Electronic supplementary information

Influence of Molecular Weight on PNIPAM Brush Modified Colloidal Silica Particles

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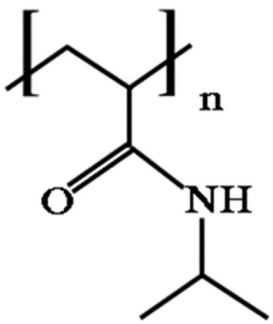

Figure S1. Molecular structure of poly(*N*-isopropylacrylamide) (PNIPAM).

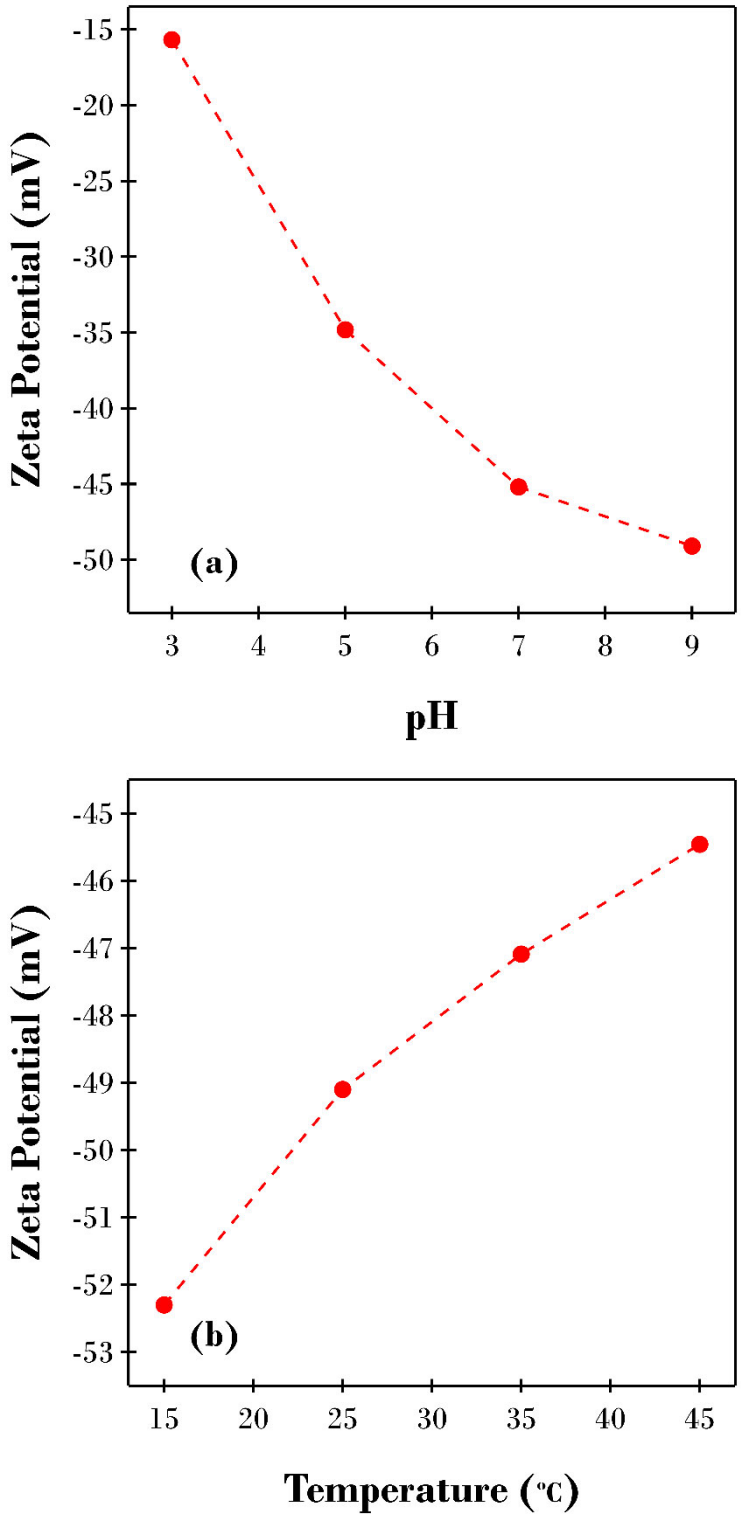

Figure S2. Zeta potential of the core silica particles (a) as a function of solution pH at 25 °C and (b) as a function of temperature at pH 9.

Details of Approach to Modelling Temperature Dependent Hydrodynamic Data of Modified Particles in Water

Owing to the unusual shape of the intensity average hydrodynamic diameter (D_{hyd}) as a function of temperature, a simple analytical model, such as a sigmoidal fit, was not adequate to calculate the mid-point temperature used to define the LCST. To accurately determine this temperature, equations SE1 to SE25 (detailed in Table S1) were used to model the increasing temperature results (15 to 45 °C) for the five PNIPAM brush modified samples displayed in Figure 2 of the main manuscript.[1] This enabled the maximum, minimum and mid-point D_{hyd} to be defined (Figure S3 shows the results for the 1 hr sample).

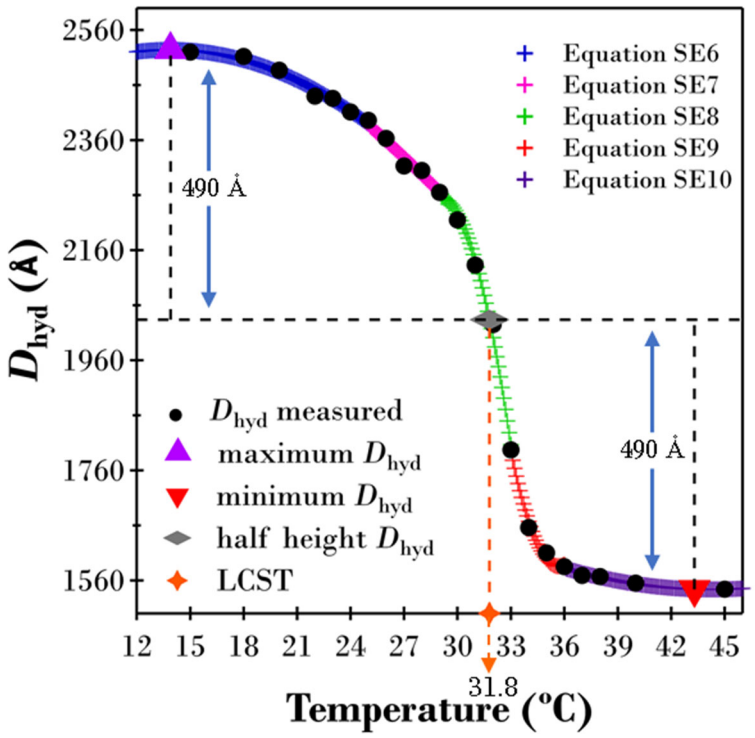

Figure S3. Intensity average hydrodynamic diameter (D_{hyd}) as a function of increasing temperature for 1 hr sample. The diameter has been modelled using the five quadratic equations (SE6 to SE10) in Table S1 and 0.1 °C increments to yield the maximum, minimum and mid-point D_{hyd} and the LCST.

Table S1. Temperature range and equations used for modelling temperature dependent hydrodynamic diameter for 0.5, 1, 2, 4 and 6 hr samples along with the calculated LCST.

Sample	Temperature range (°C)	Equation	Quadratic formula	R^2	LCST (°C)
0.5 hr	8 to 24	SE1	$y = -0.0732x^2 + 1.7228x + 235.83$	0.984	**30.72**
	24 to 29	SE2	$y = -0.5286x^2 + 24.689x - 53.383$	0.998	
	29 to 33	SE3	$y = -1.1071x^2 + 57.773x - 525.98$	0.998	
	33 to 35	SE4	$y = 1.2x^2 - 85.7x + 1696.6$	0.996	
	35 to 46	SE5	$y = 0.058x^2 - 5.1511x + 276.44$	0.967	
1 hr	8 to 25 (+)	SE6	$y = -0.1083x^2 + 2.9978x + 231.68$	0.9881	**31.80**
	25 to 29 (+)	SE7	$y = -0.0446x^2 - 0.6425x + 282.72$	0.9748	
	29 to 33 (+)	SE8	$y = -2.7286x^2 + 157.91x - 2058.9$	0.9934	
	33 to 36 (+)	SE9	$y = 2.9x^2 - 206.92x + 3849.6$	0.9898	
	36 to 46 (+)	SE10	$y = 0.0573x^2 - 5.0668x + 266.36$	0.9686	
2 hr	8 to 28	SE11	$y = -0.0742x^2 + 1.4465x + 255.77$	0.9853	**31.82**
	28 to 30	SE12	$y = -0.4196x^2 + 19.452x + 22.021$	0.999	
	30 to 33	SE13	$y = -3.45x^2 + 202.75x - 2749.9$	0.9984	
	33 to 36	SE14	$y = 3.3x^2 - 235.76x + 4369.6$	0.9948	
	36 to 46	SE15	$y = 0.0512x^2 - 4.6177x + 258.35$	0.97	
4 hr	8 to 25	SE16	$y = -0.1368x^2 + 4.0209x + 246.45$	0.982	**32.23**
	25 to 30	SE17	$y = -0.2625x^2 + 10.537x + 162.75$	0.986	
	30 to 34	SE18	$y = -2.95x^2 + 171.33x - 2241.9$	0.999	
	34 to 36	SE19	$y = 1.4x^2 - 102.9x + 2053.4$	0.989	
	36 to 46	SE20	$y = 0.0656x^2 - 5.8627x + 289.79$	0.968	
6 hr	8 to 24	SE21	$y = -0.0832x^2 + 1.4971x + 291.29$	0.9974	**32.23**
	24 to 30	SE22	$y = -0.2851x^2 + 11.608x + 165.35$	0.9970	
	30 to 34	SE23	$y = -4.2714x^2 + 254.35x - 3529.7$	0.9997	
	34 to 37	SE24	$y = 1.725x^2 - 126.63x + 2491.5$	0.9989	
	37 to 46	SE25	$y = 0.0734x^2 - 6.4359x + 305.19$	0.9592	

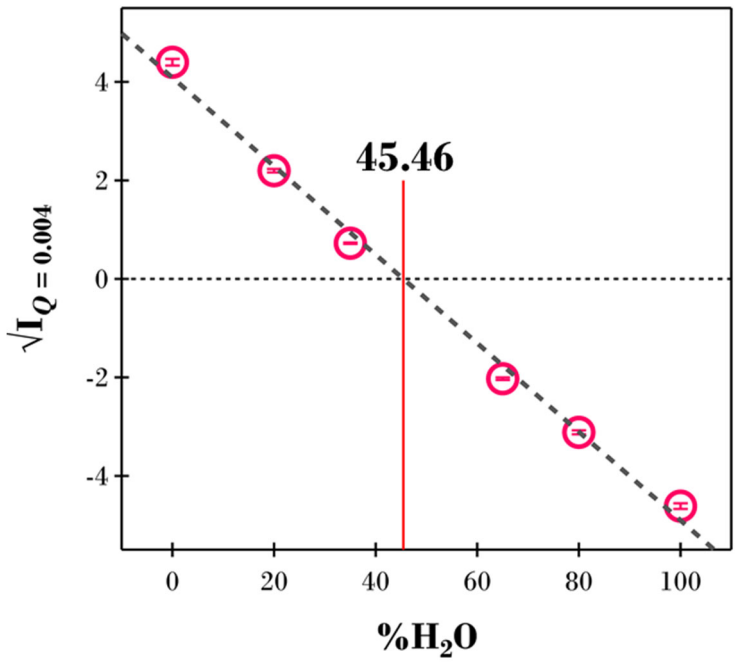

Figure S4. Contrast match results for PNIPAM brush modified particles at 18 °C with the square root of intensity (I) at $Q = 0.004$ plotted as a function of the % of H_2O in H_2O/D_2O mixture. Red vertical line indicates % H_2O at contrast matched point for the silica core (45.46%).

Preparation of SANS samples

~0.05 g of wet PNIPAM brush modified particles (approximately 50% solvent) were dispersed in 10 mL of a H_2O/D_2O solvent mixture containing 47% H_2O. The SLD of the solvent was determined during the fitting process to be 2.9×10^{-6} Å^{-2} indicating slightly more H_2O (50%) in the mixture than expected, which is ascribed to the remaining H_2O in the initial wet polymer brush modified particles. The SLD of the particles was determined to be 3.2×10^{-6} Å^{-2} which is in good agreement with Figure S4 (45.5% H_2O in the solvent mixture). The core particle radius was determined to be 650 Å.

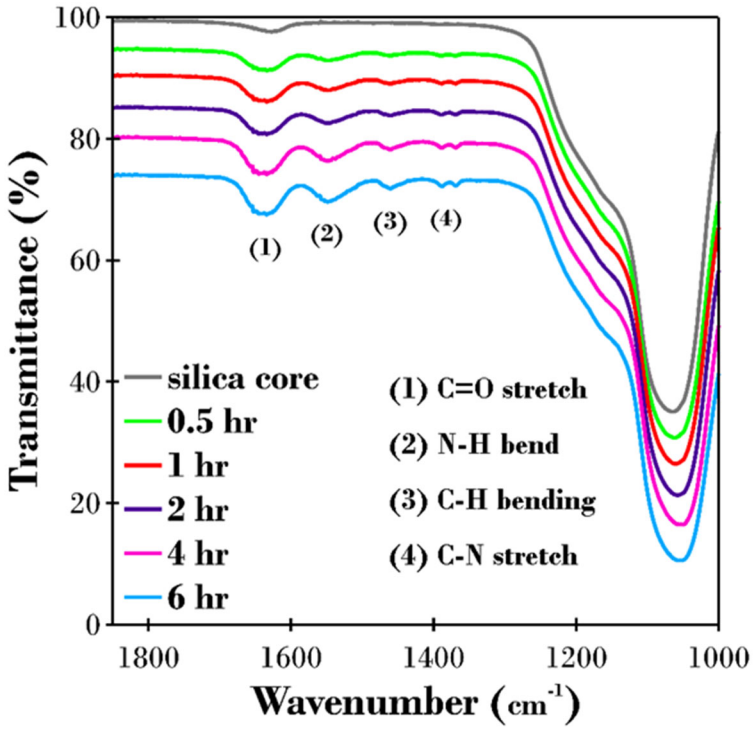

Figure S5. FTIR spectra of unmodified silica core particles, and the series of PNIPAM brush modified particles, showing the increase of peaks associated with the PNIPAM brush layer as a function of synthesis time. Data have been normalised to the SiO_2 peak at 1060 cm^{-1} and vertically offset for clarity.

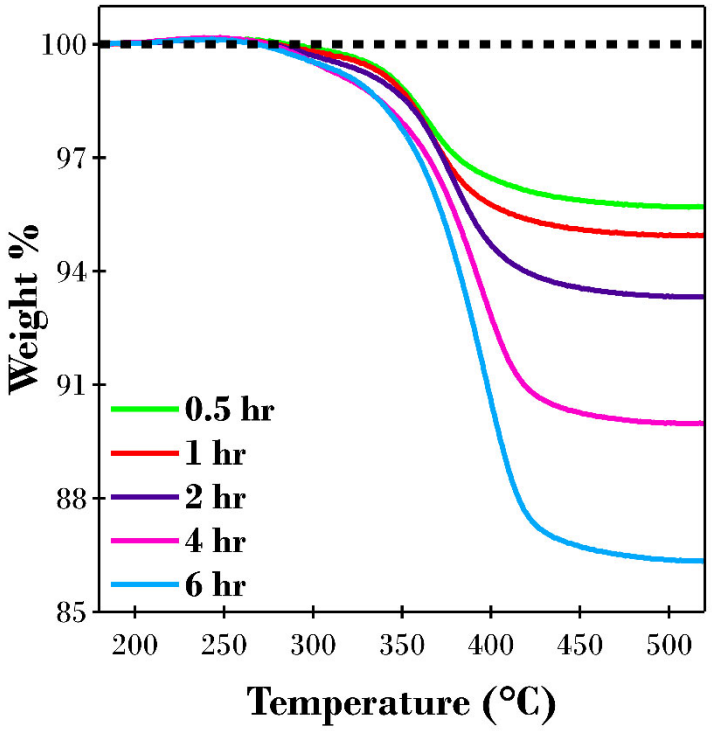

Figure S6. Percentage weight loss as a function of temperature for the series of PNIPAM brush modified particles (data normalised to the silica core at 180 °C to ensure all weight loss is due to the PNIPAM shell).

SasView sphere onion model description[2, 3]

This model provides the form factor, $P(q)$, for a multi-shell sphere where the scattering length density (SLD) of each shell is described by an exponential, linear, or constant function. The form factor is normalised by the volume of the sphere where the SLD is not identical to the SLD of the solvent. The *radius* represents the core radius r_0 and *thickness[k]* represents the thickness of the shell, $r_{k+1} - r_k$.

Table S2. Sphere onion model parameters with a description.

Parameter	Description	units
n_shells	number of shells	none
scale	source intensity	none
background	source background	cm^{-1}
sld_solvent	solvent scattering length density	$10^{-6}Å^{-2}$
sld_core	core scattering length density	$10^{-6}Å^{-2}$
radius_core	radius of core	Å
sld_in[n_shells]	scattering length density at inner radius of shell k	$10^{-6}Å^{-2}$
sld_out[n_shells]	scattering length density at outer radius of shell k	$10^{-6}Å^{-2}$
thickness[n_shells]	thickness of shell k	Å
A[n_shells]	decay rate of scattering length density for shell k	$Å^{-1}$

Definition

The 1D scattering intensity is calculated in the following way

$$P(q) = [f]^2 / V_{\text{particle}}$$

where

$$f = f_{\text{core}} + \left(\sum_{\text{shell}=1}^{N} f_{\text{shell}} \right) + f_{\text{solvent}}$$

The shells are spherically symmetric with particle density $\rho(r)$ and constant SLD within the core and solvent, so

$$f_{\text{core}} = 4\pi \int_0^{r_{\text{core}}} \rho_{\text{core}} \frac{\sin(qr)}{qr} r^2 \mathrm{d}r$$

$$f_{\text{shell}} = 4\pi \int_{r_{\text{shell}-1}}^{r_{\text{shell}}} \rho_{\text{shell}}(r) \frac{\sin(qr)}{qr} r^2 \mathrm{d}r$$

$$f_{\text{solvent}} = 4\pi \int_{r_N}^{\infty} \rho_{\text{solvent}} \frac{\sin(qr)}{qr} r^2 \mathrm{d}r$$

and the volume is $V(r) = \frac{4\pi}{3} r^3$. The volume of the particle is determined by the outer shell, so $V_{\text{particle}} = V(r_N)$.

The SLD of a shell is therefore defined by

$$\rho_{\text{shell}}(r) = Bexp(A(r - r_{\text{shell}-1})/\Delta t_{\text{shell}}) + C \;\; for\; A \neq 0$$

where $B = \frac{\rho_{\text{out}} - \rho_{\text{in}}}{e^A - 1}$ and $C = \frac{\rho_{\text{in}} e^A - \rho_{\text{out}}}{e^A - 1}$

This function becomes linear as A_shell approaches 0.

Table S3. SasView parameters used for modelling SANS data for the 2 hr PNIPAM brush modified sample as a function of temperature presented in Figure 5.

2 hr sample					
temperature (°C)	**18**	**25**	**30**	**32.5**	**40**
scale	0.0450	0.0418	0.0333	0.00704	0.00260
background	0.41	0.41	0.41	0.41	0.42
sld_solvent	2.9	2.9	2.9	2.9	2.9
sld_core	3.2	3.2	3.2	3.2	3.2
radius_core	650	650	650	650	650
sld_in1	3.2	3.2	3.2	3.2	3.2
sld_out1	2.3	2.2	2	1.7	1.65
thickness 1 (Å)	20	20	20	20	20
A1	-10	-10	-10	-10	-10
sld_in2	2.3	2.2	2	1.7	1.65
sld_out2	2.4	2.4	2.5	2.7	2.6
thickness 2 (Å)	39.738	50	68	80	105
A2	1	1	2	8	8
sld_in3	2.4	2.4	2.5	2.7	2.6
sld_out3	2.9	2.9	2.9	2.9	2.9
thickness 3 (Å)	3678.5	3479.8	3000	1450	900
A3	-14.43	-15	-12.5	-5	-14
χ^2	1.174	1.339	1.777	1.440	2.135

Table S4. SasView parameters used for modelling SANS data for the 6 hr PNIPAM brush modified sample as a function of temperature presented in Figure 5.

6 hr sample					
temperature (°C)	**18**	**25**	**30**	**32.5**	**40**
scale	0.0467	0.0327	0.0307	0.00852	0.00100
background	0.42	0.42	0.43	0.43	0.43
sld_solvent	2.9	2.9	2.9	2.9	2.9
sld_core	3.2	3.2	3.2	3.2	3.2
radius_core	650	650	650	650	650
sld_in1	3.2	3.2	3.2	3.2	3.2
sld_out1	2.3	2.2	2.035	1.8	1.65
thickness 1 (Å)	20	20	20	20	20
A1	-10	-10	-10	-10	-10
sld_in2	2.3	2.2	2.035	1.8	1.65
sld_out2	2.5	2.4	2.43	2.6	2.6
thickness 2 (Å)	160	118	97	120	170
A2	0.5	1	1.8	5	8
sld_in3	2.5	2.4	2.43	2.6	2.6
sld_out3	2.9	2.9	2.9	2.9	2.9
thickness 3 (Å)	3500	3083.7	2800	1487.4	917.71
A3	-10	-10.5	-9	-4.065	-15
χ^2	1.494	1.841	2.835	1.250	2.053

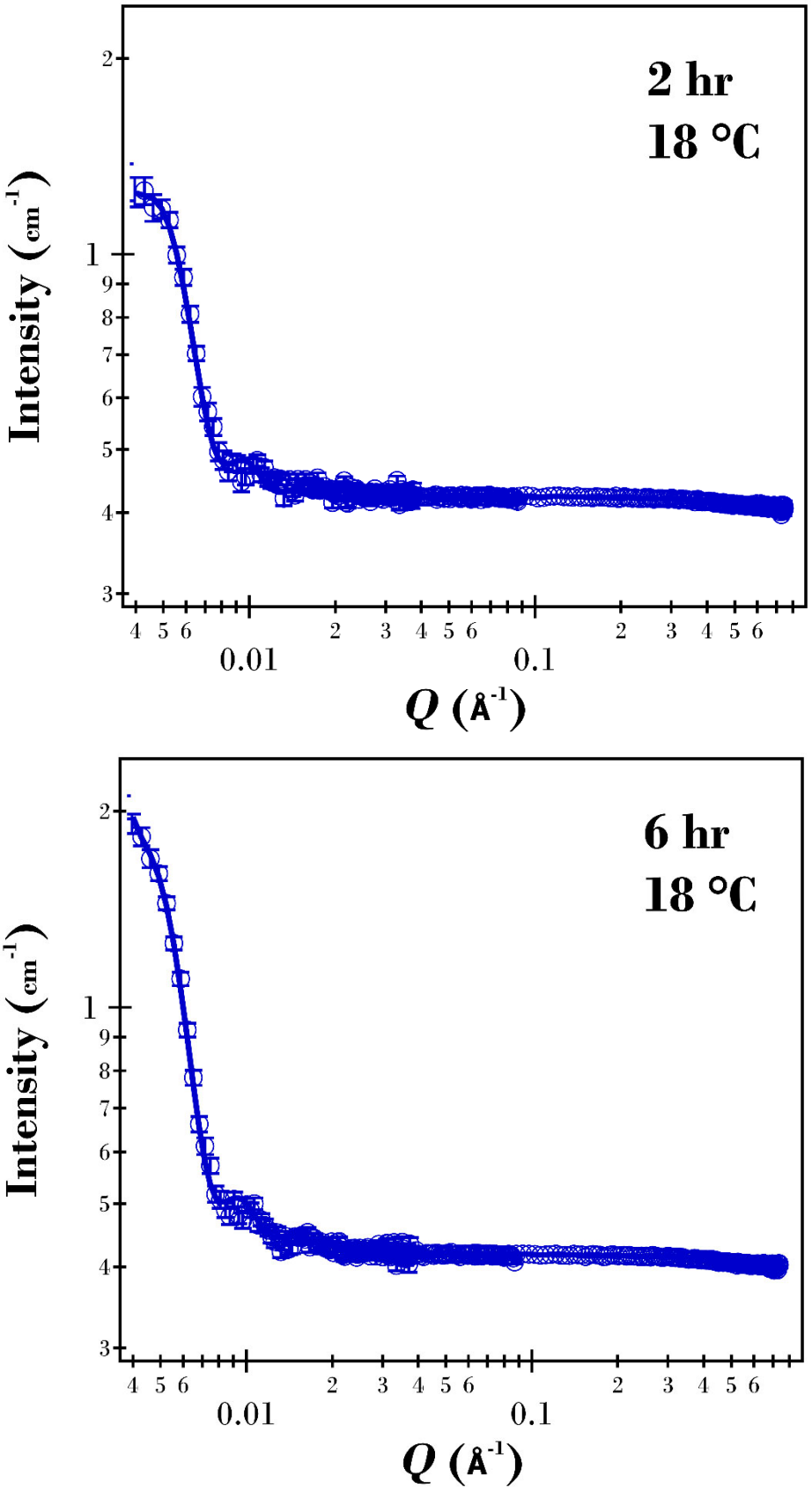

Figure S7. SANS data with fit for (top) 2 hr and (bottom) 6 hr samples at 18 °C for full *Q* range between 0.004 and 0.75 $Å^{-1}$

References

1. B. A. Humphreys, E. J. Wanless and G. B. Webber, *Journal of Colloid and Interface Science*, 2018, **516**, 153-161.
2. M. Doucet, J. H. Cho, G. Alina, J. Bakker, W. Bouwman, P. Butler, K. Campbell, M. Gonzales, R. Heenan, A. Jackson, P. Juhas, S. King, P. Kienzle, J. Krzywon, A. Markvardsen, T. Nielsen, L. O'Driscoll, W. Potrzebowski, R. Ferraz Leal, T. Richter, P. Rozycko and A. Washington, (2017, March 25) SasView version 4.1. Zenodo, https://doi.org/10.5281/zenodo.438138, DOI: (10.5281/zenodo.438138).
3. L. A. Feigin and D. I. Svergun, *Structure Analysis by Samll-Angle X-Ray and Neutron Scattering*, Plenum Press, New York, 1987.