Electronic Supplementary Information (ESI):

Photo-crosslinking polymers by dynamic covalent disulfide bonds

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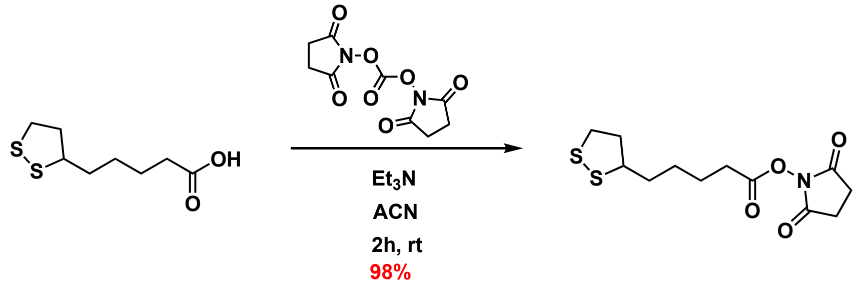
Content:

1. Materials and Methods

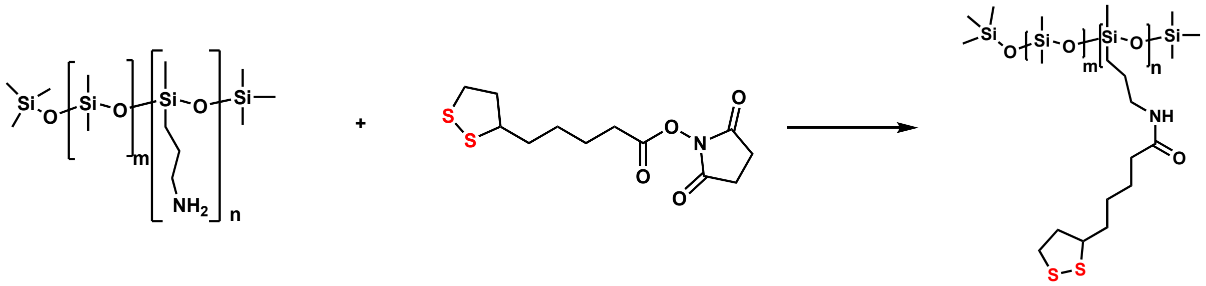
Commercial reagents and solvents: Unless stated otherwise, all available reagents and solvents were used as received from commercial sources: ABCR, Macron, Sigma-Aldrich. Thioctic acid (TA) was purchased from Aladdin company (China). Polydimethylsiloxane (PDMS) was purchased from Fluorochem (UK): PDMS-1: (6-7% aminopropylmethylsiloxane)-dimethylsiloxane copolymer, 1,800-2,200 cSt, PDMS-2: (6-7% aminopropylmethylsiloxane)-dimethylsiloxane copolymer, 80-120 cSt. Analytical TLC detection was performed on silica gel plates (Sigma, 60 F254), and visualization was enabled by UV light or staining with a $KMnO_4$ solution.

General Methods: NMR spectra were recorded at 25 °C on Varian AMX400 (^1H: 400 MHz). Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^1H NMR [$CDCl_3$: $^1H(\delta) = 7.26$ ppm]. A hand-lifting UV lamp was used for UV irradiation experiments, positioned at a distance of 3 cm from the samples. All the spectra were recorded at room temperature. UV-vis spectra were recorded by SPECORD S600 using a standard quartz cuvette (10 mm) or thin-film quartz cell. FTIR spectra were measured with a Perkin-Elmer FT-IR Spectrometer 400 using a ATR accessory. Tensile strength tests, adhesion tests were measured with Instron 5564 tensile machine.

2. Synthetic methods:



To a round-bottom flask, thioctic acid (4.8 g, 23.3 mmol, 1.0 eq) and N,N'-Disuccinimidyl carbonate (7.2 g, 28.1 mmol, 1.2 eq) was dissolved in the acetonitrile (200 mL) to obtain yellow homogeneous solution, which was then protected from light. After addition of triethylamine (10.0 mL, 71.9 mmol, 3.1 eq), the reaction mixture was stirred at room temperature for 2 h. Then, 2/3 of the solvent was evaporated, and the mixture was poured into 275 mL of 5% $NaHCO_3$ aq. Solution to form pale yellow precipitates, which was separated by filtration and drying under vacuum to afford compound TA-NHS (6.92 g, 98% yield).



PDMS-TA-2: In a round-bottom flask, TA-NHS (0.7 g, 2.31 mmol) was dissolved in THF (7.0 mL). Next (6-7% aminopropylmethylsiloxane)-dimethylsiloxane copolymer (80-120 cSt) was added (2.93 g, 3.02 mL). The reaction mixture was stirred overnight at room temperature. The resulting mixture was then washed with brine, and water phase was extracted with DCM (2 × 25 mL). The combined organic phases were washed with saturated $NaHCO_3$ aq. Solution, and dried over $MgSO_4$. After evaporating the solvent, yellow oil product (2.5 g) was obtained in 86% yield.

PDMS-TA-1: A similar procedure was applied to reaction of TA-NHS with (6-7% Aminopropylmethylsiloxane)-Dimethylsiloxane copolymer (1,800-2,200 cSt). The product was obtained as a yellow oil (2.4 g) with 83% yield.

3. Supporting Figures

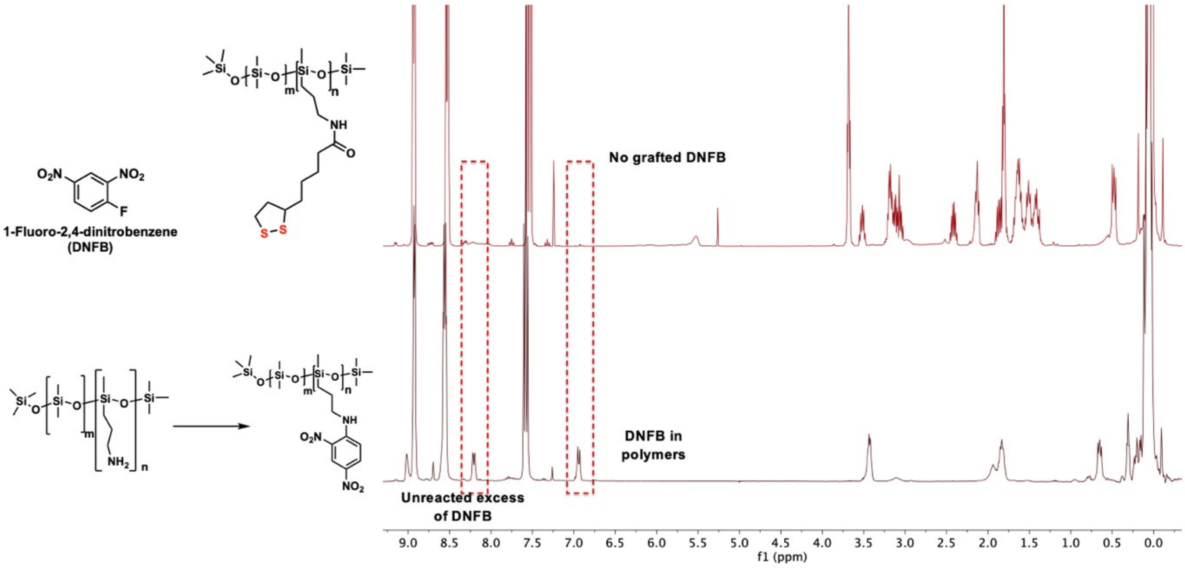
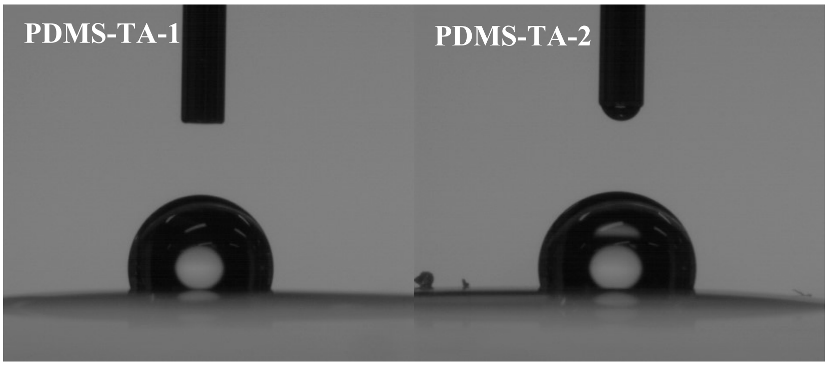


Figure S1. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of PDMS-TA and PDMS-amine mixed with 10 eq. DNFB. Spectral comparison indicates the absence of free amine groups in PDMS-TA polymers.



Contact angle	PDMS-TA-1	PDMS-TA-2
Φ_{right}	105.8 ± 1.7	102.5 ± 0.6
Φ_{left}	105.6 ± 1.7	102.6 ± 0.6

Figure S2. Contact angle measurement of the coating of PDMS-TA-1 and PDMS-TA-2

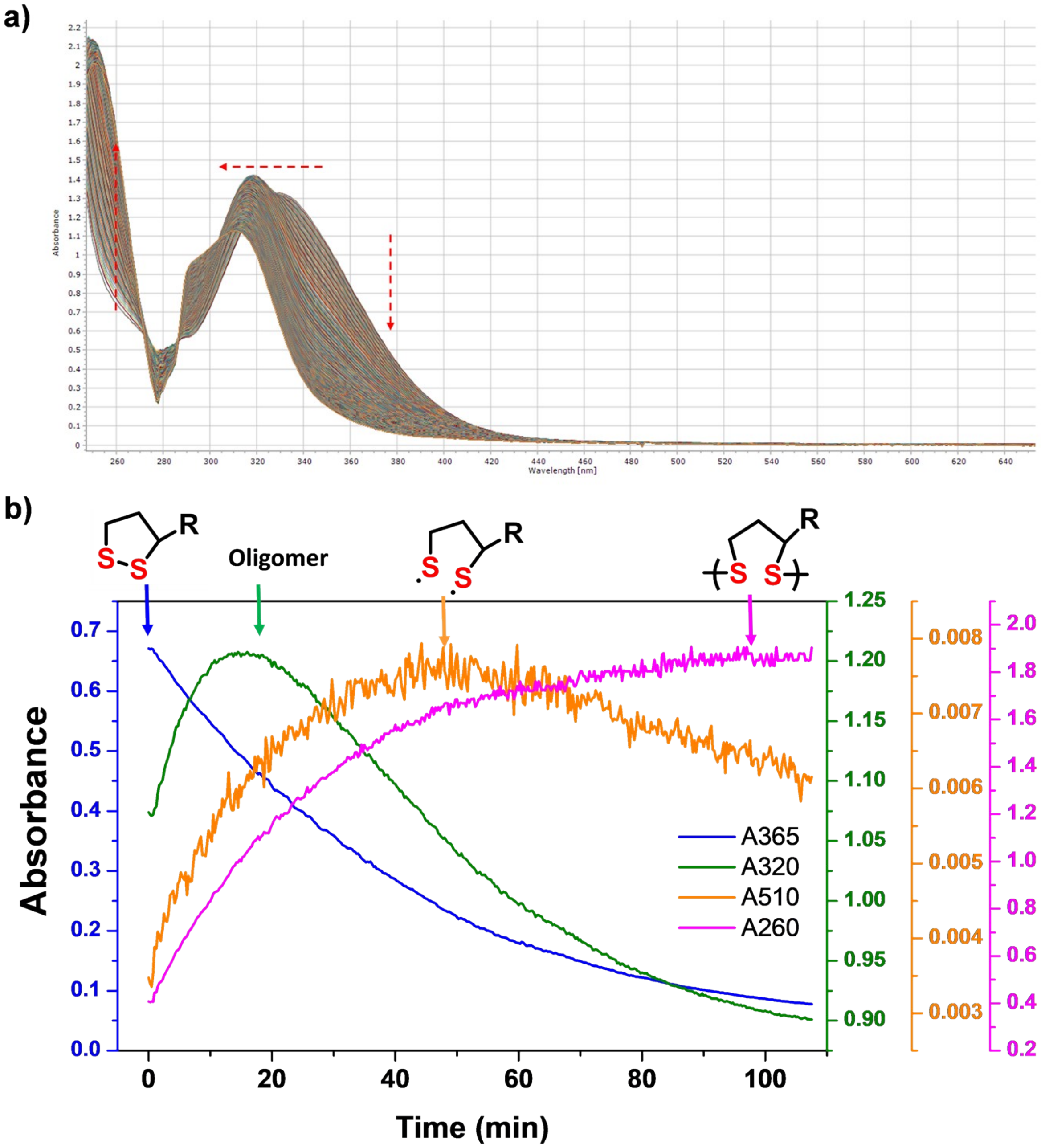


Figure S3. UV-Vis absorption spectra of the PDMS-TA-1 solution before and after irradiation using UV light (365 nm) at different times.

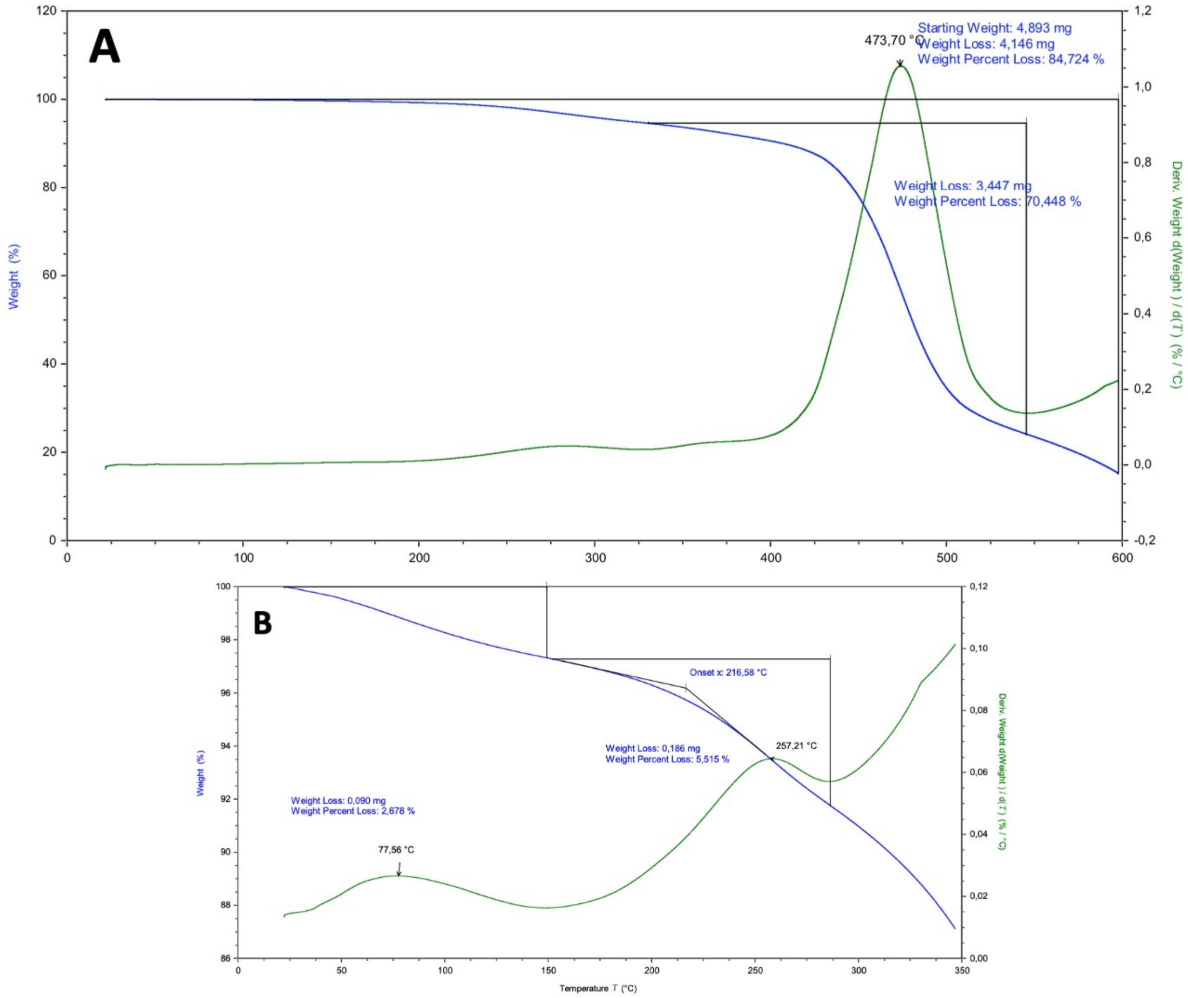


Figure S4. TGA curves of the crosslinked PDMS-TA-1 (A) and PDMS-TA-2 (B)

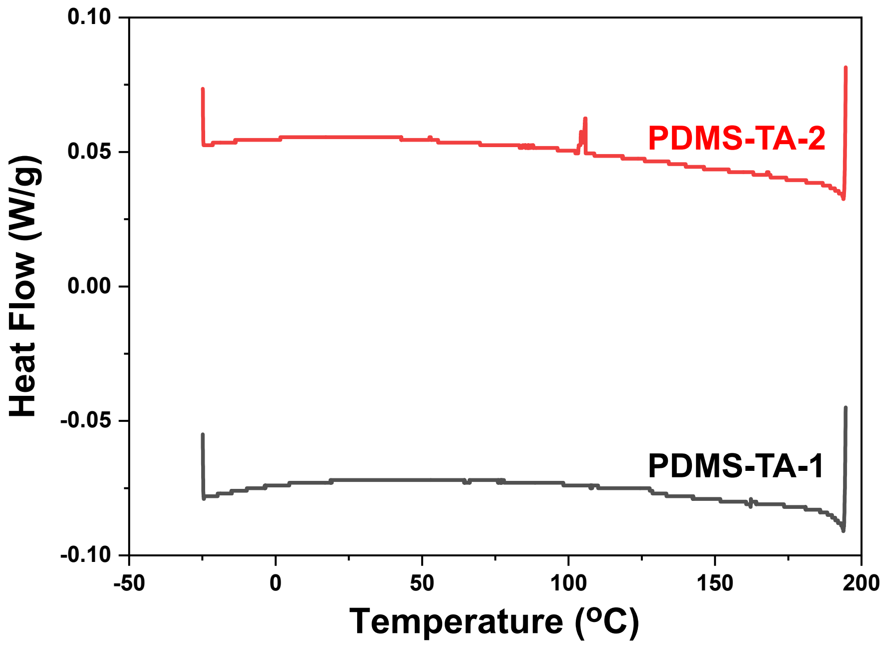
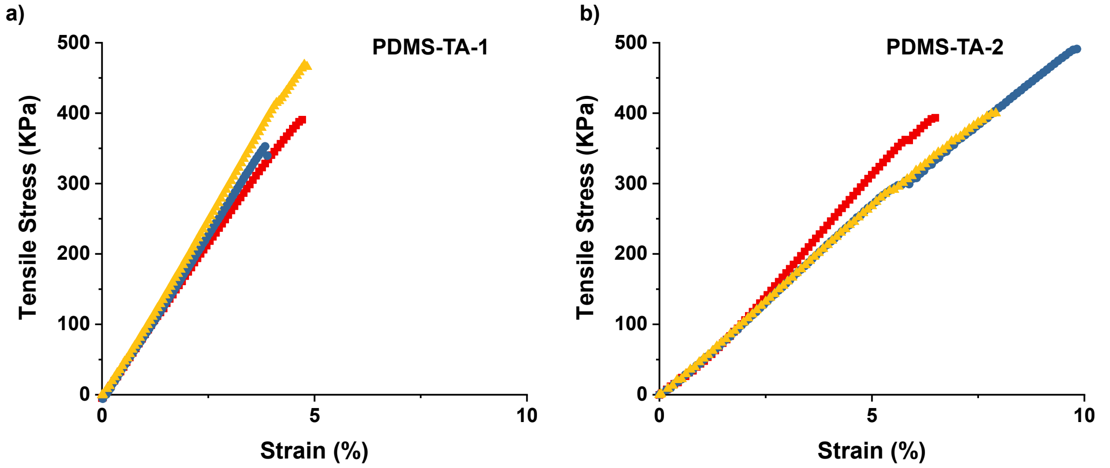


Figure S5. DSC curves of the photo-crosslinked network.



PDMS-TA network	Young's modulus [MPa]	Elongation at max strain [%]	Max stress [MPa]	Toughness [kPa]
1	9.79 ± 0.46	4.62 ± 0.68	0.41 ± 0.07	9.90 ± 0.42
2	5.61 ± 0.78	8.65 ±1.03	0.43 ± 0.06	24.74 ± 0.06

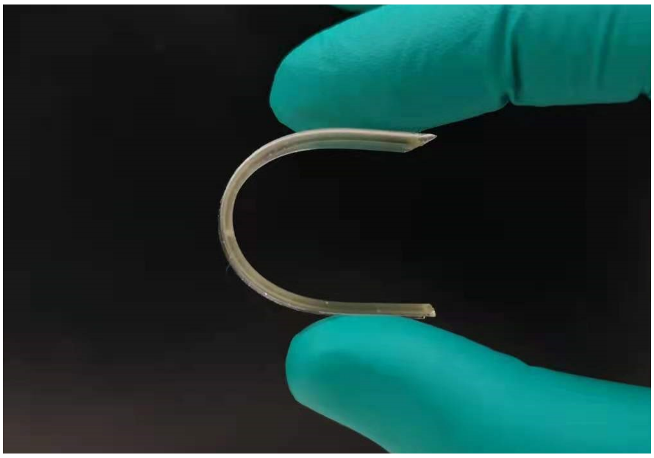


Figure S6. Tensile strength test: PDMS-TA-1 and PDMS-TA-2.

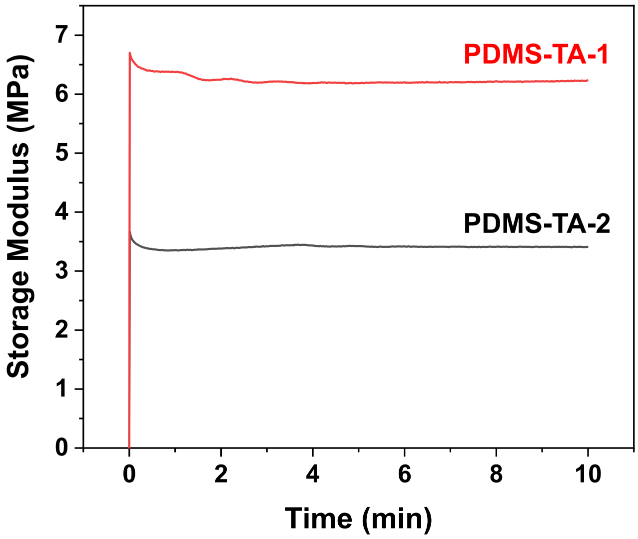


Figure S7. Stress relaxation curves of the photo-crosslinked network PDMS-TA-1 and PDMS-TA-2 with a strain at 1%.

	PDMS-TA Adhesion test	Max stress [MPa]
1	PDMS-TA-1	0.20 ± 0.09
2	PDMS-TA-2	0.52 ± 0.06

Figure S8. Lap shear test: PDMS-TA-1 and PDLMS-TA-2

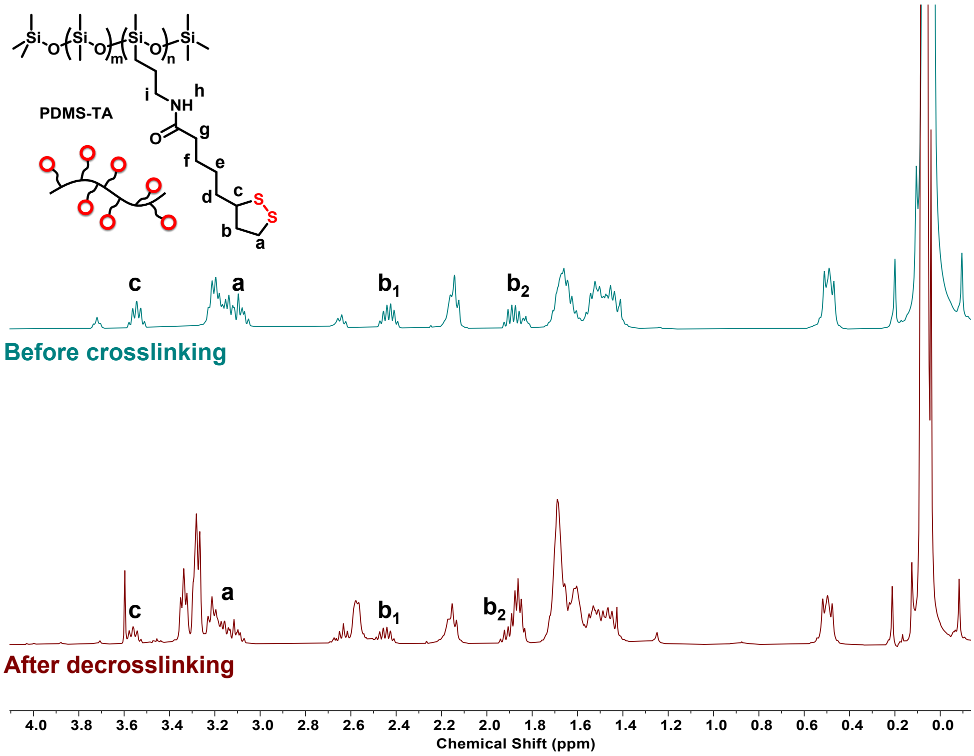


Figure S9. ^{1}H NMR spectra ($CDCl_3$) of PDMS-TA polymers before photo-crosslinking and after decrosslinking.