ARTICLE

- Supporting Information -

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Nanoscale structure and dynamics of thermoresponsive single-chain nanoparticles investigated by EPR spectroscopy

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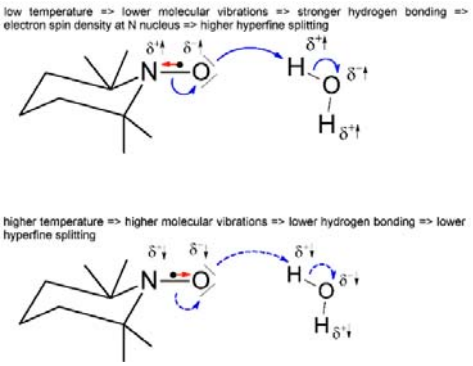
Temperature effect on hyperfine coupling

The hyperfine coupling becomes lower with increasing temperature is already known, in addition illustrated in Scheme S1.[1]

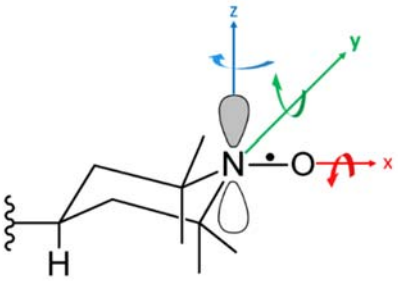


Scheme S1: Illustration for the temperature effect of the hyperfine coupling. At low temperature the molecular vibrations are lower, so the hydrogen bond interaction with TEMPO is stronger. At high temperature the molecular vibrations are higher, the hydrogen bonding is lesser. In general, the dipole is more distributed at the x,y and z axes of an Cartesian coordiante system. As a consequence, the interaction between so single electron and the nitrogen nucleus is lower at higher temperature. The associated hyperfine coupling gets lesser with higher temperature.

Calculation of the hyperfine coupling

The calculation of the hyperfine coupling is shown in (S1). The values of A_{xx}, A_{yy} and A_{zz} are used with the coordinate system of Scheme S2.

$$a_{iso}=\frac{1}{3}\cdot\left(A_{xx}+A_{yy}+A_{zz}\right) \qquad \text{(S1)}$$



Scheme S2: Illustrated rotational diffusion of nitroxide spin probes.

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Temperature series of the CW EPR-spectra

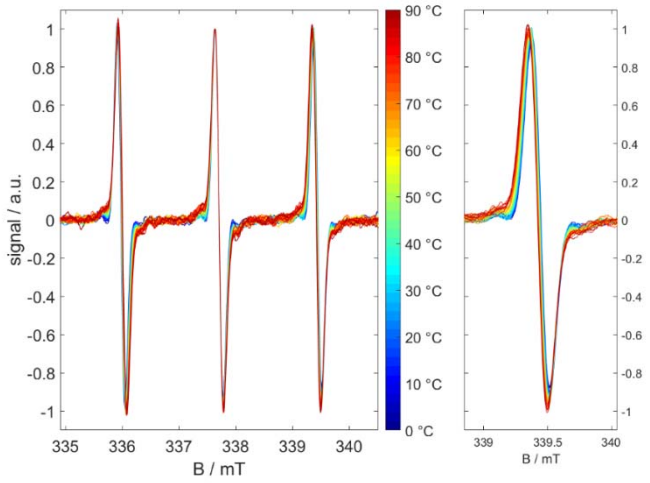

Figure S 1: Temperature series in (2 ± 0.2) K steps of the TEMPO reference.

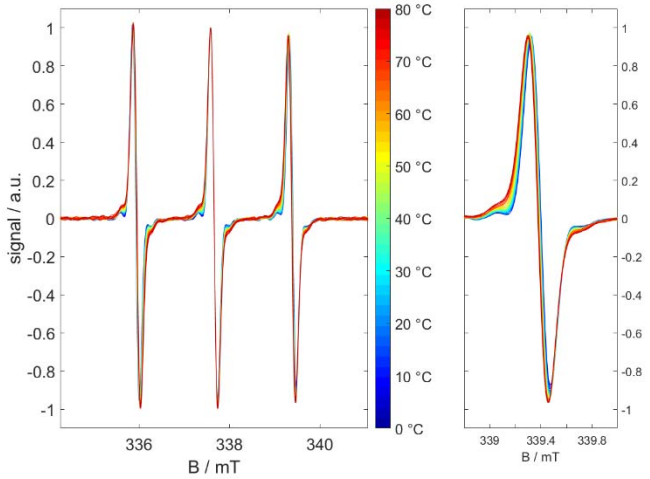

Figure S 2: Temperature series in (2 ± 0.2) K steps of Polymer I.

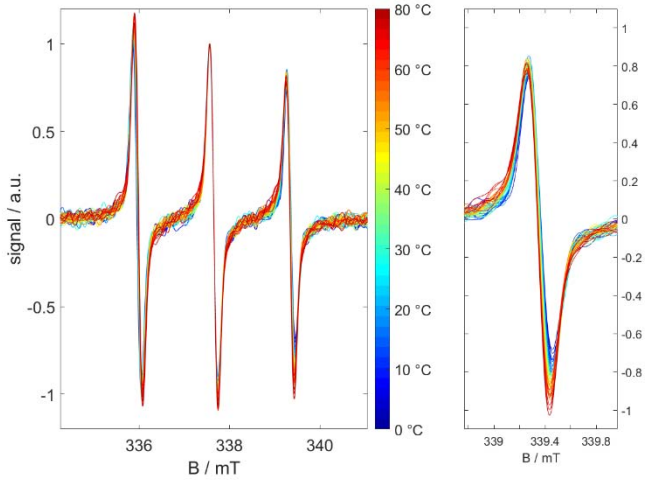

Figure S 3: Temperature series in (2 ± 0.2) K steps of SCNP I.

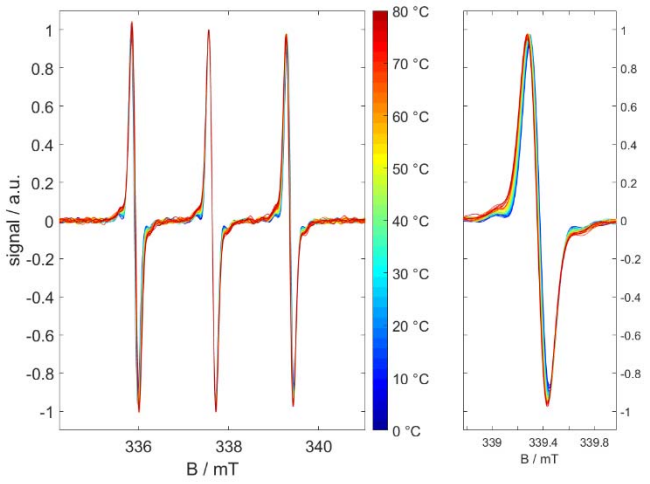

Figure S 4: Temperature series in (2 ± 0.2) K steps of SL-Polymer I.

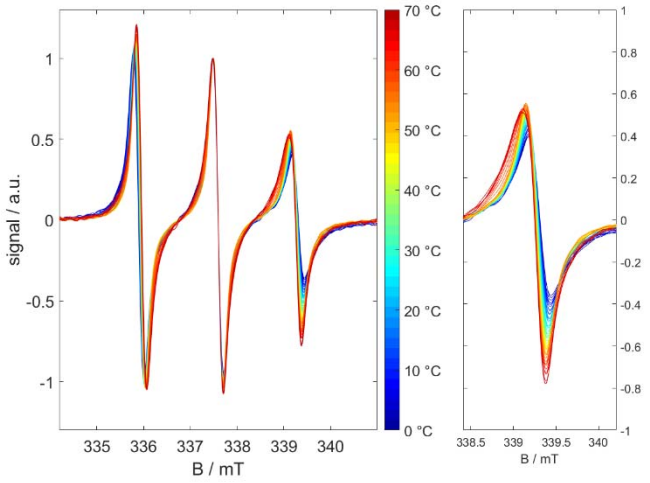

Figure S 5: Temperature series in (2 ± 0.2) K steps of SL-SCNP I.

Simulated and measured CW EPR-spectra

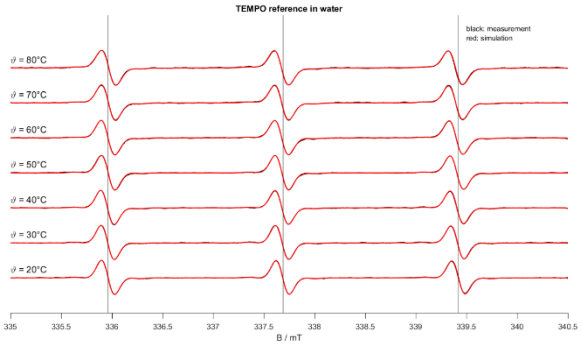

Figure S 6: Simulation (red) and measured CW EPR-spectra (black) of the TEMPO reference.

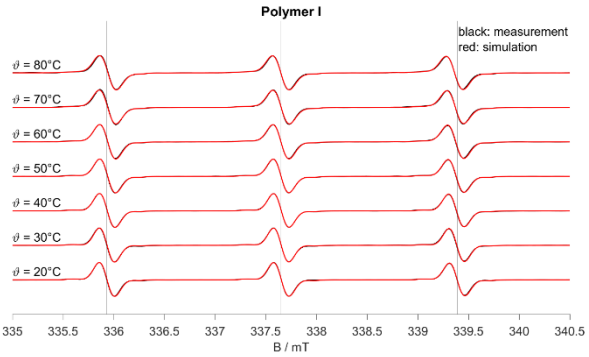

Figure S 7: Simulation (red) and measured CW EPR-spectra (black) of Polymer I.

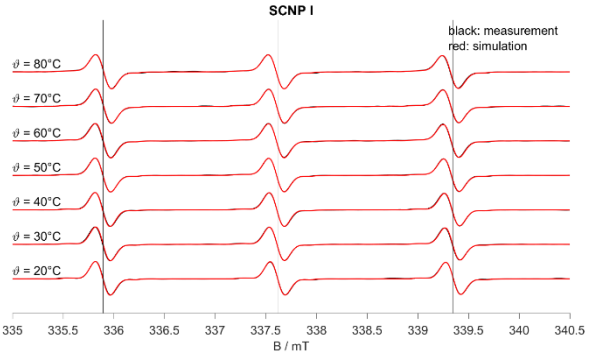

Figure S 8: Simulation (red) and measured CW EPR-spectra (black) of SCNP I.

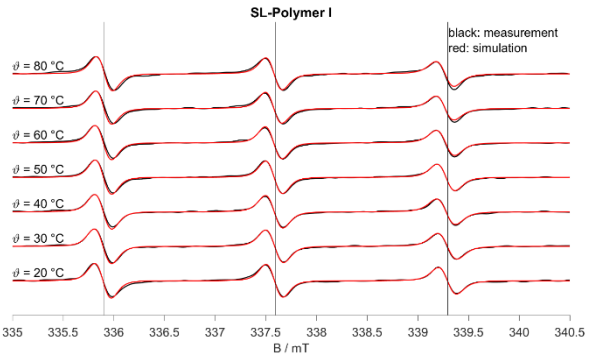

Figure S 9 Simulation (red) and measured CW EPR-spectra (black) of SL-Polymer I.

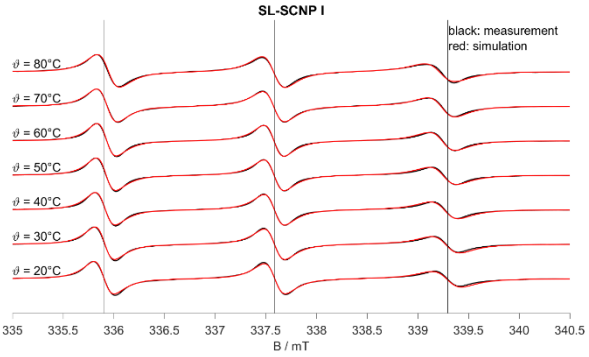

Figure S: 10 Simulation (red) and measured CW EPR-spectra (black) of SL-SCNP I.

Simulation parameters

Table S1: Diffusion tensors of all samples for each temperature.

sample	ϑ / °C	D_{xx} / s^{-1}	D_{yy} / s^{-1}	D_{zz} / s^{-1}
TEMPO reference	20	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	30	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	40	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	50	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	60	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	70	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	80	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
polymer I	20	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	30	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	40	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	50	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	60	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	70	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
	80	$1.00 \cdot 10^{11}$	$5.00 \cdot 10^{9}$	$8.00 \cdot 10^{9}$
SCNP I	20	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
	30	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
	40	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
	50	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
	60	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
	70	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
	80	$1.00 \cdot 10^{11}$	$1.00 \cdot 10^{9}$	$1.00 \cdot 10^{10}$
SL-Polymer I	20	$1.00 \cdot 10^{10}$	$1.00 \cdot 10^{9}$	$5.00 \cdot 10^{7}$
	30	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{8}$	$7.00 \cdot 10^{7}$
	40	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{8}$	$7.00 \cdot 10^{7}$
	50	$1.00 \cdot 10^{10}$	$9.00 \cdot 10^{8}$	$7.00 \cdot 10^{7}$

	60	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{8}$	$8.00 \cdot 10^{7}$
	70	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{8}$	$5.00 \cdot 10^{7}$
	80	$1.00 \cdot 10^{10}$	$8.00 \cdot 10^{8}$	$5.00 \cdot 10^{7}$
SL-SCNP I	20	$2.80 \cdot 10^{9}$	$1.40 \cdot 10^{8}$	$1.80 \cdot 10^{8}$
	30	$2.80 \cdot 10^{9}$	$1.40 \cdot 10^{8}$	$2.30 \cdot 10^{8}$
	40	$2.80 \cdot 10^{9}$	$1.40 \cdot 10^{8}$	$2.50 \cdot 10^{8}$
	50	$2.80 \cdot 10^{9}$	$1.60 \cdot 10^{8}$	$2.50 \cdot 10^{8}$
	60	$2.80 \cdot 10^{9}$	$2.00 \cdot 10^{8}$	$2.60 \cdot 10^{8}$
	70	$2.80 \cdot 10^{9}$	$1.40 \cdot 10^{8}$	$2.30 \cdot 10^{8}$
	80	$2.80 \cdot 10^{9}$	$1.80 \cdot 10^{8}$	$1.80 \cdot 10^{8}$

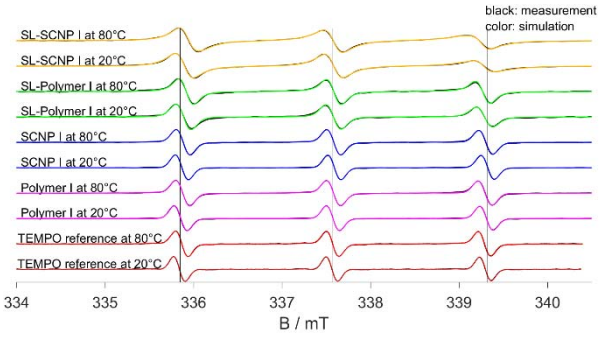

Figure S 11: Measurements and initially simulated CW EPR-spectra of spin-labeled polymeric systems: Polymer I (~~black~~magenta), SL-Polymer I (green), SCNP I (blue) and SL-SCNP I (yellow).

Table S 2 Simulated hyperfine coupling for the TEMPO reference, Polymer I, SCNP I, SL-Polymer I and SL-SCNP I.

		ϑ / °C						
		20	30	40	50	60	70	80
error	sample	a_{iso} / MHz						
± 0.25	TEMPO reference	48.20	48.20	47.92	47.92	47.92	47.64	47.64
± 0.25	Polymer I	48.48	48.48	48.20	48.20	48.20	48.20	47.92
± 0.25	SCNP I	48.48	48.48	48.48	48.20	48.20	47.92	47.92
± 0.25	SL-Polymer I	47.64	47.64	47.36	47.36	47.36	47.36	47.08
± 0.25	SL-SCNP I	47.64	47.36	47.08	47.08	46.80	46.80	46.24

Table S 3: Simulated Heisenberg spin exchange for the TEMPO reference, Polymer I, SCNP I, SL-Polymer I and SL-SCNP I.

		ϑ / °C						
		20	30	40	50	60	70	80
error	sample	J / MHz						
	TEMPO reference	-	-	-	-	-	-	-
± 0.1	Polymer I	-	-	-	-	0.2	0.5	0.6
± 0.1	SCNP I	0.1	0.2	0.2	0.5	0.6	0.7	0.8
± 0.1	SL-Polymer I	-	-	-	1.2	1.2	1.2	1.2
± 0.1	SL-SCNP I	5.7	5.7	5.7	5.7	5.7	6.6	6.3

Table S 4: Calculated rotational correlation time τ for the TEMPO reference, Polymer I, SCNP I, SL-Polymer I and SL-SCNP I.

		ϑ / °C						
		20	30	40	50	60	70	80
error	Sample	τ / ps						
± 5.2	TEMPO reference	9.0	9.0	9.0	9.0	9.0	9.0	9.0
± 5.2	Polymer I	11.0	11.0	11.0	11.0	11.0	11.0	11.0
± 5.2	SCNP I	16.7	16.7	16.7	16.7	16.7	16.7	16.7
± 25	SL-Polymer I	173	202	202	194	194	226	226
± 37	SL-SCNP I	403	372	361	346	317	372	371

Table S 5: *Calculated anisotropy of the TEMPO reference, Polymer I, SCNP I, SL-Polymer I and SL-SCNP I.*

		ϑ / °C						
		20	30	40	50	60	70	80
error	sample	Ƭ						
± 0.002	TEMPO reference	0.793	0.793	0.793	0.793	0.793	0.793	0.793

± 0.002	Polymer I	0.827	0.827	0.827	0.827	0.827	0.827	0.827
± 0.002	SCNP I	0.851	0.851	0.851	0.851	0.851	0.851	0.851
± 0.002	SL-Polymer I	0.853	0.880	0.880	0.867	0.879	0.882	0.882
± 0.002	SL-SCNP I	0.846	0.825	0.817	0.808	0.788	0.825	0.829

References

[1] a) M. Plato, H.-J. Steinhoff, C. Wegener, J. T. Törring, A. Savitsky, K. Möbius, *Molecular Physics* **2002**, *100*, 3711; b) D. Kurzbach, M. Schömer, V. S. Wilms, H. Frey, D. Hinderberger, *Macromolecules* **2012**, *45*, 7535.