Supporting information:

1. Static and Dynamic Light Scattering (SLS and DLS)

Static light scattering (SLS) and dynamic light scattering (DLS) were conducted as a function of the detection angle *Θ*. In SLS measurements, the scattering intensities for sample (I_s), toluene (I_{tol}), and PBS as solvent (I_0) were measured as a function of the scattering angle Θ (range from 30 to 130°). Furthermore, the dark current I_{dark} (detector intensity with laser switched off) was measured. The obtained intensities were converted into Rayleigh scattering (R) to obtain absolute scattering of the sample according to equation 1:

$$R(\Theta) = \left(\frac{I_s(\Theta) - I_0(\Theta)}{I_{tol}(\Theta) - I_{dark}}\right)\frac{n_s^2}{n_{tol}^2}R_{tol} \quad (1)$$

In which n_{tol} = 1.494 and n_s = 1.332 are the refractive index of the reference and solvent, respectively, and R_{tol} is the known absolute Rayleigh scattering for toluene at 632.8 nm wavelength. For R_{tol}, we used 1.02 10^{-3} m^{-1}. [1] Then, the scattering angle Θ was converted into the wave vector q based on equation 2:

$$q = \frac{4\pi n_s \sin\frac{\Theta}{2}}{\lambda} \quad (2)$$

where λ is the wavelength in vacuum.

- Therefore, R_g was obtained according to Guinier[2] by plotting $\ln(R)$ as a function of q^2 in which the slope is equal to: $\frac{R_g^2}{3}$ (results are shown in table 1)
- Hydrodynamic radius *(R_h)* was obtained by DLS. The decay rate, *Γ,* extracted from the second order cumulant was plotted as a function of q^2. For monodisperse particles this should result in a straight line with a slope equals to the diffusion coefficient D and from that R_h was obtained using the Stokes Einstein equation 3: (results are shown in table 1)

$$D = \frac{kT}{6\pi\eta R_h} \quad (3)$$

- To obtain M_w, the absolute scattering intensity R was plotted as a function of q and extrapolated to $q = 0$. The absolute scattering *R* should equal to: (results are shown in table 1)

(4) $$R = K_r C M_w\, S(q)\, P(qR)$$

At low concentration, the structure factor $S(q) \approx 1$ and at $q \to 0$ the form factor was considered $P(qR) = 1$, therefore, $R\,(q \to 0) = K_r$ *C,* M_w where K_r an optical constant (equation 5) and *C* the particle concentration in $kg.m^{-3}$.

(5) $$K_r = \frac{4 n_s^2 \pi^2}{\lambda^4 N_{Av}} \left(\frac{dn}{dc}\right)^2$$

Table 1: Characteristics of core crosslinked flower-like micelles measured at 10 and 40 °C; For comparison, micelle characteristics at other temperatures have been reported before for a slightly different polymer batch.[3]

T (°C)	R_g (nm)[a]	R_h (nm)[b]	R_g/R_h	$M_{w\,(mic.)}$ (10^6 Da)	N_{agg}[d]
10	46.0±0.8	48.2±0.9	0.95±0.00	16.3±0.4	430±10
40	30±0.8	35.4±0.4	0.85±0.01	14.8±0.2	381±10

2. Calculation of Effective Volume Fraction (φ)

$V_t = Micelles\ (mg) \times 0.83\ cm.g^{-1}\ (partial\ specific\ volume\ of\ PNIPAM)^1) + PBS\ (mL)$

$Number\ of\ micelles\ = \dfrac{Micelles\ (gr)}{N_A\ \times M_w\ micelle}$, where N_A is Avogadro constant and M_w micelle molecular weight (15.55×10^6 kDa as the average molecular weight of micelles at 10 and 40 °C was considered)

$V_m = \ number\ of\ micelles\ \times\ volume\ of\ micelles\ at\ the\ corresponding\ temperature$.

Table 2: The summary of results for calculation of φ. T_c is 28 °C.

Sample conc. (wt%)	Micelles (mg)	PBS (mL)	Sample volume (V_t) (mL)	Number of micelles (×10^{15})	Volume of micelles (V_m)(mL)		φ or ($\frac{V_t}{V_m}$)	
					Below T_c	Above T_c	Below T_c	Above T_c
7.5	75	0.925	0.987	2.89	1.34	0.52	1.36	0.53
10	100	0.900	0.983	3.86	1.79	0.69	1.82	0.7
12.5	125	0.875	0.979	4.82	2.23	0.87	2.28	0.88
15	150	0.850	0.975	5.79	2.68	1.04	2.75	1.07
20	200	0.800	0.966	7.72	3.57	1.39	3.7	1.43
30	300	0.700	0.949	11.6	5.36	2.08	5.65	2.19

1. Wu, H., Correlations between the Rayleigh ratio and the wavelength for toluene and benzene. *Chemical Physics* **2010,** *367* (1), 44-47.
2. Guinier, A.; Fournet, G., *Small-Angle Scattering of X-Rays*. John Wiley and Sons, Inc., New York, 1955.
3. Najafi, M.; Kordalivand, N.; Moradi, M. A.; van den Dikkenberg, J.; Fokkink, R.; Friedrich, H.; Sommerdijk, N.; Hembury, M.; Vermonden, T., Native Chemical Ligation for Cross-Linking of Flower-Like Micelles. *Biomacromolecules* **2018,** *19* (9), 3766-3775.
4. Sommer, C.; Pedersen, J. S.; Stein, P. C., Apparent Specific Volume Measurements of Poly(ethylene oxide), Poly(butylene oxide), Poly(propylene oxide), and Octadecyl Chains in the Micellar State as a Function of Temperature. *The Journal of Physical Chemistry B* **2004,** *108* (20), 6242-6249.