This version replaces ESI published on 13 September 2013 due to an error in the "Synthesis of tris-isocyanate-terminated prepolymer (6)" section. The mass and concentration of IPDI were originally stated as 28.86 g and 130 mmol, but were actually 45.45 g and 204.5 mmol.

Electronic Supplementary Information

Catalyst-free room-temperature self-healing elastomer based on aromatic disulfide metathesis

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Materials and methods

Poly(propylene glycol)s (PPG) **5** (M_n 6,000) and **7** (M_n 2,000) were purchased from Bayer Materials Science. Isophorone diisocyanate (IPDI, 98%), dibutyltin dilaurate (DBTDL, 95%), bis(4-aminophenyl) disulfide **1a** (98%), bis(p-tolyl) disulfide **1b** (98%), bis(4-methoxyphenyl) disulfide **2** (97%), 4,4′-ethylenedianiline **4** (> 95%) and tetrahydrofurane (THF) were purchased from Sigma-Aldrich and were used as received.

Fourier transform infrared (FTIR) spectra were registered in a Nicolet Avatar 360 spectrophotometer, using KBr disks compressed to 2 Ton cm^{-2} for 2 min as support. ^{1}H NMR spectra were registered in a Bruker AVANCE III 500 MHz spectrometer. Mechanical testing was performed using INSTRON 3365 Long travel Elastomeric Extensometer controlled by Bluehill Lite software. Tensile strength measurements were carried out according to UNE-EN-ISO 527 standard using dumbbell type test specimens and an elongation rate of 500 mm min^{-1}.

Synthesis of tris-isocyanate-terminated prepolymer (6)

A mixture of PPG **5** (390 g, 65 mmol) and IPDI (45.45 g, 204.5 mmol) were fed into a 1 L glass reactor equipped with mechanical stirrer and a vacuum inlet. The mixture was degassed by stirring under vacuum while heating at 70 ºC for 10 min. Then DBTDL (50 ppm) was added and the mixture was further stirred under vacuum at 70 ºC for 45 minutes. The reaction was monitored by FTIR spectroscopy (Figure S1). The resulting tris-isocyanate terminated prepolymer **6** was obtained in the form of a colourless liquid and stored in a tightly closed glass bottle. Yield: 398 g, 95%.

Synthesis of bis-isocyanate-terminated prepolymer (8)

A mixture of PPG **7** (250 g, 125 mmol) and IPDI (55.5 g, 250 mmol) were fed into a 1 L glass reactor equipped with mechanical stirrer and a vacuum inlet. The mixture was degassed by stirring under vacuum while heating at 60 ºC for 10 min. Then DBTDL (50 ppm) was added and the mixture was further stirred under vacuum at 60 ºC for 70 minutes. The reaction was monitored by FTIR spectroscopy

(Figure S2). The resulting bis-isocyanate terminated prepolymer **8** was obtained in the form of a colourless liquid and stored in a tightly closed glass bottle. Yield: 301 g, 98%.

Synthesis of self-healing poly(urea-urethane) elastomer (9a)

6 (35 g) and **8** (15 g) were mixed in a 250 mL glass reactor. Then, a solution of **1a** (5.12 g, 20.6 mmol) in THF (3 mL) was added. The mixture was degassed under vacuum for 15 minutes and the mixture was placed on to an open mold. The curing was allowed to proceed for 16 h at 60 ºC and was monitored by FTIR spectroscopy (Figure S3). Poly(urea-urethane) **9a** was obtained as a yellowish transparent elastomeric material. Yield: 49 g, 89%.

Synthesis of reference poly(urea-urethane) elastomer (9b)

6 (35 g) and **8** (15 g) were mixed in a 250 mL glass reactor. Then, a solution of **4** (4.41 g, 20.6 mmol) in THF (5 mL) was added. The mixture was degassed under vacuum for 15 minutes and the mixture was placed on to an open mold. The curing was allowed to proceed for 16 h at 60 ºC and was monitored by FTIR spectroscopy (Figure S4). Poly(urea-urethane) **9b** was obtained as a yellowish transparent elastomeric material. Yield: 52 g, 94%.

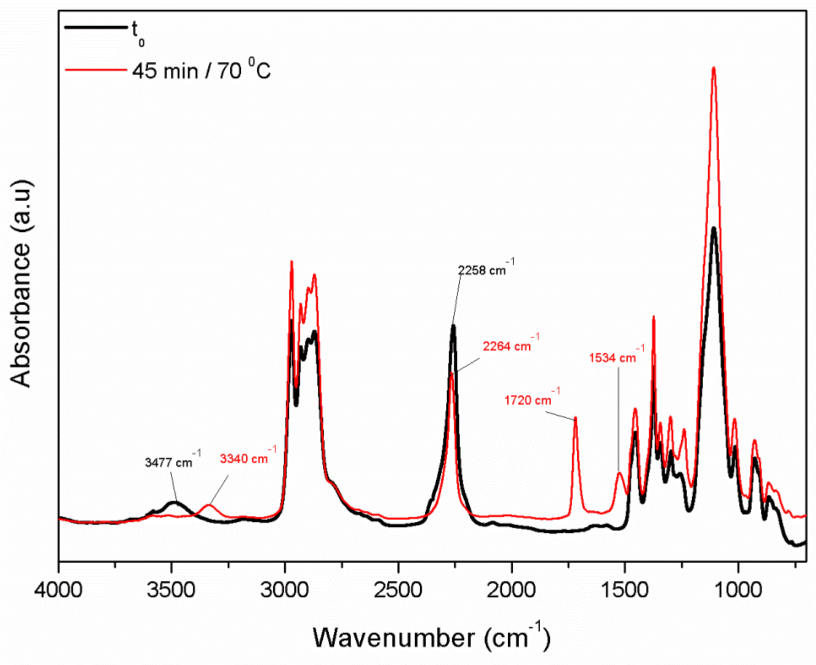

Figure S1. FTIR spectra of reaction of PPG **5** and IPDI at 70 ºC at t = 0 (black trace) and t = 45 min. (red trace), where the appearance of new bands corresponding to the carbonyl group of urethane moiety at 1720 cm^{-1} and amide II at 1534 cm^{-1} can be observed. Moreover, a decrease and displacement of the NCO stretching band from 2258 to 2264 cm^{-1} can be observed, which was used as criteria to establish that the reaction was finished.

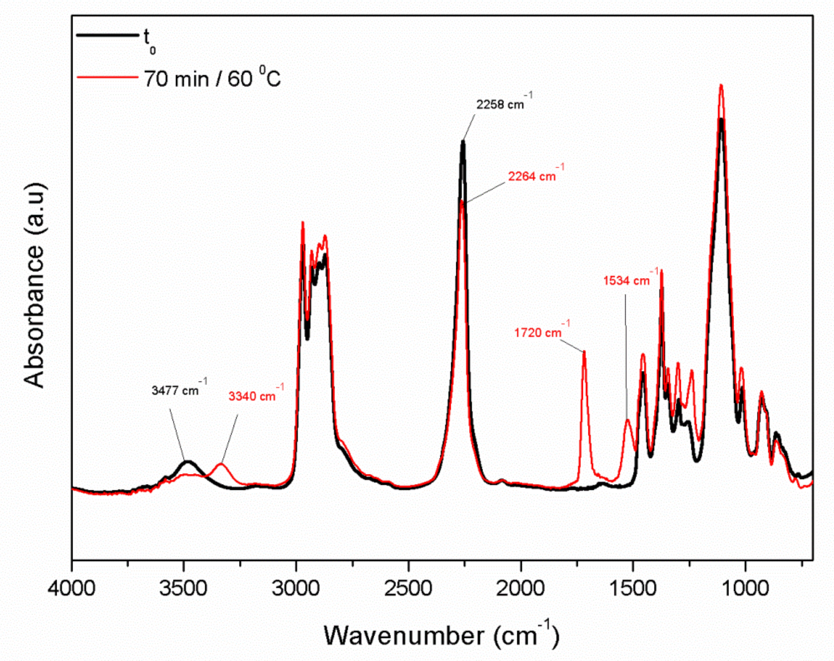

Figure S2. FTIR spectra of PPG **7** and IPDI at 60 ºC at t = 0 min (black trace) and t = 70 min. (red trace), where the appearance of new bands corresponding to the carbonyl group of urethane moiety at 1720 cm^{-1} and amide II at 1534 cm^{-1} can be observed. Moreover, a decrease and displacement of the NCO stretching band from 2258 to 2264 cm^{-1} can be observed, which was used as criteria to establish that the reaction was finished.

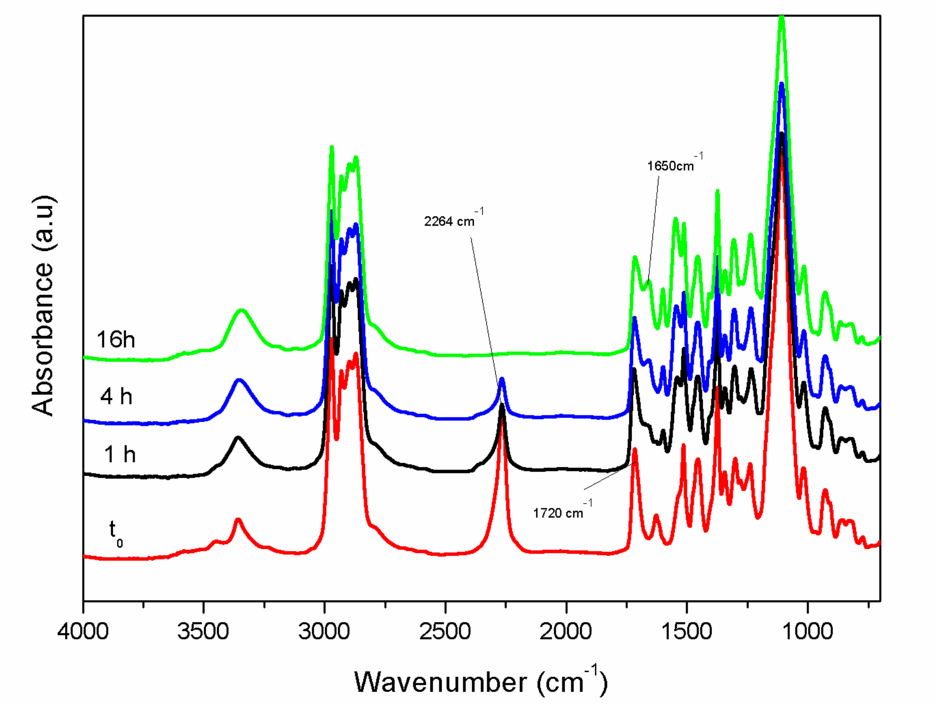

Figure S3. FTIR spectra recorded for the synthesis of **9a** at different curing times. At t = 16 h, the NCO stretching band at 2264 cm^{-1} completely disappeared and a new band corresponding to the urea appeared at 1650 cm^{-1} in the form of a shoulder. The spectra have been shifted for clarity.

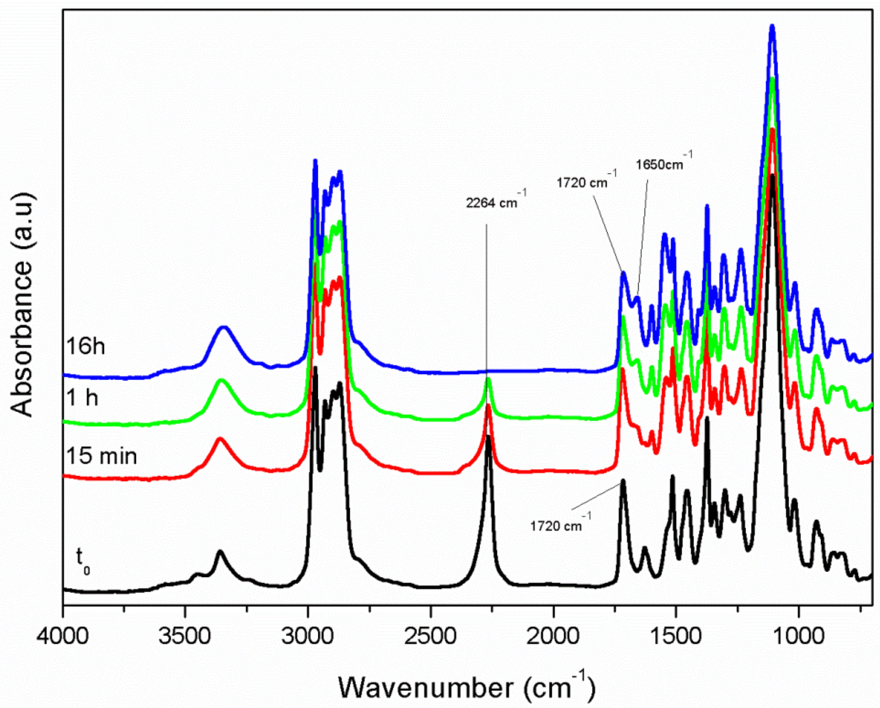

Figure S4. FTIR spectra recorded for the synthesis of **9b** at different curing times. At t = 16 h, the NCO stretching band at 2264 cm^{-1} completely disappeared and a new band corresponding to the urea appeared at 1650 cm^{-1} in the form of a shoulder. The spectra have been shifted for clarity.

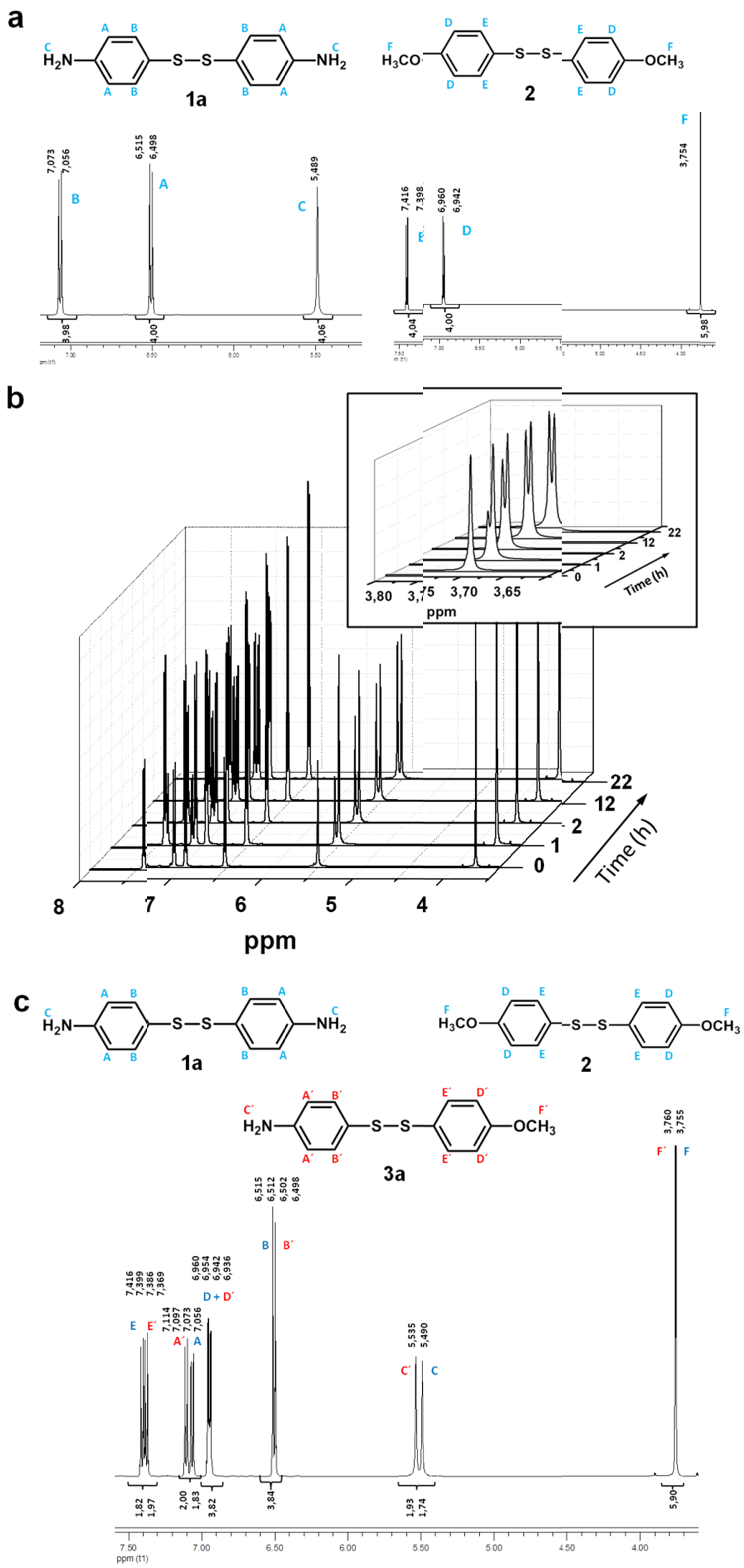

Figure S5. ^{1}H NMR spectra recorded for: a) bis(4-aminophenyl) disulfide (**1a**) and bis(4-methoxyphenyl) disulfide (**2**); b) metathesis kinetics of an equimolar mixture of **1a** and **2** at t = 0, 1, 2, 12 and 22 hours in deuterated DMSO at room temperature (inset shows the -OCH_3 protons); c) a completely equilibrated mixture of **1a** (25 mol%), **2** (25 mol%) and **3a** (50 mol%) after 22 hours.

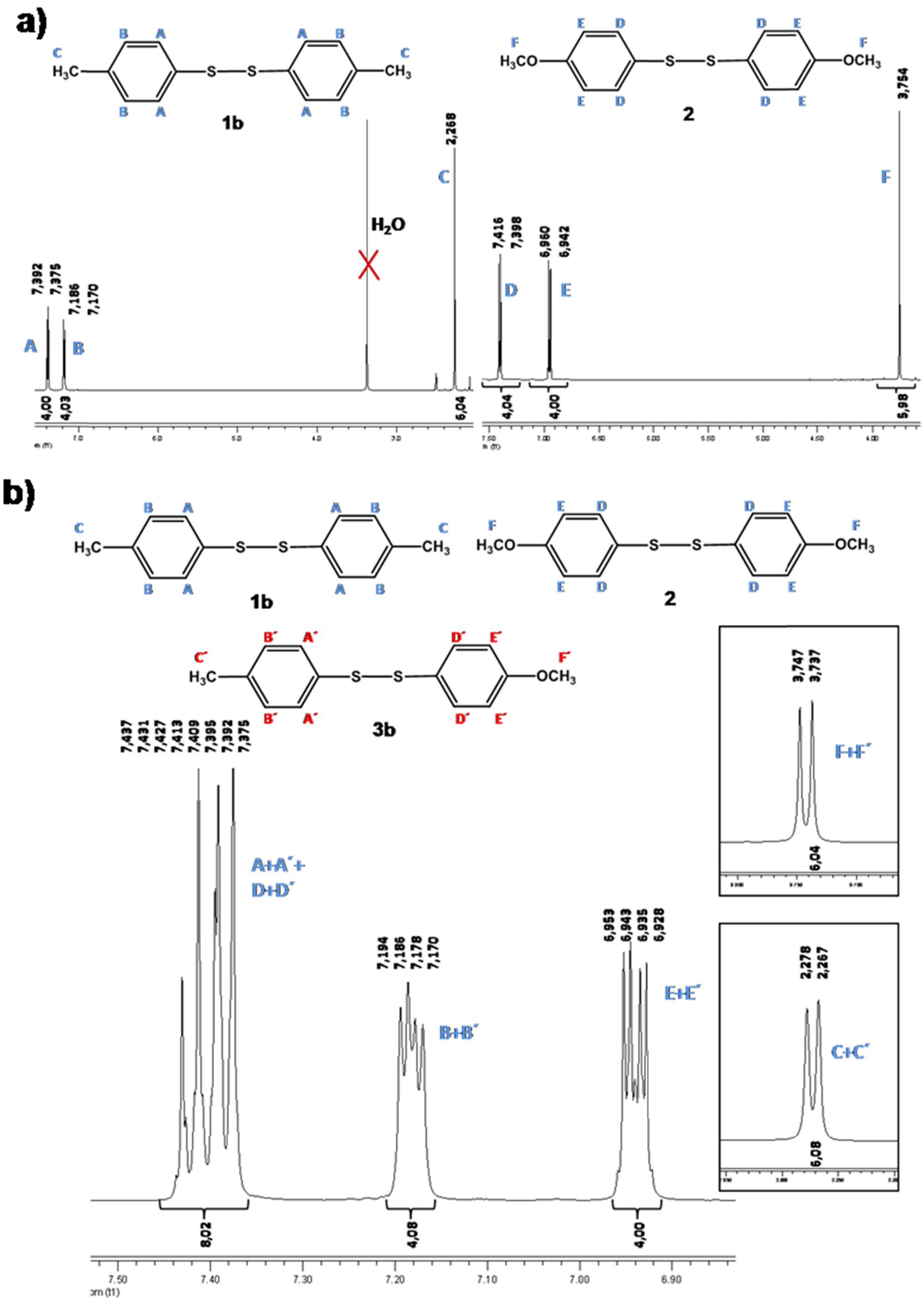

Figure S6. ^{1}H NMR spectra recorded for: a) bis(p-tolyl) disulfide (**1b**) and bis(4-methoxyphenyl) disulfide (**2**); b) a completely equilibrated mixture of **1b** (25 mol%), **2** (25 mol%) and **3b** (50 mol%) at 24 hours (the two insets show the -OCH_3 and –CH_3 protons).