Supporting Information for:

Solid-state mechanochemical activation of anthracene-maleimide adducts: the influence of the polymer matrix

Justus P. Wesseler,[‡a] James R. Hemmer,[‡a] Christoph Weder,[a] José Augusto Berrocal[a,b*]

[a]Adolphe Merkle Institute (AMI), University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland.

[b]Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), Avinguda dels Països Catalans 16, 43007 Tarragona, Spain.

[‡]equal contribution from these authors

*to whom correspondence should be addressed:

jberrocal@iciq.es

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Experimental Procedures

Materials. 9-Anthracenemethanol, furan, maleic anhydride, ethanolamine, triethylamine, 4-pentenoic acid, *N,N*-dimethylpyridin-4-amine (DMAP), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC.Cl), acryloyl chloride, α-bromoisobutyryl bromide, poly(tetrahydrofuran) (polyTHF, M_n 2,000 g/mol), 4,4'-methylenebis(phenyl isocyanate) (MDI), dibutyltin dilaurate, 1,4-butanediol, tris[2-(dimethylamino)ethyl]amine (Me_6TREN), Cu^0-wire (2.0 mm diameter), Irgacure 2959, divinylbenzene were purchased from Sigma-Aldrich and used as received unless noted otherwise. Ethanol, methanol, hexane, ethyl acetate, toluene, anhydrous tetrahydrofuran, anhydrous dichloromethane were purchased from Sigma-Aldrich and used as received. Monomers were passed through basic alumina prior to use to remove inhibitors.

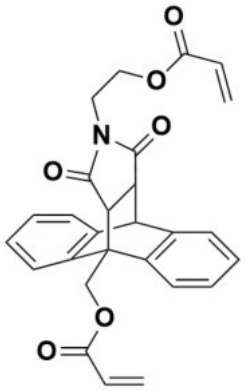
Nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy was carried out at 297.2 K on a Bruker Avance DPX 400 spectrometer at frequencies of 400.19 MHz for ^{1}H nuclei and 100.63 MHz for ^{13}C nuclei. Spectra were calibrated to the residual solvent peak of $CDCl_3$. Data were evaluated with the MestReNova software suite (v 12.0) and all chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane with coupling constant (J) in Hz (multiplicity: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad signal).

Differential scanning calorimetry (DSC) was conducted using a MettlerToledo STAR system differential scanning calorimeter at a temperature range of either -20 °C to 260 °C or -80 ˚C to 260 ˚C with a heating and cooling rate of 10 °C min^{-1}. DSC results were analysed using the STARe Evaluation software

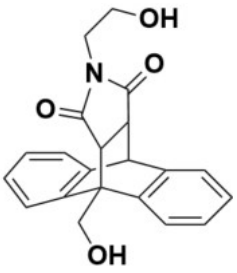
Thermogravimetric analyses (TGA) were performed with a Mettler-Toledo TGA/DSC 1 Stare System. The temperature ranged from 25 °C to 600 °C with a heating rate of 10 °C min^{-1}. TGA results were analysed using the STARe Evaluation software.

Synthesis and Characterisation of Compounds

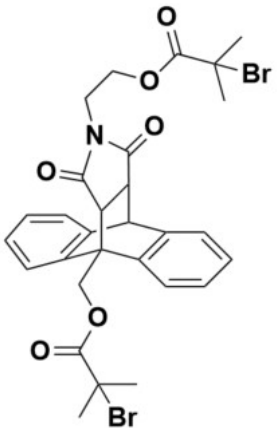
(2-Hydroxyethyl)-9-(hydroxymethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (**AM-1, diol**)[1]



(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)methyl 2-bromo-2-methylpropanoate (**AM-2**)[2]

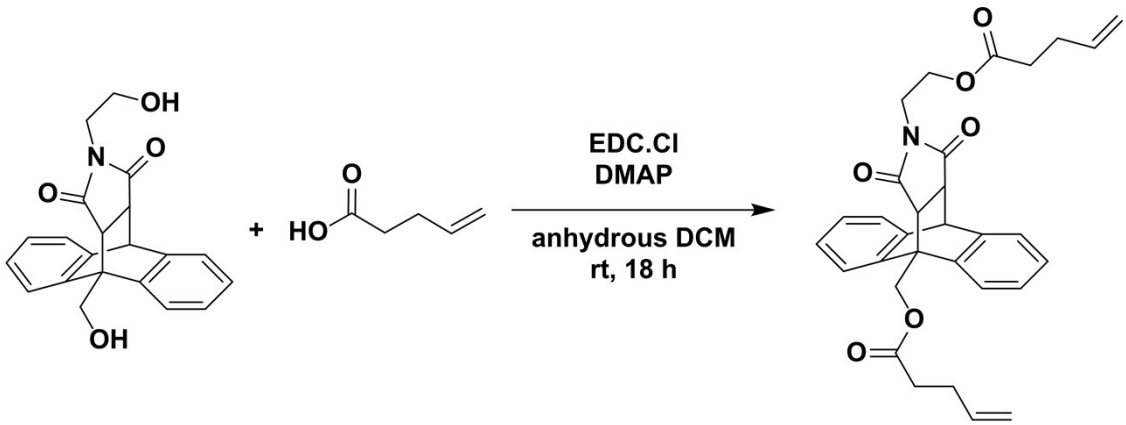


(2-(acryloyloxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)methyl acrylate (**AM-3**)[1]



were all synthesized according to previous literature reports.[1,2]

Synthesis of 12,14-dioxo-13-(2-(pent-4-enoyloxy)ethyl)-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)methyl pent-4-enoate (AM-4)



Anthracene-maleimide diol **AM-1** (264 mg, 0.75 mmol), 4-pentenoic acid (307 µL, 3 mmol), and EDC.Cl (577 mg, 3 mmol) were added to a 50 mL round-bottomed flask equipped with a magnetic stirring bar under positive nitrogen flow, and dissolved in anhydrous DCM (10 mL). DMAP (18.4 mg, 0.15 mmol) was added to the reaction mixture under positive nitrogen flow. The flask was sealed with a rubber septum, and the reaction mixture was stirred for 18 hours at room temperature. The reaction mixture was concentrated by removing the solvent *in vacuo*. The crude material was suspended in hexane (50 mL), and the suspension was washed with water. The organic phase was recovered and the solvent was removed. The residue was purified by column chromatography on silica gel with 1:2 EtOAc/hexane as the mobile phase to yield **AM-4** a white powder (150 mg, 38.7%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 (m, 1H), 7.30 (m, 2H), 7.21-7.17 (m, 5H), 5.95-5.75 (m, 2H), 5.50 (m, 2H), 5.12-5.00 (m, 4H), 4.78 (d, *J* = 2.7 Hz, 1H), 3.65-3.45 (m, 2H), 3.39 (m, 4H), 2.58-2.54 (m, 2H), 2.51-2.45 (m, 2H), 2.33-2.30 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.21, 175.12, 172.82, 172.53, 141.88, 141.18, 138.63, 136.64, 136.49, 127.18, 127.12, 126.86, 126.67, 125.33, 124.15, 123.08, 122.11, 115.76, 115.52, 61.70, 60.55, 47.70, 46.18, 45.69, 37.17, 33.62, 33.25, 28.89, 28.56.

HRMS (ESI+) *m/z* 536.2042 (536.2044 calc'd for $C_{13}H_{31}NO_6Na^+$ $[M + Na]^+$)

^{1}H and ^{13}C NMR Spectra

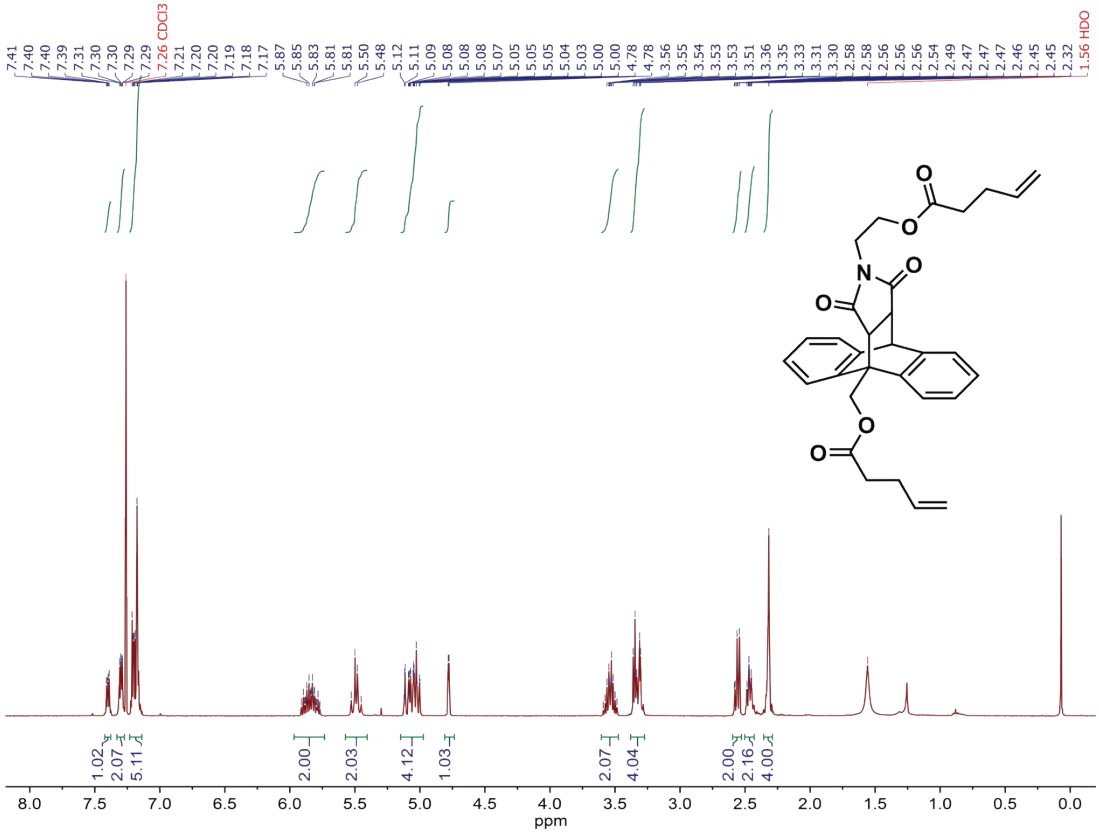


Figure S1. ^{1}H NMR spectrum of **AM-4** in $CDCl_3$.

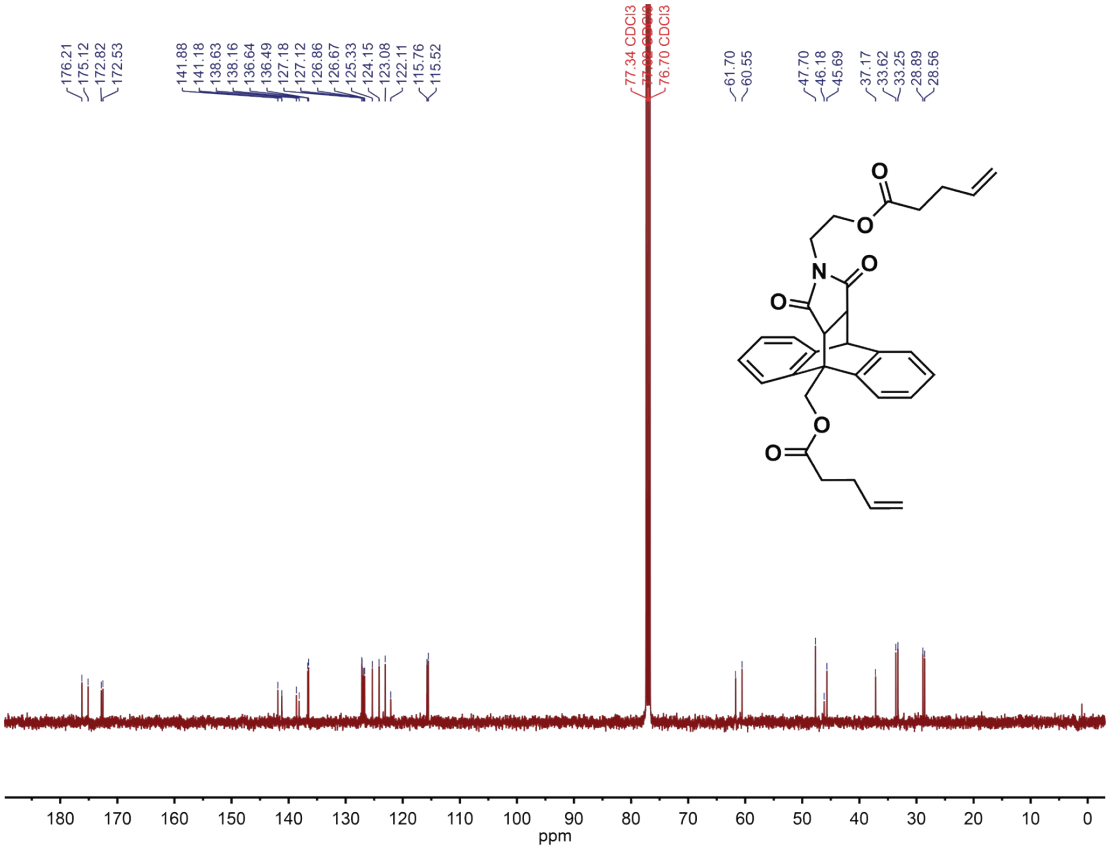


Figure S2. ^{13}C NMR spectrum of **AM-4** in $CDCl_3$.

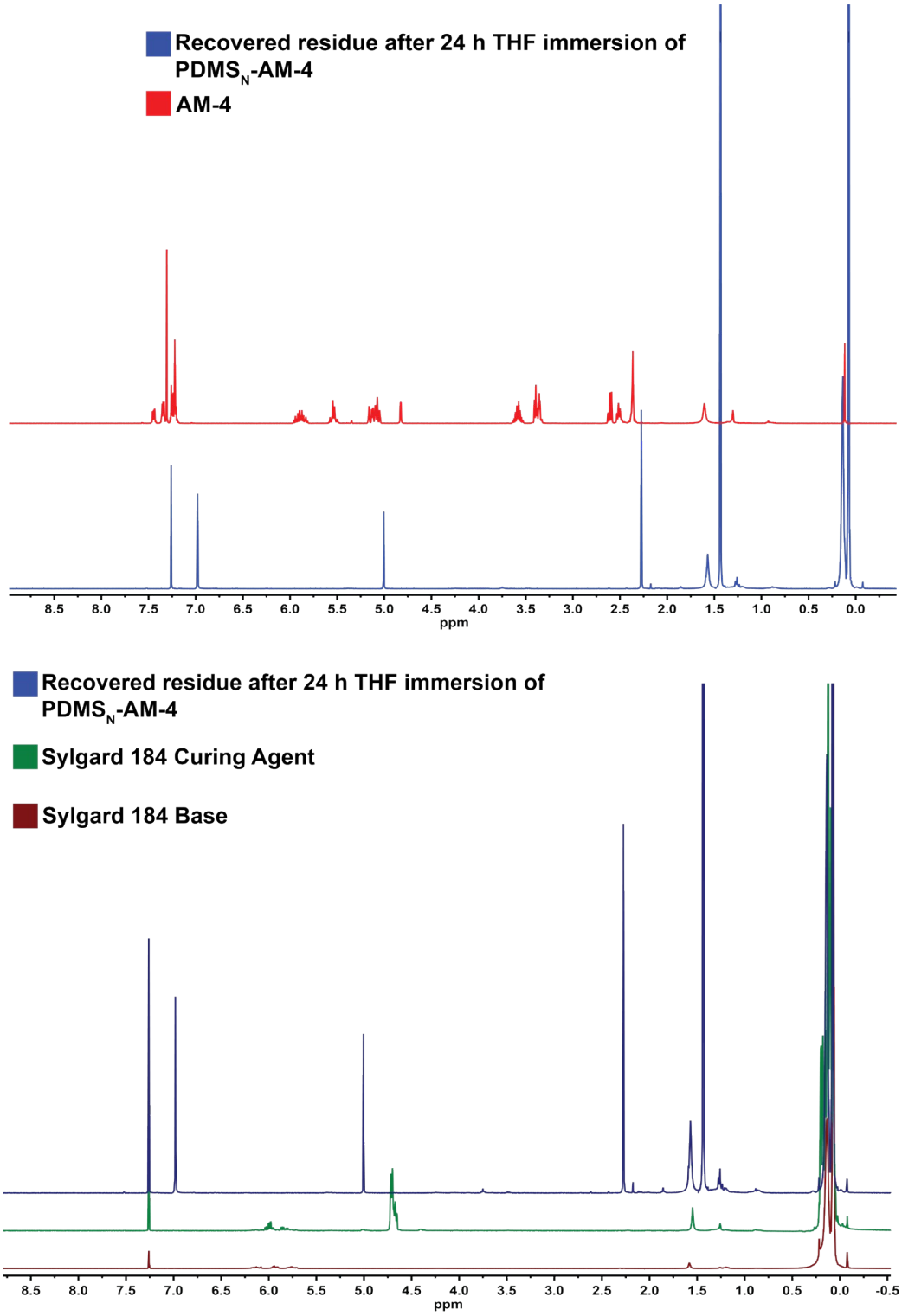


Figure S3. Top: ^{1}H NMR spectra (400 MHz, 20 °C, $CDCl_3$) of **AM-4** (red trace) and the recovered material obtained by swelling **PDMS$_N$-AM-4** in THF overnight, retrieving the solution and removing the solvent *in vacuo* (blue trace). The absence of **AM-4** peaks in the recovered material indicates the successful incorporation of the mechanophore into the PDMS network. Bottom: ^{1}H NMR spectra (400 MHz, 20 °C, $CDCl_3$) of the recovered material obtained by swelling **PDMS$_N$-AM-4** in THF overnight and removing the solvent *in vacuo* (blue trace) compared to the ^{1}H NMR spectra (400 MHz, 20 °C, $CDCl_3$) of Sylgard 184 base (maroon trace) and curing agent (green trace). Characteristic peaks of siloxane species can be seen in the 0.05 – 0.20 ppm range. The base and curing agent also display peaks further downfield (4.70 – 6.50 ppm) due to the presence of vinyl and Si-H groups.

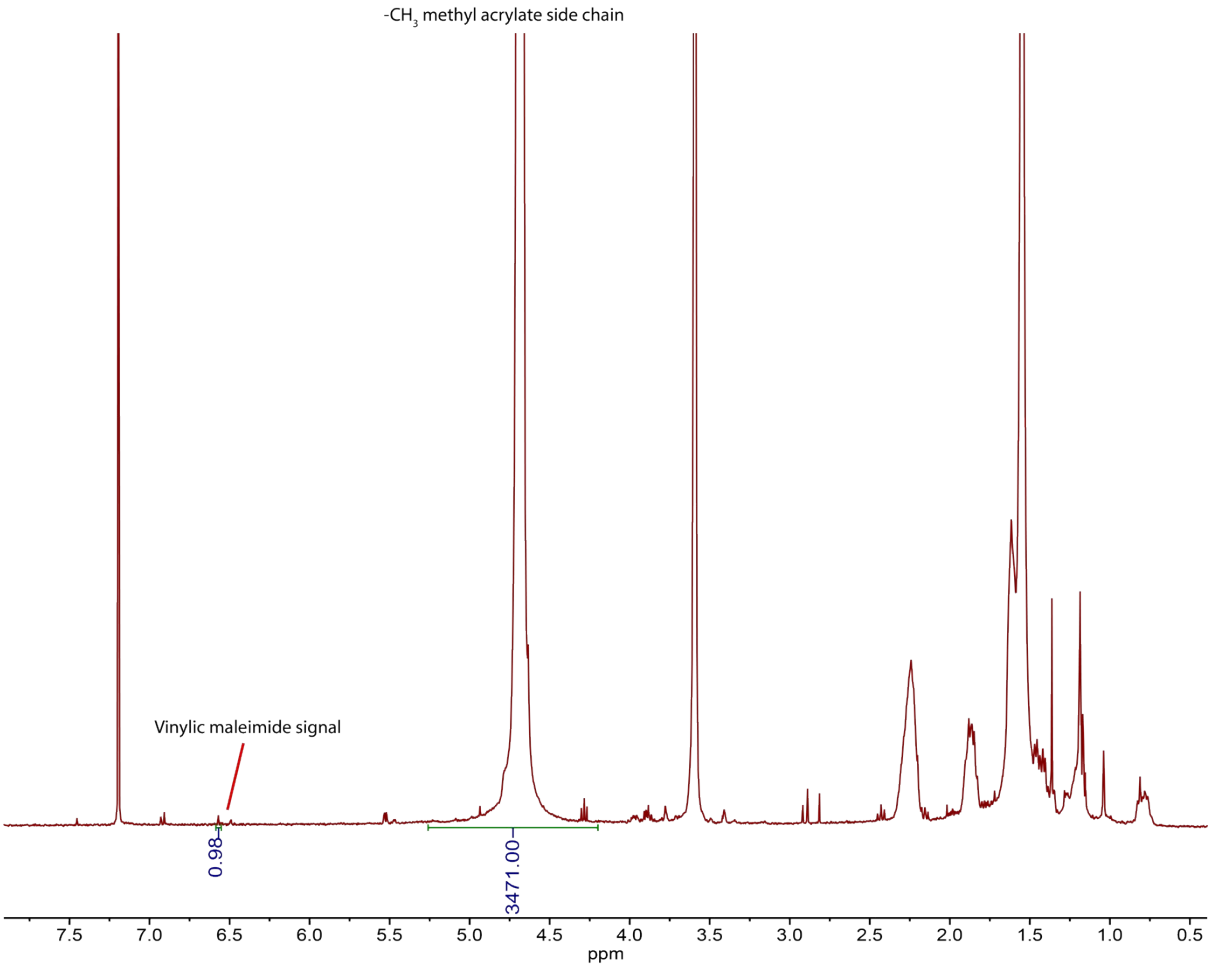


Figure S4. ^{1}H NMR spectrum (400 MHz, 20 °C, $CDCl_3$) of **PMA_L-AM-4** after 150 minutes of effective sonication time. The vinylic signal of maleimide (blue) could be compared to the -CH_3 side chain of PMA to determine the amount of cleaved **AM** species. The signals of aromatic anthracene moiety were not intense enough for a reliable integration.

The quantity of cleaved AM was determined as follows: Molecular weight of polymer: Molecular $weight_{SEC}$ – molecular $weight_{AMfragment}$ = 100,000 – 487 = 99,513

No. repeat units = 99,513 / 86 = 1157

Using the peak of the CH_3 side chain of methyl acrylate, the integral is: 1157 x 3 = 3471

Integrating the signal of the vinylic protons of maleimide liberated during **AM** cleavage gives a value of 0.98. At full **AM** cleavage the expected integral value would correspond to 2.

Therefore the %**AM** activation is: (Int_{MalNMR} / Int_{MalMax}) * 100 = 49.0%

Accounting for the 1.7% degraded **AM**, the mechanically activated **AM** is 47.3%

The discrepancy between NMR and UV-detector SEC analysis is due to the inherently low concentration of **AM** in the polymer, which results in their associated cleaved product signals to have poor S/N ratio in NMR analysis.

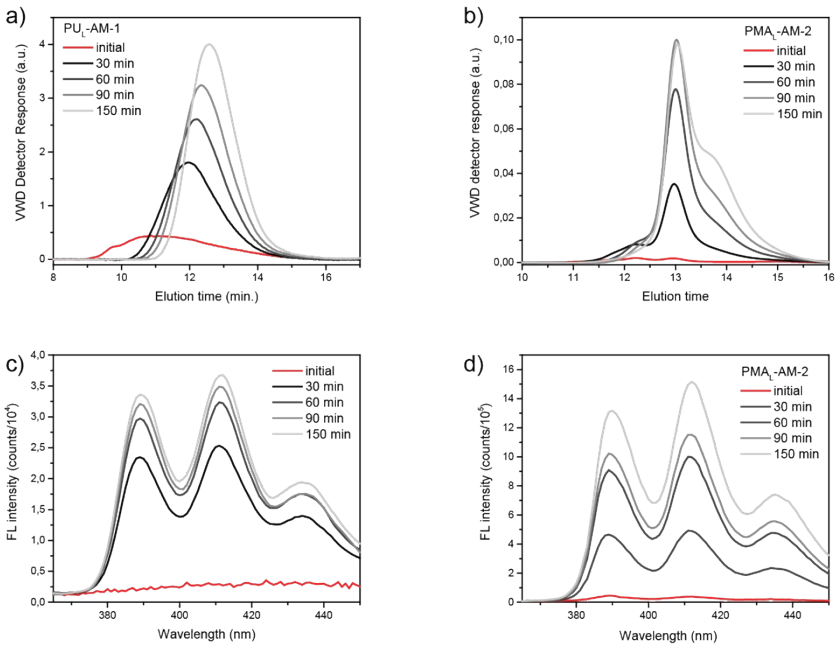


Figure S5. SEC traces (VWD) of (a) **PU$_L$-AM-1** (347 nm) and (b) **PMA$_L$-AM-2** (254 nm) measured at time zero and after being exposed to 30, 60, 90, and 150 min of ultrasonication. 347 nm was selected for **PU$_L$-AM-1** due to the polyurethane itself absorbing strongly at 254 nm. Fluorescence spectra of (c) **PU$_L$-AM-1** and (d) **PMA$_L$-AM-2** measured at time zero and after being exposed to 30, 60, 90 and 150 min of ultrasonication**.**

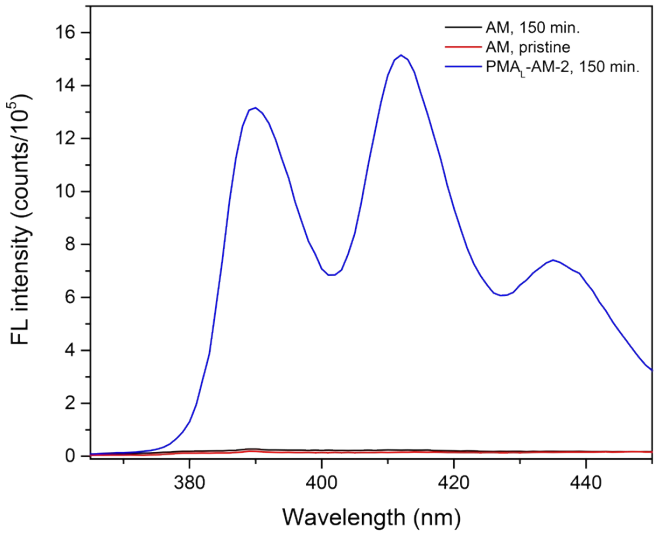


Figure S6. Fluorescence spectra of a small molecule **AM-4** solution in THF (15 µg/mL) before and after being exposed to 150 minutes of effective sonication time, compared to the fluorescence spectrum of **PMA$_L$-AM-2** after 150 minutes of effective sonication time.

Quantifying mechanophore activation

PU_L-AM-1. The final aliquot (150 minutes effective sonication time) was transferred to a UV-Vis spectroscopy cuvette and its absorbance spectra was measured. From the absorbance value at λ = 347 nm, using the molar extinction coefficient of anthracene in THF at this wavelength (ε = 6100 M^{-1} cm^{-1}), the concentration of anthracene and consequently the amount of activated **PU_L-AM-1** could be determined. Knowing the mass of polymer material in the aliquot and the initial **AM** loading for **PU_L-AM-1** (0.014 mmol/g), the maximum amount of **AM** was calculated and finally the activated **AM%** could be determined.

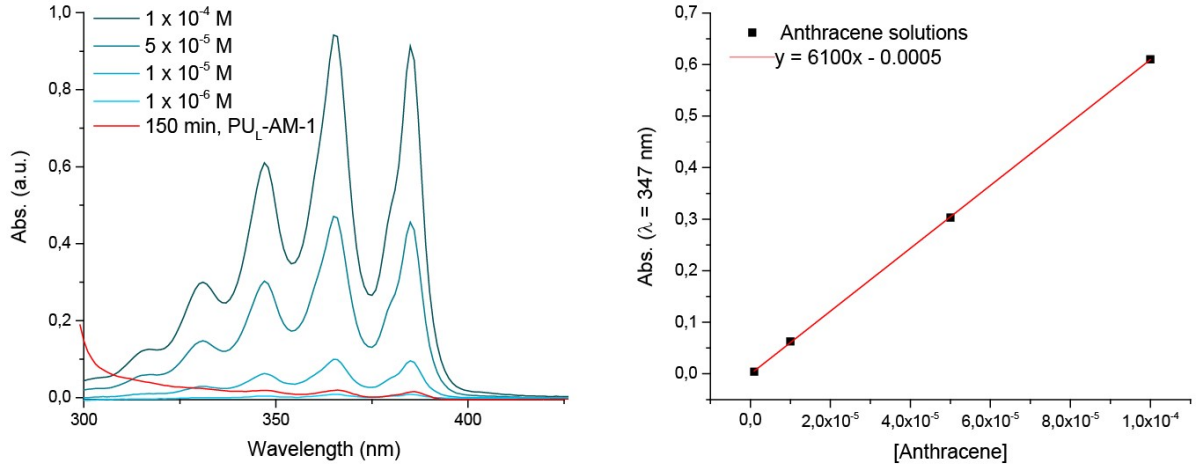


Figure S7. (left) UV-Vis spectra of anthracene solutions (THF) of known concentrations and **PU_L-AM-1** after 150 minutes of effective sonication time (red curve). (right) Plot of anthracene absorbance at 347 nm in THF *vs* anthracene concentration to determine molar extinction coefficient.

PMA_L-AM-2. The amount of **AM** activated was quantified according to the previous method described by Diesendruck *et al.*[3] Briefly, the total number of chains injected was calculated based on the aliquot concentration and GPC inject volume and divided by the polymer's original Mw.

$$n_{total} = \frac{2\ mg\ ml^{-1} \times 100\ \mu L}{100\ kg\ mol^{-1}} = 8.04 \times 10^{-10}$$

Integrating the chromatogram of each aliquot using the limits of the half-molecular-weight polymer peak ($\int AdV$), the number of **AM**-cleaved chains could be determined:

$$n_{AM-cleaved} = \frac{\int AdV}{\varepsilon d}$$

Where ε is the extinction coefficient of anthracene in THF at 254 nm (113,000 $M^{-1}cm^{-1}$), d is the path length (1 cm).

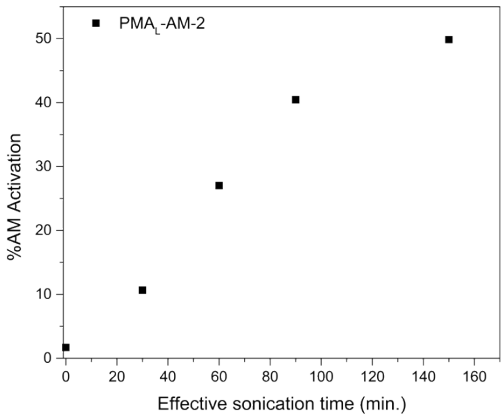


Figure S8. Plot of %AM activation against effective sonication time for **PMA_L-AM-2**

The amount of **AM** activated at T0 was subtracted from all **%AM** activation values of subsequent timepoints to account for the degraded adducts.

Thermal characterization of AM-polymer samples

Differential Scanning Calorimetry

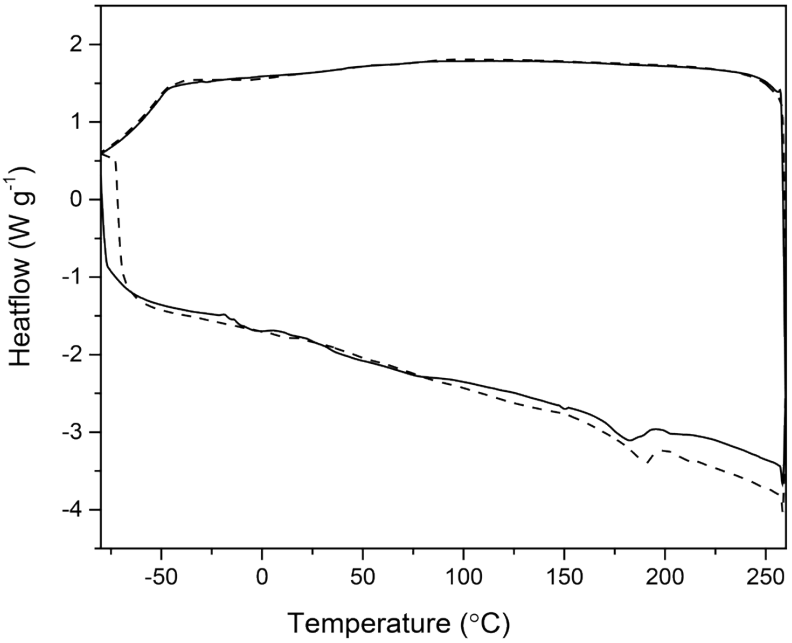


Figure S9. DSC traces of **PU_L-AM-1**. Bold solid line: first heating/cooling cycle, dashed line: second heating/cooling cycle.

PU_L-AM-1

PMA_L-AM-2

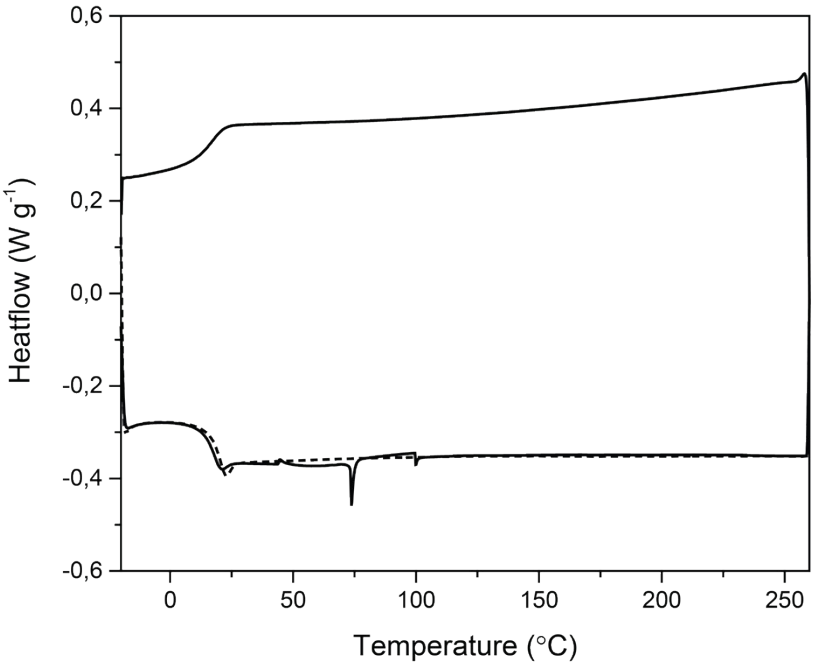


Figure S11. DSC traces of **PMA_N-AM-3**. Bold solid line: first heating/cooling cycle, dashed line: second heating cycle.

PMA_N-AM-3

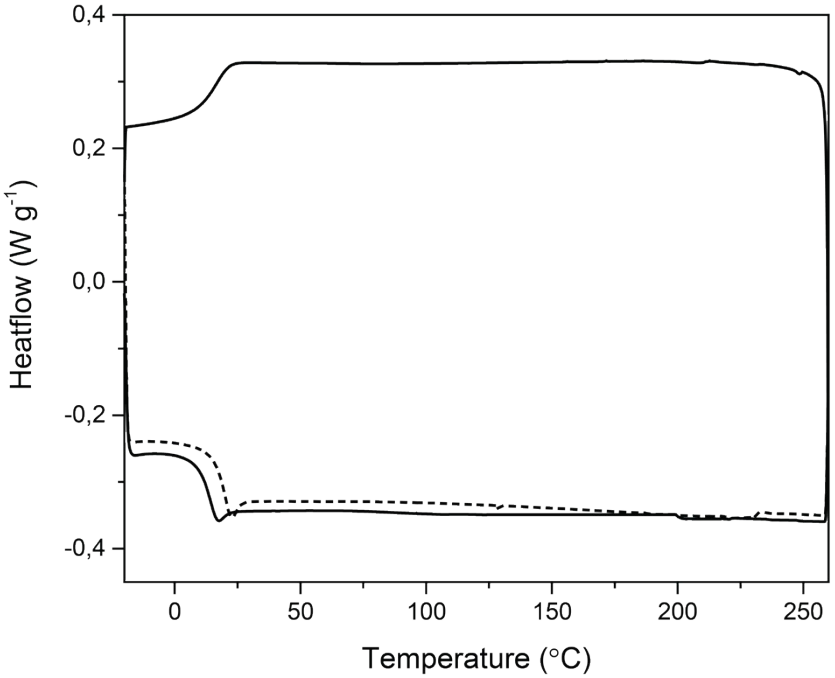


Figure S10. DSC traces of **PMA_L-AM-2**. Bold solid line: first heating/cooling cycle, dashed line: second heating cycle.

$PDMS_N$-AM-4

Thermogravimetric Analysis

PU_L-AM-1

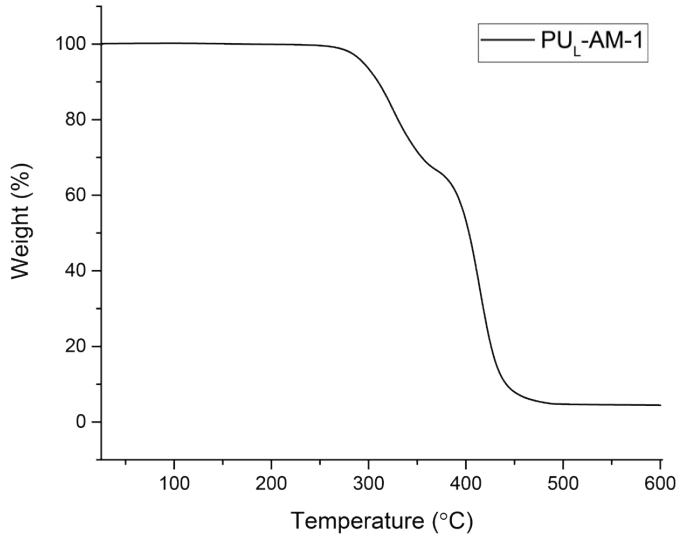


Figure S13. TGA curve of **PU_L-AM-1**.

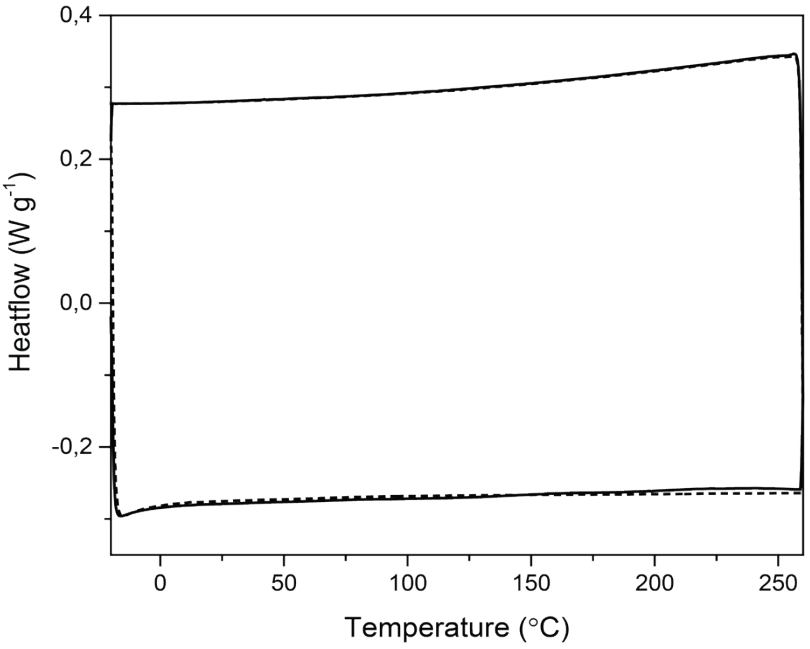


Figure S12. DSC traces of **$PDMS_N$-AM-4**. Bold solid line: first heating/cooling cycle, dashed line: second heating cycle.

PMA_L-AM-2

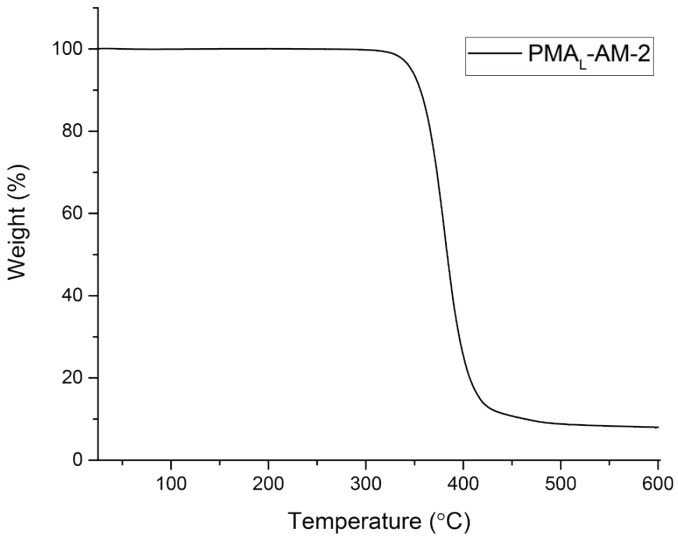


Figure S14. TGA curve of **PMA$_L$-AM-2**.

PMA$_N$-AM-3

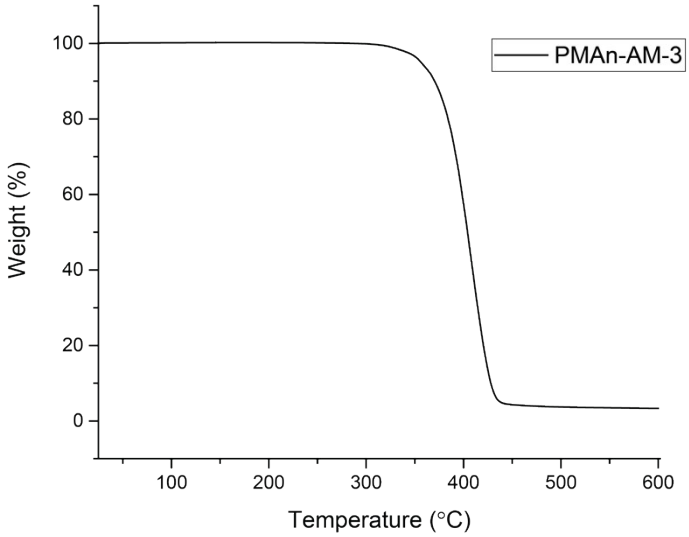


Figure S15. TGA curve of **PMA$_N$-AM-3**.

PDMS$_N$-AM-4

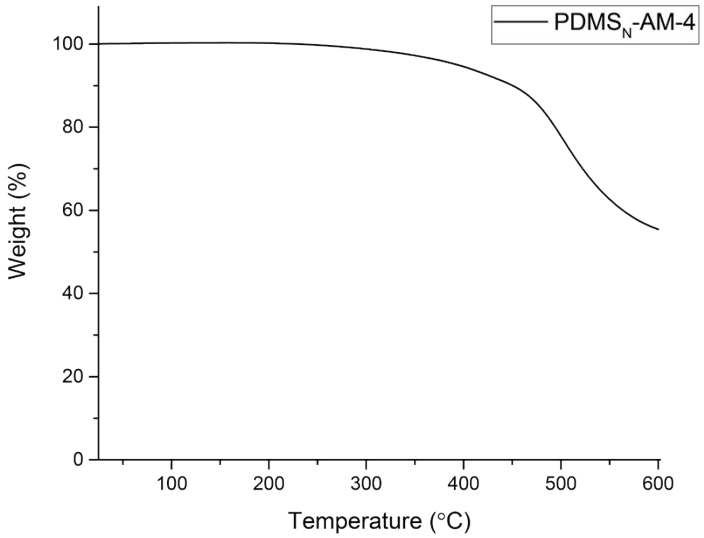


Figure S16. TGA curve of **PDMS$_N$-AM-4**.

Optical fibre fluorescence of solid-state stretched samples PU$_L$-AM-1

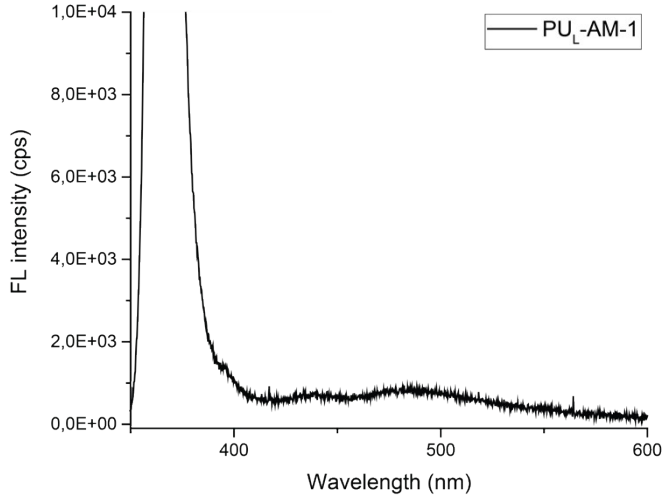


Figure S17. Fluorescence spectrum of a **PU$_L$-AM-1** film after elongation to failure.

PMA_L-AM-2

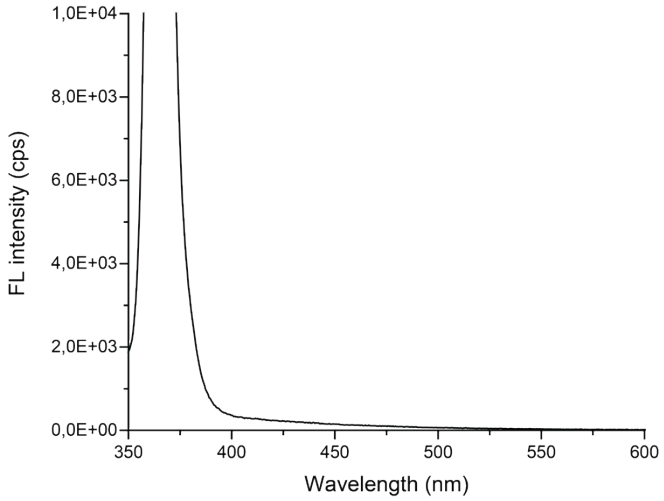


Figure S18. Fluorescence spectrum of a **PMA_L-AM-2** film after elongation to failure.

$PDMS_N$-AM-4

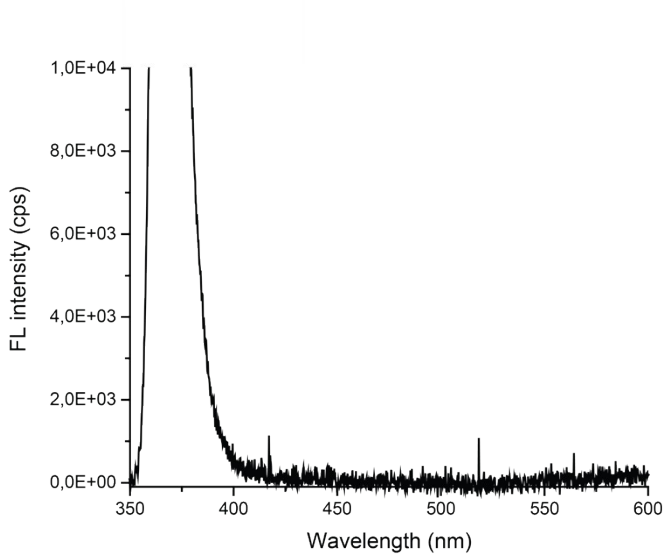


Figure S19. Fluorescence spectrum of a **$PDMS_N$-AM-4** film after elongation to failure.

Tensile tests

Table S1. Stress at break (σ_B) and strain at break (ε_B) determined for **PU_L-AM-1**, **PMA_L-AM-2**, **PMA_N-AM-3**, and **$PDMS_N$-AM-4** in the tensile testing (measurements carried out in triplicates, at 25°C, at a strain rate of 10.5% s^{-1}).

Sample	σ_B (MPa)	ε_B(%)
PU_L-AM-1	58 ± 2.6	762 ± 62
PMA_L-AM-2	0.49 ± 0.09	1778 ± 194
PMA_N-AM-3	19 ± 3.2	773 ± 93
$PDMS_N$-AM-4	3.7 ± 0.21	127 ± 14

References

1 C. P. Kabb, C. S. O'Bryan, C. D. Morley, T. E. Angelini and B. S. Sumerlin, *Chem. Sci.*, 2019, **10**, 7702–7708.

2 J. Li, T. Shiraki, B. Hu, R. A. E. Wright, B. Zhao and J. S. Moore, *J. Am. Chem. Soc.*, 2014, **136**, 15925–15928.

3 C. E. Diesendruck, L. Zhu and J. S. Moore, *Chem. Commun.*, 2014, **50**, 13235–13238.