

# **Dissassembly of Elastomers: Poly (olefin sulfone) – Silicones with Switchable Mechanical Properties**

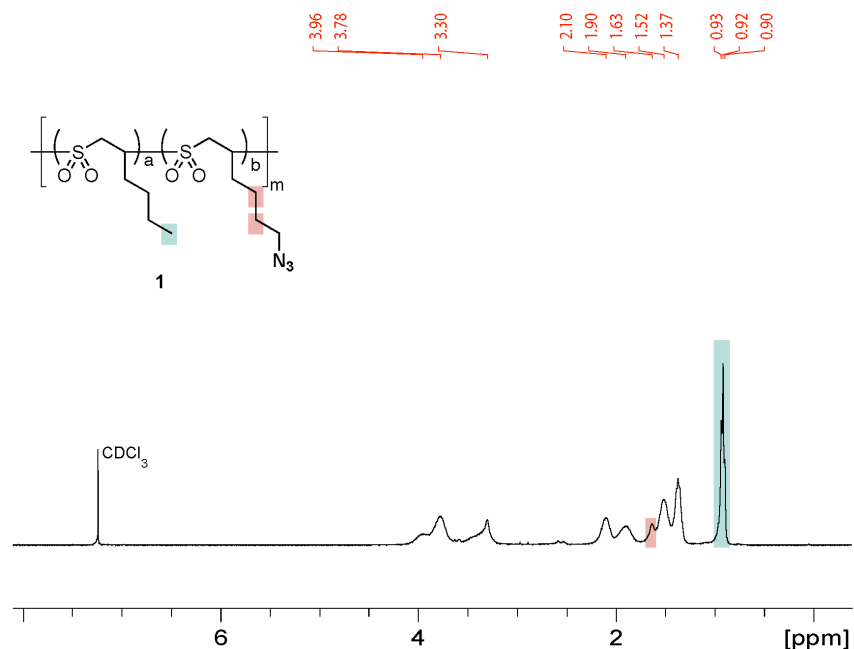
## **Supporting Information**

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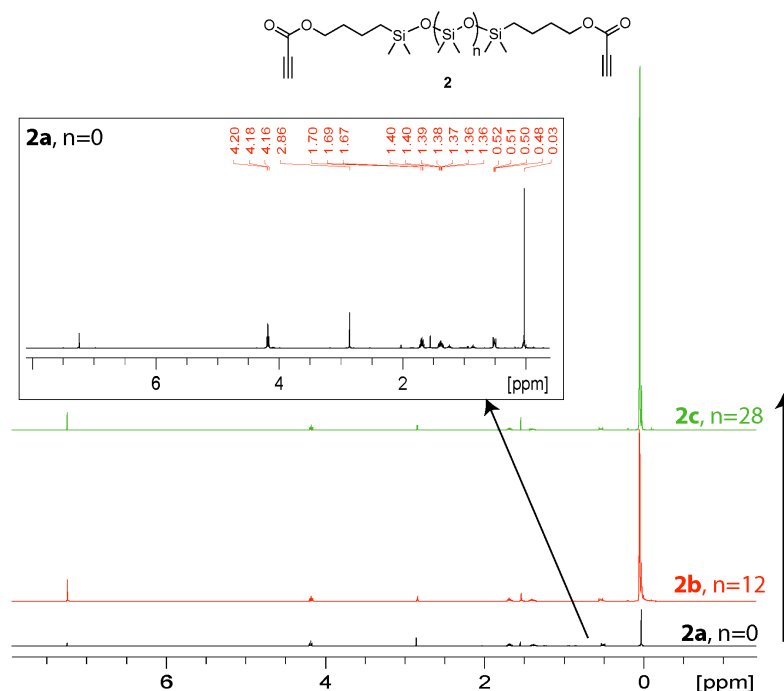
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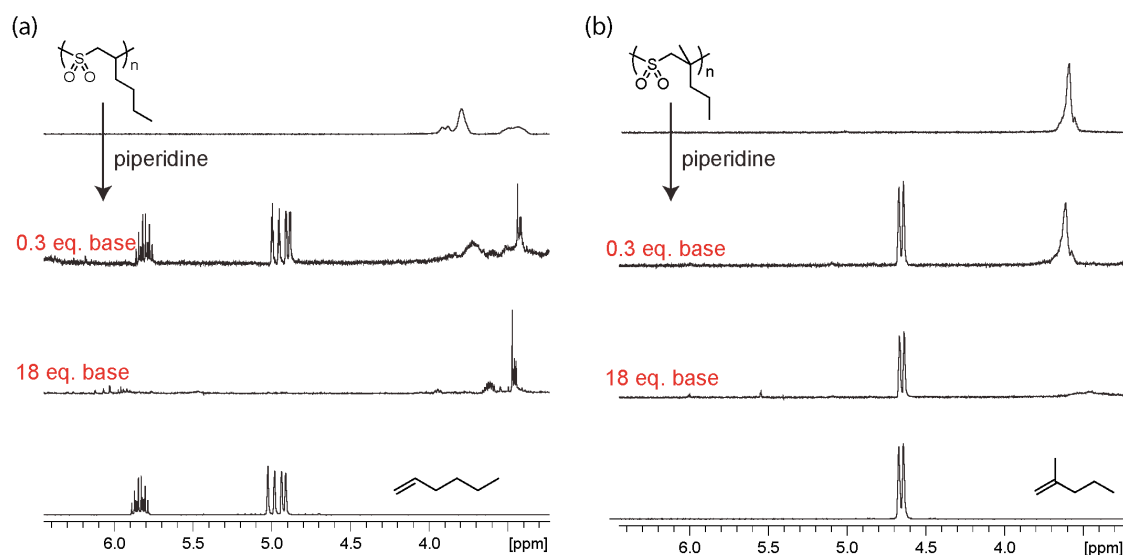
<b>Figure</b>	<b>Page</b>
<b>S1    <sup>1</sup>H-NMR Determination of Azide Content for POS polymers (1)</b>	<b>SI1</b>
<b>S2    <sup>1</sup>H-NMR Determination of polymer length for polymers 2</b>	<b>SI1</b>
<b>S3, S4    Influence of base concentration and conditions on rate of unzipping</b>	<b>SI2</b>
<b>S5    IR spectra of composites</b>	<b>SI3</b>
<b>S6    Hardness of composites with varying POS/silicone ratios and chain lengths</b>	<b>SI4</b>
<b>Synthesis of Alkynyl-FBB</b>	<b>SI5</b>



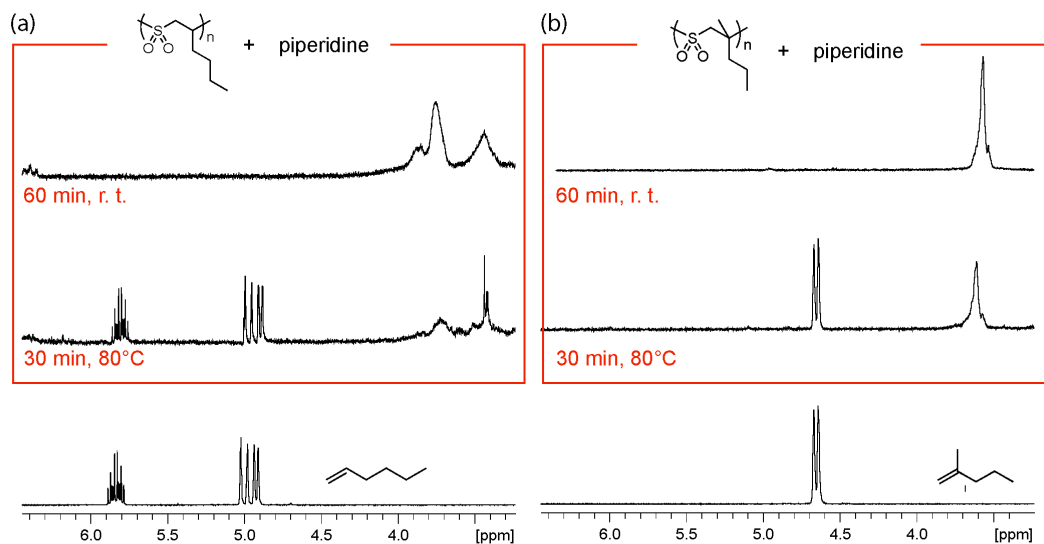
**Figure S1.**  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) of compound **1**. The 6-azido-hexenyl content was determined from the relative integration of the peak highlighted in red, compared to the peak highlighted in blue.



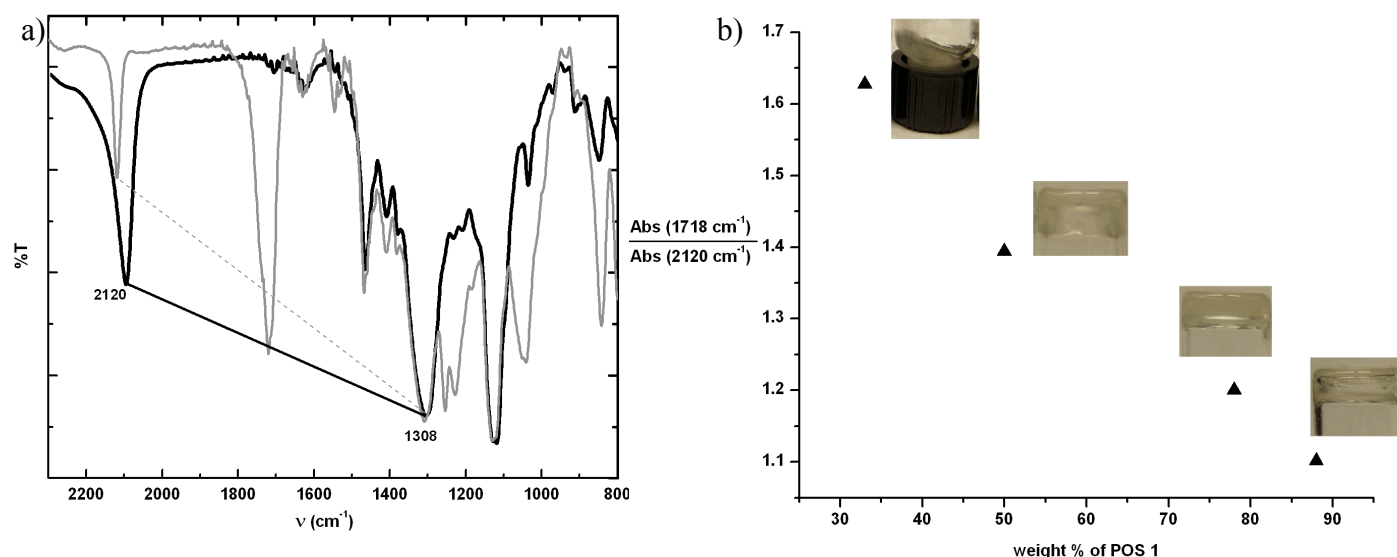
**Figure S2.**  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) of compounds **2a**, **2b**, **2c**. The length of the dimethylsiloxane chain can be determined from the integration of the peak at 0.03 ppm (the spectra have been normalized to the intensity of the rest of the signals in the molecule). Inset: detail and chemical shifts of the spectrum of **2a**.



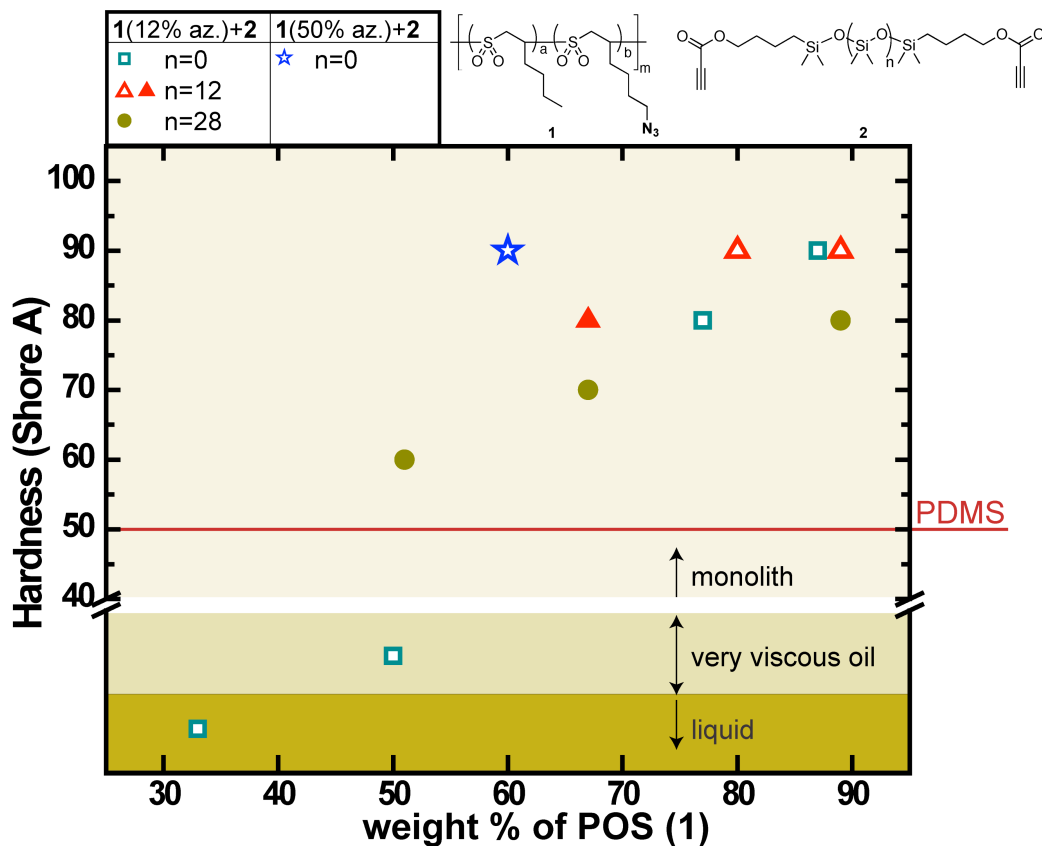
**Figure S3.** Unzipping of **P1HS** (a) and **P2MPS** (b) into their olefinic monomers as seen by  $^1\text{H}$ -NMR (acetonitrile- $d_6$ ) with different amounts of piperidine at  $80^\circ\text{C}$ . **P1HS** unzips into its monomers faster than **P2MPS**: a larger amount of base is needed for **P2MPS** to completely decompose into its olefinic monomer under the same conditions as **P1HS**. The olefinic monomer reacts with the excess base when using an excess of base for **P1HS**.



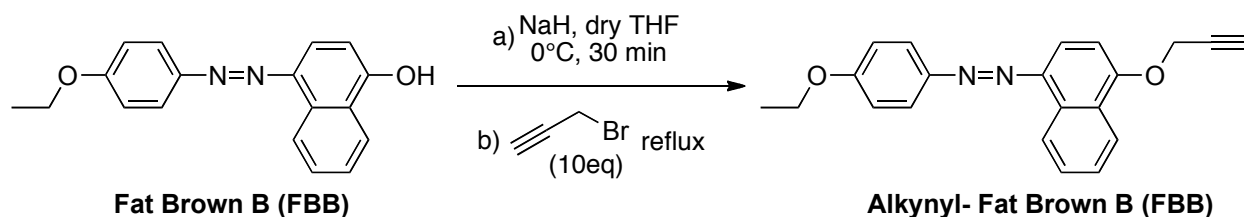
**Figure S4.** Unzipping of **P1HS** (a) and **P2MPS** (b) into their olefinic monomers by action of 0.3 eq. of piperidine as seen by  $^1\text{H}$ -NMR (acetonitrile- $d_6$ ) under different conditions (time, temperature). Both polymers require a higher temperature to start depolymerizing into its monomers. The extent of degradation is higher for **P1HS** than for **P2MPS** at  $80^\circ\text{C}$  under the same conditions of degradation time and base concentration.



**Figure S5.** IR spectra of composites of POS **1** and silicone **2a**. a) IR spectrum of POS **1** (bold) and a composite containing 88 weight % of POS **1** and 12 weight % of **2a** (light gray). The degree to which crosslinking takes place can be related to the amount of side-chain azide groups reacted, estimated by the decrease in intensity of the azide band (2120 cm<sup>-1</sup>) compared to one of the sulfone bands (1308 cm<sup>-1</sup>), and the number of azide groups per polymer chain (for this polymer a calculated average of 5 azide groups per polymer chain was determined considering the azide % and the length of the polymer). b) Relative intensity of the IR alkynyl band (1718 cm<sup>-1</sup>) over the intensity of IR azide band (2120 cm<sup>-1</sup>) plotted versus the weight % of POS (inset: pictures of the corresponding composites). The higher the content of POS **1**, the more crosslinked the composites will be, which can be seen by the relative decrease in intensity of the band at 1718 cm<sup>-1</sup> compared with the band at 2120 cm<sup>-1</sup>, and the fact that the composites flow or form monoliths, depending on the composition.



**Figure S6.** Shore A hardness of composites formed from POS **1** and silicone **2**, with varying proportions of each component, different % of azide-containing repeat unit in the POS backbone, and different silicone lengths (each formulation with a different silicone chain length or azide content is denoted by a different geometrical shape, see legend). The properties of the composite can be tuned by changing these variables. The hardness of PDMS is given as a reference value (red line). Unfilled data points represent formulations where the final composite was transparent and colorless; for filled data points the composite was opaque, probably due to phase segregation and microdomain formation. It can be seen that the higher the content of silicone, or the longer the chain of the silicone component, the more opaque the composite is, so more phase segregation was induced. In general, the higher the weight content of POS, the higher the hardness, which correlates with the  $T_g$  values. A higher hardness of composites formed of **1**(12%azide) and **2**(n=0), represented with squares as compared to the composites formed of **1**(12%azide) and **2**(n=12) represented with triangles, can be attributed to a higher degree of cross-linking, since the mixtures are in general more homogenous and the click reaction will go to a higher extent. The higher hardness of composites formed of **1**(50%azide) and **2**(n=0), represented with a star as compared to the composites formed of **1**(12%azide) and **2**(n=0) represented with squares, can be attributed to the higher number of azide functionalities per POS chain, which results in a higher degree of cross-linking.



### Synthesis of 1-(4-ethoxyphenyl)-2-(4-(prop-2-yn-1-yloxy)naphthalen-1-yl)diazene (Alkynyl

**Fat Brown B):** To a solution of Fat Brown B (FBB) (100 mg, 0.34 mmol) in anhydrous THF (6ml) was added NaH (9 mg, 0.37mmol) at 0°C. The solution was stirred at 0°C for 30 min and propargyl bromide (80% in toluene, 0.2ml, 1.8 mmol) was added. The reaction was refluxed for 6h, after which another fraction of propargyl bromide (80% in toluene, 0.2ml, 1.8 mmol) was added. After removal of the solvent under vacuum, the crude was purified by column chromatography using hexanes: ethyl acetate (9:1) as the eluent to give **alkynyl-FBB** as a dark orange powder (110 mg, 98%).

$\delta_H$  (CDCl<sub>3</sub>) 1.46 (3H, t, J=6.8 Hz), 2.56 (1H, t, J=2.4 Hz), 4.12 (2H, q, J=6.8 Hz), 4.95 (2H, d, J=2.4 Hz), 7.01 (d, 2H, J=9.2 Hz), 7.56-7.64 (4H, m), 7.82 (1H, d, J=8.4 Hz), 7.98 (2H, d, J=9.2 Hz), 8.31 (1H, d, J=8.4 Hz), 8.91 (1H, d, J=8.4 Hz);  $\delta_C$  (CDCl<sub>3</sub>) 15.03, 56.52, 64.05, 76.21, 77.45, 105.58, 112.28, 114.92, 115.63, 121.46, 122.29, 123.49, 124.96, 125.95, 126.15, 127.53, 132.66, 142.71, 147.85, 155.67, 161.35; IR 3217, 2919, 2112, 1602, 1576, 1501, 1256, 1233, 1088, 921, 833, 823, 761 cm<sup>-1</sup>; m/z (HR-MS) found (M+H)<sup>+</sup> 331.26, theoretical 331.14.

