

One pot synthesis of responsive sulfobetaine nanoparticles by RAFT polymerisation: the effect of branching on the UCST cloud point.

Helen Willcock, Annhelen Lu, Claire F. Hansell, Emma Chapman, Ian R. Collins and Rachel K. O'Reilly.

Supporting Information.

Figure S1 - SEC traces showing the overlap of the RI and UV (309 nm) traces in the SEC of polymer 3a.

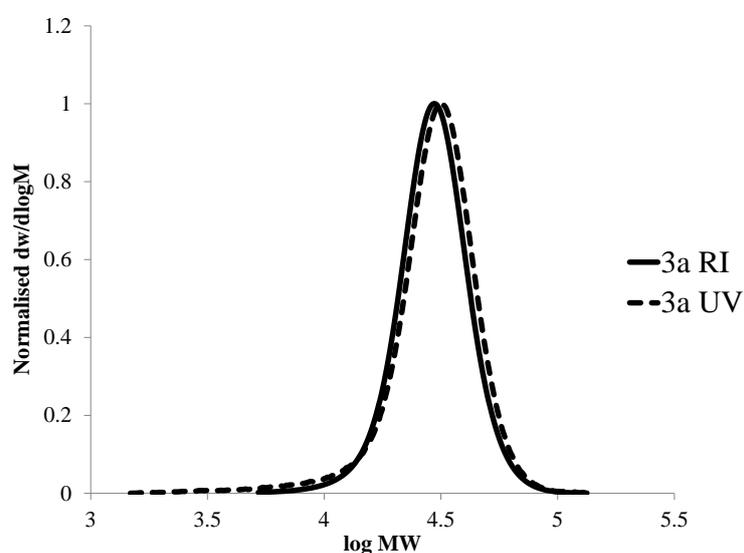


Figure S2 – Cloud point measurements of 4a in water at 1 mg/mL (measured cloud point 23°C).

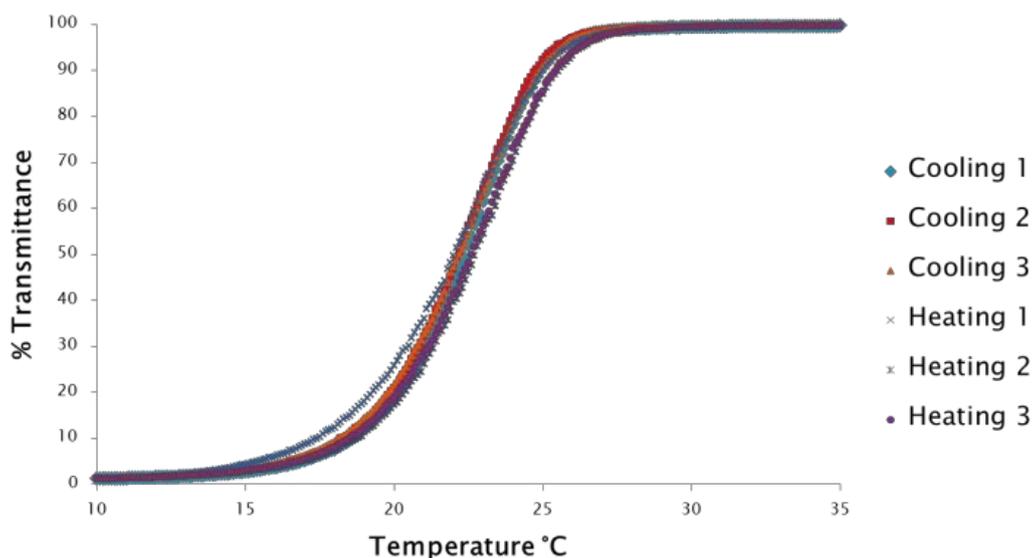


Figure S3 – Correlation function and DLS number, volume and intensity size data for **4b**. $D_{h(\text{number})}$ 10 nm, \bar{D} 0.217.

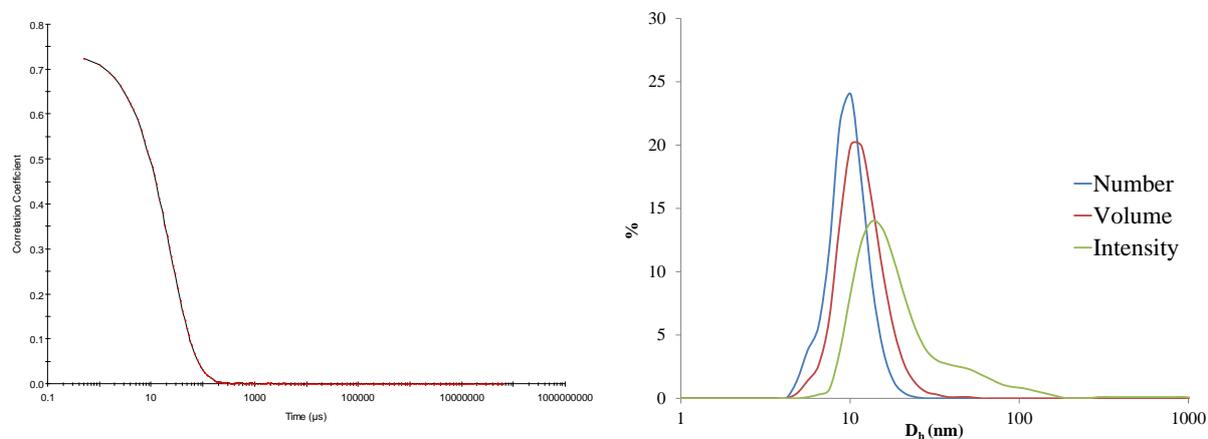


Figure S4 – Correlation function and DLS number, volume and intensity size data for **4c**. $D_{h(\text{number})}$ 11 nm, \bar{D} 0.474.

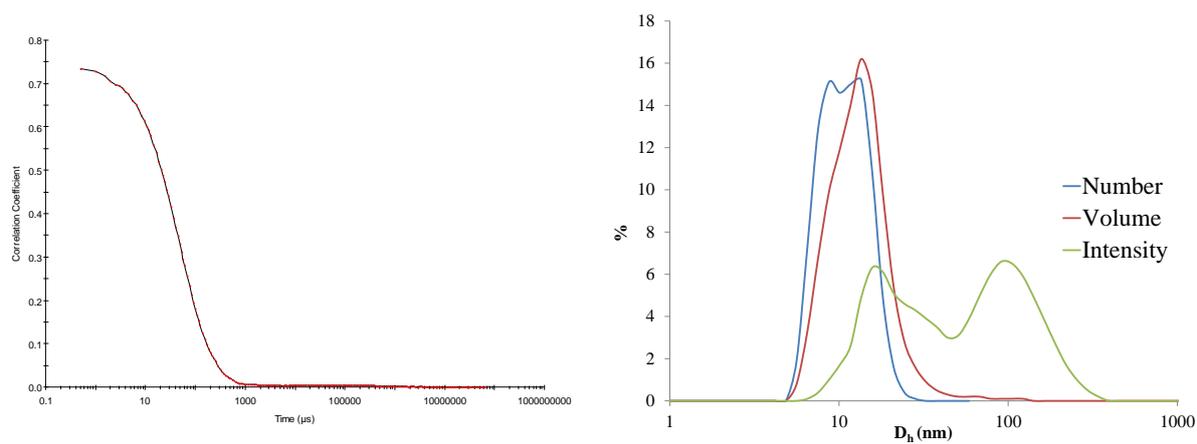


Figure S5 – Correlation function and DLS number, volume and intensity size data for **5b**. $D_{h(\text{number})}$ 15 nm, \bar{D} 0.322.

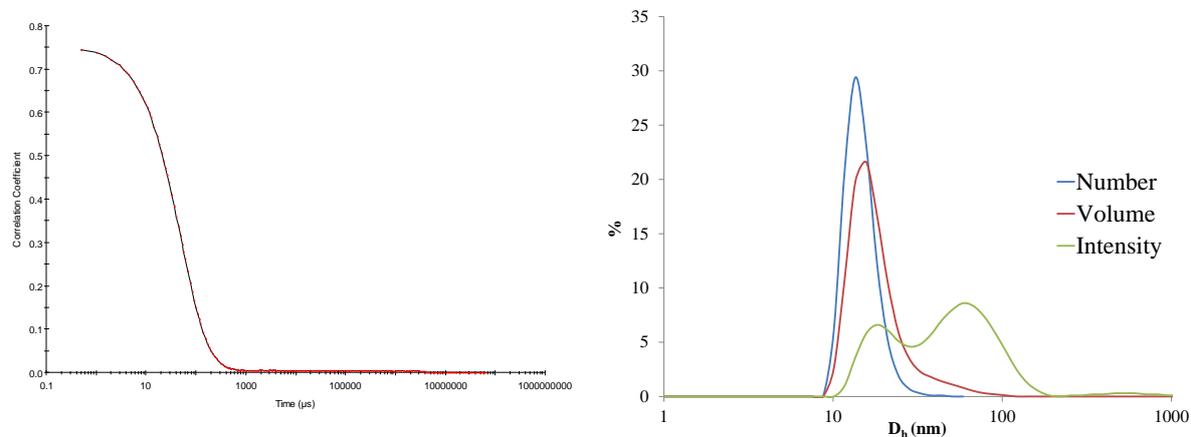


Figure S6 – Correlation function and DLS number, volume and intensity size data for **5c**. $D_{h(\text{number})}$ 14 nm, \bar{D} 0.362.

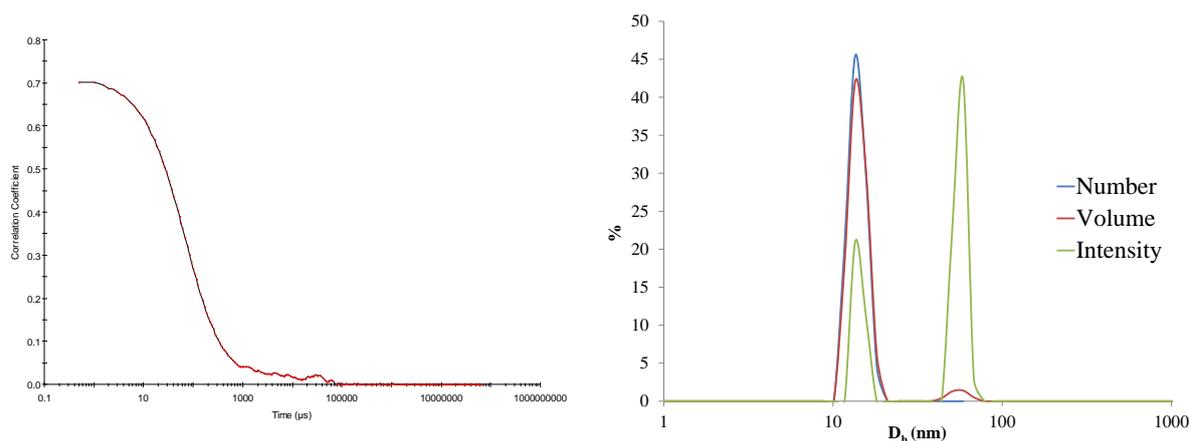


Figure S7 – Correlation function and DLS number, volume and intensity size data for **6b** @ 25°C. $D_{h(\text{number})}$ 20 nm, \bar{D} 0.246.

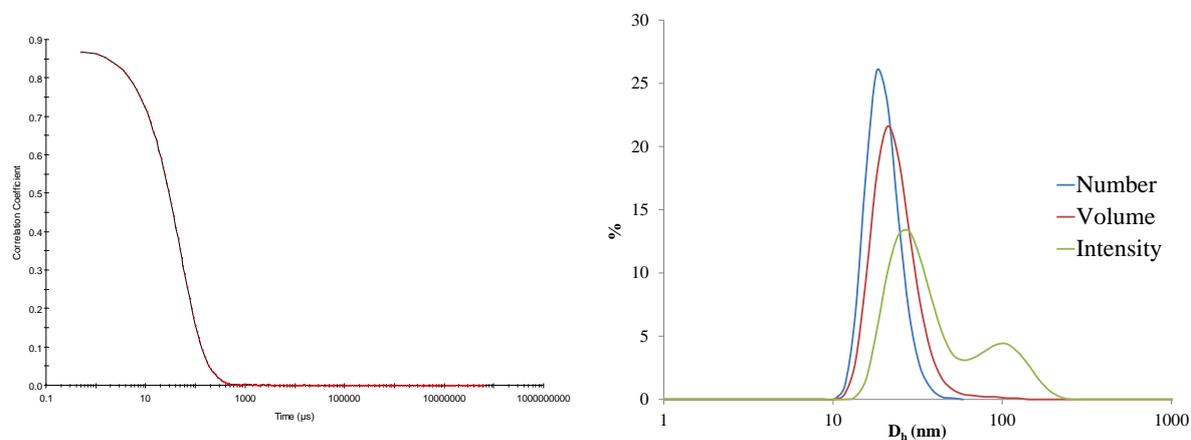


Figure S8 – Correlation function and DLS number, volume and intensity size data for **6b** @ 90°C.
 $D_{h(\text{number})}$ 25 nm, \bar{D} 0.206.

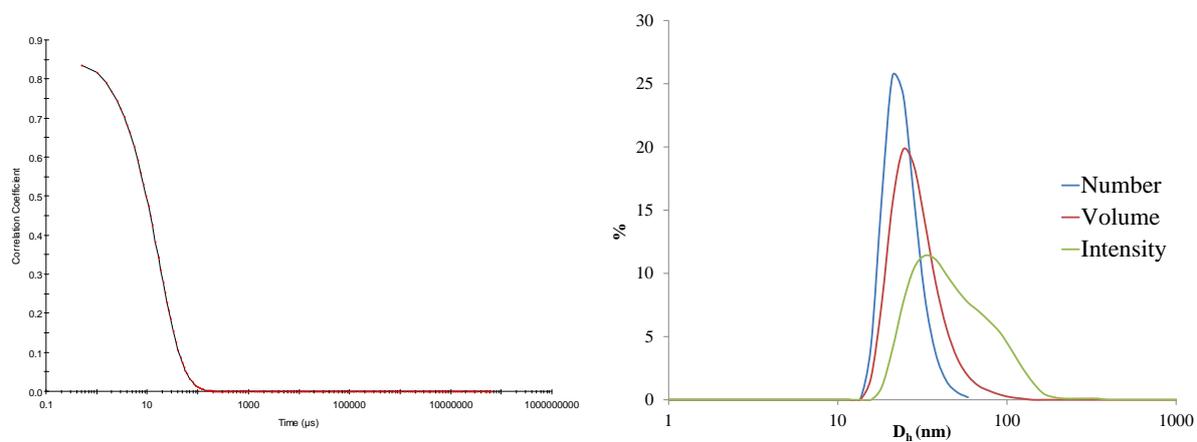


Figure S9 – Representative TEM image of **4c**.

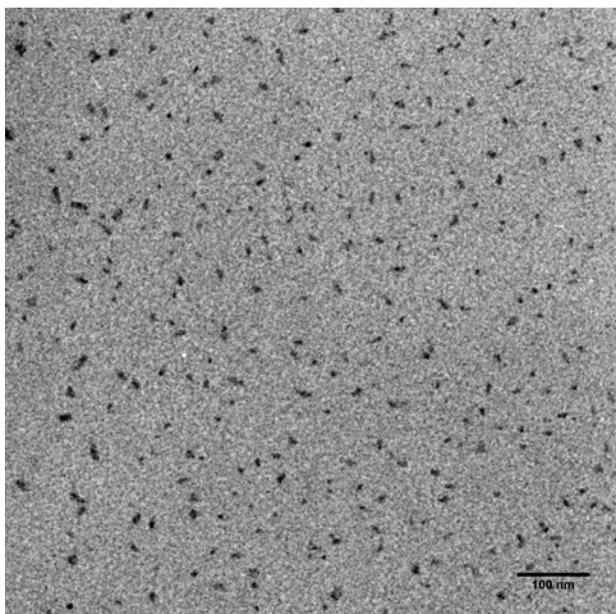


Figure S10 – Representative TEM image of **5b**.

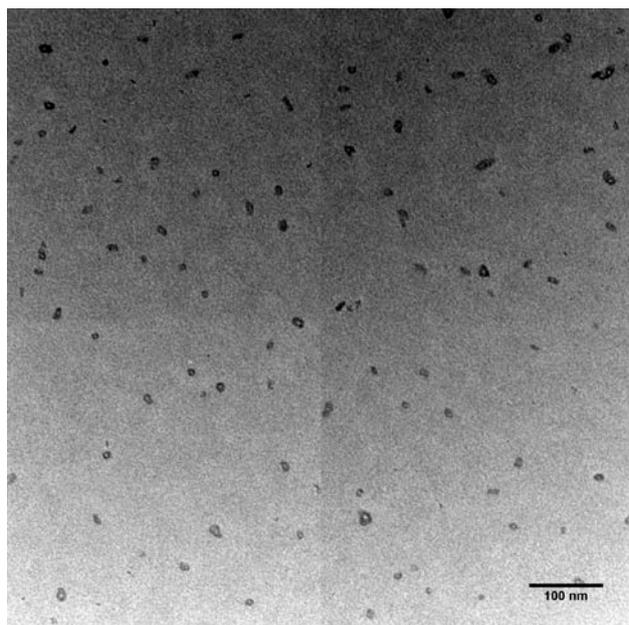


Figure S11 – Representative TEM image of **5c**.

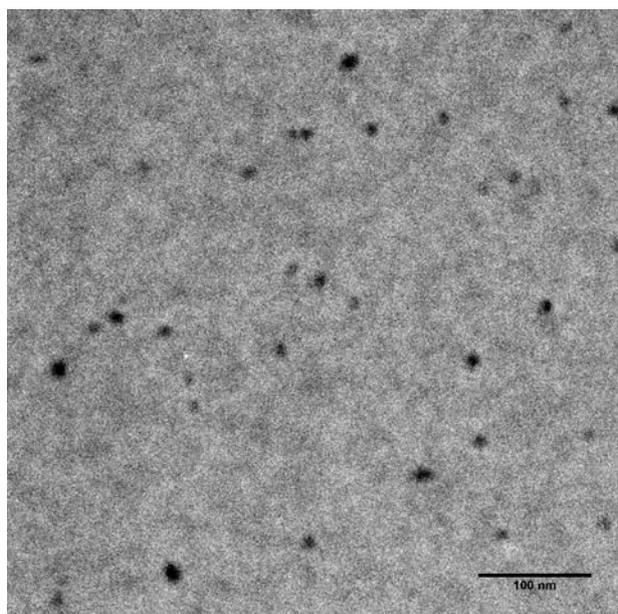


Figure S12 – Representative TEM image of **6c**.

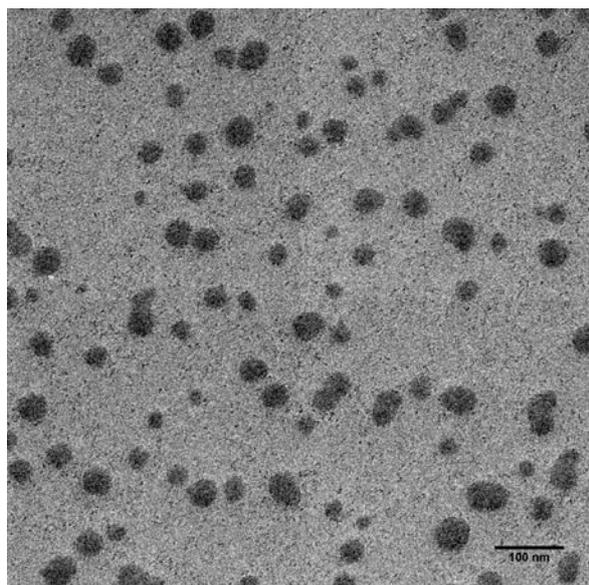


Figure S13 – Representative data from SLS measurements plotted as Kc/R_θ versus q^2 for **6a** in 0.5 M NaCl solution, where the data was extrapolated to zero angle for each concentration *via* a linear fit.

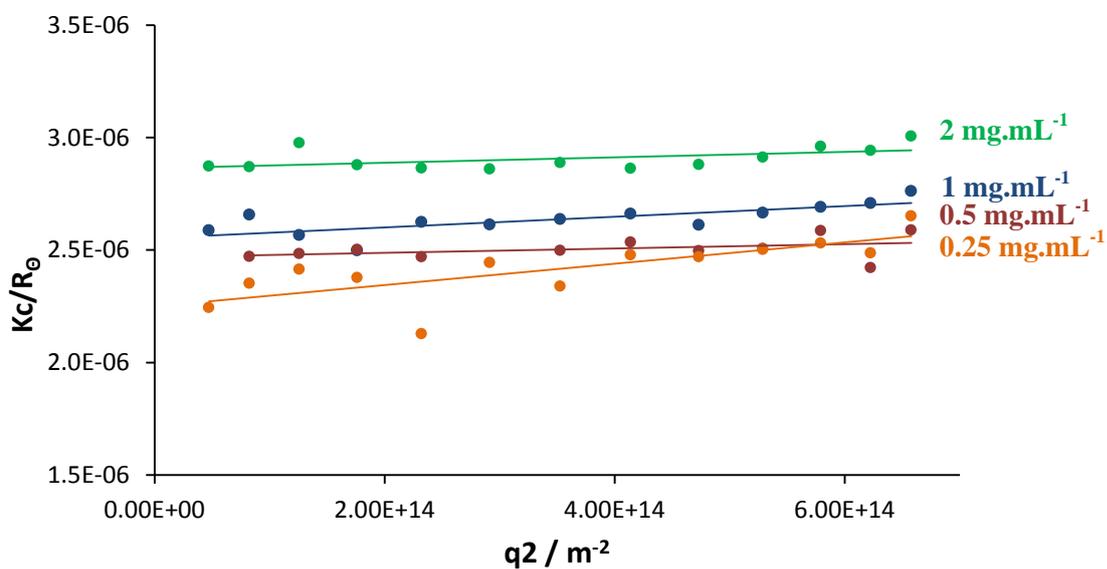


Figure S14 - SLS data plotted as Kc/R_0 versus concentration where the M_w was determined from the intercept of a linear fit.

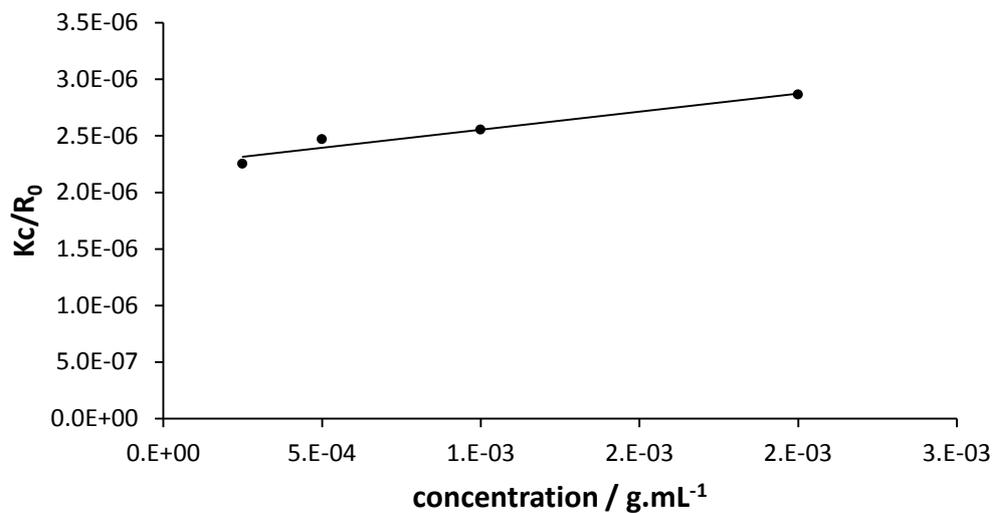


Figure S15 – DOSY NMR analysis of **6b** in D₂O.

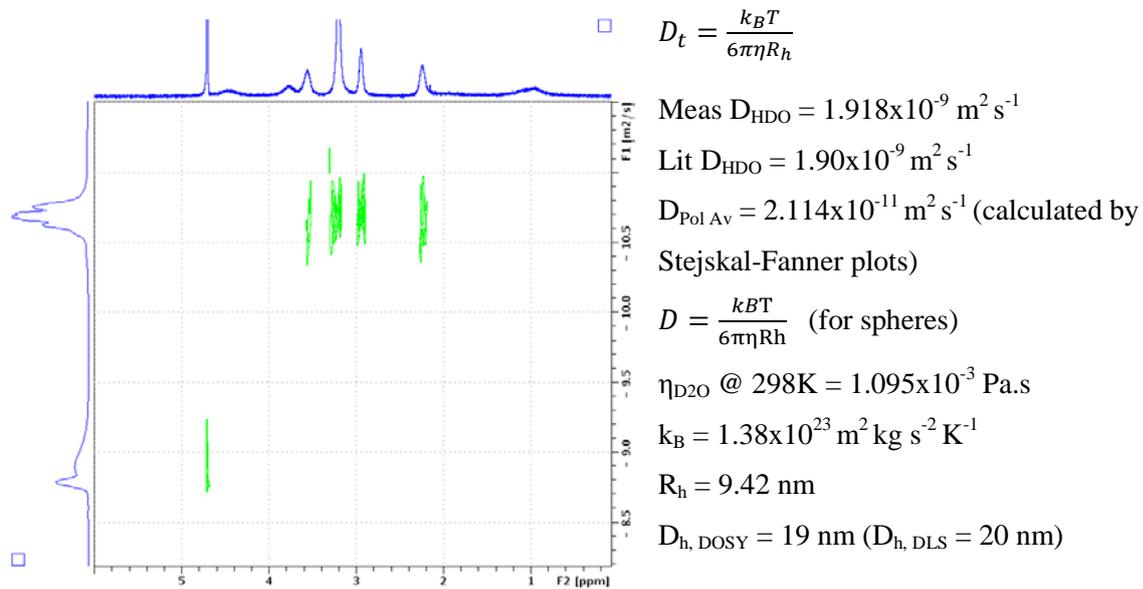


Table S1 – Temperature response of polymers **4b-6b** in H₂O at 0.25 mg/mL by DLS.

#	D_h (nm)	
	H ₂ O 25°C	H ₂ O 90°C
4b	10	13
5b	15	17
6b	20	25

Figure S16 – SEC traces of **6a** compared to a polymer synthesised by free radical polymerisation demonstrating the narrower *D* obtained when using RAFT polymerisation.

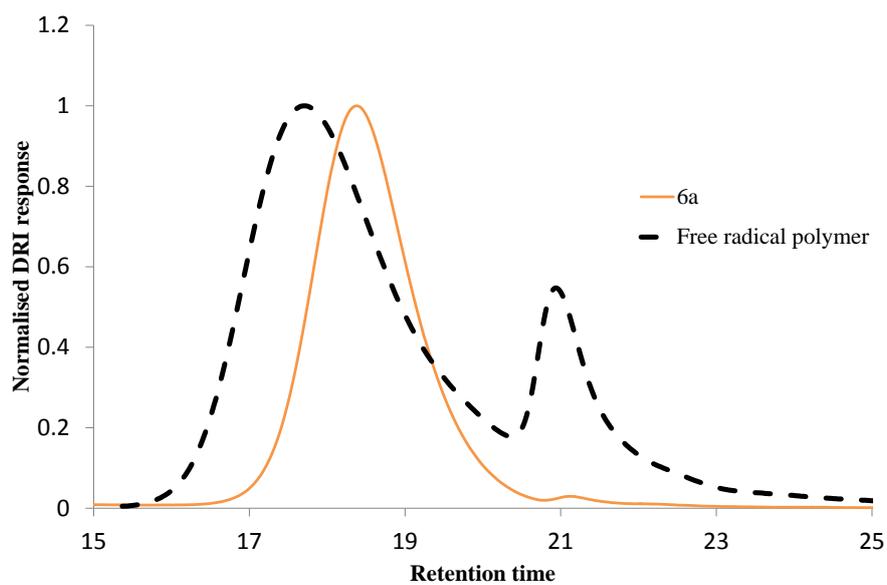


Figure S17 – Representative branched polymer ^1H NMR spectra in 0.5M NaCl in D_2O .

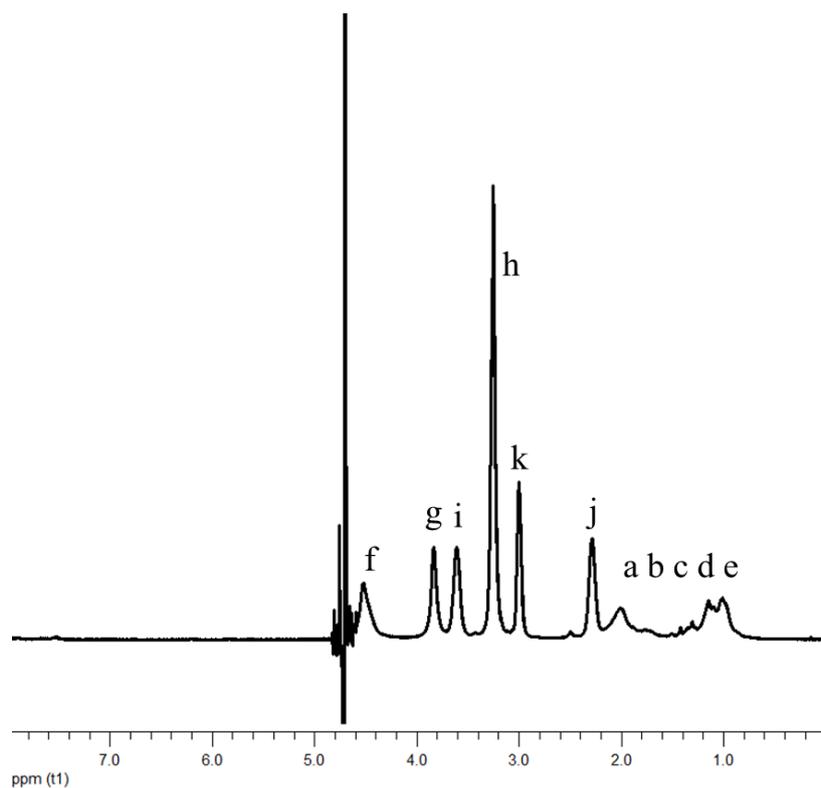


Figure S18 – Representative branched PDMAPS/PEGMA copolymer ^1H NMR spectra in 0.5M NaCl in D_2O .

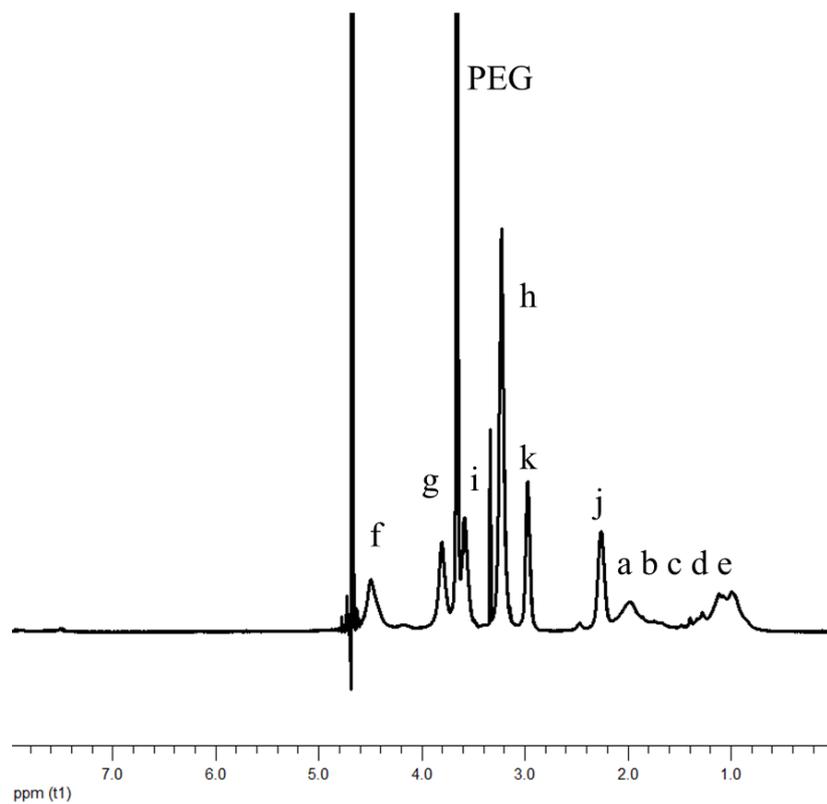


Table S2 – Additional cloud point data for branched polymers (X = no cloud point observed down to 4°C). n.b. measured by eye in fridge (^a) or water bath (^b).

Description	Cloud point at given concentration (°C)			
	50 mg/mL	20 mg/mL	10 mg/mL	1 mg/mL
20 kDa branched PDMAPS	4-8 ^a	4-8 ^a	X	X
20 kDa branched PEG/PDMAPS	X	X	X	X
100 kDa branched PDMAPS	>50 ^b	42 ^b	33 ^b	X
100 kDa branched PEG/PDMAPS	X	X	X	X
500 kDa branched PDMAPS	>50 ^b	48	36 ^b	X
500 kDa branched PEG/PDMAPS	X	X	X	X