## Molecular environment and reactivity in gels and colloidal solutions under identical conditions

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## **Electronic Supplementary Information.**

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**Figure S1**:  $PEG_{2000}$ -Tyr<sub>6</sub> determination of cmc by DLS count rate. Average of 3 measurements shown. Error bars indicate 95% confidence levels.



Figure S2a: Q-band EPR spectrum of spin labelled PEG<sub>2000</sub>-Tyr<sub>6</sub> at 88 K



**Figure S2b**: Power saturation experiment showing change in EPR signal intensity for spin labelled  $PEG_{2000}$ -Tyr<sub>6</sub> at 88 K with microwave power at Q-band



**Figure S3**: A Q-band EPR spectrum of  $PEG_{2000}$ -Tyr<sub>6</sub> micelle system and a 3-component simulation using parameters obtained by fitting the X-band spectrum of the same solution.

	Gaussian	Lorentzian	log D <sub>₂</sub> / s <sup>-1</sup>	Log D <sub>  </sub> / s <sup>-1</sup>	Relative
	Linewidth / mT	Linewidth / mT			contribution
"Fast"	0.2198	0.0000	9.5476	9.6372	1.0000
"Slow" A	0.2682	0.4919	7.1023	7.4527	6.5881
"Slow" B	0.6356	0.3140	7.9136	8.4558	6.3433

**Table S1a**: Optimised parameters for nitroxide components of X band EPR spectrum of labelled  $PEG_{2000}$ -Tyr<sub>6</sub> micelles at 20 °C

Table S1b: Optimised parameters for nitroxide components of X band EPR spectrum of labell	ed
PEG <sub>2000</sub> -Tyr <sub>6</sub> gel	

	Gaussian	Lorentzian	Log(D <sub>2</sub> / s <sup>-1</sup> )	Log(D <sub>  </sub> / s <sup>-1</sup> )	Relative
	Linewidth / mT	Linewidth / mT			contribution
"Fast"	0.2116	0.0169	9.3478	9.4372	1.0000
"Slow" A	0.3732	0.1060	7.0551	7.5709	6.5185
"Slow" B	0.9312	0.0416	7.8551	8.2275	4.9886



**Figure S4a**: DLS measurements of sealed 10 mg/ml  $PEG_{2000}$ -Tyr<sub>6</sub> sample before (1), after 30 (2) and 60 (3) seconds of heating at 65 °C



**Figure S4b**: Change in average particle size (hydrodynamic radius) upon heating a  $PEG_{2000}$ -Tyr<sub>6</sub> 10 mg/ml sample to 65 °C



**Figure S5:** Comparison of EPR spectra of  $PEG_{2000}$ -Tyr<sub>6</sub> micellar solution: fresh solution (red) and a micellar solution obtained from the polymer that formed a gel at 60 °C, the gel was dissolved in methanol, solution was evaporated and dry polymer redispersed in water (black).



Figure S6: UV/vis absorbance spectra for  $PEG_{2000}$ -Tyr<sub>6</sub> 5 mg/ml micelle and gel samples.



**Figure S7.** EPR spectrum of  $PEG_{2000}$ -Tyr<sub>6</sub> in methanol is dominated by the fast-tumbling component suggesting that the copolymer aggregation in this solvent is at least partially suppressed.