Electronic Supplementary Information

Room temperature self-healing power of silicone elastomers having silver nanoparticles as crosslinkers

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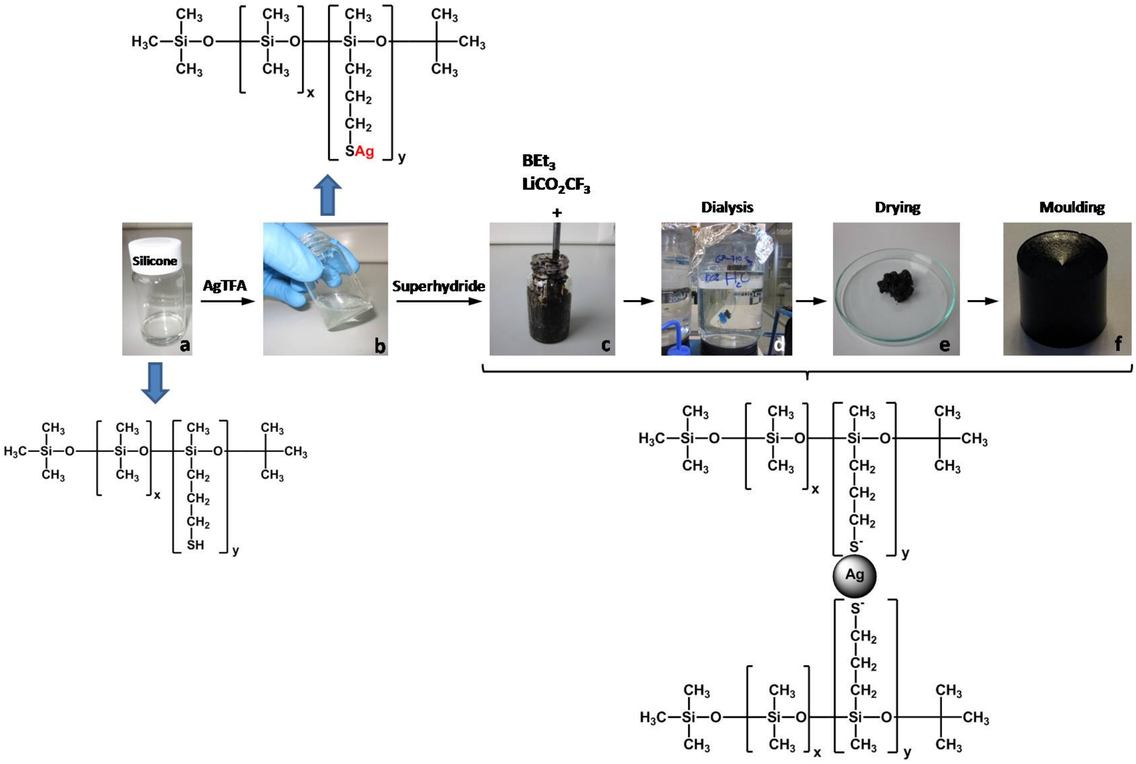
Materials and instrumentation

Thiol-functionalised silicone-oils **1a** (average M_w 70 KD_a PI = 1.99) and **1b** (average M_w 3,6 KD_a PI = 1.70) were purchased from Genesee Polymer Corporation and used as-received, without further purification. All the rest of reagents and solvents were commercial products from Sigma-Aldrich® and were also used as-received.

Dialysis was performed using Thermo Scientific SnakeSkin Dialysis Tubing, 3.5K MWCO. UV/vis spectra were recorded in transmission mode on a Shimadzu UV-vis spectrophotometer. The samples were placed in UV quality quartz cuvettes, 1 cm path length. Fourier transform infrared (FT-IR) spectra were registered in a Nicolet Avatar 360 spectrophotometer, using KBr disks compressed to 2 Ton x cm^{-2} for 2 min as support. Scanning electron microscopy (SEM) micrographs were recorded on a JEOL JSM5610-LV microscope. The specimens were coated with a thin layer of gold. Compression Strain-Stress tests were carried out in using INSTRON Long travel Elastomeric Extensometer (Cat No.2603-080) controlled by Bluehill Lite software. TEM images were registered using a 200 kV JEOL JSM-2100 Transmission Electron Microscope. Specimens were prepared onto carbon-coated Cu grids (150 mesh).

Synthesis of AgNPs-crosslinked silicone elastomers 2a-g

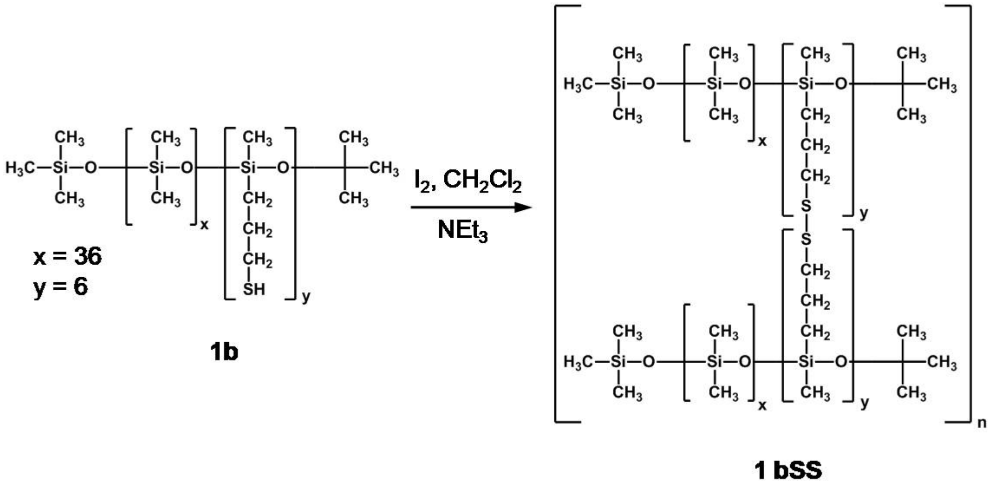
In a typical preparation procedure, appropriate quantities of **1a** and **1b** (total mass 3 g) were mixed in a capped round bottom flask under magnetic stirring. Then, a solution of silver trifluoroacetate (1, 3, 5, 10 or 15 equivalents respect to thiol groups) in the minimum volume of THF (1-2 mL) was added to the silicone-oil mixture. After homogenization, 1.2 equivalents of triethylborohydride (Super-Hydride ©) were added under vigorous stirring. Immediately after the addition of the reducing agent, a black colour evolved due to the formation of silver nanoparticles, and the arising black solids were obtained as swollen elastomers. Purification was carried out by dialyzing the solid samples using "Thermo Scientific SnakeSkin Dialysis Tubing, 3.5K MWCO" against water and water/THF mixtures (50:50 vol:vol) for 72 h. The solids were then dried under ambient conditions and shaped in a cylindrical mould, to give **2a-g** in the form of cylindrical black rubbery materials.



Scheme S1 Images of the different stages of the synthesis of silicone elastomers having silver nanoparticles as crosslinkers. A solution of silver trifluoroacetate (AgTFA) in THF was added to the silicone-oil mixture (a) resulting in a transparent fluid (b); then, triethylborohydride (Super-Hydride©) was added (c) and immediately, a black colour evolved due to the formation of Ag NPs, and the arising black solids were obtained as swollen elastomers which were submitted to dialysis (d). The solids were dried under ambient conditions (e) and moulded to give a black cylindrical elastomer (f).

Synthesis of disulfide-crosslinked silicone reference 1bSS.

A solution of **1b** (3 g), triethylamine (1.5 mL) and anhydrous dichloromethane (CH_2Cl_2, 25 mL) was placed in a capped round bottom flask cooled down to 0 ºC with an ice bath. Then, a solution of I_2 (0.5 M in CH_2Cl_2) was slowly dropped under vigorous stirring over the silicone solution. Immediately after the addition of the reducing agent, I_2 solution colour evolved from purple to colourless due to I_2 reduction. Addition was carried out until no further decolouration of I_2 was observed. The reaction mixture was then washed with aqueous HCl 0.1 M and distilled water until neutral pH. The organic phase was dried with $MgSO_4$, filtered and the solvent removed under vacuum to obtain a white powder. The material did not present self-healing behaviour (Figure S1).



Scheme S2 Synthetic procedure to obtain disulfide-crosslinked silicone **1bSS.**

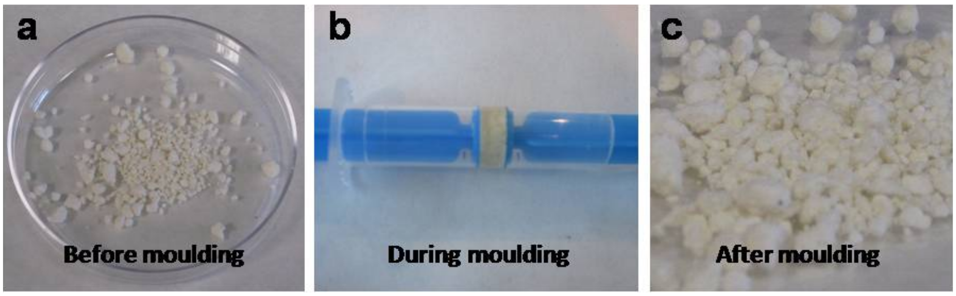


Figure S1 Photographs of **1bSS** during a self-healing experiment: (a) pristine material, (b) moulding and (c) the resulting **non-healed** material.

Characterization of starting silicone-oils

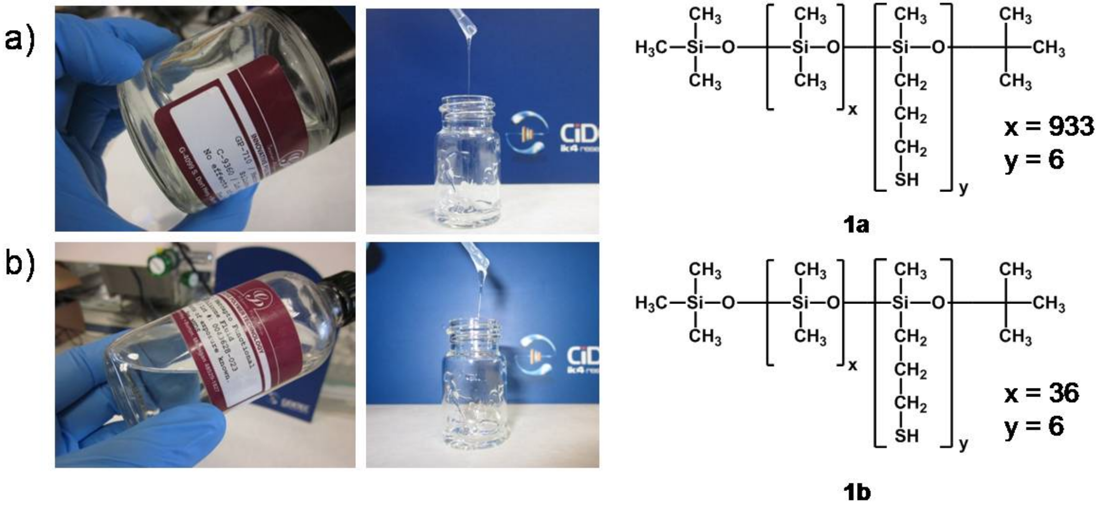
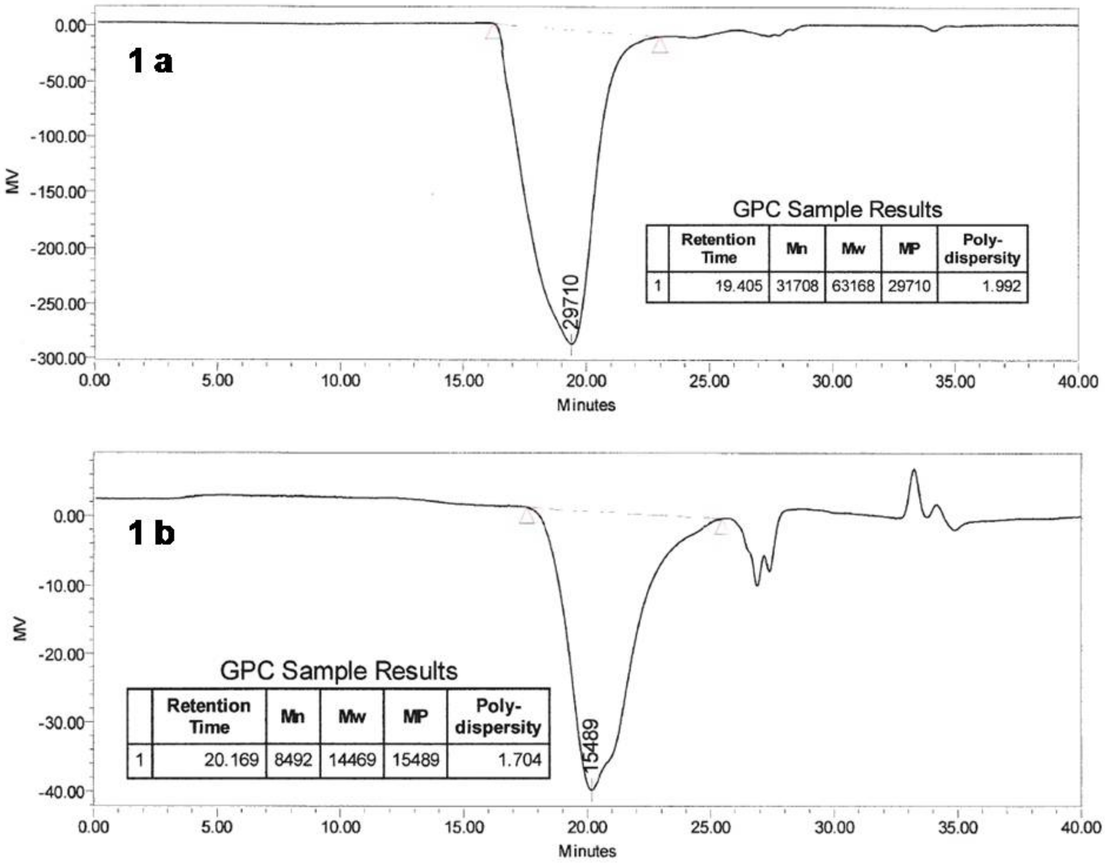


Figure S2 Photographs of starting silicone-oils showing their fluidity and structure: (a) **1a** (M_w 70,000) and (b) **1b** (M_w 3,600).



GPC Sample Results

	Retention Time	Mn	Mw	MP	Poly-dispersity
1	19.405	31708	63168	29710	1.992

GPC Sample Results

	Retention Time	Mn	Mw	MP	Poly-dispersity
1	20.169	8492	14469	15489	1.704

Figure S3 GPC chromatograms kindly provided by Genesee Polymers Corp. (USA) for starting silicone-oils **1a** (average M_w 70,000) and **1b** (average M_w 3,600).

According to these chromatograms the apparent molecular weights of silicone-oils **1a** and **1b** are 63168 and 14469 g·mol^{-1} respectively. In case of **1a** the weights are as close as could be expected. However, in **1b**, the high relative concentration of mercapto functionality is interacting with the column filler, causing an artificially high reading. ^{1}H NMR spectra were in good accordance with the expected molecular weights, namely 70,000 and 3,600, respectively for **1a** and **1b**.

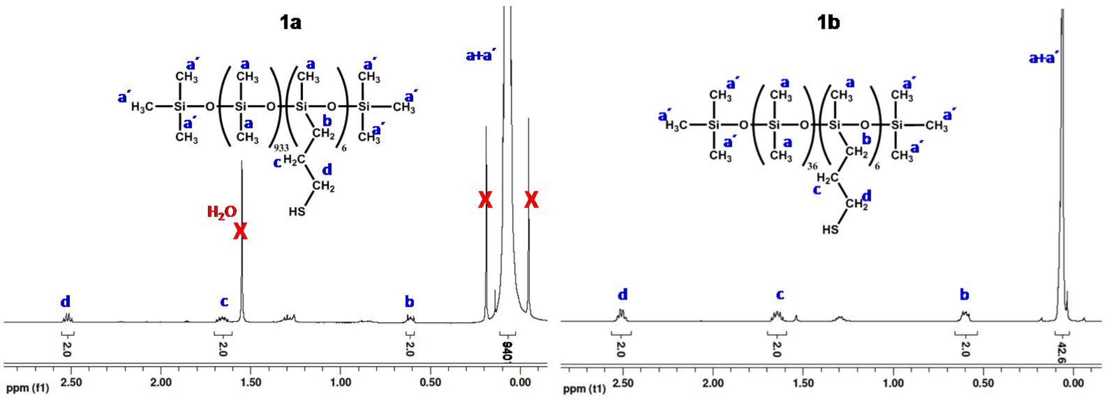


Figure S4 ^{1}H RMN spectra recorded for starting silicone-oils **1a** (average M_w 70,000) and **1b** (average M_w 3,600). Each spectra shows assignation and integral values of the corresponding signals.

Characterization of silicone elastomers 2a-g

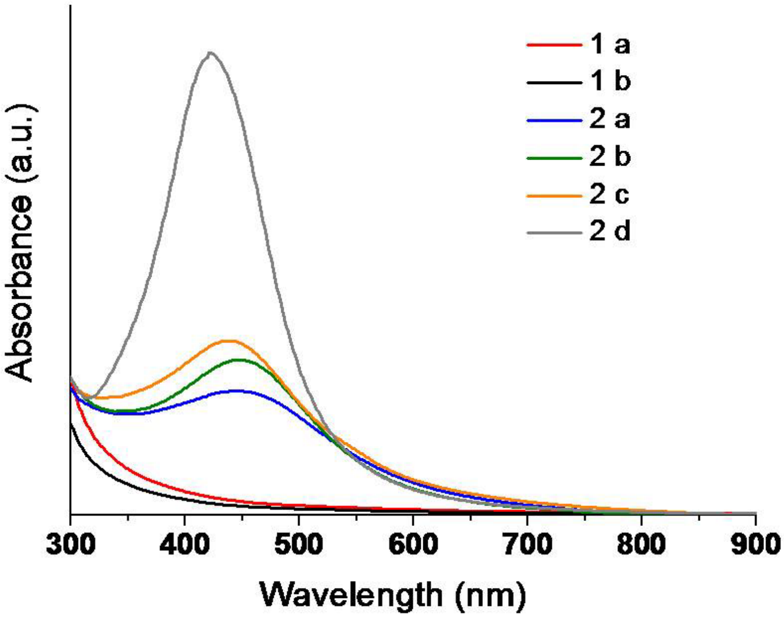


Figure S5 UV-Vis transmission spectra recorded for starting silicone-oils **1a** (red) and **1b** (black) and those of synthesized silicone elastomers **2a** (blue), **2b** (green), **2c** (orange) and **2d** (grey).

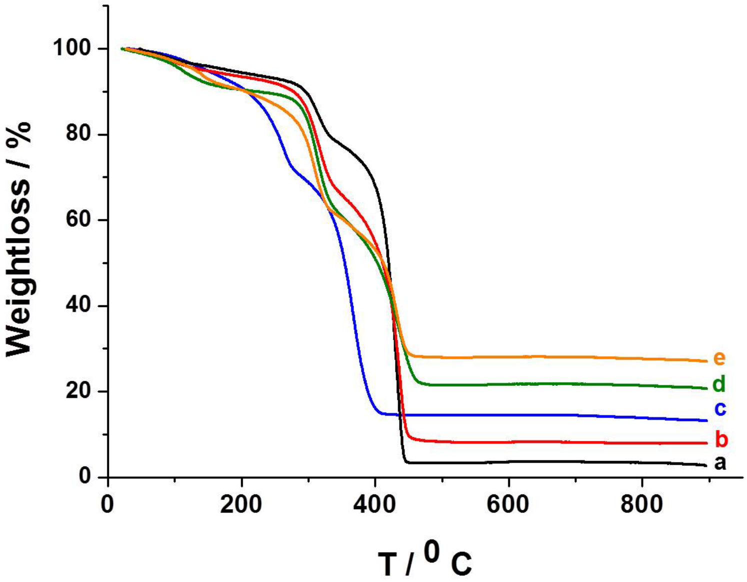


Figure S6 TGA of synthesized silicone elastomers **2a** (a), **2b** (b), **2c** (c), **2d** (d) and **2e** (e).

Table S1 Comparison between the calculated values of the TGA residue and the experimental ones for all synthesized materials. Obtained values were in good agreement with the theoretical ones.

Compound	Ag/thiol molar ratio	Theoretical residue (%)	Experimental residue (%)
2a	1	2.7	2.63
2b	3	7.6	7.8
2c	5	12.1	13.4
2d	10	21.5	21.0
2e	15	29	27.2
2f	5	14.5	13.4
2g	5	16.1	18.2

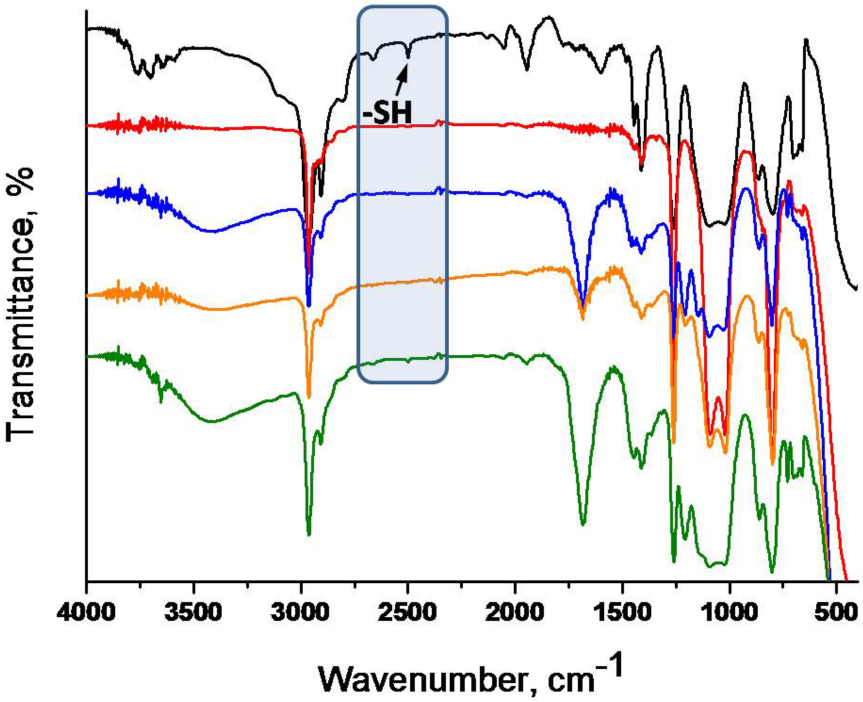


Figure S7 FT-IR spectra recorded for starting silicone-oils **1a** (black) and **2a** (red), and those of synthesized silicone elastomers **2a** (blue), **2c** (orange) and **2e** (green).

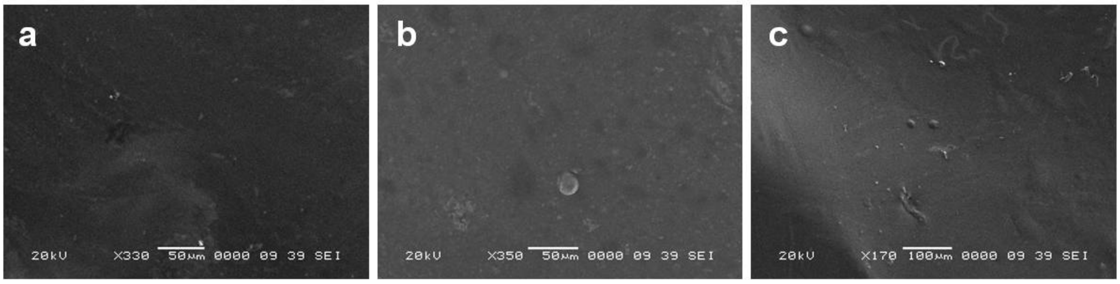


Figure S8 SEM micrographs of freshly cut surfaces obtained for samples **2c** (a), **2f** (b) and **2g** (c).

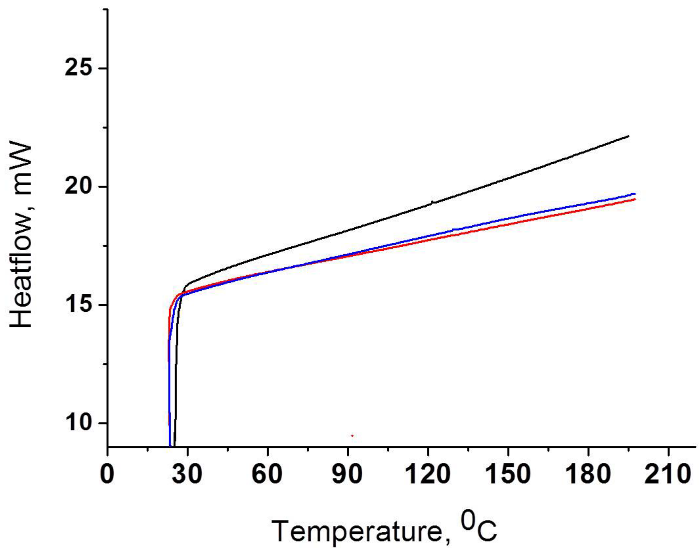


Figure S9 Differential Scan Calorimetry (DSC) profiles recorded for samples **2c** (red), **2f** (blue) and **2g** (black).