Fine-tuning the architecture of microgels by varying the initiator addition time

Supplementary Information

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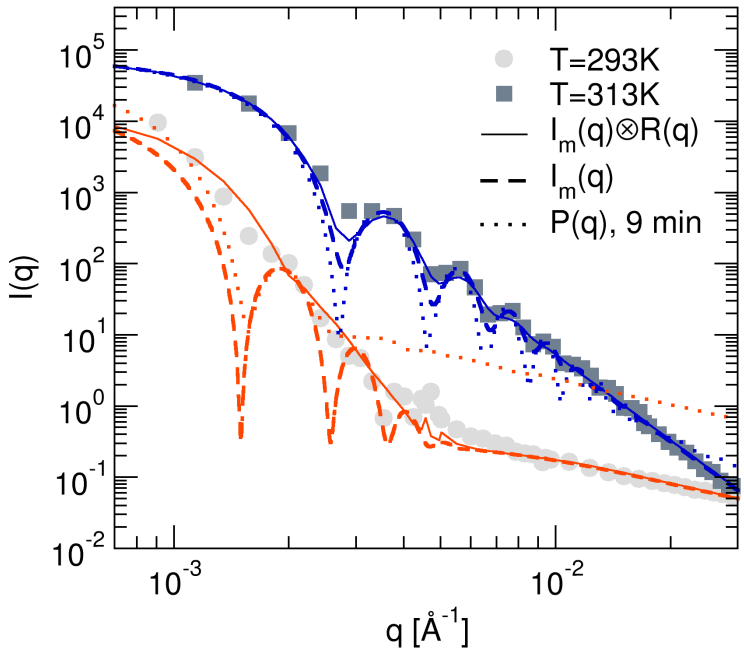

Figure S1: Experimental scattering intensity measured on the D22 diffractometer for microgels synthesised in the absence of surfactants in D_2O with KPS added in $t_{add} = 9$ min in the collapsed (313 K, dark gray squares) and in the swollen (293 K, light gray circles) state. Thin solid lines represent the best fits obtained as described in the main text and the resolution-free $I_m(q)$ curves are shown as thick dashed lines. Dotted lines are for simulations with the same model described in the main text for $t_{add} = 9$ min.

Table S1: Structural parameters obtained from the analysis of the SANS data, measured at 293 K and 313 K, for the microgels synthesised in the absence of surfactants in D_2O with KPS added in $t_{add} = 9$ min.

T $[K]$	t_{add} [min]	R $[nm]$	σ_f $[nm]$	$R + 2\sigma_f$ $[nm]$	$R/(R + 2\sigma_f)$
293	9.0	300 ± 50	40 ± 5	380 ± 60	0.79 ± 0.03
313	9.0	170 ± 3	0	170 ± 3	1

Table S2: Structural parameters obtained from the analysis of the SANS data, measured at 293 K and 313 K, for the microgels synthesised in the presence of surfactants in D_2O with KPS added at different t_{add} times.

T $[K]$	t_{add} [min]	R $[nm]$	σ_f $[nm]$	$R + 2\sigma_f$ $[nm]$	$R/(R + 2\sigma_f)$
293	0.2	250 ± 10	32 ± 6	310 ± 20	0.80 ± 0.03
293	1.0	173 ± 4	28 ± 4	230 ± 10	0.76 ± 0.03
293	9.0	155 ± 4	32 ± 5	220 ± 10	0.71 ± 0.03
313	0.2	112 ± 2	0	112 ± 2	1
313	1.0	96 ± 1	0	96 ± 1	1
313	9.0	86 ± 1	0	86 ± 1	1

Table S3: First- (Γ_1) and second-order (Γ_2) coefficients determined from the analysis of the intensity autocorrelation functions for the DLS data measured at 293 K and 313 K for microgels synthesized in the presence of surfactants, with KPS added at different t_{add} times. The parameters were obtained using the relation $g_2(t) - 1 = Ae^{-2\Gamma_1 t}(1 + \Gamma_2 t^2)^2$, where A is a scale factor.[1] In this framework, the polydispersity index (PDI) is calculated as $PDI = \frac{\Gamma_2}{\Gamma_1^2}$. These results, which align well with the analysis performed using the stretched exponential function described in the main text, indicate that the samples are monodisperse in both the swollen and collapsed states.

t_{add} [min]	Γ_1^{293K} $[s^{-1}]$	Γ_2^{293K} $[s^{-1}]$	PDI^{293K}	Γ_1^{313K} $[s^{-1}]$	Γ_2^{313K} $[s^{-1}]$	PDI^{313K}
0.2	273	3025	0.04	1019	14714	0.01
0.5	263	762	0.01	1025	22310	0.02
1	305	997	0.01	1159	5753	0.004
4	344	1975	0.02	1288	33601	0.02
9	375	3383	0.02	1277	10624	0.006

Table S4: Inverse of the first-order coefficient ($1/\Gamma_1$) and relaxation time (τ) determined from DLS measurements at 293 K and 313 K for microgels synthesized with KPS added at different t_{add} times. The overlap of these two quantities indicates that the sample can be considered monodisperse.

t_{add} [min]	$1/\Gamma_1^{293K}$ $[s]$	τ^{293K} $[s]$	$1/\Gamma_1^{313K}$ $[s]$	τ^{313K} $[s]$
0.2	0.00366	0.00372	9.80×10^{-4}	9.82×10^{-4}
0.5	0.00379	0.00366	9.75×10^{-4}	9.84×10^{-4}
1	0.00328	0.00320	8.62×10^{-4}	8.64×10^{-4}
4	0.00290	0.00284	7.75×10^{-4}	7.78×10^{-4}
9	0.00266	0.00270	7.82×10^{-4}	7.88×10^{-4}

References

(1) B. J. Frisken, *Applied Optics*, 2001, **40**, 4087–4091.