Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Silicone vitrimers prepared by vulcanisation of pendant vinylpolysiloxanes with elemental sulfur

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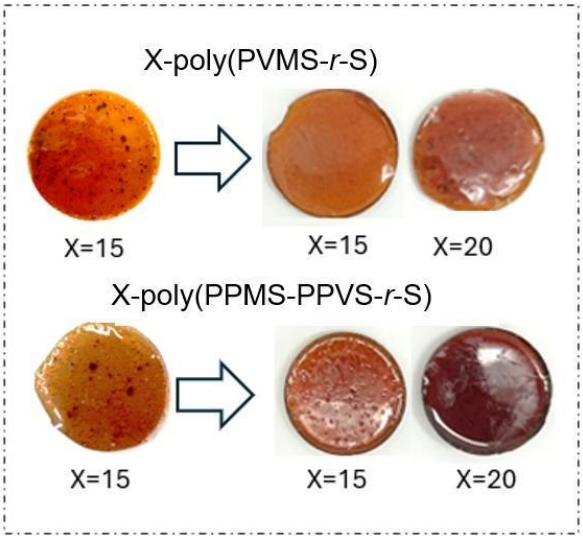

Figure S1- Comparison of sulfur addition strategies in vinyl polysiloxanes. Left: single-step sulfur addition causing phase separation. Right: portion wise sulfur addition (5 wt% sulfur increments every 15 min) yielding more homogeneous networks.

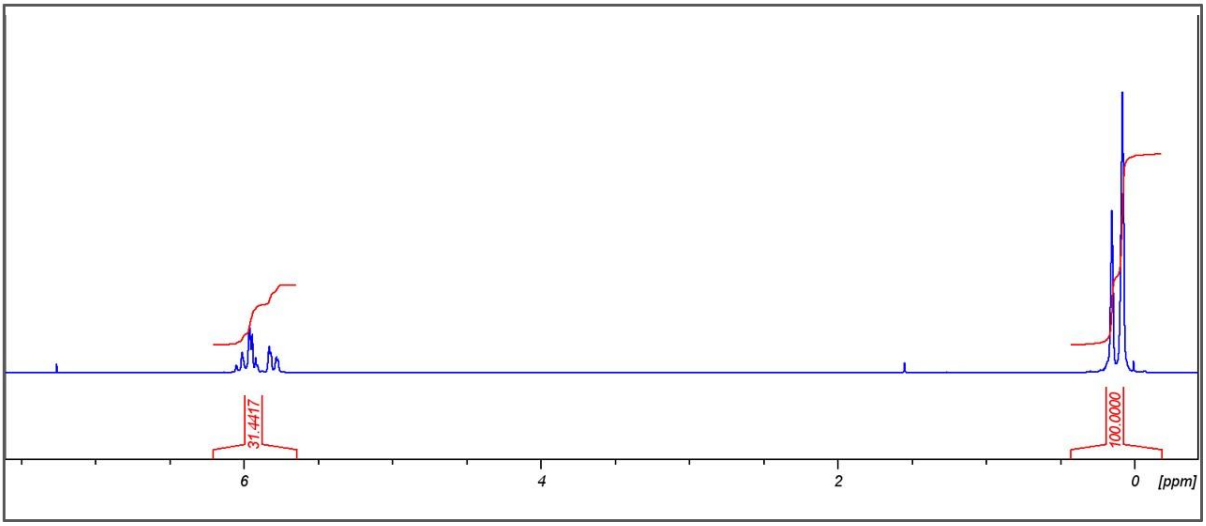

Figure S2- ^{1}H NMR spectrum of 0-poly(PDMS-PVMS-r-S) in $CDCl_3$ at t = 0 min with integrated vinyl and methyl signals

Table S1- Correlation of viscosity, vinyl-to-methyl proton integration, vitrification time, and vinyl-group consumption for the 7 and 10 wt % sulfur-cross-linked networks

Sample	Viscosity (cSt)	Initial vinyl/ Me	Vitrification time (min)	Vinyl/Me at vitrification	Vinyl/Me after solidification	% vinyl-group reduction at vitrification (%)	% vinyl-group reduction after solidification (%)
7-poly(PDMSPVMS-*r*-S)	4500 – 5500	31	35	30	29	5	9
10-poly(PVMS-*r*-S)	7 – 15	27	140	43	31	36	54
10-poly(PPMSPPVS-*r*-S)	80 – 150	62	240	43	n.d.*	31	n.d.

n.d. : not determined owing to severe peak broadening in the SS ^{1}H NMR spectrum after full curing.

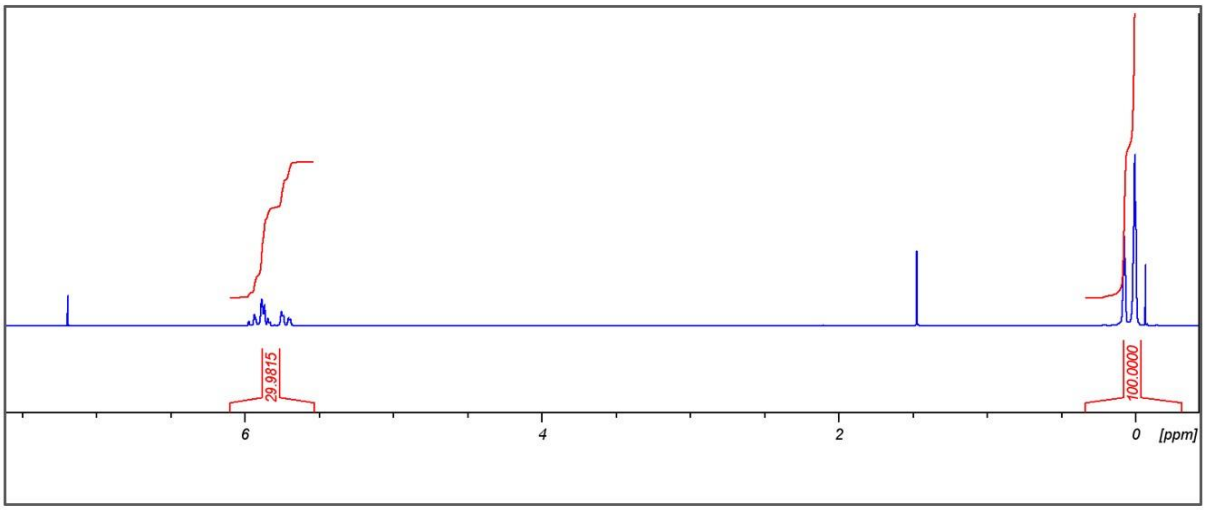

Figure S3- ^{1}H NMR spectrum of 7-poly(PDMS-PVMS-r-S) in $CDCl_3$ at the vitrification point (35 min), showing integrated vinyl and methyl signal

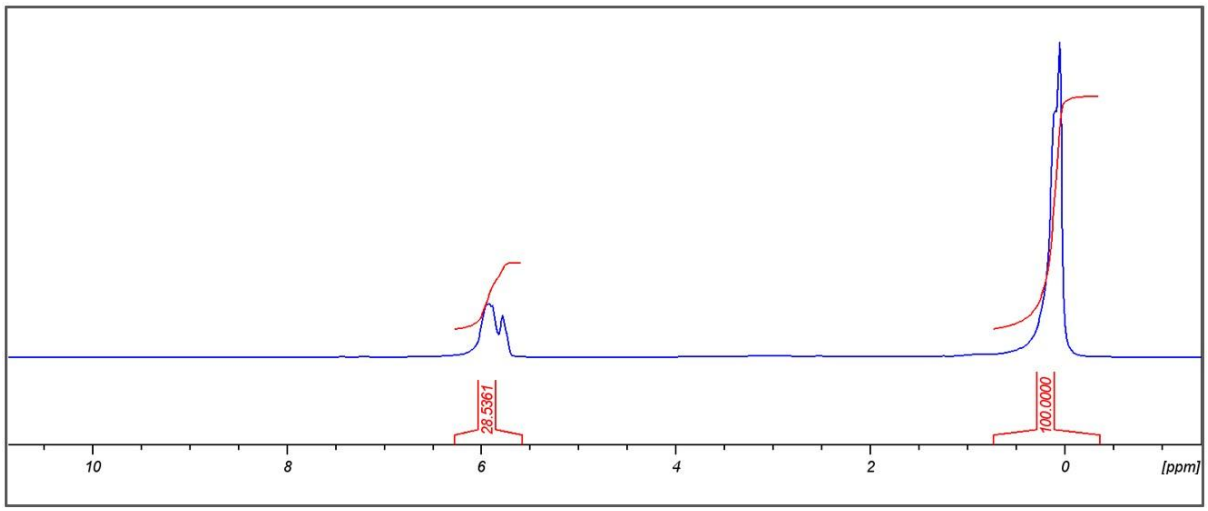

Figure S4- SS ^{1}H NMR spectrum of 7-poly(PDMS-PVMS-r-S) in $CDCl_3$ after full solidification, showing integrated vinyl and methyl signals

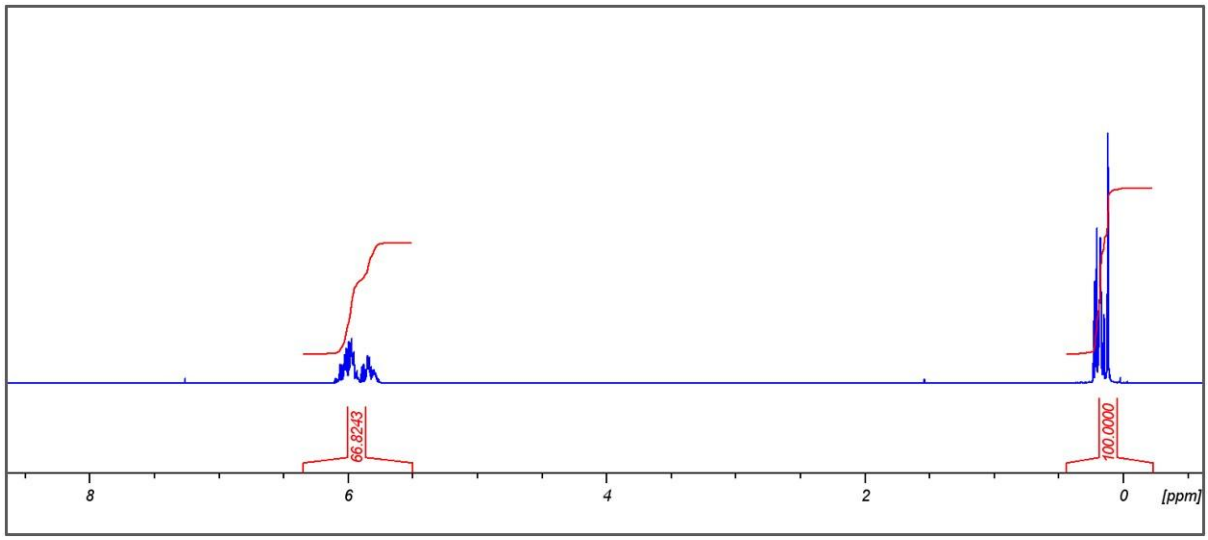

Figure S5-¹H NMR spectrum of 0-poly(PVMS-r-S) in $CDCl_3$ at t = 0 min, showing integrated vinyl and methyl signals

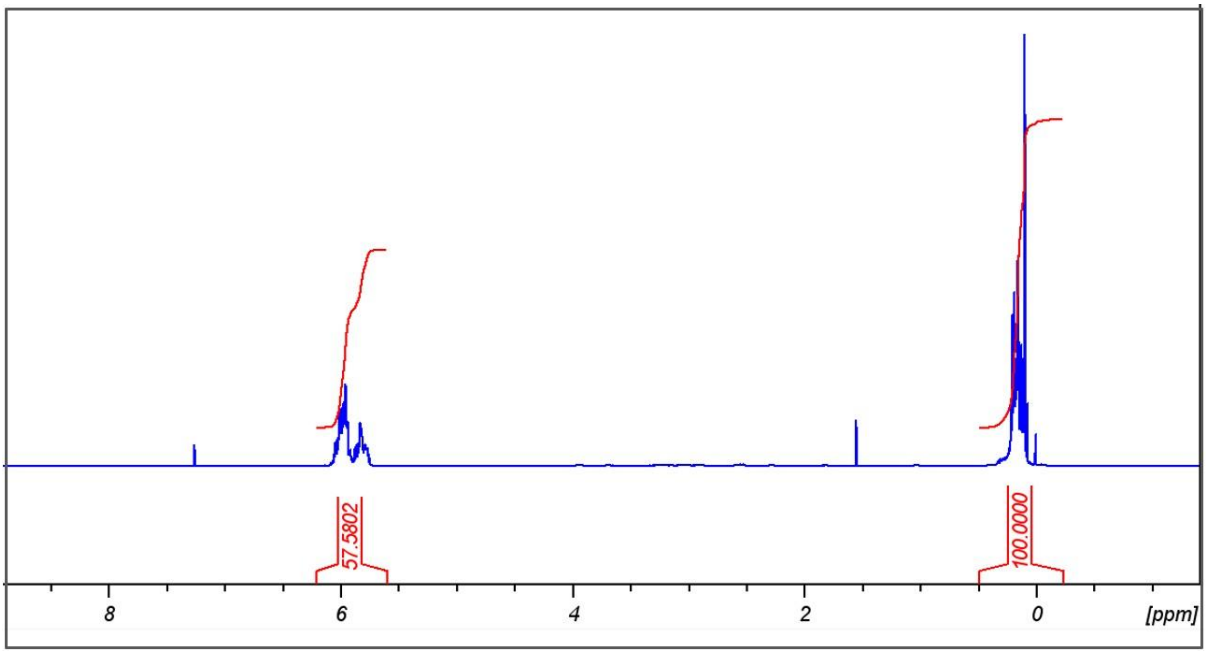

Figure S6- ¹H NMR spectrum of 10-poly(PVMS-r-S) in $CDCl_3$ at vitrification (140 min), showing integrated vinyl and methyl signals

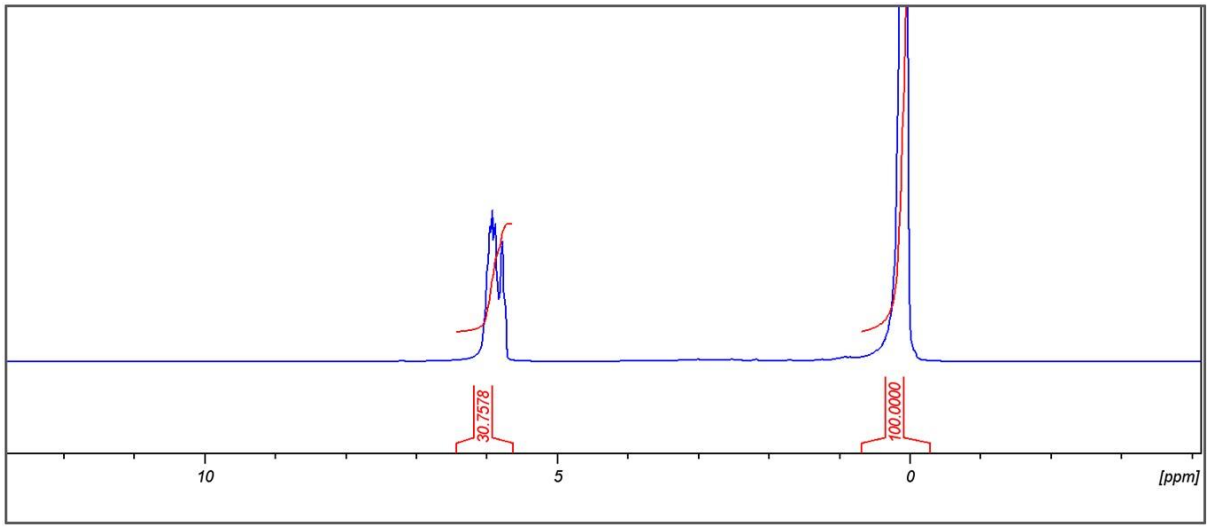

Figure S7- SS ^{1}H NMR spectrum of 10-poly(PVMS-r-S) after full solidification, showing integrated vinyl and methyl signals

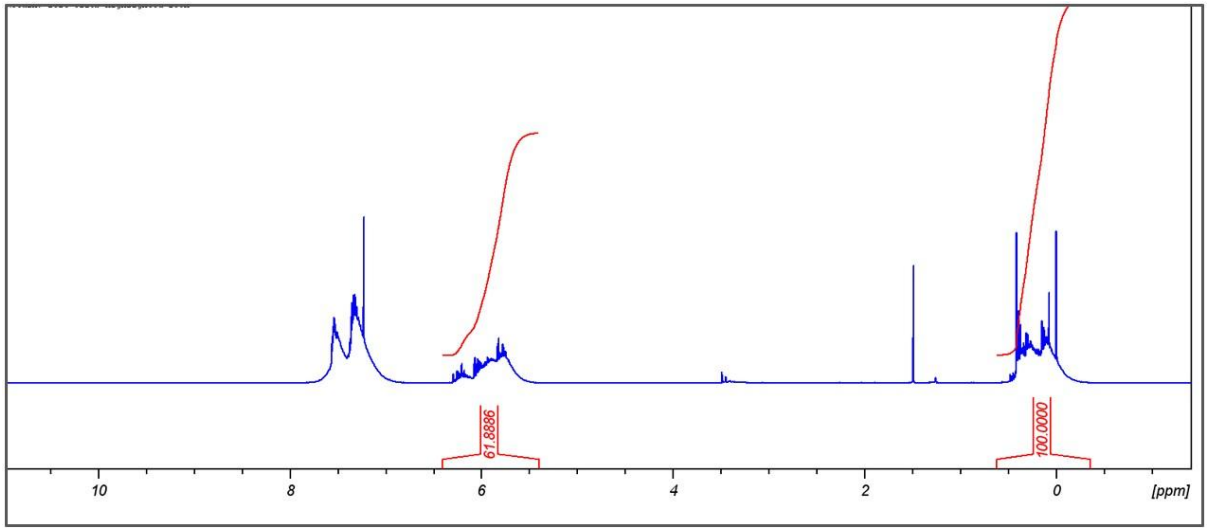

Figure S8- ^{1}H NMR spectrum of 0-poly(PPMS-PPVS-r-S) in $CDCl_3$ at t = 0 min, showing integrated vinyl and methyl signals

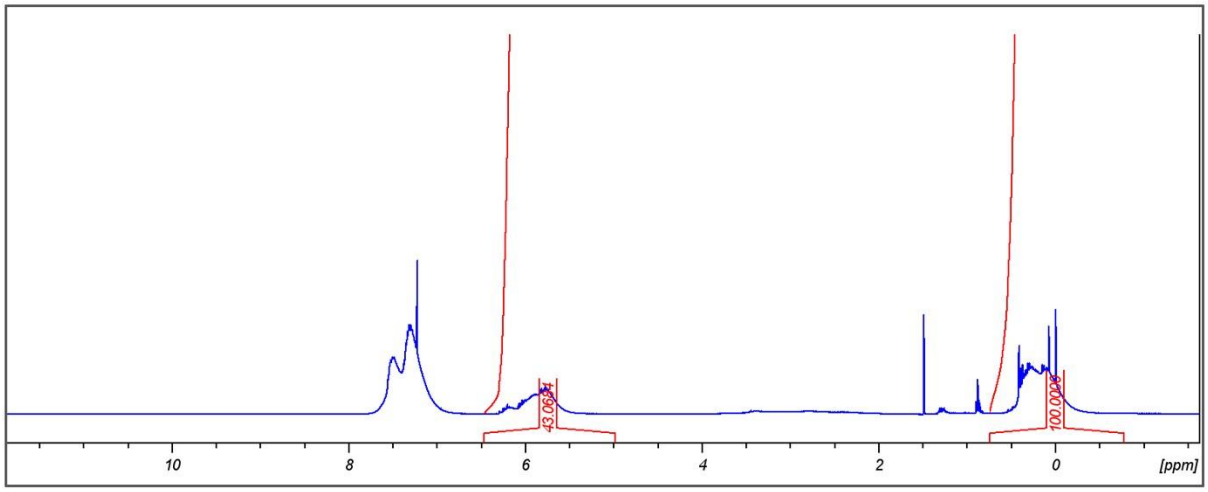

Figure S9- ^{1}H NMR spectrum of 10-poly(PPMS-PPVS-r-S) in $CDCl_3$ at vitrification (240 min), showing integrated vinyl and methyl signals

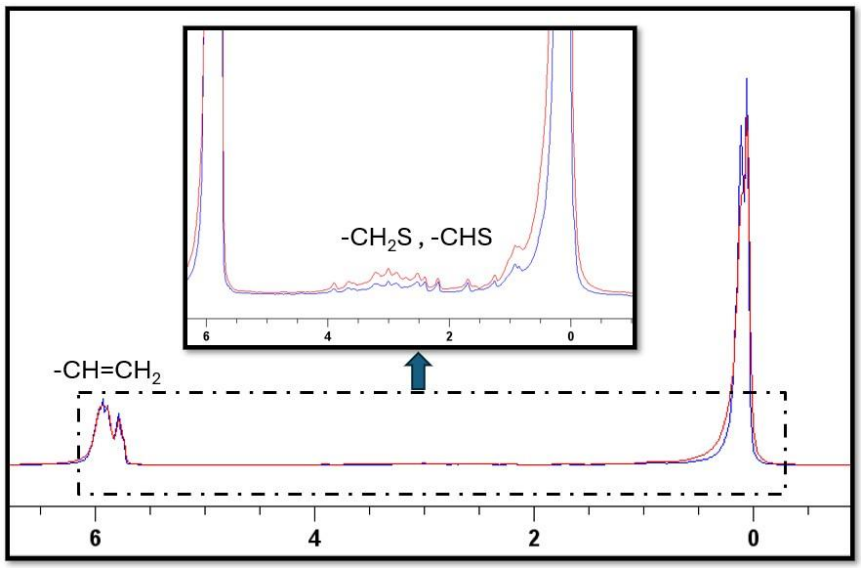

Figure S10- Comparison of SS ^{1}H NMR spectra of 5-poly(PDMS-PVMS-r-S) (blue) and 7-poly(PDMS-PVMS-r-S) (red)

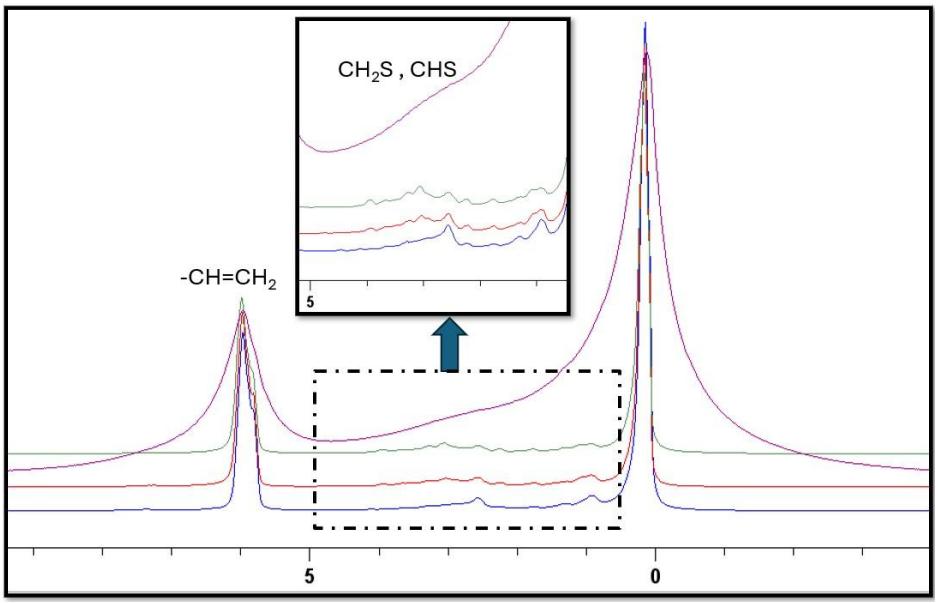

Figure S11- Comparison of SS ^{1}H NMR spectra of 5-poly(PVMS-r-S) (blue), 10-poly(PVMS-r-S) (red), 15-poly(PVMS-r-S) (green), and 20-poly(PVMS-r-S) (purple)

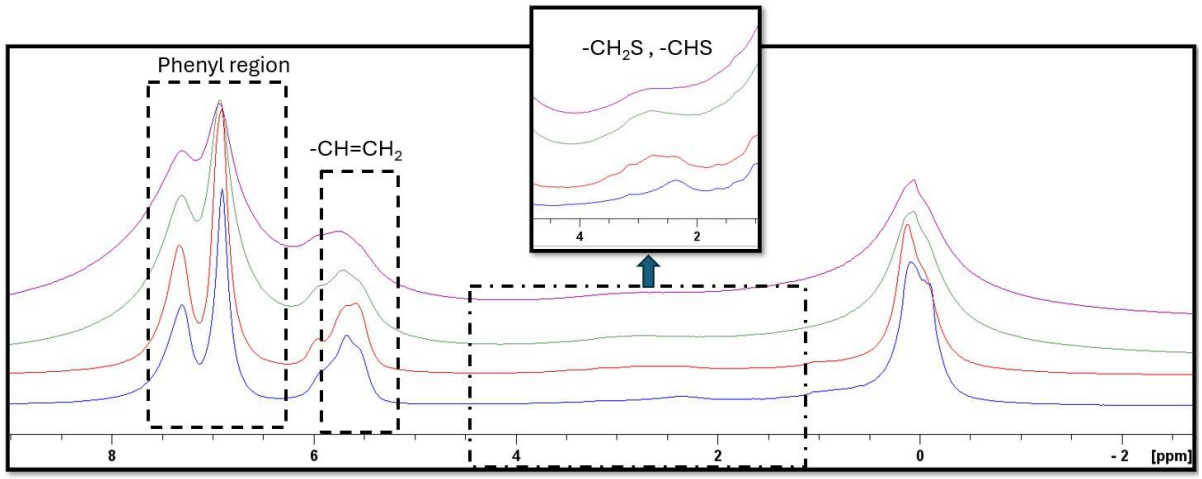

Figure S12- Comparison of SS ^{1}H NMR spectra of 5-poly(PPMS-PPVS-r-S) (blue), 10-poly(PPMS-PPVS-r-S) (red), 15poly(PPMS-PPVS-r-S) (green), and 20-poly(PPMS-PPVS-r-S) (purple)

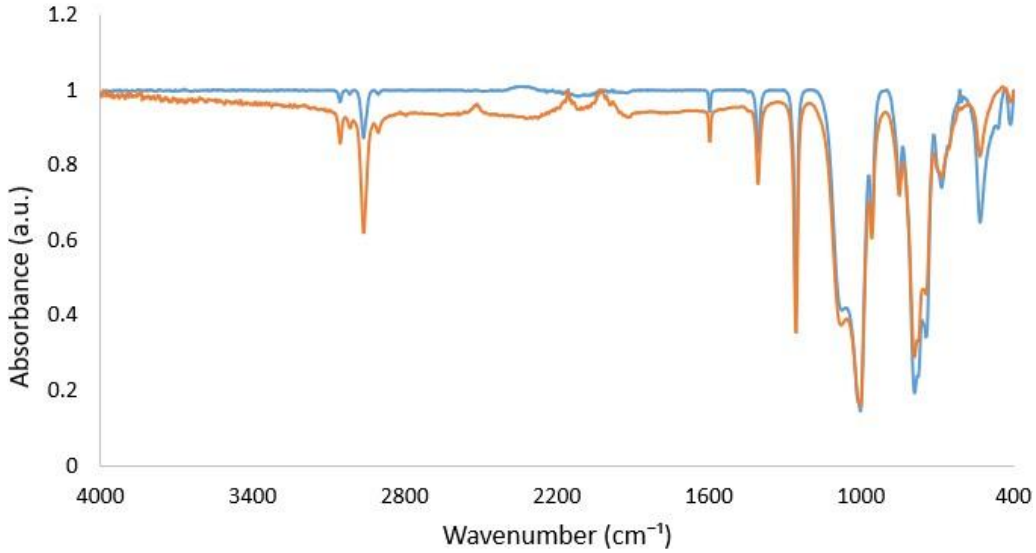

Figure S13- FT-IR spectra of 5-poly(PPMS-PPVS-r-S) before (blue) and after (orange) crosslinking

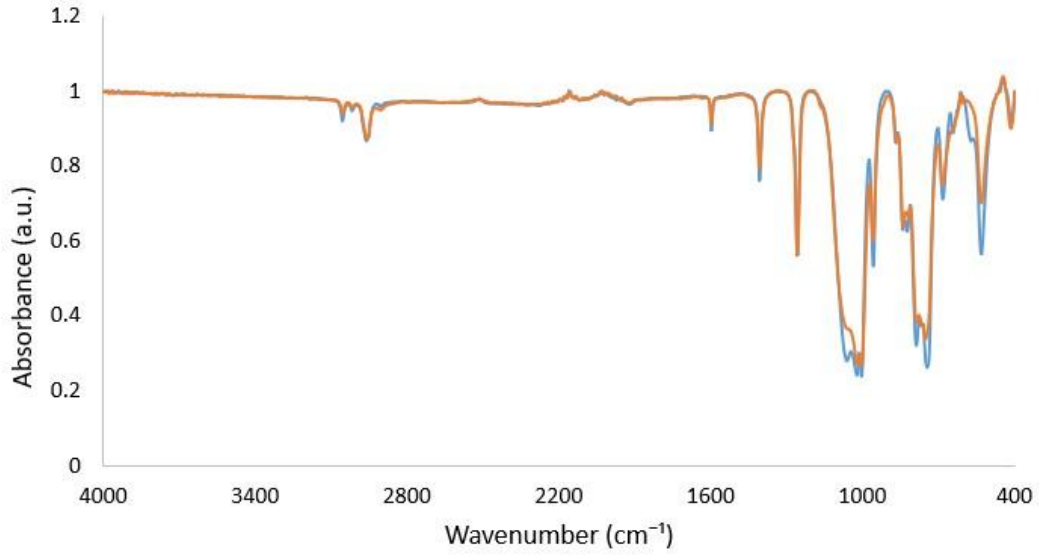

Figure S14- FT-IR spectra of 10-poly(PVMS-r-S) before (blue) and after (orange) sulfur crosslinking

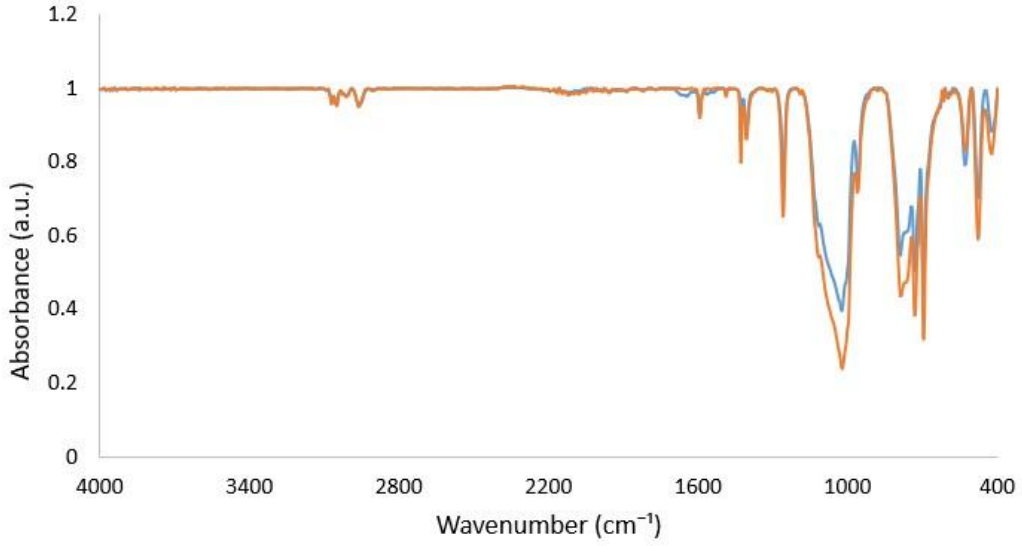

Figure S15- FT-IR spectra of 10-poly(PPMS-PPVS-r-S) before (blue) and after (orange) sulfur crosslinking Table S2- water contact angles (°) of X-poly(PDMS-PVMS-r-S), X-poly(PVMS-r-S), and X-poly(PPMS-PPVS-r-S) at different sulfur loadings (X). Values represent the mean of three independent measurements.

Sample	Sulfur loading (X, wt %)	Contact angle (°)
X-poly(PDMS-PVMS-*r*-S)	5	102.6
X-poly(PDMS-PVMS-*r*-S)	7	106.8
X-poly(PVMS-*r*-S)	5	101.4
X-poly(PVMS-*r*-S)	10	102.4
X-poly(PVMS-*r*-S)	15	103.4

X-poly(PVMS-*r*-S)	20	104.4
X-poly(PPMS-PPVS-*r*-S)	5	104.8
X-poly(PPMS-PPVS-*r*-S)	10	106.2
X-poly(PPMS-PPVS-*r*-S)	15	109.4
X-poly(PPMS-PPVS-*r*-S)	20	111.2

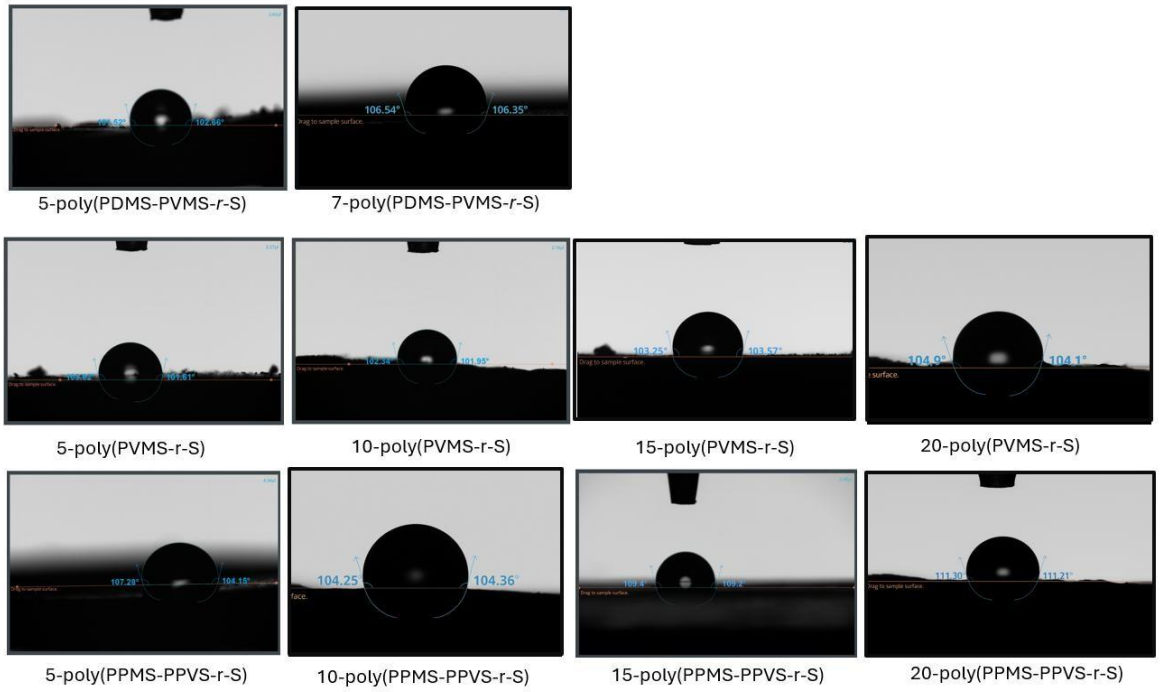

Figure S16- Examples of the contact angle measurements for X-poly(PDMS-PVMS-r-S) (5 and 7 wt% S), X-poly(PVMSr-S) (5–20 wt% S), and X-poly(PPMS-PPVS-r-S) (5–20 wt% S).

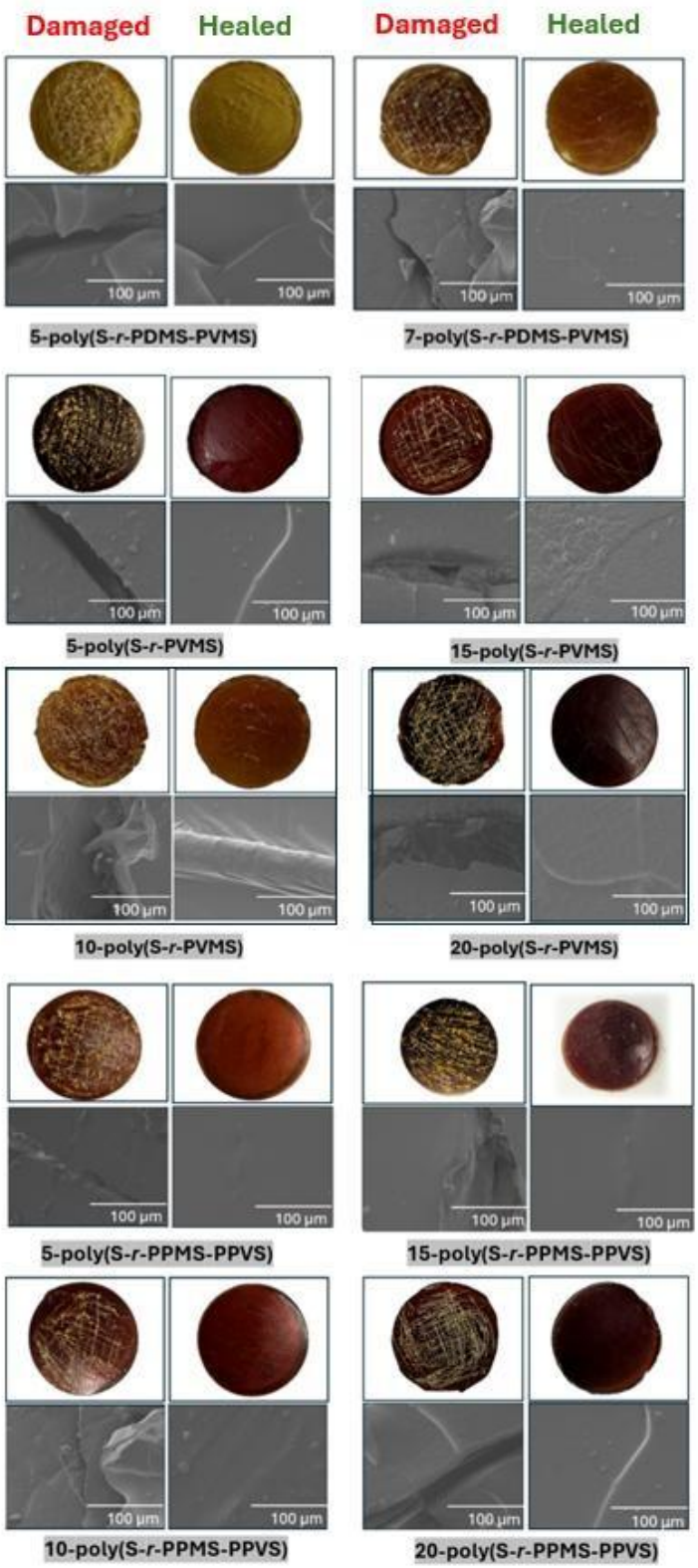

Figure S17- Visual and SEM characterisation of thermal self-healing for X-poly(PDMS-PVMS-r-S) (5 and 7 wt% S), X-poly(PVMS-r-S) (5–20 wt% S), and X-poly(PPMS-PPVS-r-S) (5–20 wt% S) after mechanical damage and thermal repair at 120°C for 48-50 h.

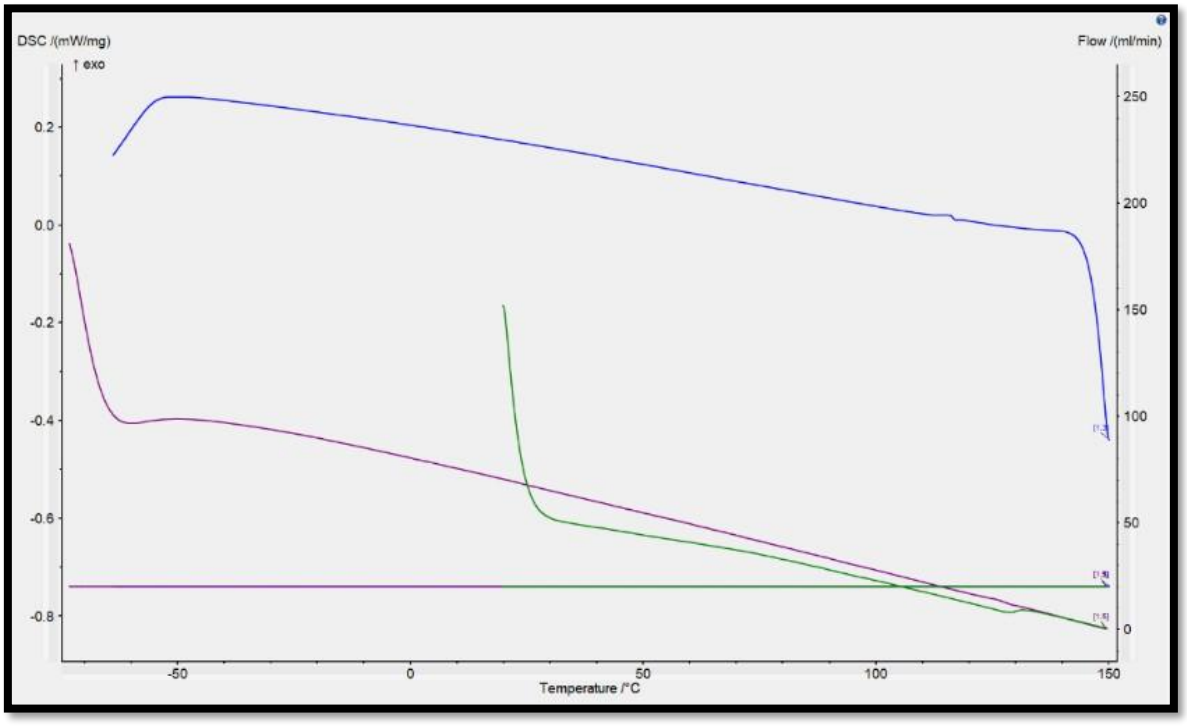

Figure S18- DSC thermogram of 5-poly(PDMS-PVMS-r-S)

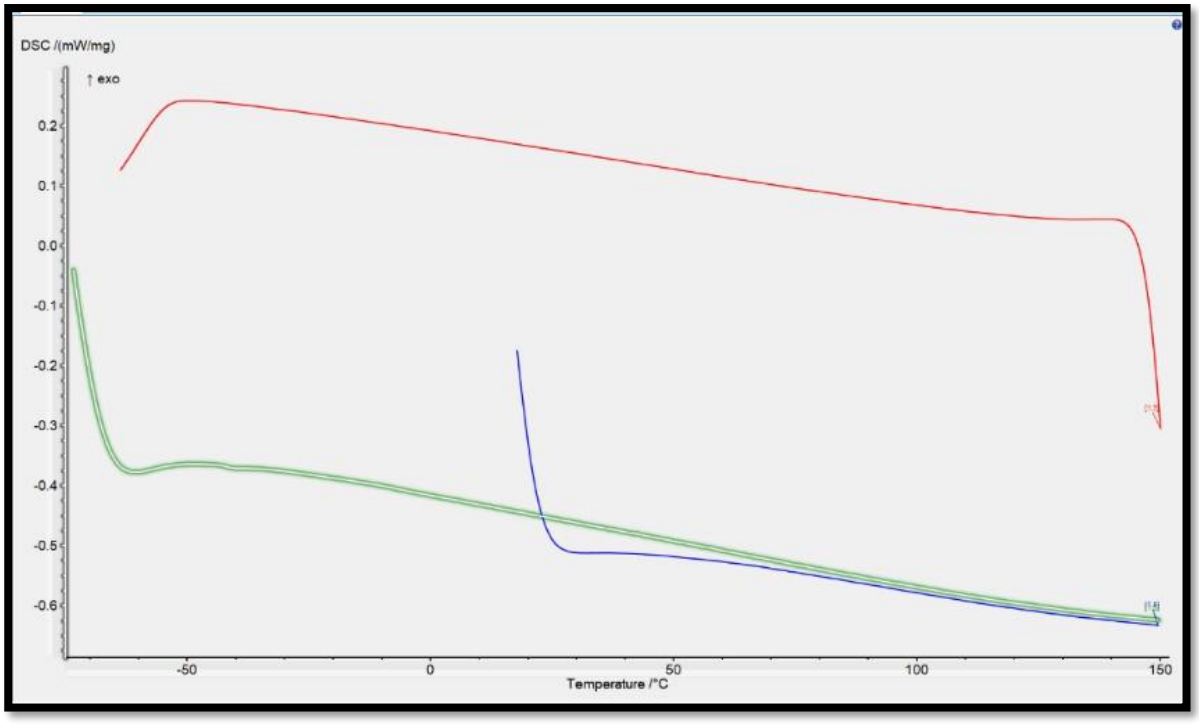

Figure S19- DSC thermogram of 7-poly(PDMS-PVMS-r-S)

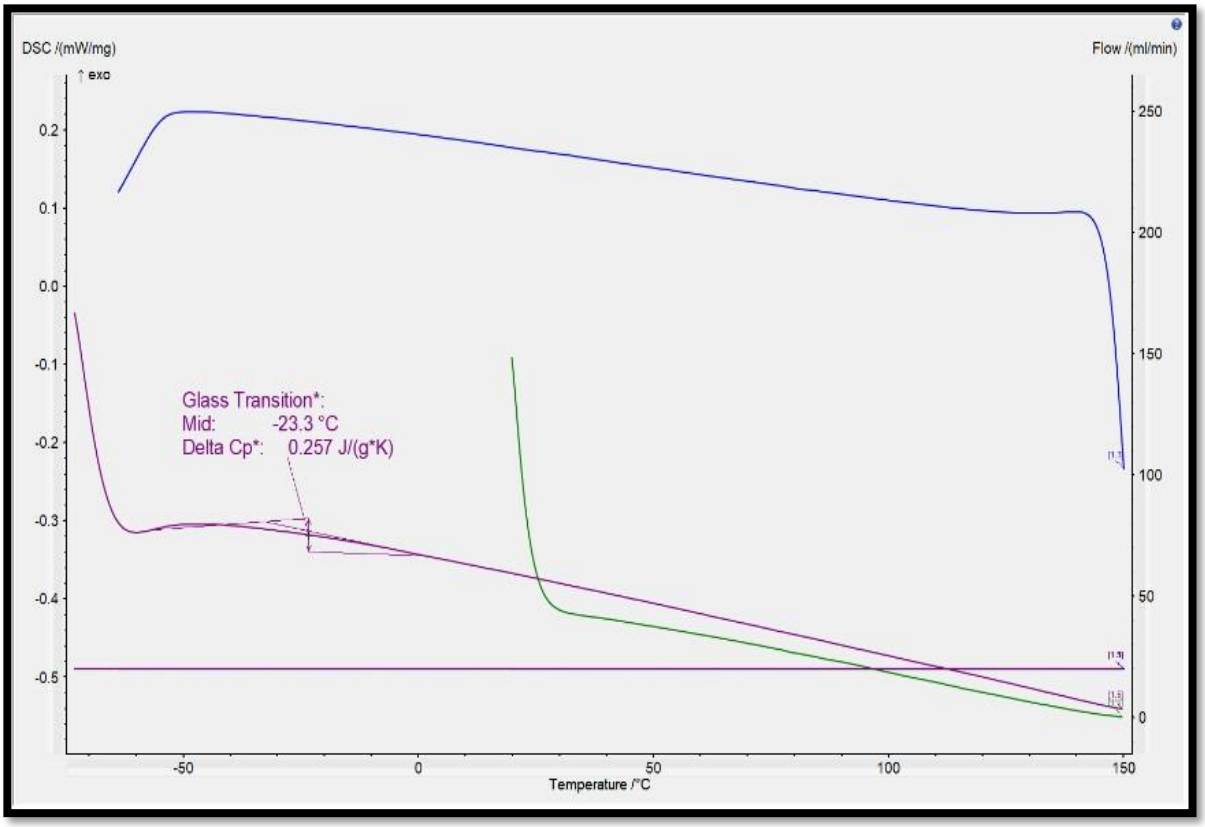

Figure S20- DSC thermogram of 5-poly(PVMS-r-S)

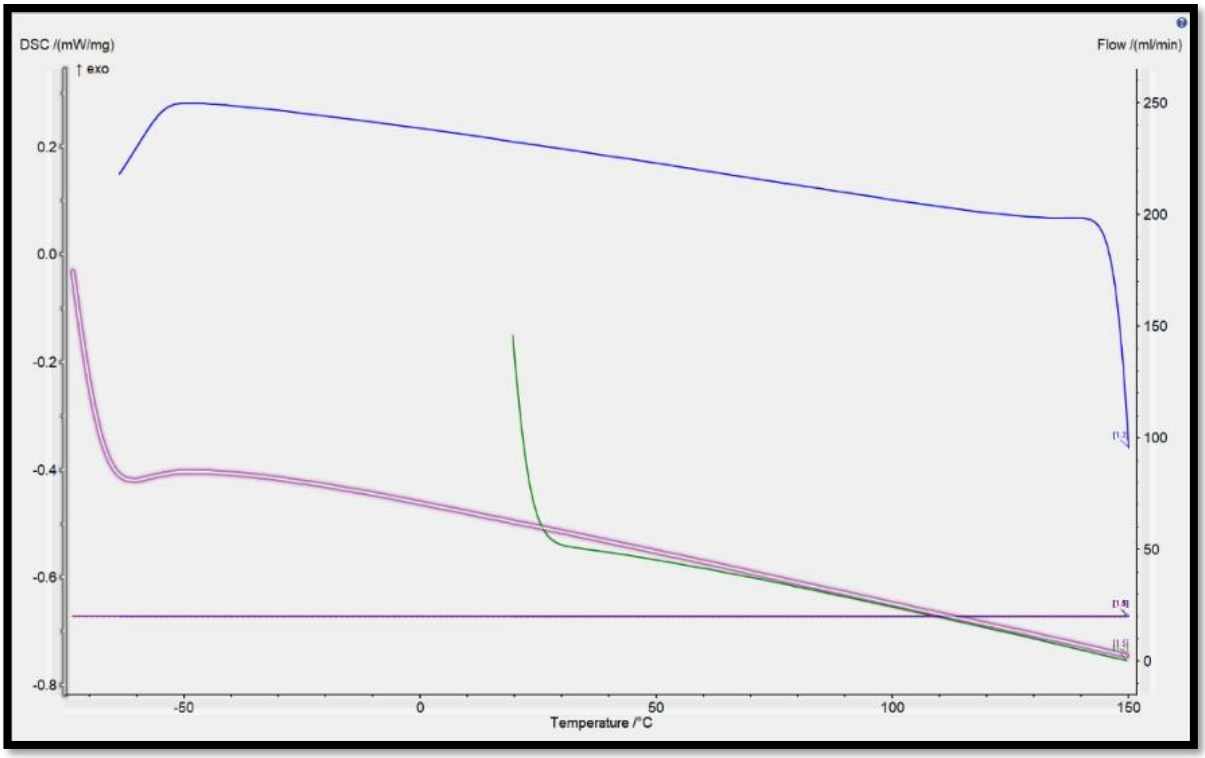

Figure S21- DSC thermogram of 10-poly(PVMS-r-S)

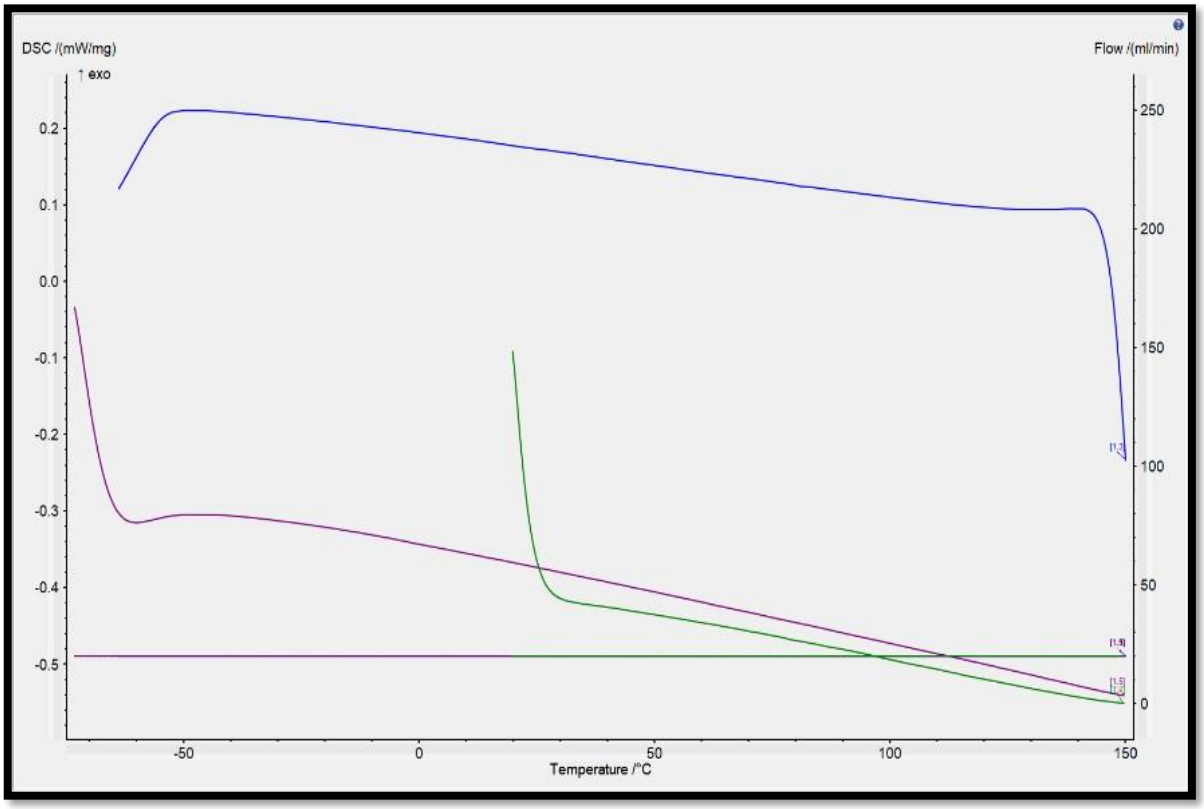

Figure S22- DSC thermogram of 15-poly(PVMS-r-S)

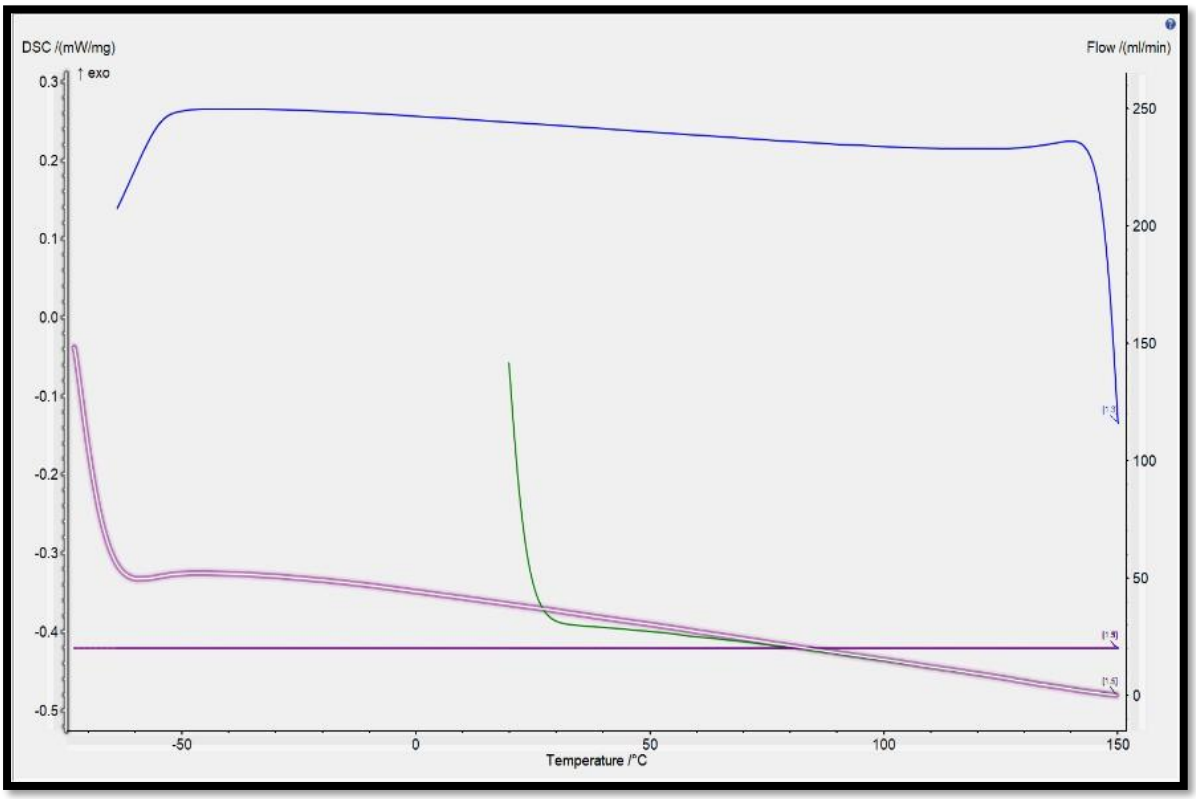

Figure S23- DSC thermogram of 20-poly(PVMS-r-S)

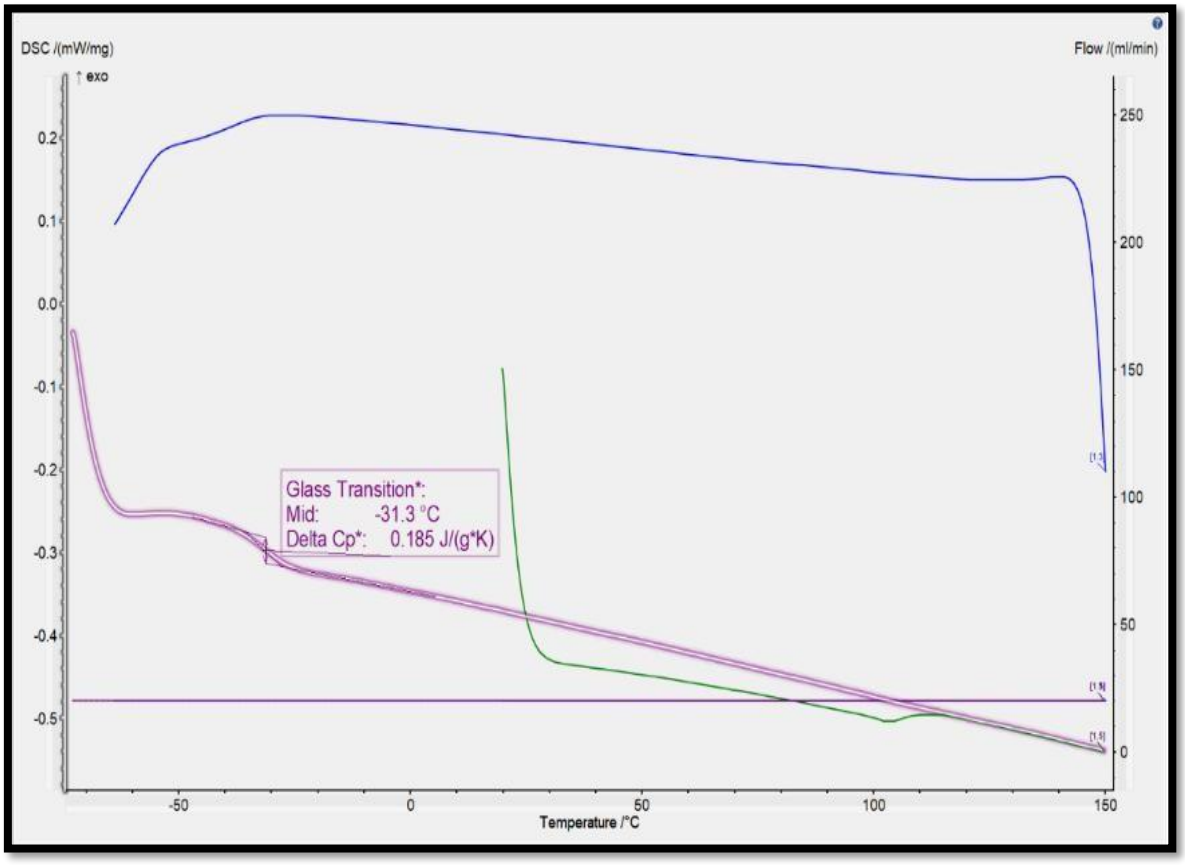

Figure S24- DSC thermogram of 5-poly(PPMS-PPVS-r-S)

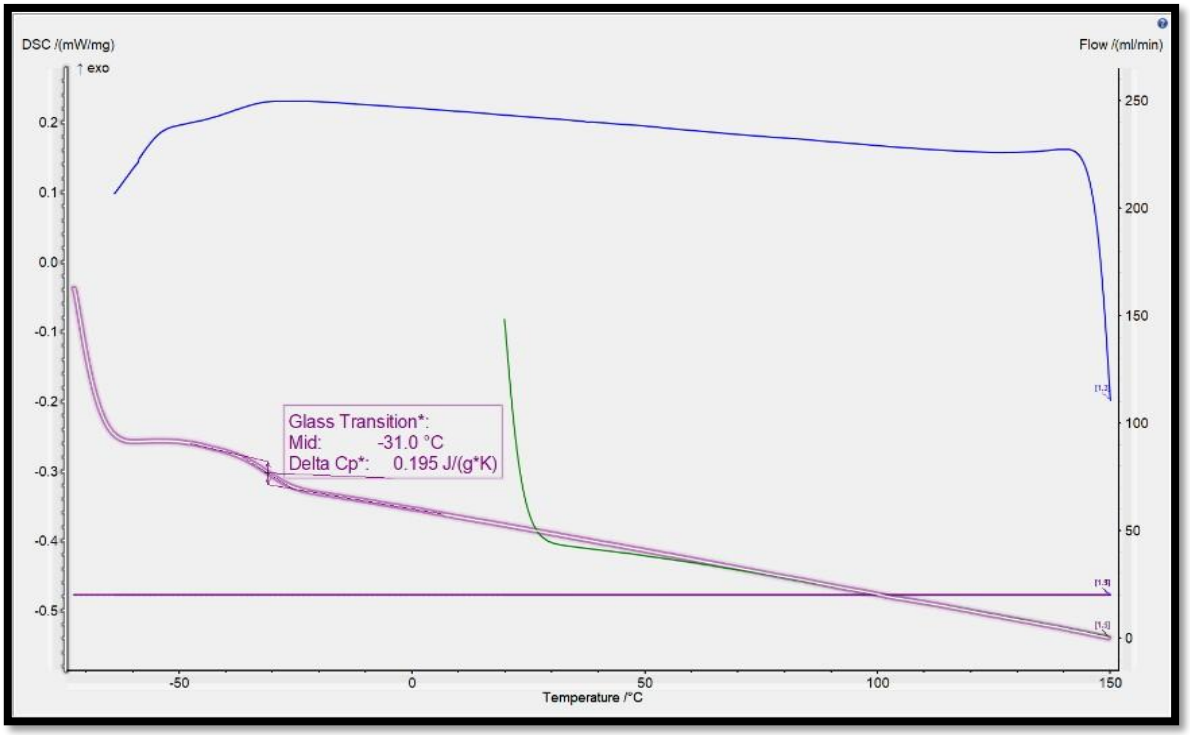

Figure S25- DSC thermogram of 10-poly(PPMS-PPVS-r-S)

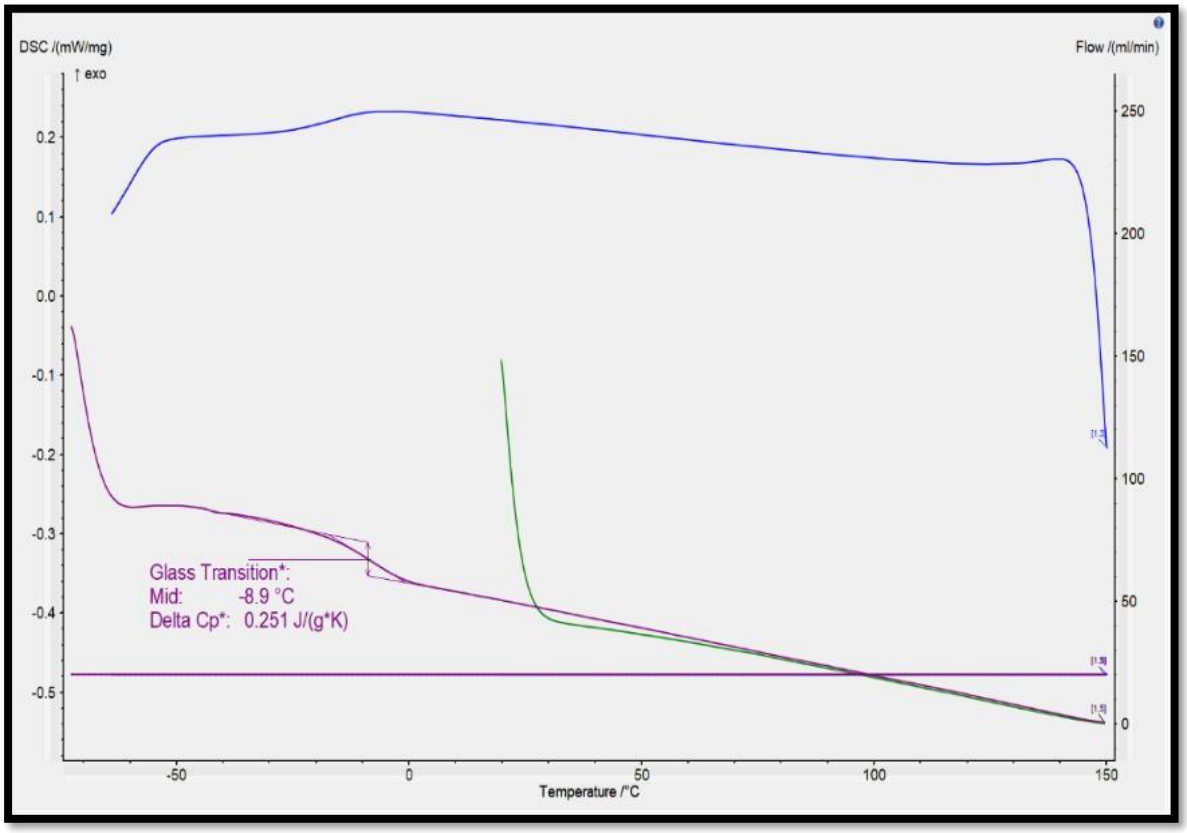

Figure S26- DSC thermogram of 15-poly(PPMS-PPVS-r-S)

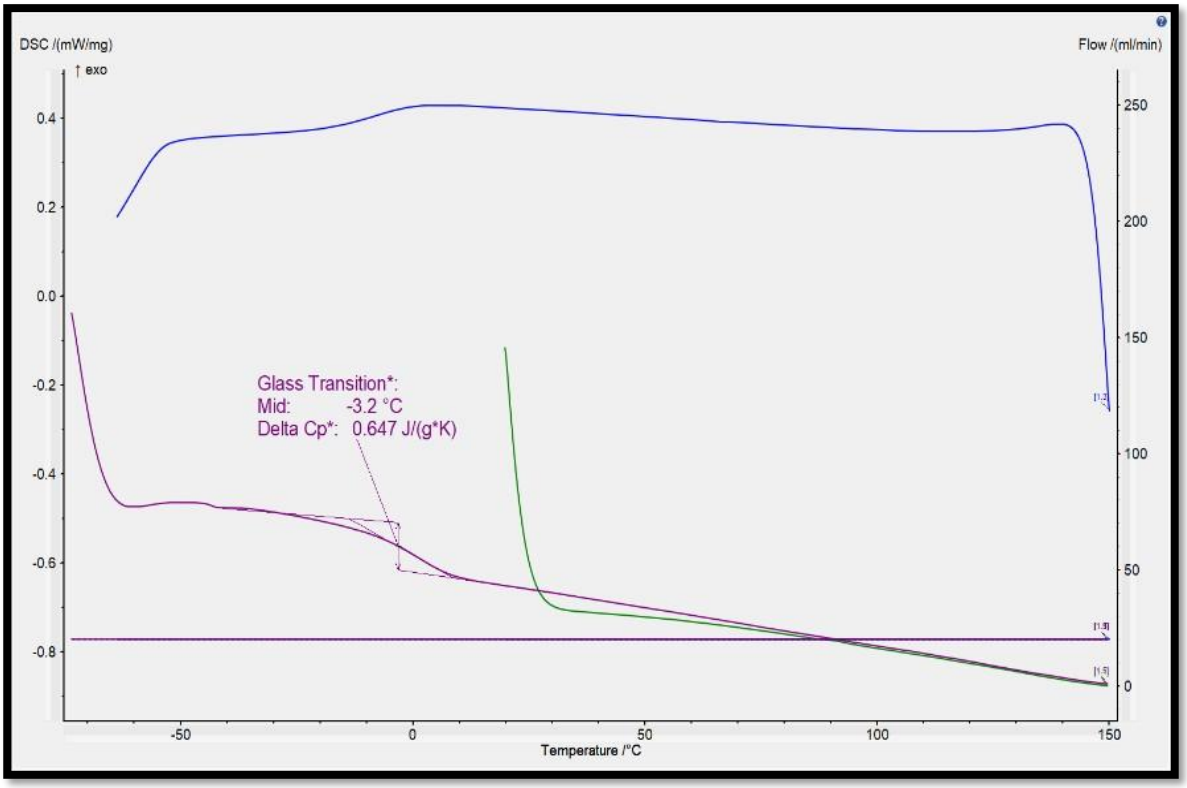

Figure S27- DSC thermogram of 20-poly(PPMS-PPVS-r-S)

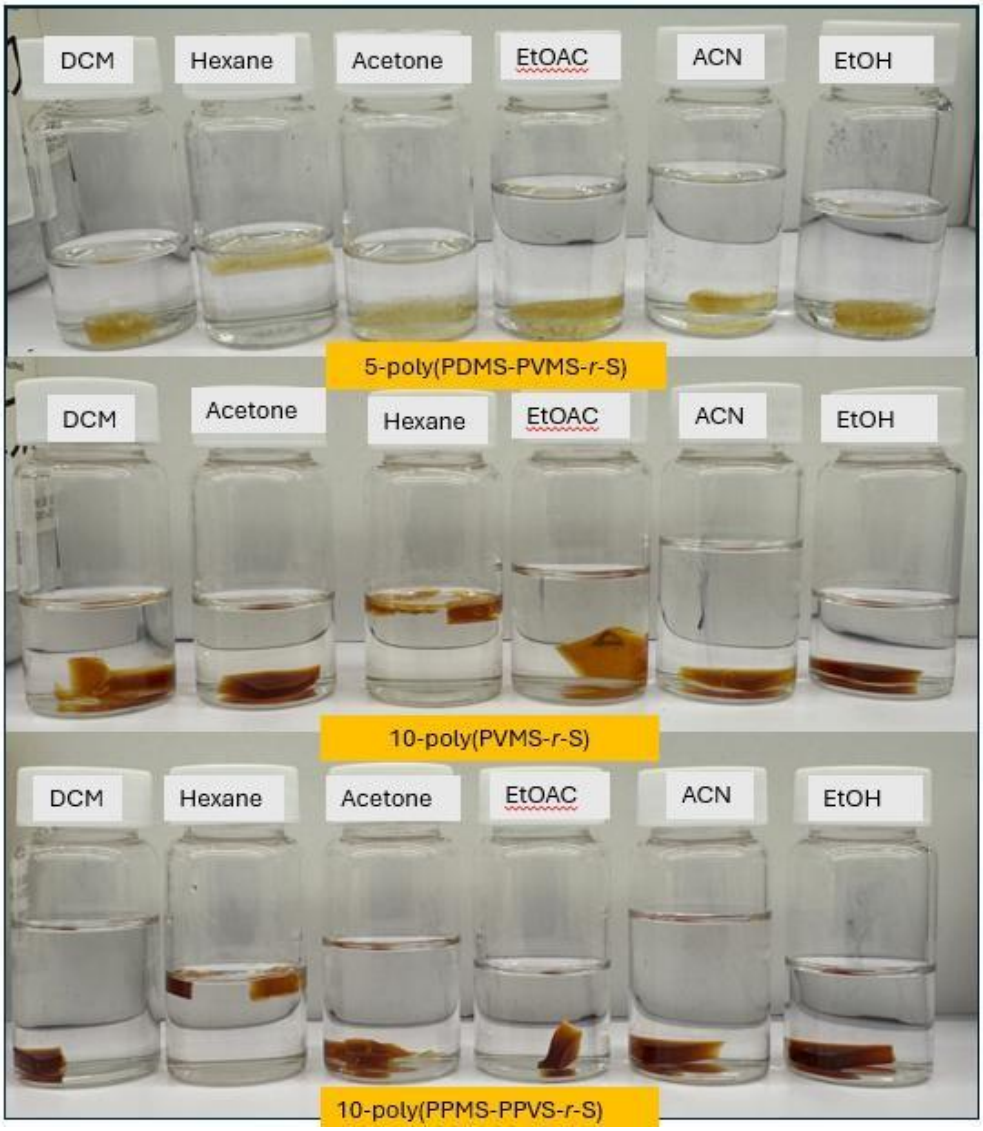

Figure S28- Solubility screening of sulfide crosslinked polysiloxanes in common organic solvents

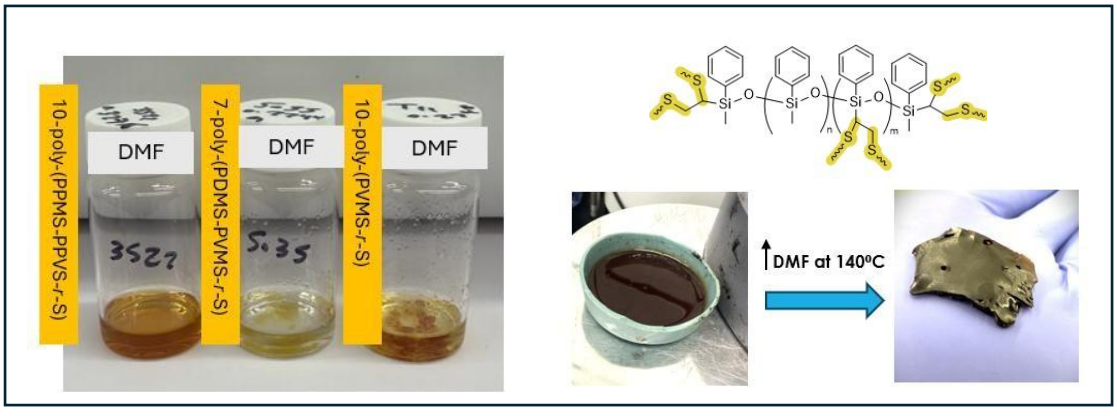

Figure S29- Solubility of synthesised polymers in DMF showing complete dissolution of 10-poly(PPMS-PPVS-r-S) and partial solubility of 5-poly(PDMS-PVMS-r-S) and of 10-poly(PVMS-r-S) (left). Removal of DMF from the dissolved 10poly(PPMS–PPVS-r-S) followed by heating at 140°C regenerates a cohesive solid network (right).

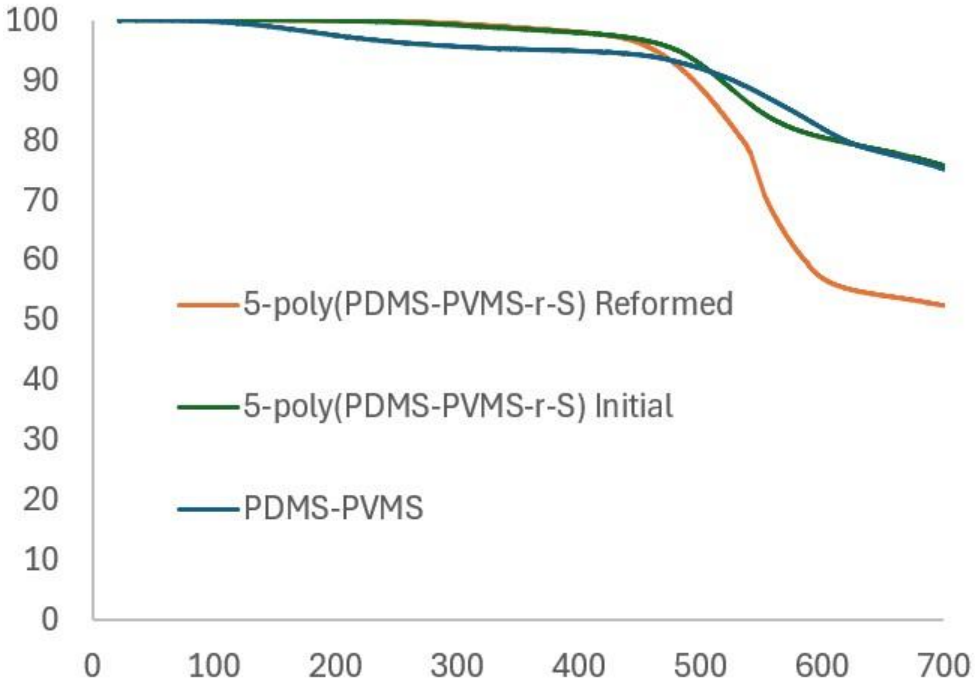

Figure S30- TGA results of PDMS-PVMS oil (blue) of 5-poly(PDMS-PVMS-r-S) before (green) and after reformation (orange)

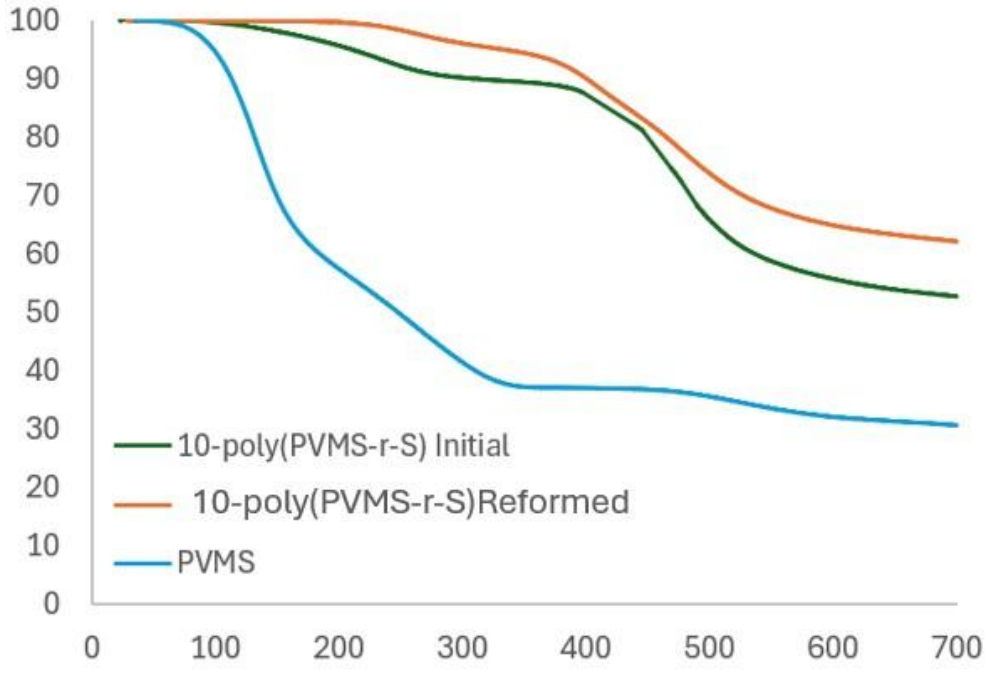

Figure S31- TGA results of PVMS oil (blue), 10-poly(PVMS-r-S) before (green) and after reformation (orange)

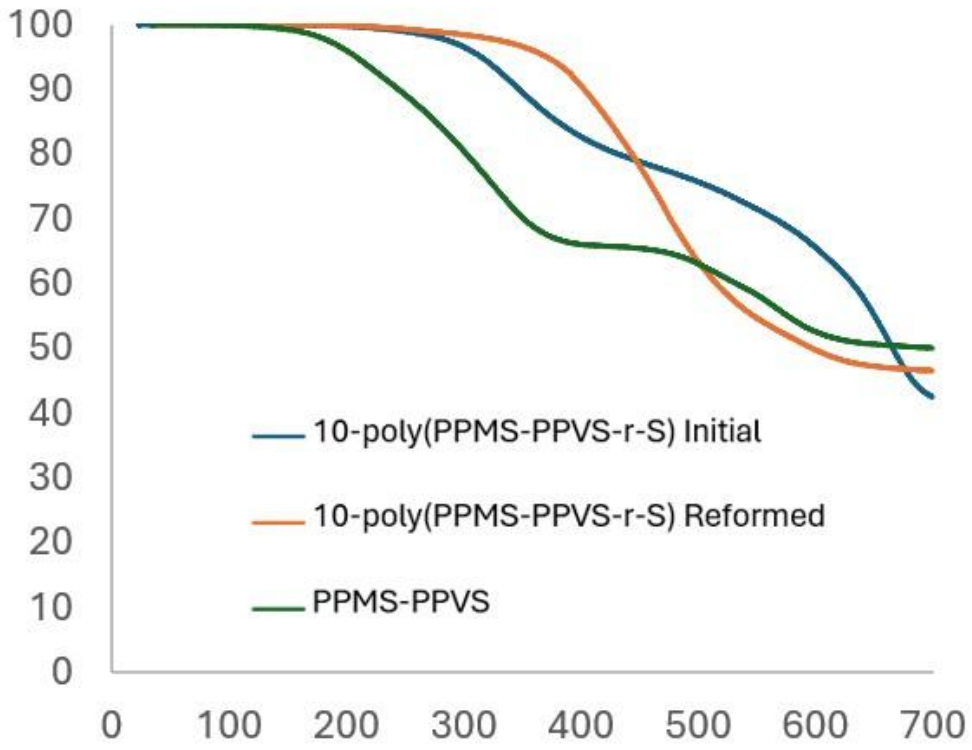

Figure S32- TGA results of PPMS-PPVS oil (green),10-poly(PPMS-PPVS-r-S) before (blue) and after reformation (orange).

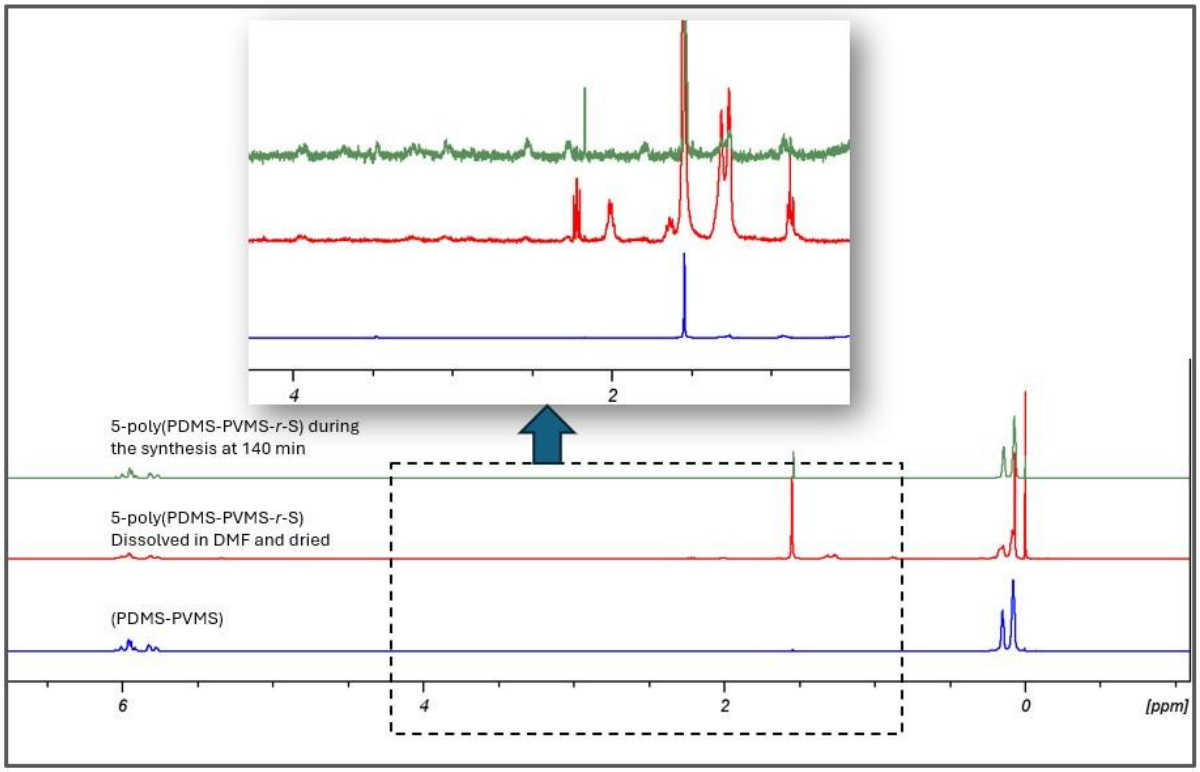

Figure S33- ^{1}H NMR spectra of 5-poly(PDMS-PVMS-r-S) at three stages: precursor oil, final reaction aliquot at 35 min (vitrification), and DMF-treated (dried) sample in $CDCl_3$

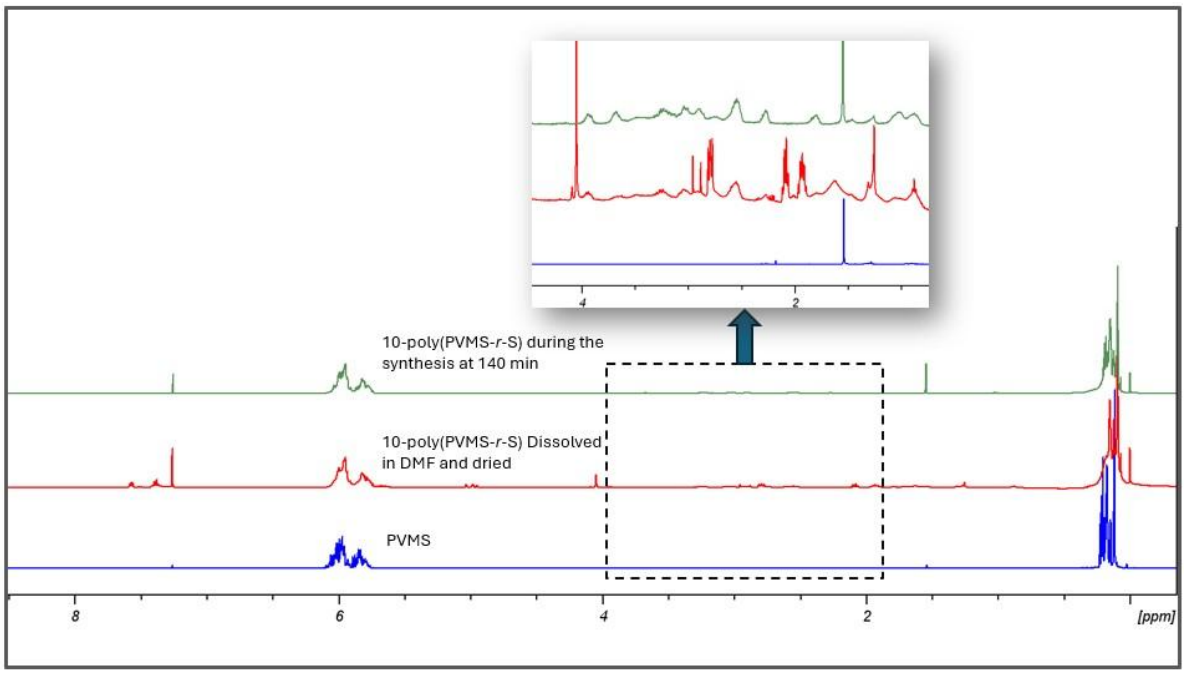

Figure S34-¹H NMR spectra of 5-poly(PVMS-r-S) at three stages: precursor oil, final reaction aliquot at 140 min (vitrification), and DMF-treated (dried) sample in $CDCl_3$

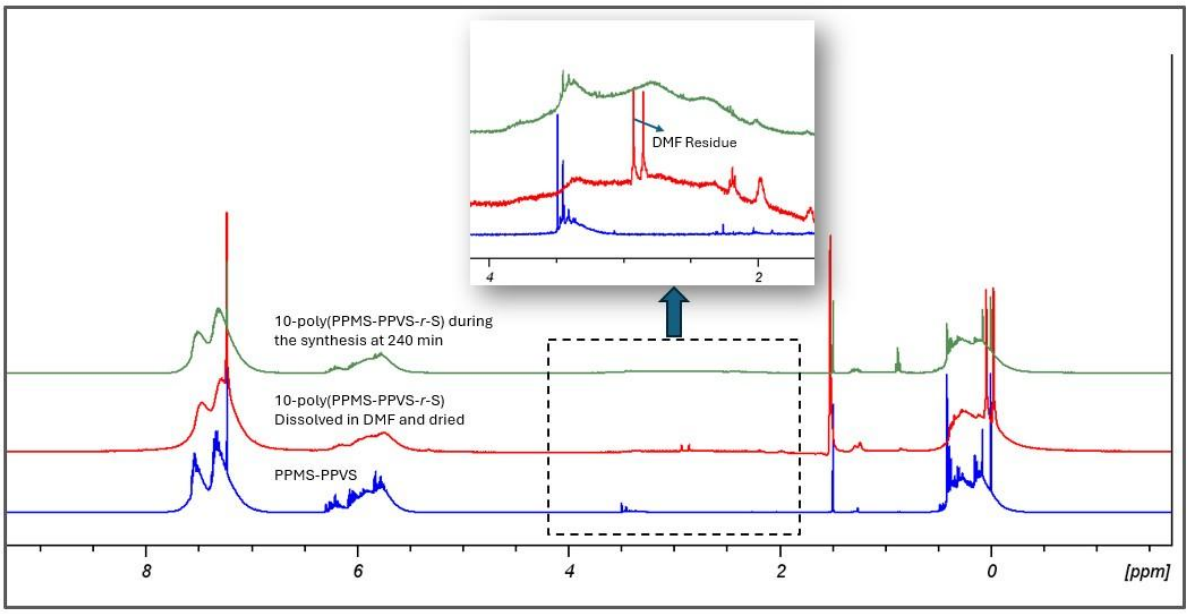

Figure S35- ¹H NMR spectra of 10-poly(PPMS-PPVS-r-S) at three stages: precursor oil (blue), final reaction aliquot at 240 min (vitrification, green), and DMF-treated sample (dried, red) in $CDCl_3$

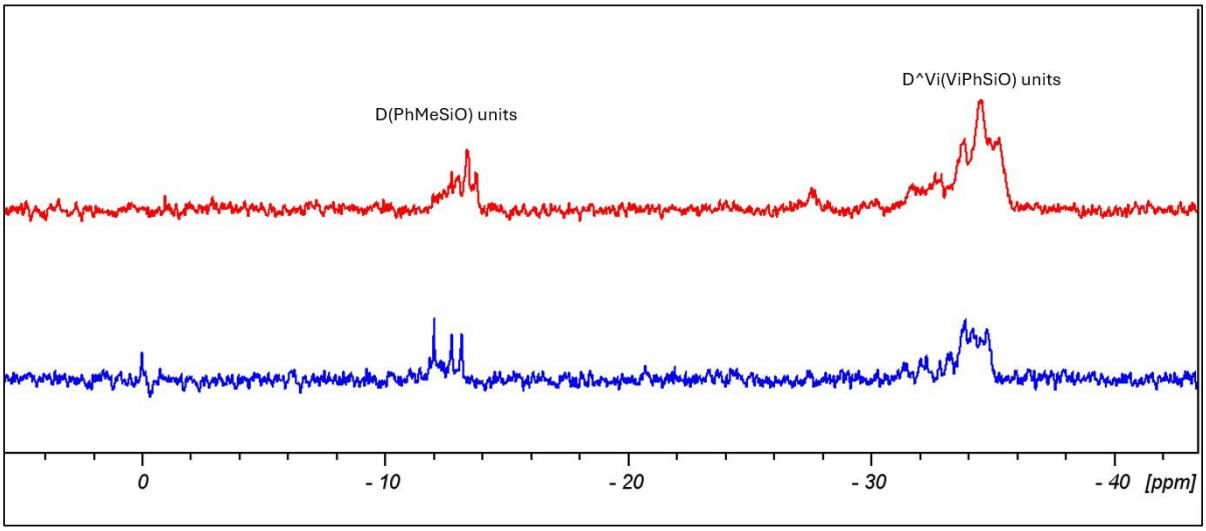

Figure S36-[29]Si DEPT NMR spectrum of PVMS oil (blue) and 10-poly(PVMS-r-S) (red) in $CDCl_3$ after DMF-induced cleavage

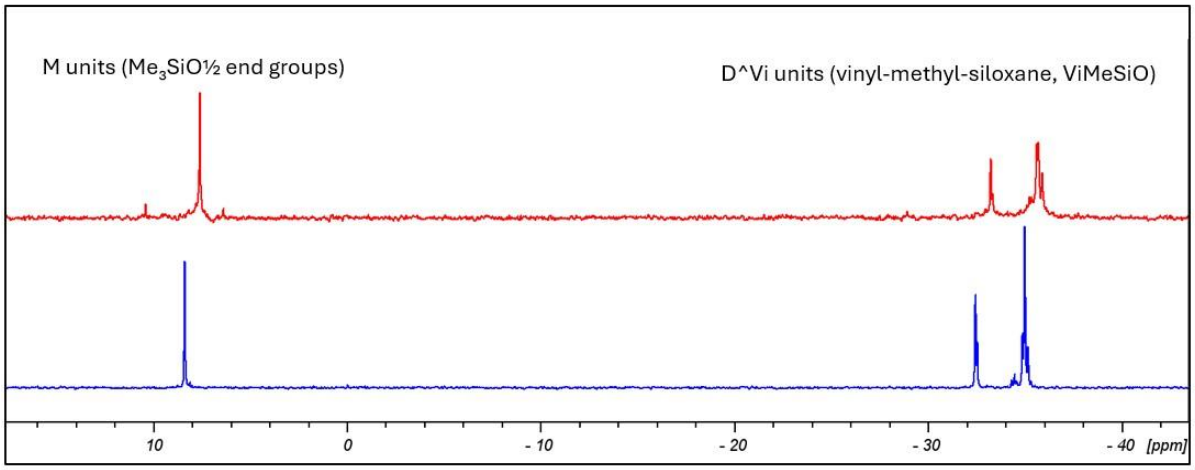

Figure S37 - [29]Si DEPT NMR spectrum of PPMS-PPVS oil (blue) and 10-poly(PPMS-PPVS-r-S) (red) in $CDCl_3$ after DMF induced cleavage

Estimating the average polysulfide rank (r) in network bridges

To estimate the average polysulfide rank (number of S atoms per bridge), we assume each bridge forms from two vinyl groups, thus:

$$r = \frac{2nS(atoms)}{n\ vinyl, concs}$$

When $2nS(atoms)$ is the mmol of sulfur atoms added (and incorporated) and $n\ vinyl, concs$ is the mmol of vinyl groups consumed, measured by ^{1}H NMR spectroscopy. (Note: for PPMS-PPVS, the value refers to the vitrification stage.)

For the 10 wt% batches, the sulfur charge was m(S_8) = 0.420 g for PVMS ;13.10 mmol and m(S_8) = 0.431 g for PPMS-PPVS: 13.44 mmol). For the 7 wt% batch, m(S_8) = 0.285 g: 8.89 mmol. Vinyl conversion fractions from ^{1}H NMR spectroscopy were ≈ 54% (PVMS), ≈ 31%(PPMS-PPVS, measured at

vitrification) and ≈ 9% (PDMS-PVMS). Vinyl site counts per chain were estimated from the precursor compositions and the measured M_n.

Table S6- Vinyl consumption and estimated average sulfur rank (r) for sulfur crosslinked polysiloxane networks

Sample	Vinyls per chain (estimate)	Vinyls (initial, mmol)*	Vinyls consumed (mmol)*	S added (mmol atoms)	Sulfur rank (r)
10-poly(PVMS-*r*-S)	~14.5	~43.96	~23.74	13.10	1.10
10-poly(PPMS-PPVS-*r*-S)	~6.5	~24.62	~7.63	13.44	3.52
7-poly(PDMS-PVMS-*r*-S)	~3.12	~23.39	~2.11	8.89	8.43

*Vinyls initial (mmol) = $\left(m^{polymer}/M_n\right) \times v_0$

*Vinyls consumed (mmol) $= \left(m^{polymer}/M_n\right) \times v_0 \times f_{vinyl}$

Where $m_{polymer}$ is the polymer mass in (g), M_n is the number-average molar mass (g·mol^{-1}), and v_0 = vinyls per chain and $f_{vinyl} =$ ^{1}H NMR conversion