Supplementary Material
Self-Healing Redox-Active Coatings Based on Ferrocenyl-Containing Polysiloxanes ‡

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‡ In commemoration of the 300th anniversary of St Petersburg State University's founding.

Content

S1. NMR and HRMS spectra

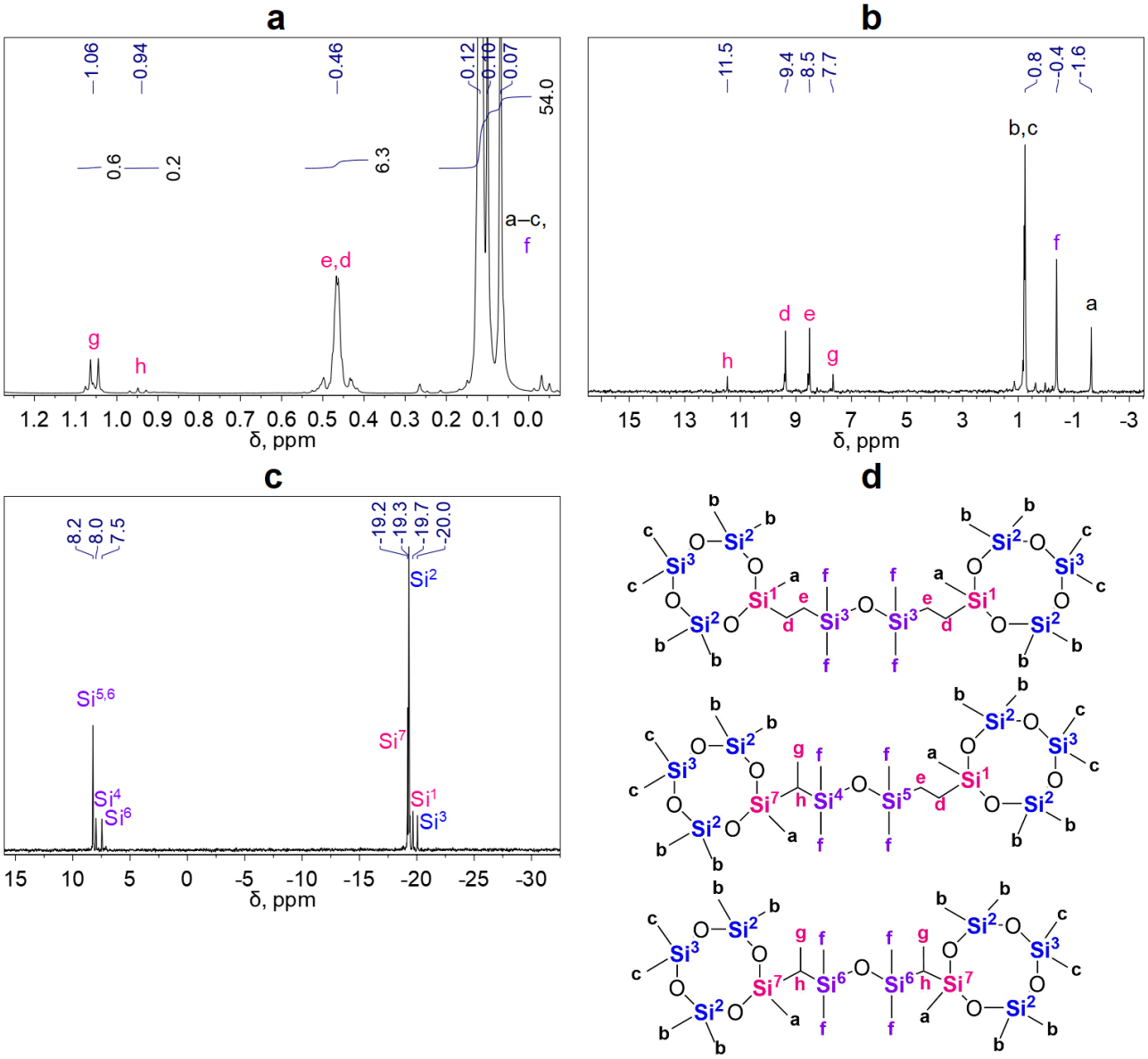

Figure S1. ^{1}H (**a**), ^{13}C (**b**), and ^{29}Si NMR spectra (**c**) of *bis*-D$_4$ and its isomers (**d**).

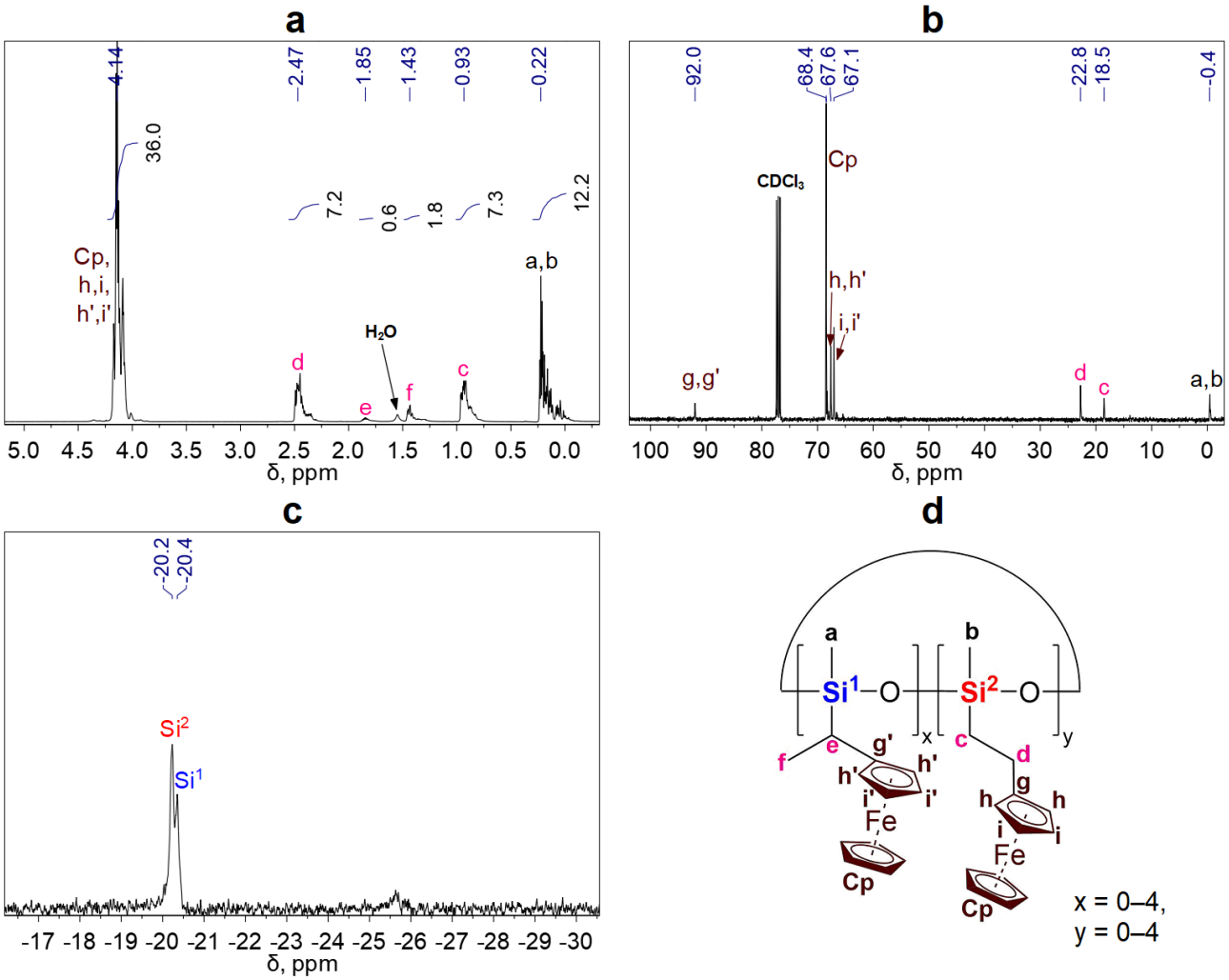

Figure S2. ^{1}H (**a**), ^{13}C (**b**), and ^{29}Si NMR spectra (**c**) of Fc_4D_4 and its general structure (**d**).

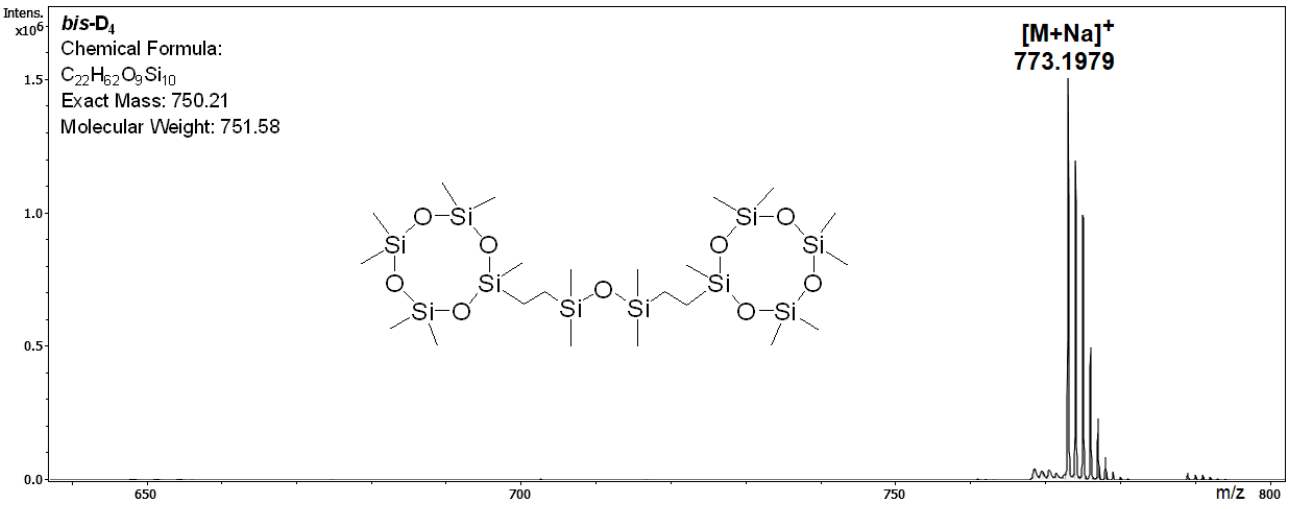

Figure S3. HRMS spectrum of *bis*-D_4.

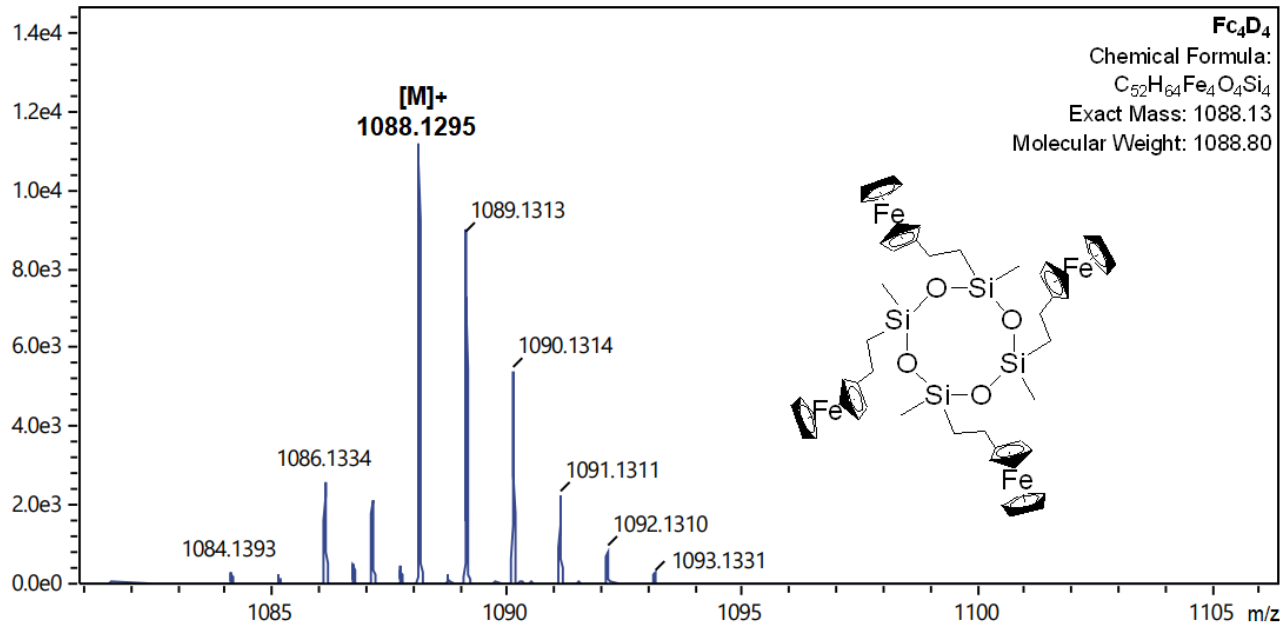

Figure S4. HRMS spectrum of Fc_4D_4.

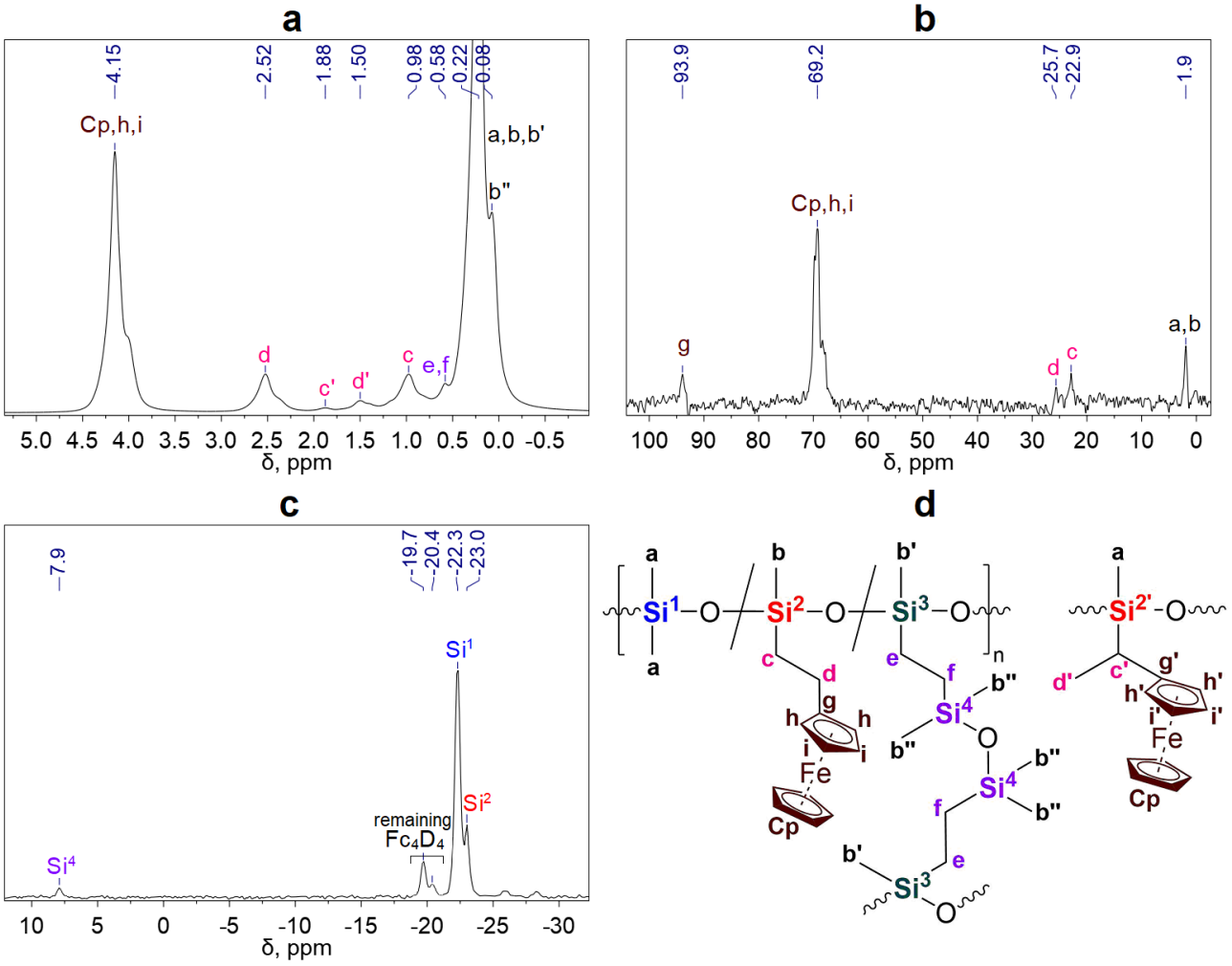

Figure S5. ^{1}H (**a**), ^{13}C (**b**), and ^{29}Si SSNMR spectra (**c**) of FSR25 and the fragment of its 3D polymer network (**d**).

S2. Swelling and tensile properties of MSRs

The cross-linking degree of the model silicone rubbers (with *bis*-D_4 concentrations of 0.5, 0.75, and 1.0 wt.%) was estimated by swelling measurements as in the case of FSRs. As expected (Table S1), the soluble fraction (ω_{sol}) decreases and the gel fraction rises with an increase in the concentration of the *bis*-D_4 cross-linking agent (due to an increase in the number of cross-links in the 3D polymer network). The M_c parameter (the "distance" between the cross-links) declines in the PDMSbisD$_4$-0.5%–PDMSbisD$_4$-0.75%–PDMSbisD$_4$-1.0% series.

Table S1. Swelling and tensile properties of the MSRs.

Silicone rubber	ρ_p, g·mL^{-1}	Swelling properties				Tensile properties	
		s, %	ω_{sol}, %	υ	M_c	σ, MPa	ε, %
PDMSbisD$_4$-0.5%	1.00±0.03	450±40	43±7	0.15±0.04	32300	0.10±0.02	1600±200
PDMSbisD$_4$-0.75%	1.01±0.03	570±50	11±2	0.18±0.05	15500	0.15±0.04	300±40
PDMSbisD$_4$-1.0%	1.01±0.03	570±50	7±2	0.19±0.05	14100	0.16±0.02	220±20

It can be seen from the mechanical properties presented in the Table S1, the MSR with the lowest cross-linking degree is the most stretchable (ε = 1600%), while the least robust (σ = 0.10 MPa). With an increase in the concentration of *bis*-D_4, the tensile strength (σ) rises with a decrease in the elongation at break (ε) in the PDMSbisD$_4$-0.5%–PDMSbisD$_4$-0.75%–PDMSbisD$_4$-1.0% series.

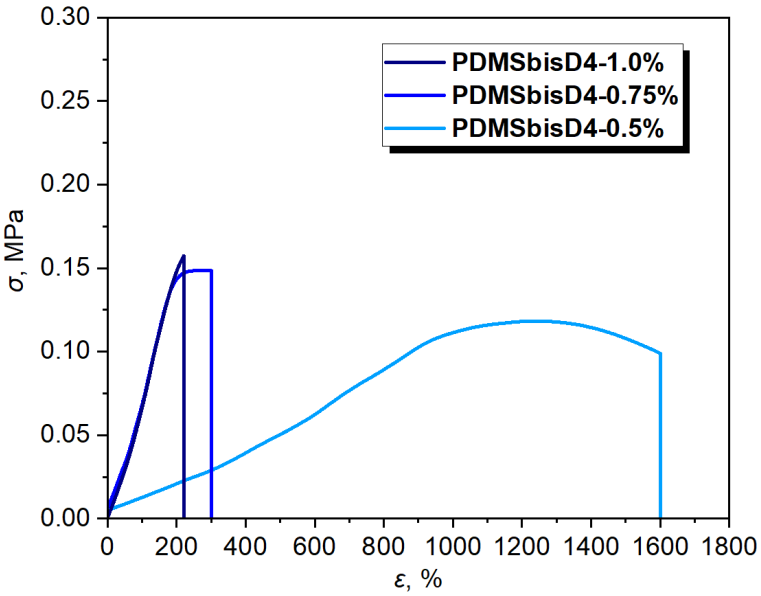

Figure S6. Stress–strain curves of the MSRs at a stretching speed of 40 mm·min^{-1}.

S3. Self-healing properties of FSRs and MSRs

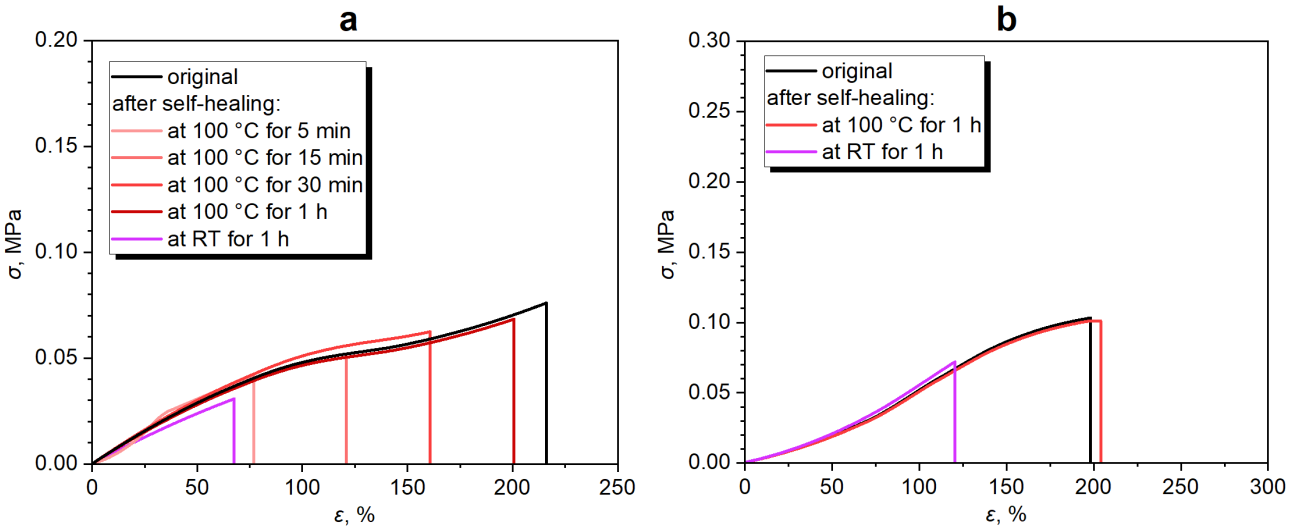

Figure S7. Stress–strain curves of the original and healed FSR25 (**a**) and FSR50 (**b**) at a stretching speed of 40 mm·min^{-1}.

The self-healing efficiency of MSRs was estimated after 24 h at RT and 100 °C after 15 min.The maximum value of η parameter is observed in the sample with the lowest cross-linking degree (PDMSbisD$_4$-0.5%) and reaches 90% at RT. The self-healing ability and η parameter sharply drop down to 0% in the PDMSbisD$_4$-0.5%–PDMSbisD$_4$-0.75%–PDMSbisD$_4$-1.0% series (Table S2, Figure S8). It can be concluded that an increase in the concentration of *bis*-D$_4$ negatively affects the self-healing of samples.

Table S2. Self-healing properties of the MSRs.

Silicone rubber	Healing temperature, °C	Healing time	η, %
PDMSbisD$_4$-0.5%	RT	24 h	90
	100	15 min	100
PDMSbisD$_4$-0.75%	RT	24 h	15
PDMSbisD$_4$-1.0%	RT	24 h	0

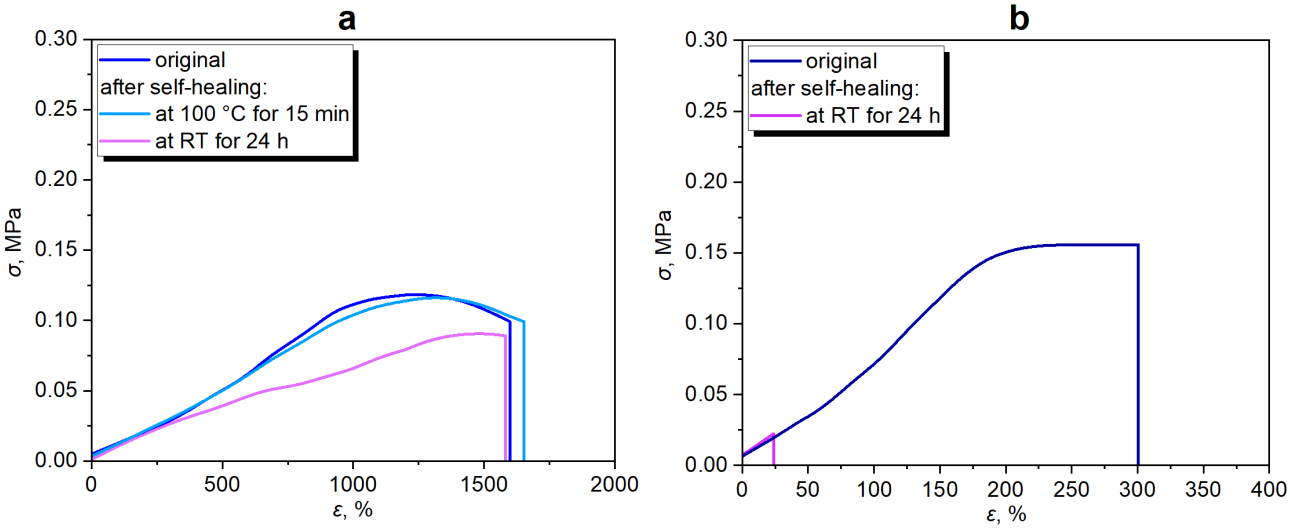

Figure S8. Stress–strain curves of the original and healed MSRs: PDMSbisD$_4$-0.5% (**a**) and PDMSbisD$_4$-0.75% (**b**) at a stretching speed of 40 mm·min^{-1}.

S4. Thermal properties of MSRs

In the case of self-healing MSRs (PDMSbisD$_4$-0.5%) (Figure S9), there is an endothermic peak (30.22 J·g^{-1}) at –39 °C, corresponding to melting, and an exothermic peak (–27.97 J·g^{-1}) at –77 °C, corresponding to crystallization. At the same time, the T_g of the polymer is approximately –128 °C, which is similar to pure polydimethylsiloxane.

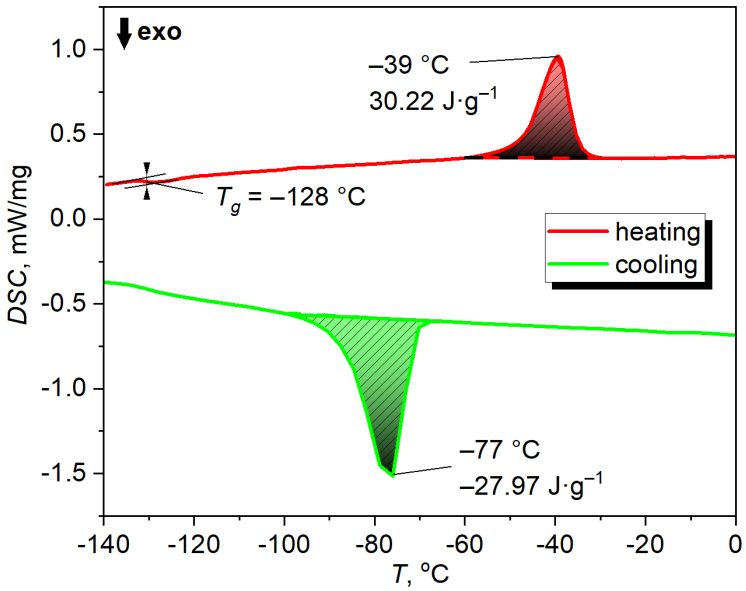

Figure S9. DSC curves for PDMSbisD$_4$-0.5% from –140 to 0 °C.