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## Electronic Supplementary Information

# Synthesis and characterization of polysulfides formed by the inverse vulcanisation of cyclosiloxanes with sulfur

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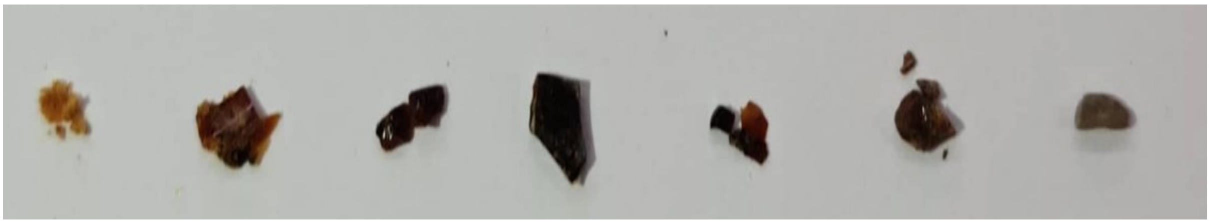

**Figure S1:** Photo of X-poly(S-*r*-TVTSi) series (X = wt% S). From left to right: X = 20, 30, 40, 50, 60, 70 and 80.

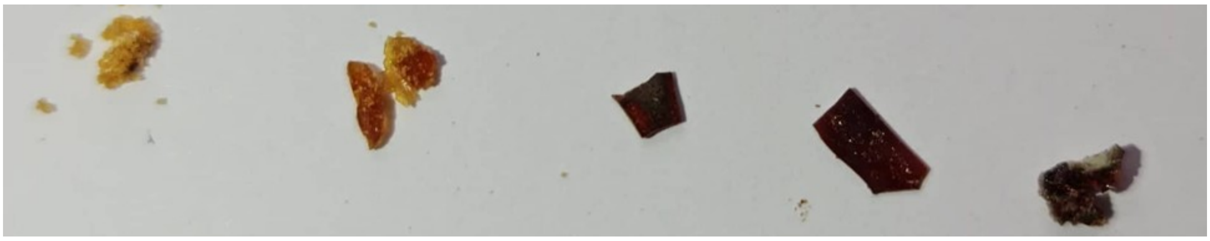

**Figure S2:** Photo of X-poly(S-*r*-PVPSi) series (X = wt% S). From left to right: X = 10, 20, 30, 40, 50.

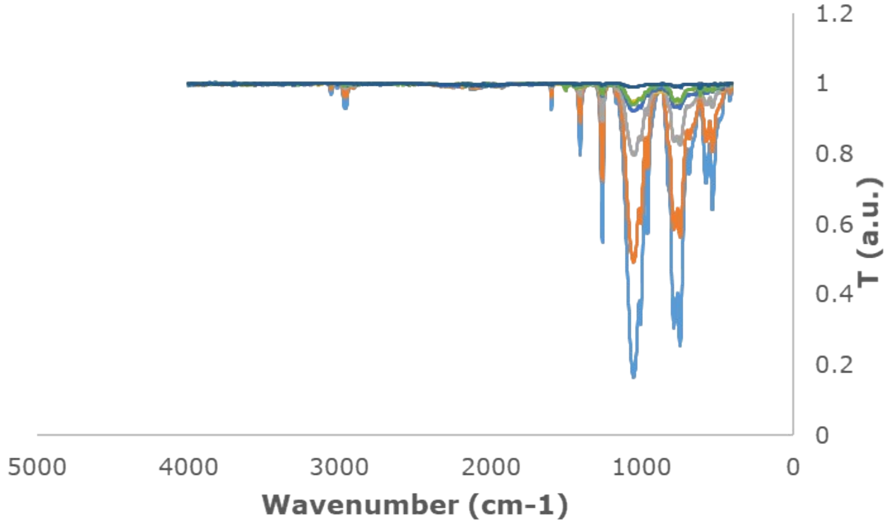


**Figure S3:** FTIR spectra of X-poly(S-*r*-TVTSi) (X = wt % S), X = 20 (light blue), X = 30 (orange), X = 40 (grey), X = 50 (yellow), X = 60 (blue), X= 70 (green), X= 80 (navy)

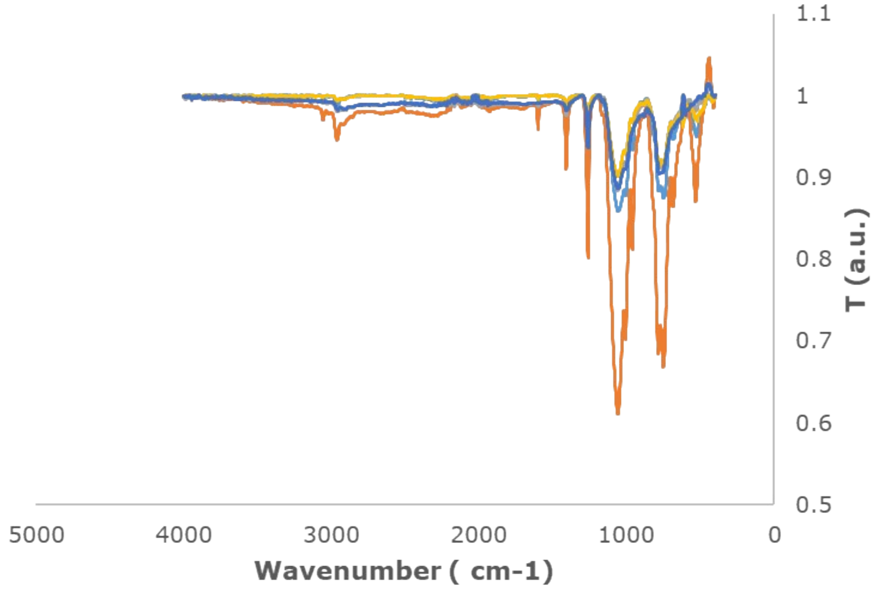


**Figure S4:** FTIR spectra of X-poly(S-*r*-PVPSi) (X = wt % S), X = 10 (light blue), X = 20 (orange), X = 30 (grey), X = 40 (yellow), X = 50 (dark blue).

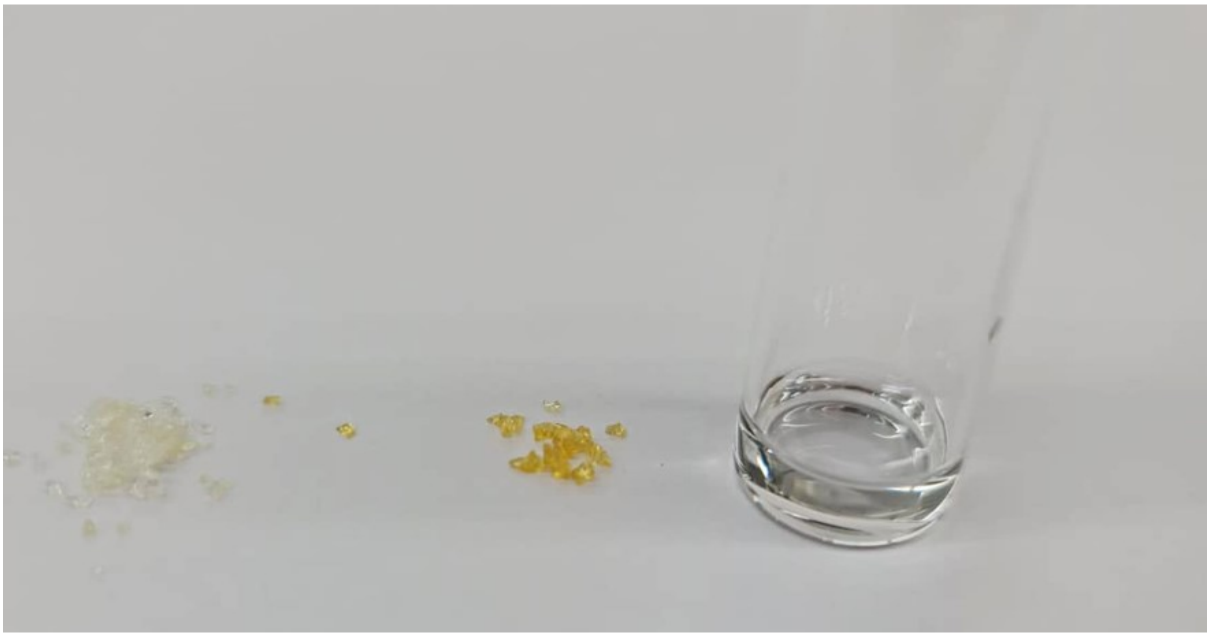

**Figure S5:** Tetravinyl-tetramethyl-cyclotetrasiloxane (TVTSi) after heating at 230°C for 3h (left), pentavinyl-pentamethyl-cyclopentasiloxane (PVPSi) after heating at 230°C for 3 h (middle) and unheated TVTSi (right).

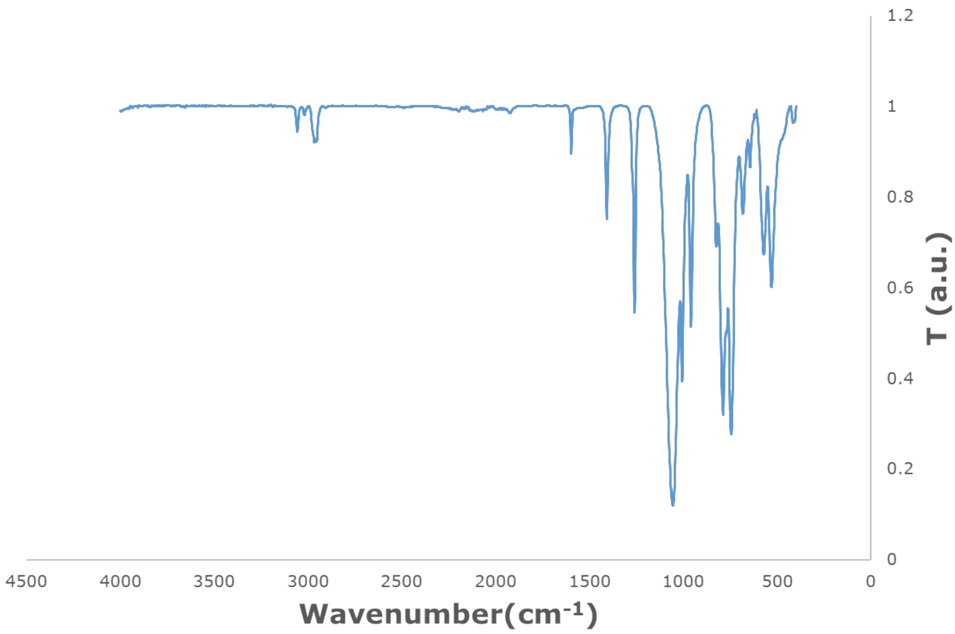


**Figure S6:** FTIR spectrum of TVTSi.

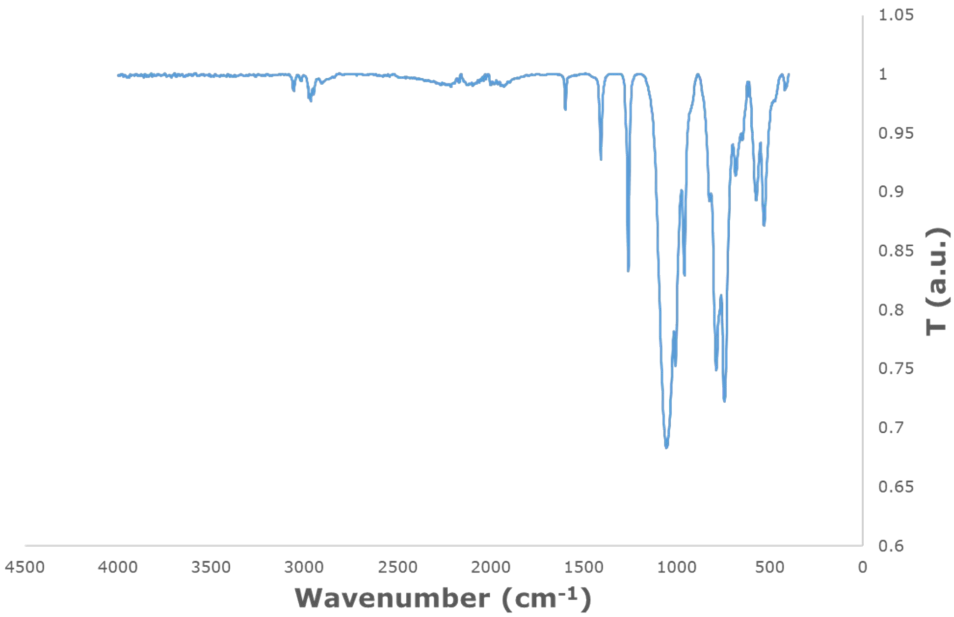


**Figure S7:** FTIR spectrum of TVTSi heated.

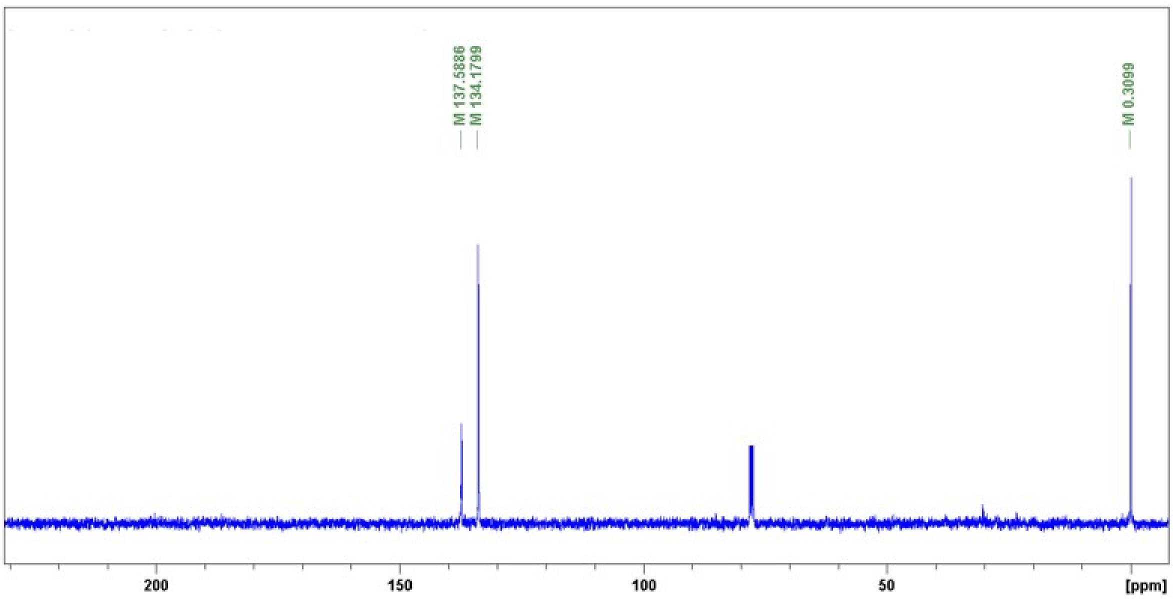


**Figure S8:** $^{13}C\{^1H\}$ NMR spectrum of tetravinyl-tetramethyl-cyclotetrasiloxane in $CDCl_3$.

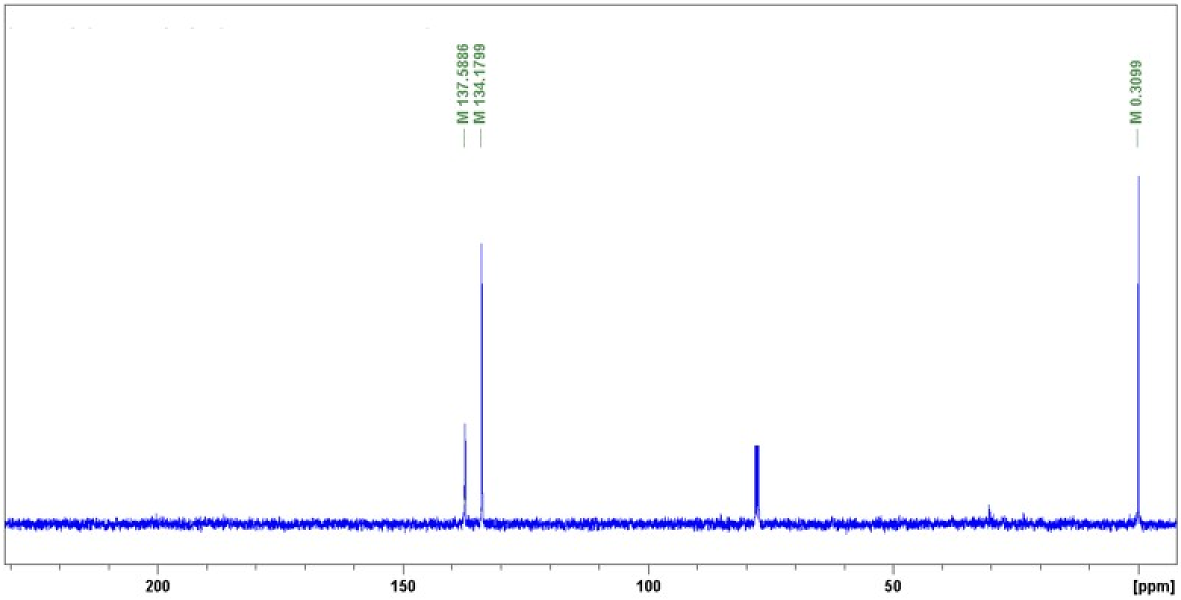


**Figure S9:** $^{13}C\{^{1}H\}$ NMR spectrum of pentavinyl-pentamethyl-cyclopentasiloxane in $CDCl_3$.

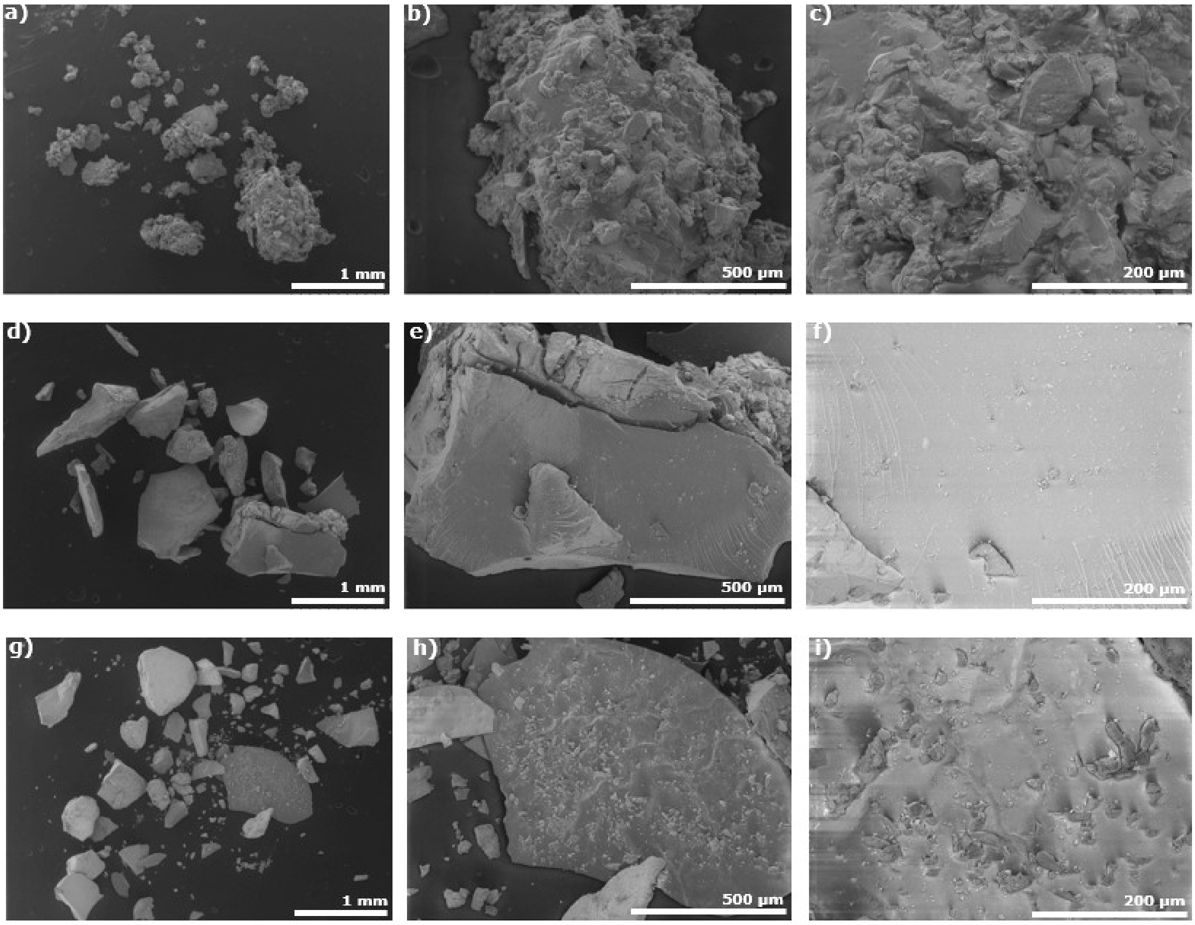


**Figure S10:** Representative SEM images for different wt% S polysulfides; top row: 20-poly(S-*r*-TVTSi), middle row: 40-poly(S-*r*-TVTSi), bottom row: 80-poly(S-*r*-TVTSi).

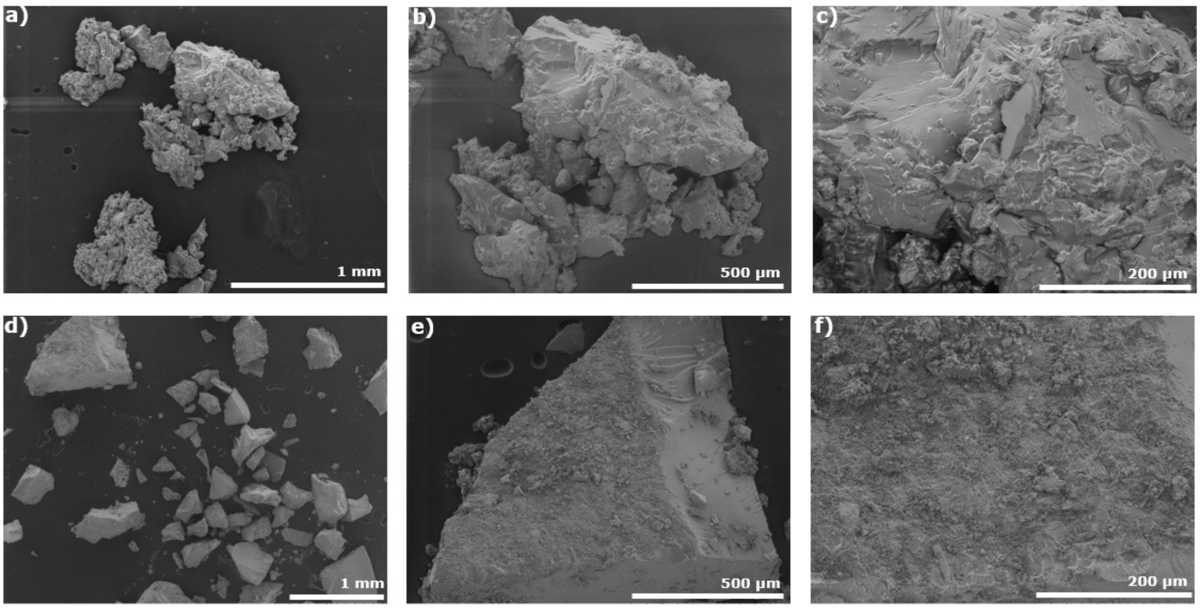


**Figure S11:** Representative SEM images for different wt % S polysulfides; top row: 20-poly(S-*r*-PVPSi), bottom row: 40-poly(S-*r*-PVPSi)

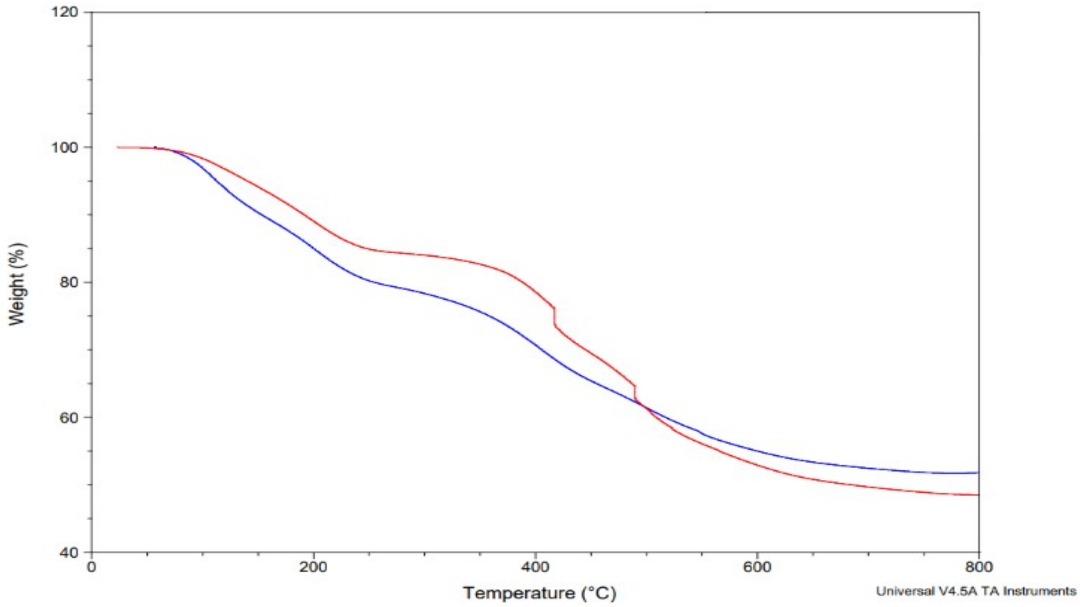


**Figure S12:** Thermogram of 20-poly(S-*r*-TVTSi) repeated twice.

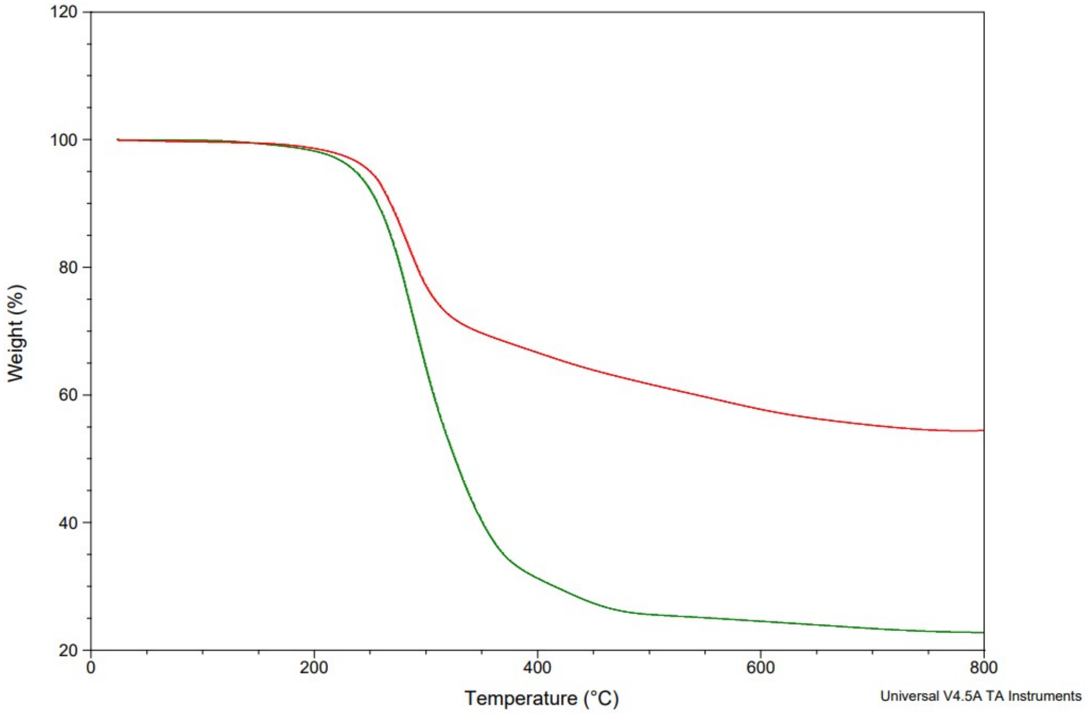


**Figure S13:** Thermogram comparison of 80-poly(S-*r*-TVTSi) before (green) and after (red) washing with $CS_2$.

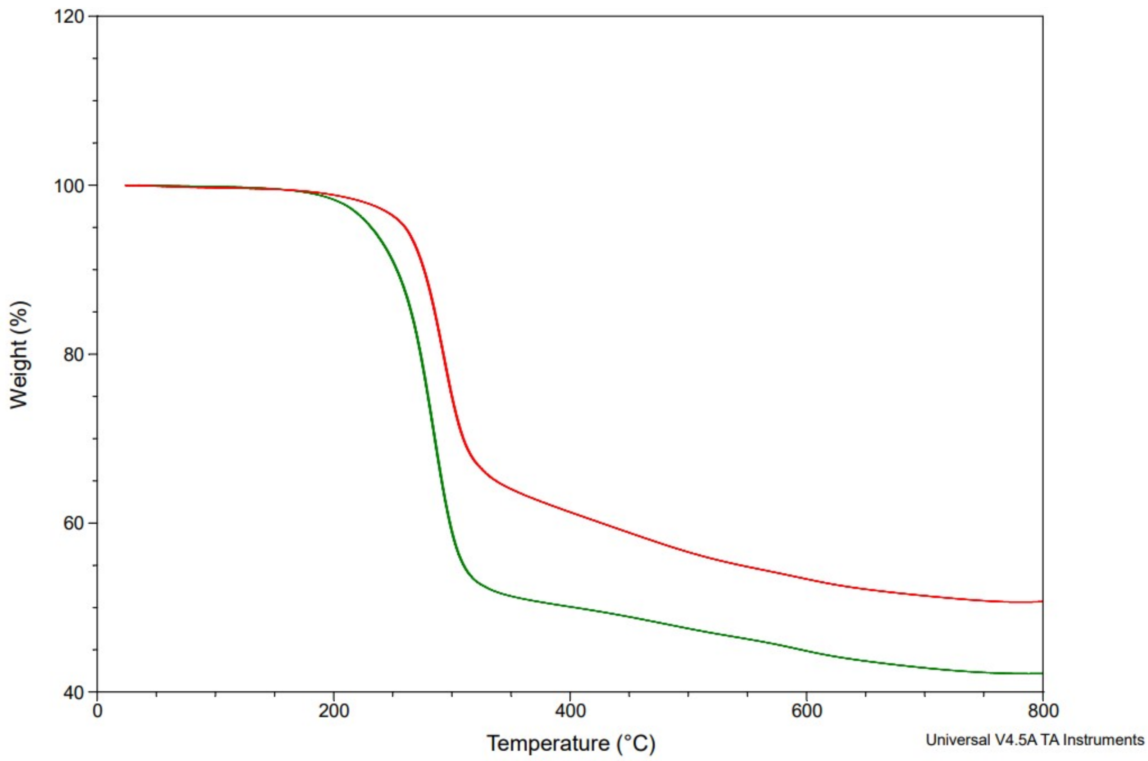


**Figure S14:** Thermogram comparison of 50-poly(S-*r*-PVPSi) before (green) and after (red) washing with $CS_2$.

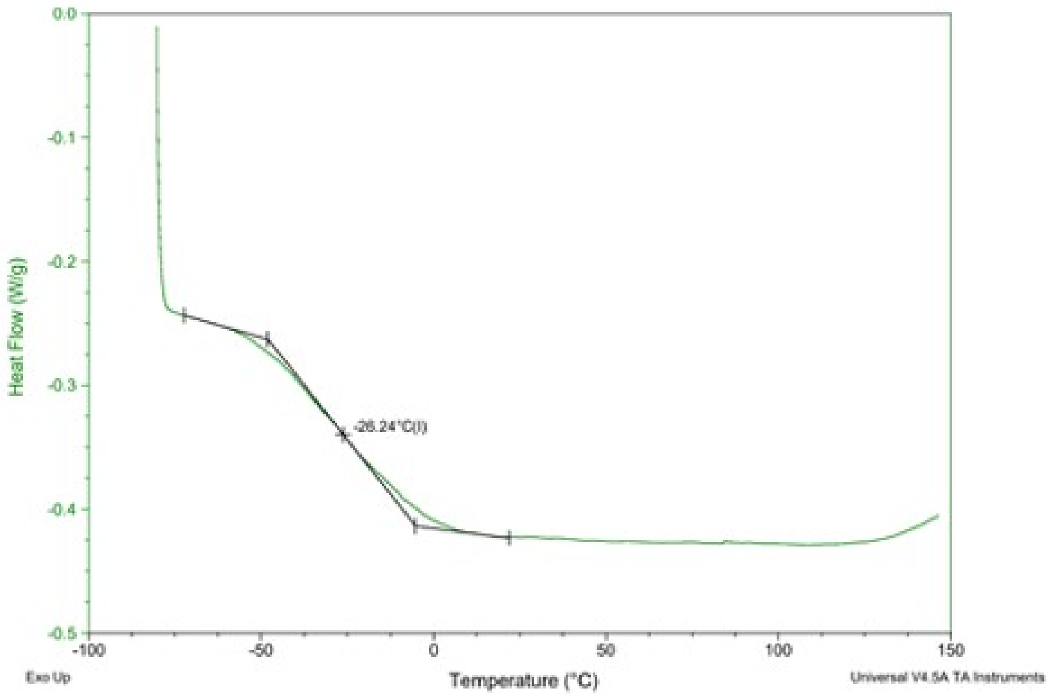


**Figure S15:** DSC scan of 20-poly(S-*r*-TVTSi) with $T_g$ measured at -26.24°C

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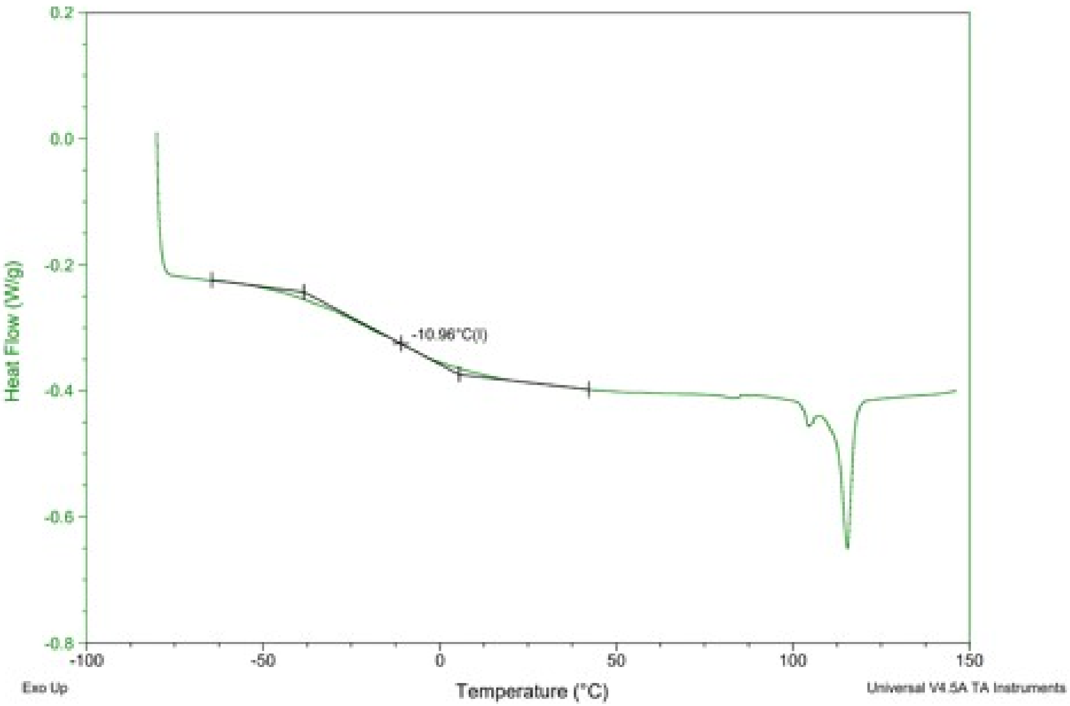


**Figure S16:** DSC scan of 30-poly(S-*r*-TVTSi) with $T_g$ measured at -10.96°C and elemental sulfur shown to melt at 120°C.

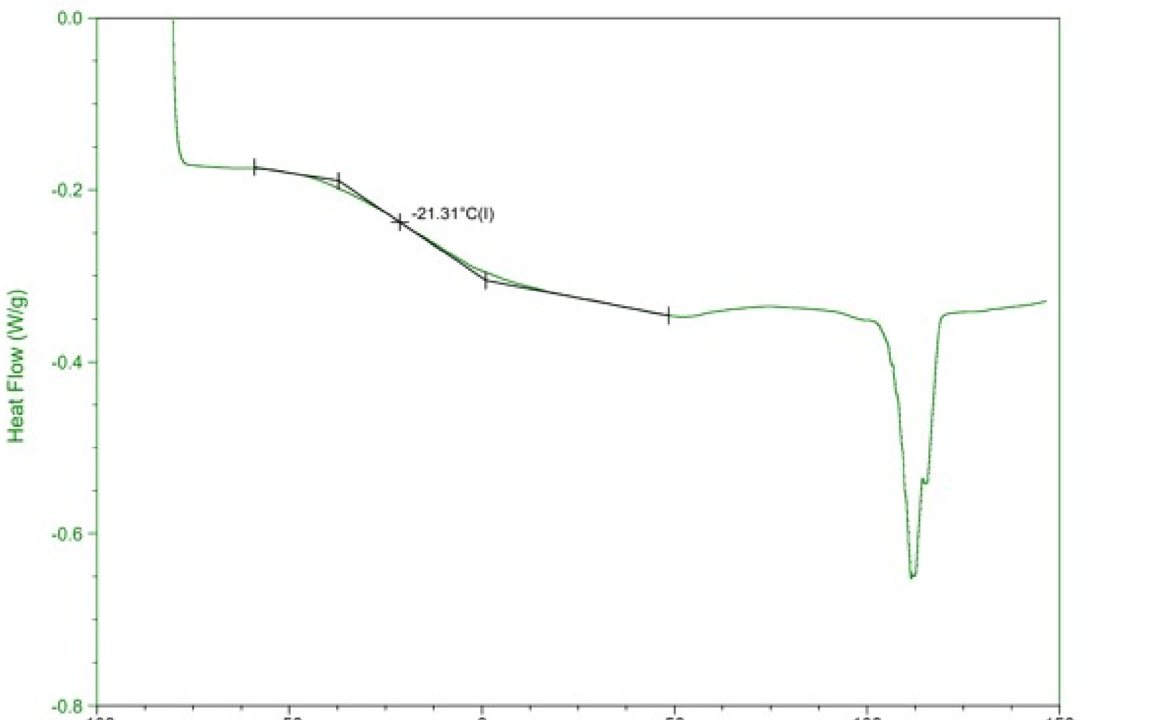


**Figure S17:** DSC scan of 40-poly(S-*r*-TVTSi) with $T_g$ measured at -21.31°C and elemental sulfur shown to melt at 120°C.

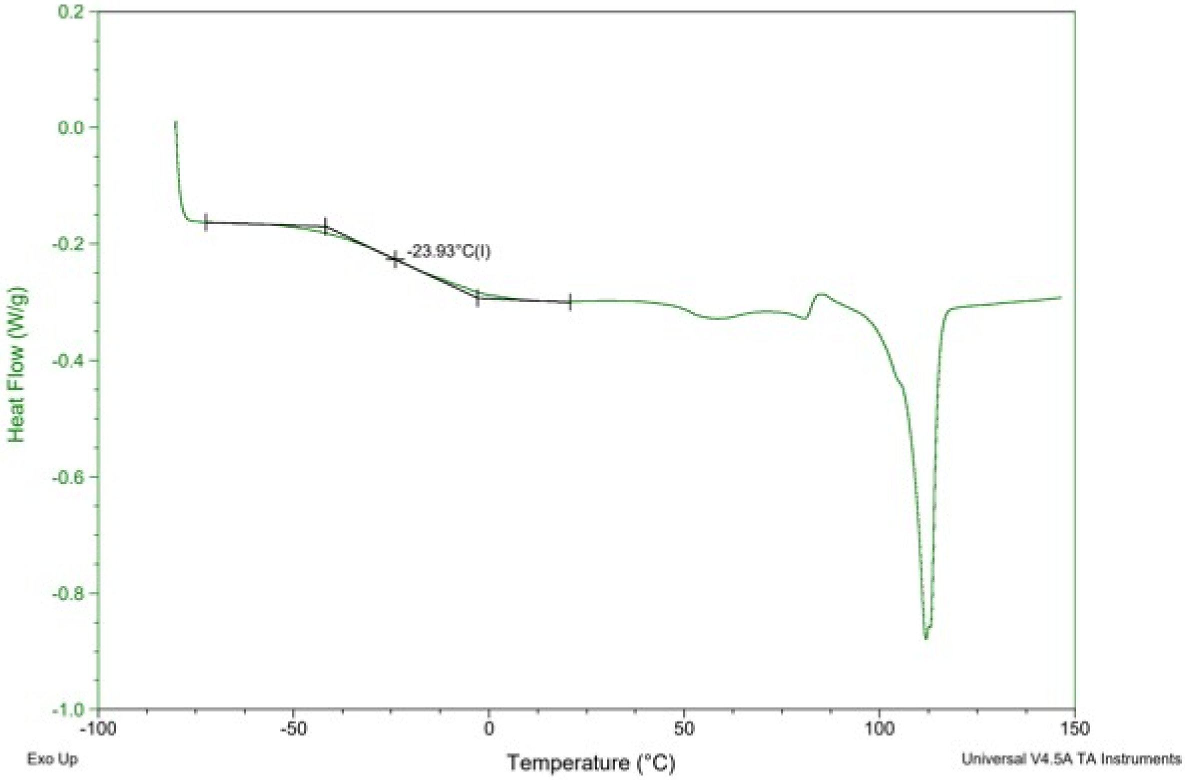


**Figure S18:** DSC scan of 50-poly(S-*r*-TVTSi) with $T_g$ measured at -23.93°C and elemental sulfur shown to melt at 120°C.

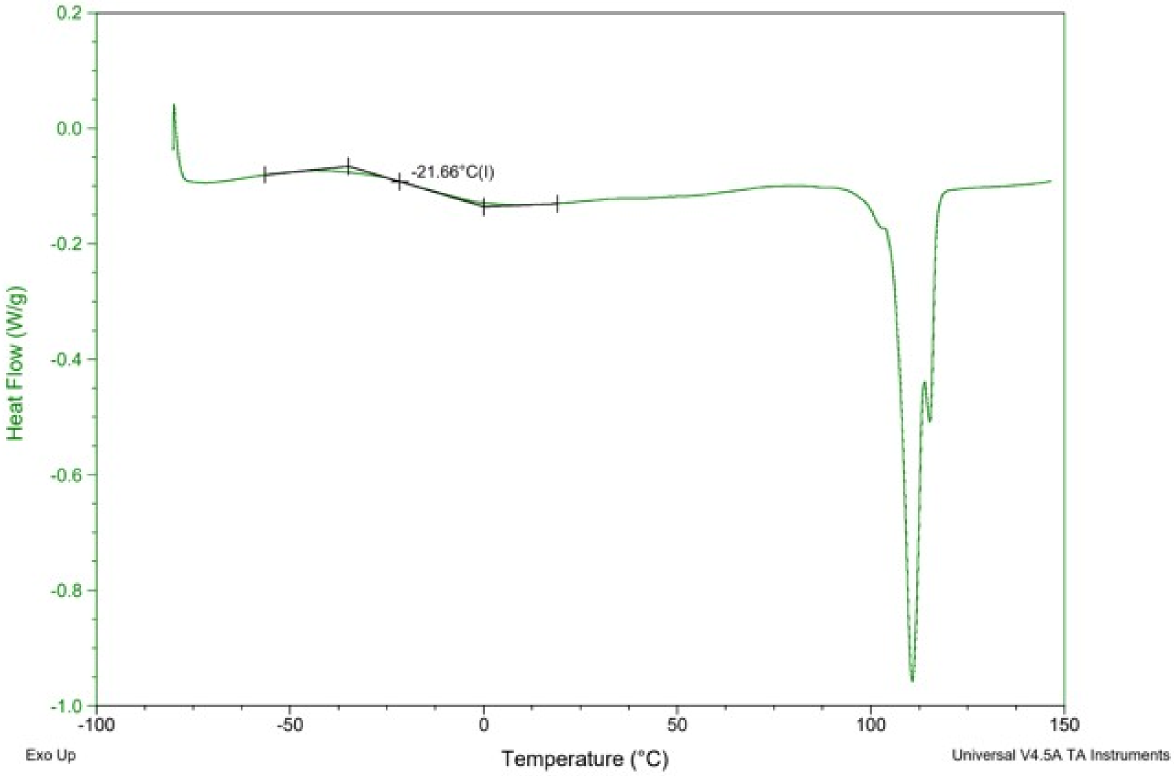


**Figure S19:** DSC scan of 60-poly(S-*r*-TVTSi) with $T_g$ measured at -21.66°C and elemental sulfur shown to melt at 120°C.

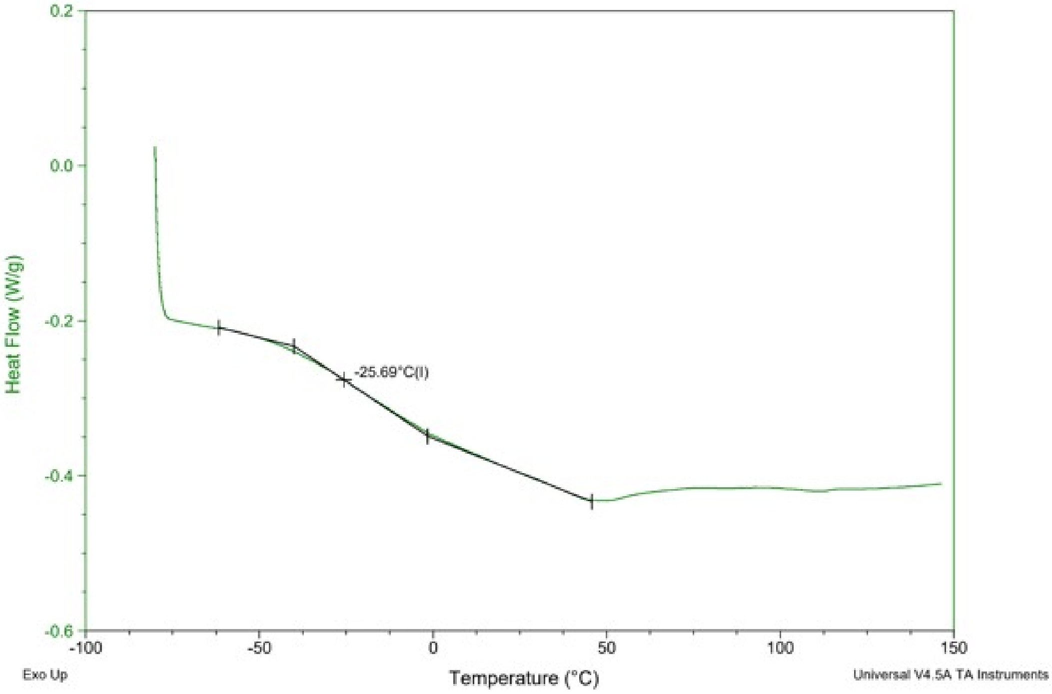


**Figure S20:** DSC scan of 70-poly(S-*r*-TVTSi) with $T_g$ measured at -25.69°C.

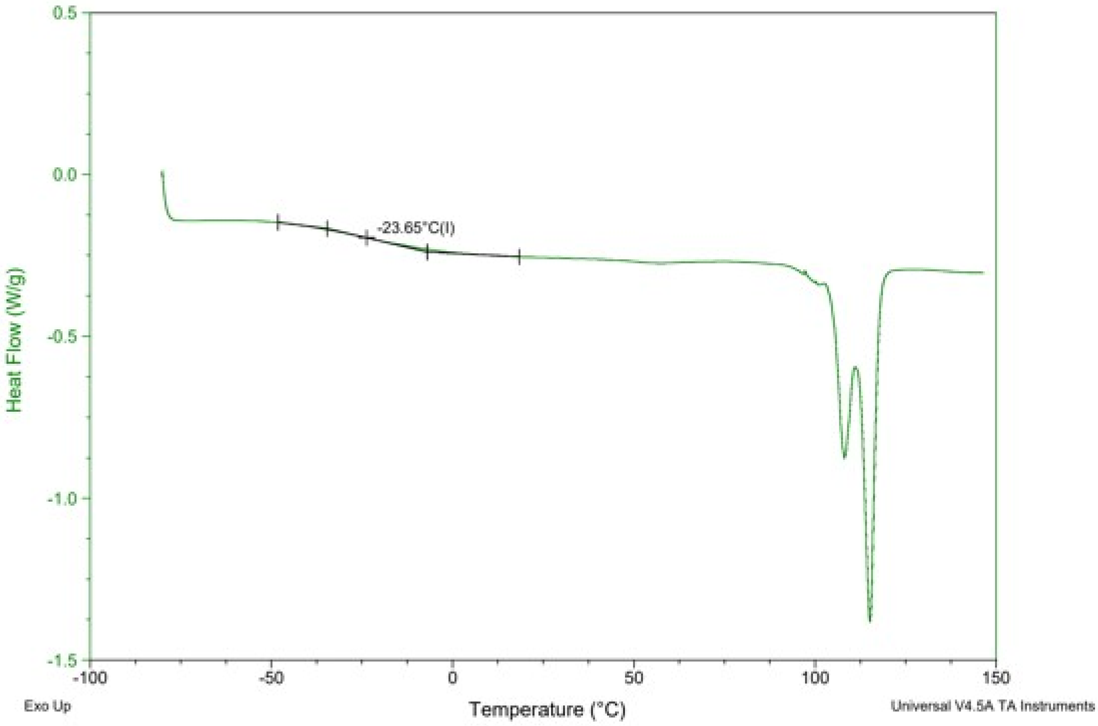


**Figure S21:** DSC scan of 80-poly(S-*r*-TVTSi) with $T_g$ measured at -23.65°C and elemental sulfur shown to melt at 120°C.

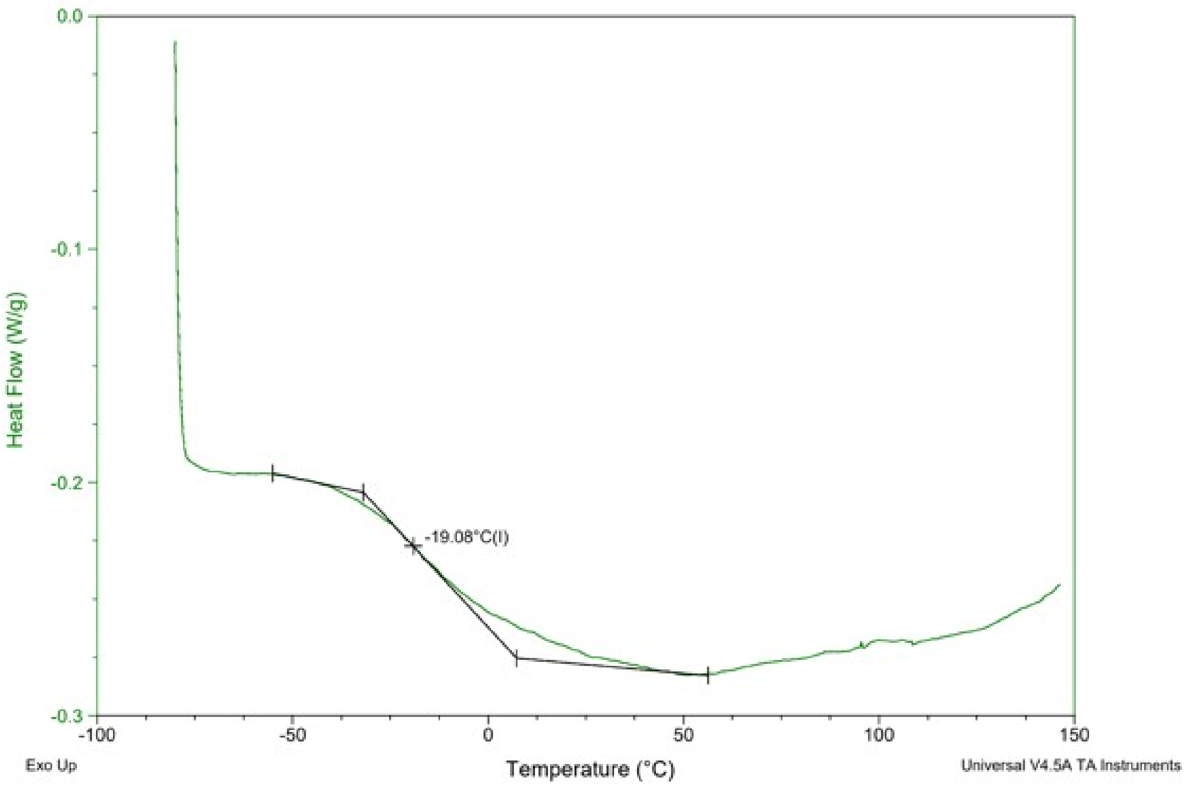


**Figure S22:** DSC scan of 10-poly(S-*r*-PVPSi) with $T_g$ measured at -19.08°C.

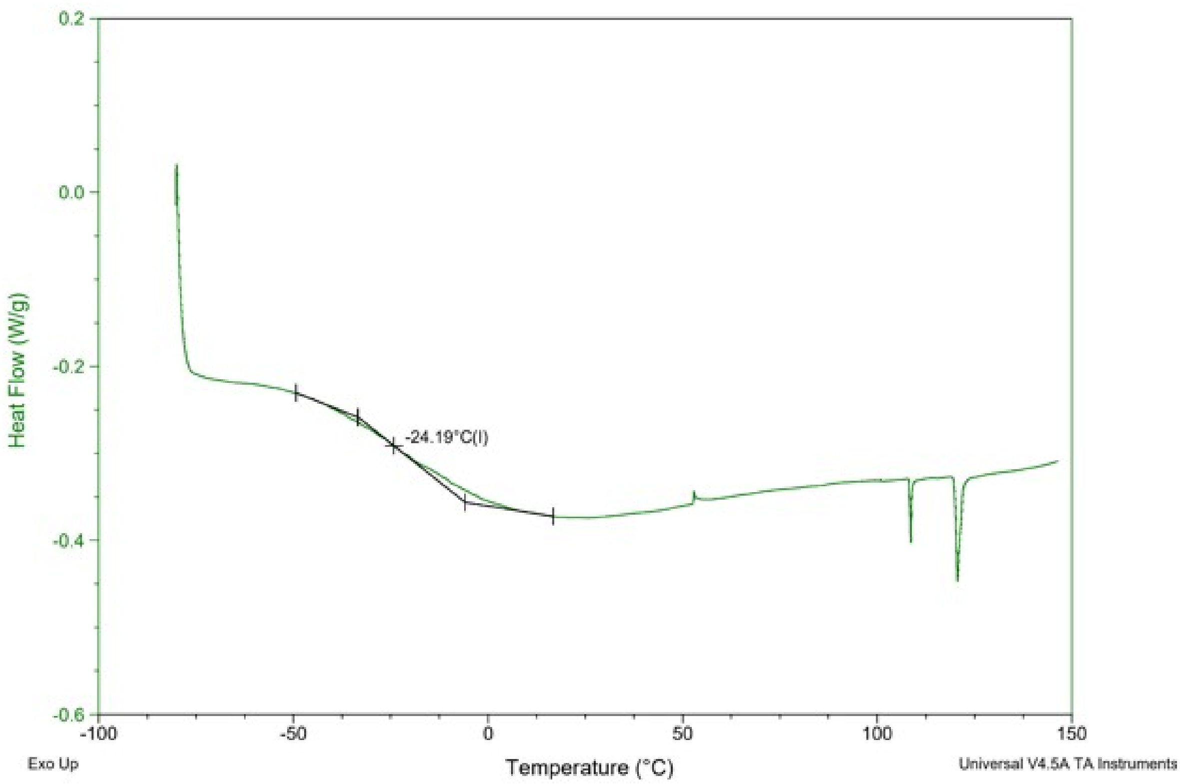


**Figure S23:** DSC scan of 20-poly(S-*r*-PVPSi) with $T_g$ measured at -24.19°C and elemental sulfur shown to melt at 120°C.

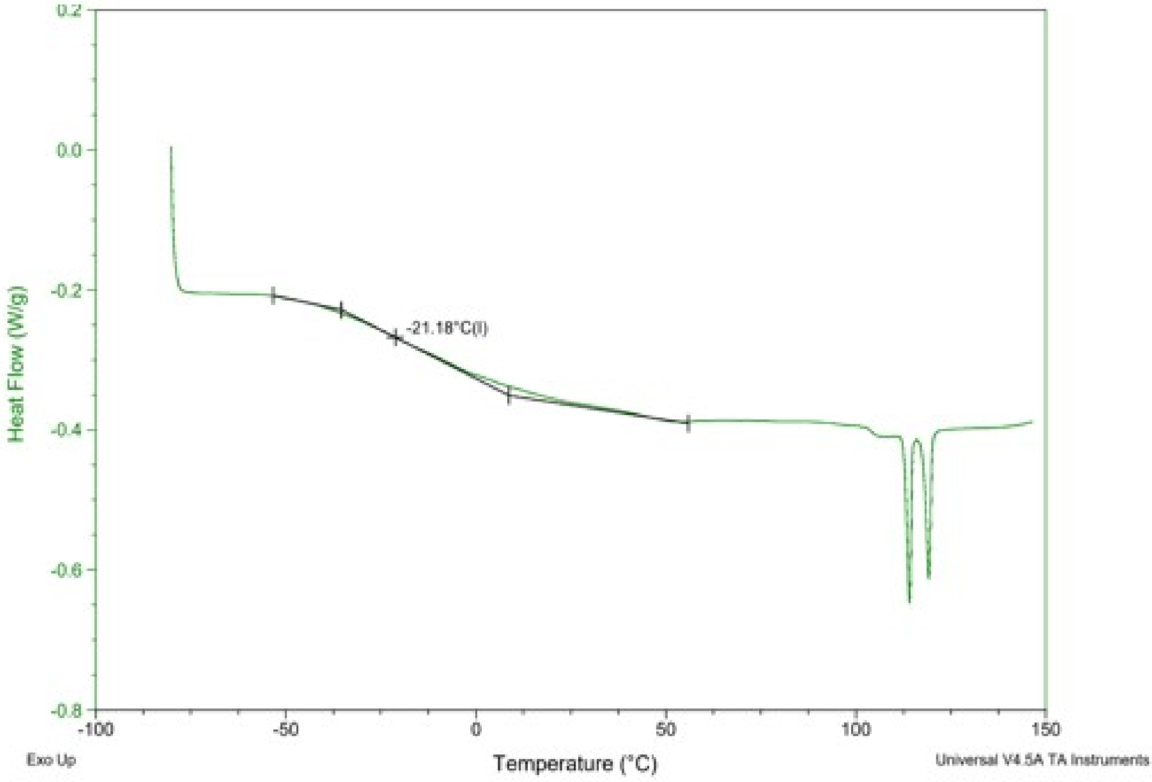


**Figure S24:** DSC scan of 30-poly(S-*r*-PVPSi) with $T_g$ measured at -21.18°C and elemental sulfur shown to melt at 120°C.

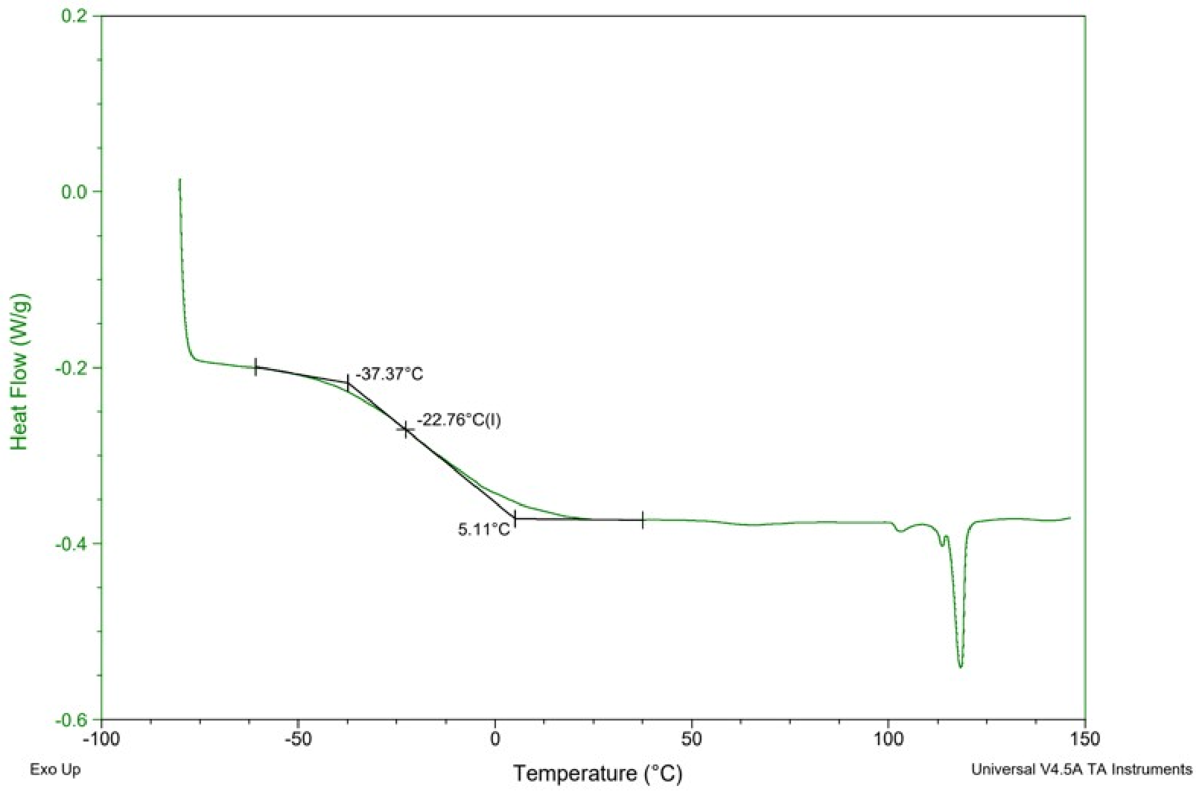


**Figure S25:** DSC scan of 40-poly(S-*r*-PVPSi) with $T_g$ measured at -22.76°C and elemental sulfur shown to melt at 120°C.

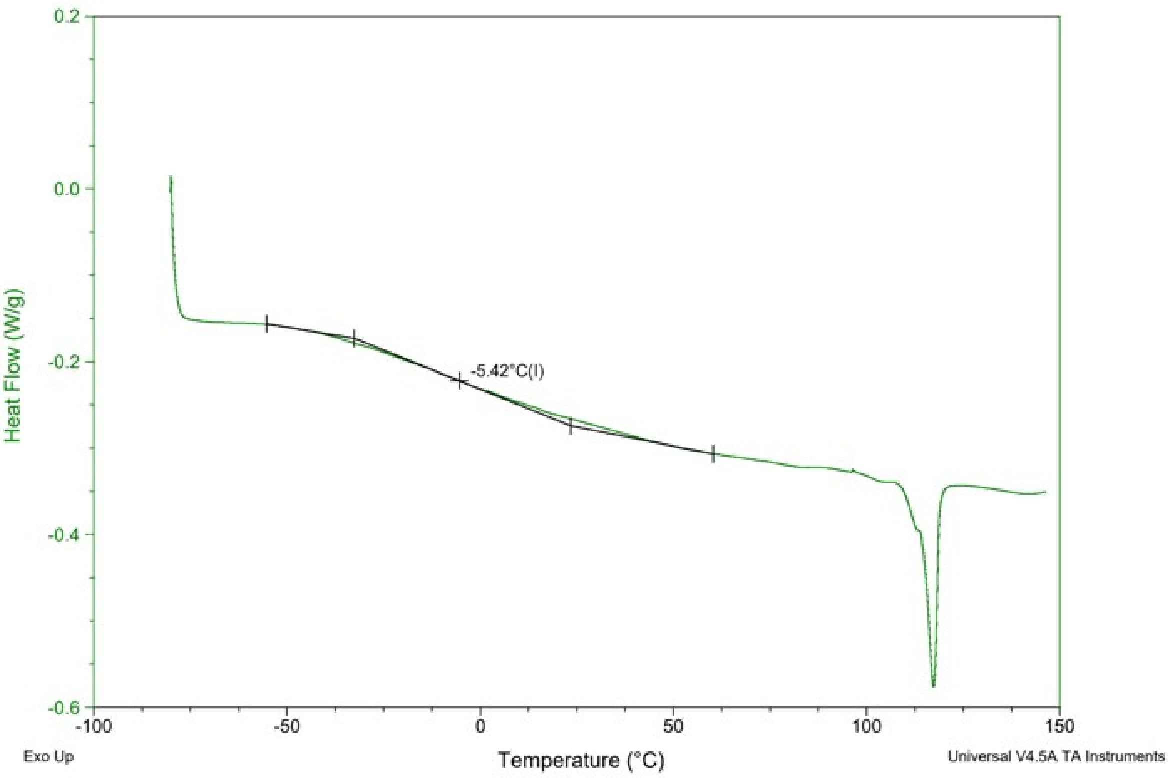


**Figure S26:** DSC scan of 50-poly(S-*r*-PVPSi) with $T_g$ measured at -5.42°C and elemental sulfur shown to melt at 120°C.

| polysuflide mass before (g) | solvent | solvent volume (mL) | time/h | polysulfide mass after(g) | mass difference (g) | swelling (%) | volume absorbed(mL) |
|---|---|---|---|---|---|---|---|
| 0.02 | Et2O | 1 | 24 | 0.0268 | 0.0068 | 34 | 0.009537167 |
| 0.0198 | Et2O | 1 | 24 | 0.0369 | 0.0171 | 86.36363636 | 0.02398317 |
| 0.0199 | Et2O | 1 | 24 | 0.0362 | 0.0163 | 81.90954774 | 0.02286115 |
| 0.0205 | DCM | 1 | 24 | 0.065 | 0.0445 | 217.0731707 | 0.033458647 |
| 0.0203 | DCM | 1 | 24 | 0.0753 | 0.055 | 270.9359606 | 0.041353383 |
| 0.0203 | DCM | 1 | 24 | 0.0731 | 0.0528 | 260.0985222 | 0.039699248 |
| 0.0191 | hexane | 1 | 24 | 0.0248 | 0.0057 | 29.84293194 | 0.00870229 |
| 0.0205 | hexane | 1 | 24 | 0.0272 | 0.0067 | 32.68292683 | 0.010229008 |
| 0.0206 | hexane | 1 | 24 | 0.0273 | 0.0067 | 32.52427184 | 0.010229008 |
| 0.0198 | toluene | 1 | 24 | 0.0258 | 0.006 | 30.3030303 | 0.006920415 |
| 0.0209 | toluene | 1 | 24 | 0.0265 | 0.0056 | 26.79425837 | 0.006459054 |
| 0.0202 | toluene | 1 | 24 | 0.0269 | 0.0067 | 33.16831683 | 0.007727797 |
| 0.0201 | benzene | 1 | 24 | 0.0386 | 0.0185 | 92.039801 | 0.021118721 |
| 0.0204 | benzene | 1 | 24 | 0.0381 | 0.0177 | 86.76470588 | 0.020205479 |
| 0.0203 | benzene | 1 | 24 | 0.044 | 0.0237 | 116.7487685 | 0.027054795 |
| 0.0206 | octane | 1 | 24 | 0.0247 | 0.0041 | 19.90291262 | 0.005832148 |
| 0.0206 | octane | 1 | 24 | 0.0242 | 0.0036 | 17.47572816 | 0.00512091 |
| 0.0197 | octane | 1 | 24 | 0.0225 | 0.0028 | 14.21319797 | 0.00398293 |
| 0.02 | water | 1 | 24 | 0.02 | 0 | 0 | 0 |
| 0.0208 | water | 1 | 24 | 0.0208 | 0 | 0 | 0 |
| 0.0207 | water | 1 | 24 | 0.0208 | 1E-04 | 0.483091787 | 1E-04 |
| 0.0202 | ethanol | 1 | 24 | 0.0202 | 0 | 0 | 0 |
| 0.0203 | ethanol | 1 | 24 | 0.0203 | 0 | 0 | 0 |
| 0.02 | ethanol | 1 | 24 | 0.02 | 0 | 0 | 0 |
| 0.02 | methanol | 1 | 24 | 0.02 | 0 | 0 | 0 |
| 0.0204 | methanol | 1 | 24 | 0.0204 | 0 | 0 | 0 |
| 0.0197 | methanol | 1 | 24 | 0.0197 | 0 | 0 | 0 |

**Table S1:** Data for the initial absorbance testing of 20-poly-(S-*r*-TVTSi)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 0.02 | Et2O | 1 | 24 | 0.0298 | 0.0098 | 49 | 0.013744741 |
| 0.0203 | Et2O | 1 | 24 | 0.0289 | 0.0086 | 42.36453202 | 0.012061711 |
| 0.0201 | Et2O | 1 | 24 | 0.0297 | 0.0096 | 47.76119403 | 0.013464236 |
| 0.0199 | DCM | 1 | 24 | 0.038 | 0.0181 | 90.95477387 | 0.013609023 |
| 0.0202 | DCM | 1 | 24 | 0.0382 | 0.018 | 89.10891089 | 0.013533835 |
| 0.0203 | DCM | 1 | 24 | 0.0376 | 0.0173 | 85.22167488 | 0.013007519 |
| 0.02 | hexane | 1 | 24 | 0.0266 | 0.0066 | 33 | 0.010076336 |
| 0.02 | hexane | 1 | 24 | 0.0262 | 0.0062 | 31 | 0.009465649 |
| 0.0201 | hexane | 1 | 24 | 0.0284 | 0.0083 | 41.29353234 | 0.012671756 |
| 0.0202 | toluene | 1 | 24 | 0.0386 | 0.0184 | 91.08910891 | 0.021222607 |
| 0.0201 | toluene | 1 | 24 | 0.0415 | 0.0214 | 106.4676617 | 0.024682814 |
| 0.0202 | toluene | 1 | 24 | 0.0419 | 0.0217 | 107.4257426 | 0.025028835 |
| 0.02 | benzene | 1 | 24 | 0.0292 | 0.0092 | 46 | 0.010502283 |
| 0.02 | benzene | 1 | 24 | 0.0329 | 0.0129 | 64.5 | 0.014726027 |
| 0.0203 | benzene | 1 | 24 | 0.0315 | 0.0112 | 55.17241379 | 0.012785388 |
| 0.02 | octane | 1 | 24 | 0.0316 | 0.0116 | 58 | 0.016500711 |
| 0.0199 | octane | 1 | 24 | 0.0315 | 0.0116 | 58.29145729 | 0.016500711 |
| 0.02 | octane | 1 | 24 | 0.0305 | 0.0105 | 52.5 | 0.014935989 |
| 0.02 | water | 1 | 24 | 0.02 | 0 | 0 | 0 |
| 0.0206 | water | 1 | 24 | 0.0206 | 0 | 0 | 0 |
| 0.0207 | water | 1 | 24 | 0.0207 | 0 | 0 | 0 |
| 0.02 | ethanol | 1 | 24 | 0.02 | 0 | 0 | 0 |
| 0.0196 | ethanol | 1 | 24 | 0.0196 | 0 | 0 | 0 |
| 0.0201 | ethanol | 1 | 24 | 0.0201 | 0 | 0 | 0 |
| 0.02 | methanol | 1 | 24 | 0.02 | 0 | 0 | 0 |
| 0.0203 | methanol | 1 | 24 | 0.0203 | 0 | 0 | 0 |
| 0.0209 | methanol | 1 | 24 | 0.0211 | 0.0002 | 0.956937799 | 0.000252525 |

**Table S2:** Data for the initial absorbance testing of 20-poly-(S-*r*-PVPSi)

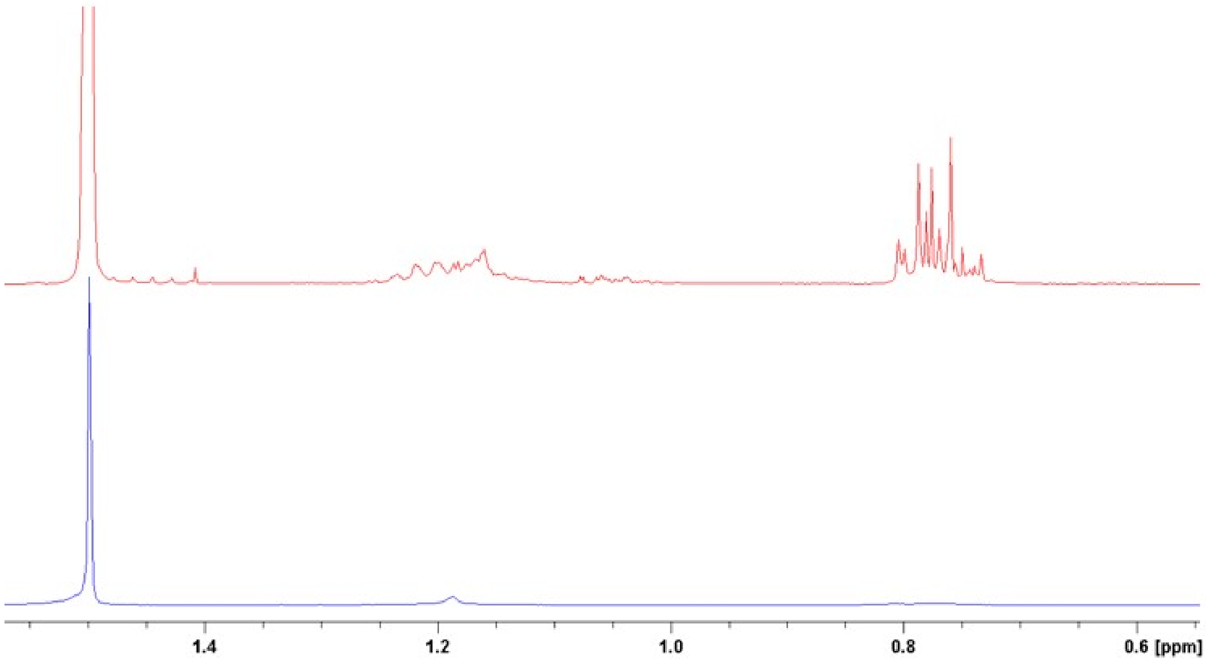


**Figure S27:** Comparison of $^{1}H$ NMR spectra ($CDCl_3$) of a 5000 ppm hexane solution in water before (top, red) and after (bottom, blue) the addition of 20-poly-(S-*r*-TVTSi) for 24 hours.

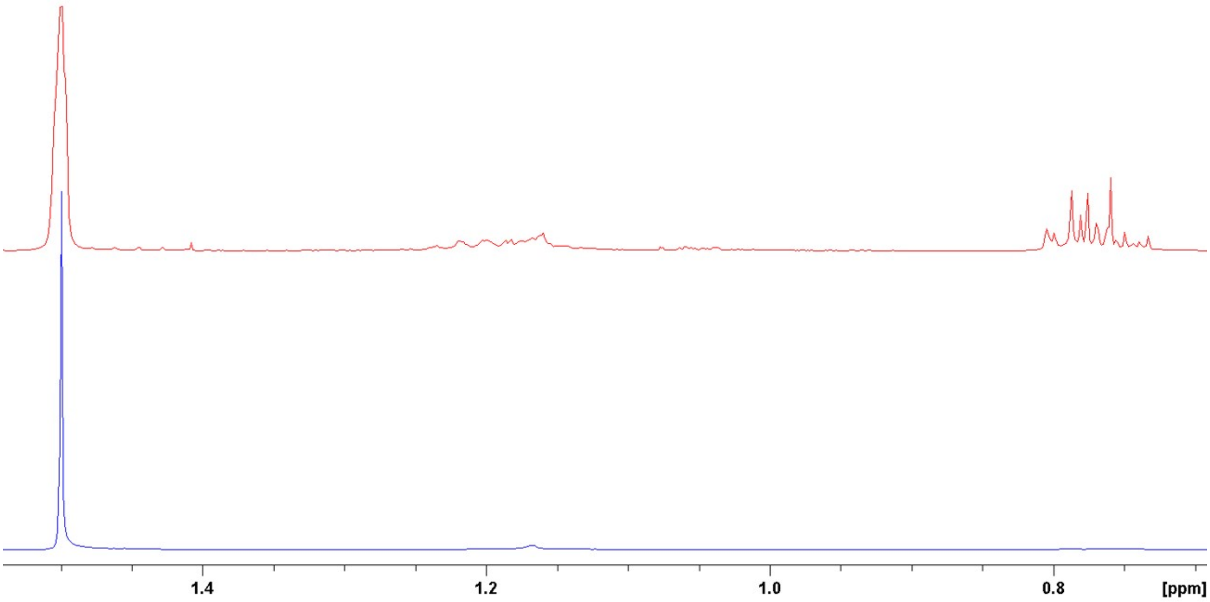


**Figure S28:** Comparison of [1]H NMR spectra ($CDCl_3$) of a 5000 ppm hexane solution in water before (top, red) and after (bottom, blue) the addition of 20-poly-(S-*r*-PVPSi) for 24 hours.

| Sample | Integration at 1.28ppm | Difference of hexane integration from stock (%) |
|---|---|---|
| 5000 ppm Stock solution | 1.627 | 0 |
| 1st | 0.4883 | 69.98770744 |
| 2nd | 0.4487 | 72.42163491 |
| 3rd | 0.4718 | 71.00184388 |
| 4th | 0.4604 | 71.70251998 |

**Table S3:** Analysis and calculation % hexanes removed for recycling testing of 20-poly(S-*r*-PVPSi) in different batches of contaminated water.

| Sample | Integration at 1.28ppm | Difference of hexane integration from previous addition (%) | Difference of hexane integration from stock (%) |
|---|---|---|---|
| 5000 ppm Stock solution | 1.627 | 0 | 0 |
| 1st | 0.4928 | 69.71112477 | 69.71112477 |
| 2nd | 0.4829 | 2.008928571 | 70.31960664 |
| 3rd | 0.4819 | 0.207082212 | 70.38106945 |
| 4th | 0.4779 | 0.830047728 | 70.62692071 |

**Table S4:** Analysis and calculation of total % hexanes removed for multiple cycles of adding 20-poly(S-*r*-PVPSi) to the same 5000 ppm hexanes in water solution.