Supplementary information to the article "Chain collapse and dynamics of inhomogeneities in aqueous solutions of poly(N-isopropylacrylamide) and its block copolymers with polyethylene glycol"

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EPR spectra processing and simulation

The amplitudes and linewidths of the spectral lines were measured using the EsrD program (Chemistry Faculty of Lomonosov Moscow State University).[1] All spectra simulations were performed using homemade scripts for the EasySpin (v. 6.0.2) open-source MATLAB toolkit.[2,3] Simulation quality was determined by calculation of the root mean square deviation (RMSD) value between simulated and experimental spectra. The following values were taken as the initial values of diagonalized **g**- and **A**-tensors: g_x = 2.0092, g_y = 2.0062, g_z = 2.0022; A_{xx} = 0.71 mT, A_{yy} = 0.70 mT, A_{zz} = 3.71 mT.

Spin-Hamiltonian and dynamic parameters of TEMPO in PNIPA-1 inhomogeneities (type **B** particles) were determined from their individual EPR spectrum obtained via Cu^{2+} ions addition and were used in simulation of total spectra without variations. In the case of TEMPO in PEG1-*b*-PNIPA and PEG2-*b*-PNIPA inhomogeneities (type **C** and type **D** particles, respectively), where suppression of type **A** particles (TEMPO in solution) signal by copper ions isn't applicable due to complexation with polymers functional groups, parameters of type **B** particles were used as an initial approximation and were varied in simulation. In addition to hyperfine splitting on the ^{14}N nuclei, the spectra contain satellite lines arising from hyperfine coupling with the six ^{13}C nuclei (I = ½) located close enough to the N-O group in the TEMPO molecule. To describe this feature, the ^{13}C nucleus with an increased abundance is six times and a_{iso} = 0.54 mT was added to the simulation.

The 'chili' function in EasySpin utilizing the Schneider–Freed theory[4,5] for slowly tumbling nitroxides was used to simulate TEMPO spectra. The anisotropic values of the spin Hamiltonian parameters (the **g**-tensor and **A**-tensor) were averaged to obtain the g_{iso} and a_{iso} values. The

rotational correlation time (t_{corr}) was calculated from the averaged rotational diffusion constant as described in ref. [5]:

$$g_{iso} = \frac{1}{3}(g_x + g_y + g_z); a_{iso} = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz}); t_{corr} = \frac{1}{6\sqrt[3]{D_{xx}D_{yy}D_{zz}}}$$

In the case of the spectra containing two types of the particles (probe in bulk solution (type **A**) and inside polymer inhomogeneities (types **B/C/D,** denoted in the formula as type **X**) fraction of the latter probes type was calculated from weight values of type **X** particles in the full EPR spectra, considering that the weight of type **A** particles is equal to 1:

$$x(X) = \frac{w(X)}{1 + w(X)}$$

The uncertainties for the simulated parameters were estimated as follows:

$$g_{iso} \pm 0.00003;\ a_{iso} \pm 0.01mT; x \pm 1\%; t_{corr} \pm 0.1ns$$

Table S1 shows the parameters of all particles encountered in this work. Parameters of type **E** particles, belonging to PNIPA-2 polymer, are presented for comparison. All parameters are taken at T = 60 °C.

Table S1. Magnetic and dynamic parameters of particles used in present work, T = 60 °C.

Particle Type	**Environment**	**a_{iso}, mT**	**t_x, ns**	**t_y, ns**	**t_z, ns**	**t_{iso}, ns**	**x, %**
A	Bulk solution	1.73	0.01	0.01	0.01	0.01	-
B	PNIPA-1	1.62	24.0	0.5	1.7	2.7	35
C	PEG1-b-PNIPA	1.62	31.1	0.3	2.3	2.9	41
D	PEG2-b-PNIPA	1.62	30.2	0.5	1.9	3.3	56
E	PNIPA-2 [6]	1.60	17.8	0.3	1.8	2.1	63

References

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