

### S1: Self-healing setup

Healing experiments were performed by punching dumbbell-shaped tensile bars according to ISO 527-2, slicing them in half, leaving 150  $\mu$ m attached, after which the bars where placed in the setup schematically represented in Fig. S1. By tightening the screw (orange in figure), the bars are slightly compressed (this was not done for thermoset T3). The setup is subsequently heated in an oven for a given time. The healed bars are compared to virgin bars by performing tensile test (grip to grip separation: 50 mm, testing speed: 10 mm/min, or 20 mm/min for T3 samples) on both and comparing the stress at break. One bar was cut and not healed to be able to compensate for the 150  $\mu$ m of material that was not cut.



Fig. S1: Schematic representation of the healing setup.

## S2: Aliphatic disulfide exchange

Table S.1: Retention time of the different thiols and disulfides in GC-MS

Material	Retention time (min)
Propanethiol (3S)	1.92
Butanethiol (4S)	2.95
Pentanethiol (5S)	4.41
Dipropyldisulfide (3SS3)	9.4
Propyl-Butyldisulfide (3SS4)	10.99
Dibutyldisulfide (4SS4)	12.48
Propyl-Pentyldisulfide (3SS5)	12.5
Butyl-pentyldisulfide (4SS5)	13.91
Dipentylsulfide (5SS5)	15.22

#### Table S.2: Experimental values of exchange experiments varying the amounts of DPDS, DBDS, PT and DBU.

		Sample content grams Molar ratio							Relative	peak siz	ze (%)							
Sample	Time - Temperature	DPDS	DBDS	PT	DBU	DPDS	DBDS	PT	DBU	35	4S	5S	3SS3	3SS4	4SS4	3SS5	4SS5	5SS5
P1B1 RT	1 h - 20 °C	0.999	1.182			1.00	1.00						50.20	0.47	49.33			
P1T1 RT	1 h - 20 °C	1.062		0.698		1.00		0.95		2.00		39.72	51.96			6.11		0.21
B1T1 RT	1 h - 20 °C		1.189	0.687			1.00	0.99			1.42	38.97	55.48				3.95	0.18
P1B1T1 RT	1 h - 20 °C	1.004	1.194	0.719		1.00	1.00	1.03		0.44	0.46	26.67	33.12	0.6	37.08		1.49	0.14
P1B1T01 RT	1 h - 20 °C	1.004	1.188	0.092		1.00	1.00	0.13		0.15	0.11	5.21	45.06	0.57	48.54			0.36
P1B1 DBU RT	1 h - 20 °C	0.999	1.187		0.069	1.00	1.00		0.07				47.59	1.07	51.34			
P1T1 DBU RT	1 h - 20 °C	1.002		0.692	0.065	1.00		1.00	0.06	17.22		12.45	25.54			30.9		13.9
B1T1 DBU RT	1 h - 20 °C		1.188	0.695	0.075		1.00	1.00	0.07		17.45	12.98			25.63		31.7	12.2
P1B1T1 DBU RT	1 h - 20 °C	1	1.189	0.69	0.068	1.00	1.00	1.00	0.07	6.17	6.34	4.03	12.21	22.09	13.37	13.9	16.4	5.49
P1B1T01 DBU RT	1 h - 20 °C	0.999	1.189	0.089	0.077	1.00	1.00	0.13	0.08	1.36	1.31		23.11	41.22	24.53	3.85	4.62	
P1B1 60	1 h - 20 °C + 1 h - 60 °C	0.999	1.182			1.00	1.00						47.47	0.32	52.21			
P1T1 60	1 h - 20 °C + 1 h - 60 °C	1.062		0.698		1.00		0.95		1.85	40.72		51.84			5.41		0.18
B1T1 60	1 h - 20 °C + 1 h - 60 °C		1.189	0.687			1.00	0.99			2.12	37.74			53.94		5.96	0.24
P1B1T1 60	1 h - 20 °C + 1 h - 60 °C	1.004	1.194	0.719		1.00	1.00	1.03		0.64	0.36	26.72	35.31	0.48	35.81		0.68	
P1B1T01 60	1h - RT + 1h - 60ºC	1.004	1.188	0.092		1.00	1.00	0.13		0.12	0.07	4.79	45.33	0.39	48.96		0.34	
P1B1 DBU 60	1 h - 20 °C + 1 h - 60 °C	0.999	1.187		0.069	1.00	1.00		0.07				46.58	2.88	50.54			
P1T1 DBU 60	1 h - 20 °C + 1 h - 60 °C	1.002		0.692	0.065	1.00		1.00	0.06	15.01		10.73	26.59			33.2		14.5
B1T1 DBU 60	1 h - 20 °C + 1 h - 60 °C		1.188	0.695	0.075		1.00	1.00	0.07		15.54	11.06			27.03		34	12.4
P1B1T1 DBU 60	1 h - 20 °C + 1 h - 60 °C	1	1.189	0.69	0.068	1.00	1.00	1.00	0.07	5.78	5.98	3.96	12.22	22.63	13.47	13.9	16.6	5.46
P1B1T01 DBU 60	1 h - 20 °C + 1 h - 60 °C	0.999	1.189	0.089	0.077	1.00	1.00	0.13	0.08	1.01	0.85		23.26	42.03	24.35	4.03	4.36	0.11

Table S.3: Experimental values of exchange experiments varying the amount of additives.

Sample content (g)									Molar		Relative peak size (%)													
Sample	Time - Temperature	DPDS	DBDS	PT	Base	DOx	EtAc P	rOH	DPDS	DBDS	PT	Base	DOx	EtAc	PT	35	4S	5S	3553	3SS4	4SS4	3SS5	4SS5	5555
P1B1T1 DMAPA 60	1h - 60⁰C	1.03	1.19	0.7	0.028				1	0.97	0.98	0.04				0.72	0.23	20.55	37.8	0.11	40.04		0.55	
P1B1T1 DMAP 60	1h - 60⁰C	0.994	1.19	0.693	0.031				1	1.01	1.01	0.04				0.09	0.11	22.77	35.4	1.21	39.82		0.6	
P1B1T1 DBU 60	1h - 60ºC	0.999	1.193	0.693	0.029				1	1.01	1.00	0.03				5.12	4.68	3.14	11.41	25.72	12.43	16.66	16.75	4.09
P1B1T1 DMAP DOx t=0	0h	0.197	0.24	0.137	0.01	0.468			1	1.03	1.00	0.06	4.82						47.1		52.9			
P1B1T1 DMAP DOx t=60	1h - 60⁰C	0.197	0.24	0.137	0.01	0.468			1	1.03	1.00	0.06	4.82						44.32	0.99	52.79		1.9	
P1B1T1 DMAP DOx t=1080	18h - 60⁰C	0.197	0.24	0.137	0.01	0.468			1	1.03	1.00	0.06	4.82				0.75	14.75	32.34	7.88	40.56		3.1	0.62
P1B1T1 EtAc PrOH DOx DMAP 60	1h - 60⁰C	0.42	0.49	0.29	0.02	0.41	0.24	0.16	1	0.98	1.00	0.06	1.98	0.97	0.95		0.29	20.74	36.42	1.83	39.27		1.45	

### S3: Disulfide exchange of structures resembling thermoset structure Table S.4: Experimental values of exchange experiments with the corresponding SEC

spectrum.

	Product							Amount (g)										Amount (mmol)									
sample	nr	Time - Temperature	Mn	Mw	PDI	T20	T44	T130	PMT I	DMAP	DMAPA	DBDS	FDA D	TDA POI	I T20	T44	T130	PMT	DMAP D	MAPA	DBDS	FDA DTD	а рон				
T20	1		2242	5539	2.47																						
T44	2		1126	2021	1.79																						
T130	3		5094	13370	2.62																						
T44 DMAP	4	1h - 60°C	1048	1867	1.78		2.40			0.12						2.13			0.98								
T44 T130	5	1h - 60°C	3458	12668	3.66		0.83	3.41								0.74	0.67										
T44 T130 DMAP	6	1h - 60°C	2985	6891	2.31		0.76	3.20			0.04					0.67	0.63			0.39							
T44 T130 DMAPA	7	1h - 60ºC	2676	6141	2.29		0.90	3.31			0.05					0.80	0.65			0.49							
T44 T130 DMAPA B	7	5 d - 60°C 25h - 60°C	2259	5520	2.44		0.90	3.31			0.05					0.80	0.65			0.49							
T20T130 DMAPA	8	1h - 60°C	3589	8709	2.43	2.90		4.00			0.09				1.29		0.79			0.88							
T130 DBDS	9	1h - 60°C	5224	13828	2.65			2.40				0.08					0.47				0.42						
T130 DBDS DMAPA	10	1h - 60°C	3368	7577	2.25			4.30			0.07	0.14					0.84			0.69	0.78						
T130 DBDS DMAPA B	10	7 d - 60°C 25h - 60°C	2295	5337	2.33			4.30			0.07	0.14					0.84			0.69	0.78						
T130 PMT DMAPA	11	1h - 60°C	1231	2499	2.03			4.28	0.35		0.05						0.84	0.81		0.49							
T130 PMT DMAPA B	11	25h - 60ºC	1329	2688	2.02			4.28	0.35		0.05						0.84	0.81		0.49							
T130 DTDA DMAPA	12	1h - 60ºC	2592	6217	2.40			4.03						0.17			0.79					0.6	6				
T130 DTDA DMAPA B	12	25h - 60ºC	2597	6291	2.42			4.03						0.17			0.79					0.6	6				
T130 FDA	13	1h - 60°C	5478	15768	2.88			3.50					0.09				0.69					0.86					
T130 FDA DMAPA	14	1h - 60°C	4272	12314	2.88			3.20			0.05		0.08				0.63			0.49		0.77					
T130 FDA POH	15	1h - 60°C	4251	12288	2.89			2.90					0.05	0.0	3		0.57					0.51	0.50				
T130 FDA POH DMAPA	16	1h - 60°C	4461	12319	2.76			3.20			0.04		0.06	0.0	3		0.63			0.39		0.58	0.50				





## S4: Monitoring of the curing reaction by FTIR spectroscopy

Figure S.2: FTIR data for the curing reaction of T25 with PTM1 (Production of Thermoset T2).



Figure S.3: FTIR data for the curing reaction of T25 with PTM2 (Production of Thermoset T4).