

Supporting Information

Molecular assembly in block copolymer-surfactant nanoparticle dispersions: Information on molecular exchange and apparent solubility from high resolution and PFG NMR.

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Particles labeled with HMDSO

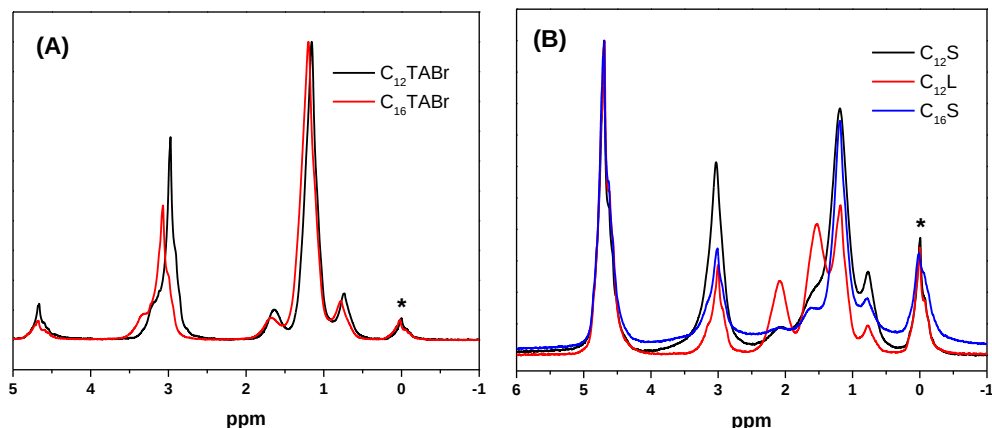


Figure S1. Low resolution ^1H NMR spectra for samples labeled with the hydrophobic probe HMDSO. (A) micellar solutions of C_{12}TABr and C_{16}TABr at 25 mM. (B) BCPCS *intact* dispersions at 1.0 wt%. In all cases, the surfactant-to-HMDS molar ratio is 0.01. For both cases, * denotes the peak used to measure the self-diffusion of HMDSO.

Conductivity

Aqueous solutions of C_{12}TABr and C_{16}TABr surfactant, as a function of surfactant ion concentration were prepared, and their conductivity was measured in a digital conductivity meter. The results are displayed in Figure S2. The conductivity of the C_{12}S , C_{16}S and C_{12}L *intact* samples at 1 wt% is also displayed in the same figure (horizontal lines). If one assumes $\alpha = 0.3$ (see text in the main article), the concentration of dissociated surfactant ions in the solution would be around 6 mM, 5.4 mM and 4 mM for C_{12}S , C_{16}S and C_{12}L , respectively (based on the molecular weight of a BCPCS unimer - diblock copolymer chain with its associated surfactant counterions). Clearly, the results in Figure S2 show that the measured conductivities of *intact* samples at 1 wt% corresponds to much lower concentrations of free surfactant ions.

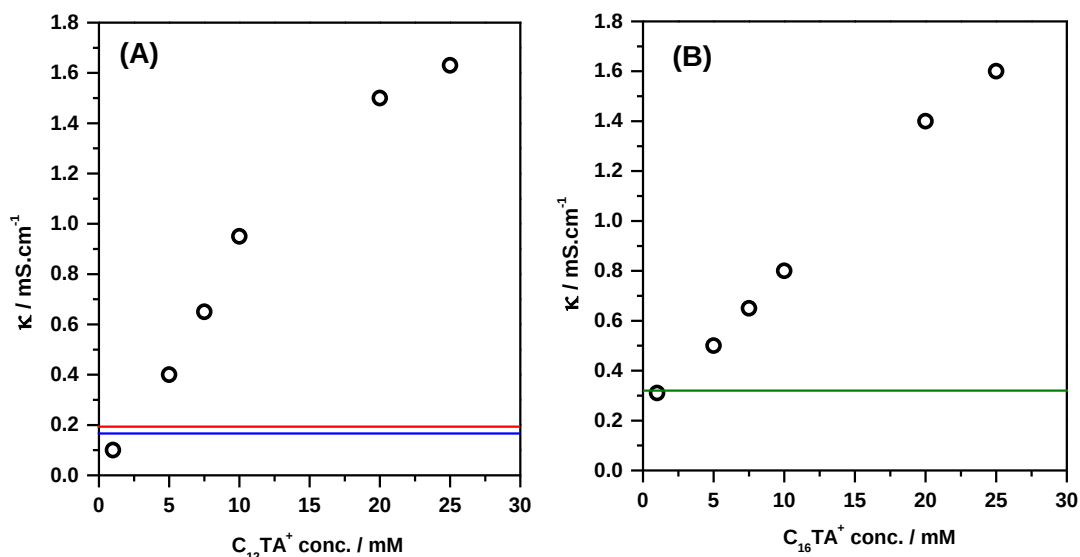


Figure S2. (A). Conductivity (κ) of $C_{12}TABr$ solutions as a function of $C_{12}TA^+$ surfactant ion concentration (open symbols). The horizontal lines denote the conductivity of $C_{12}S$ (red) and $C_{12}L$ (blue) *intact* samples at 1 wt%. (B). Conductivity (κ) of $C_{16}TABr$ solutions as a function of $C_{16}TA^+$ surfactant ion concentration (open symbols). The horizontal green line denotes the conductivity of $C_{16}S$ *intact* sample at 1 wt%.

Self-diffusion measurements as a function of time of sample preparation

A 1 wt% $C_{12}S$ *intact* sample was prepared in D_2O and in a mixture of (30:70) $H_2O:D_2O$. Soon after preparation, the samples were analyzed by PFG NMR at time 0 (few minutes after sample preparation) and at different time intervals. The obtained D values for both surfactant ion and polyion are presented in Figure S3. Clearly, the obtained values increase with time. The low-resolution spectra used for self-diffusion measurements in D_2O were also registered as a function of time and are presented in Figure S4. After 3 days, the samples were gently mixed and measured again. The results (Table S1 and Figure S5) shows that the obtained self-diffusion coefficients and line shapes are remarkably similar to the ones obtained at time 0.

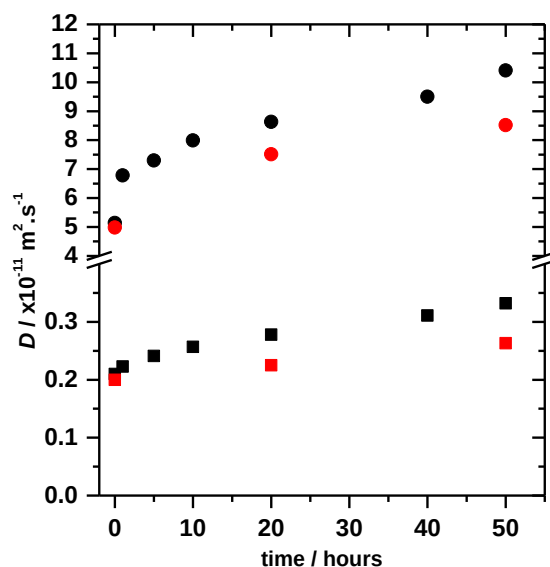


Figure S3. Self-diffusion coefficients (D) for surfactant ion (circles) and polyion (squares) in an *intact* 1.0 wt. % C_{12}S as a function of time for a sample prepared in D_2O . Red points refer to a sample in which the solvent is a 30:70 $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixture.

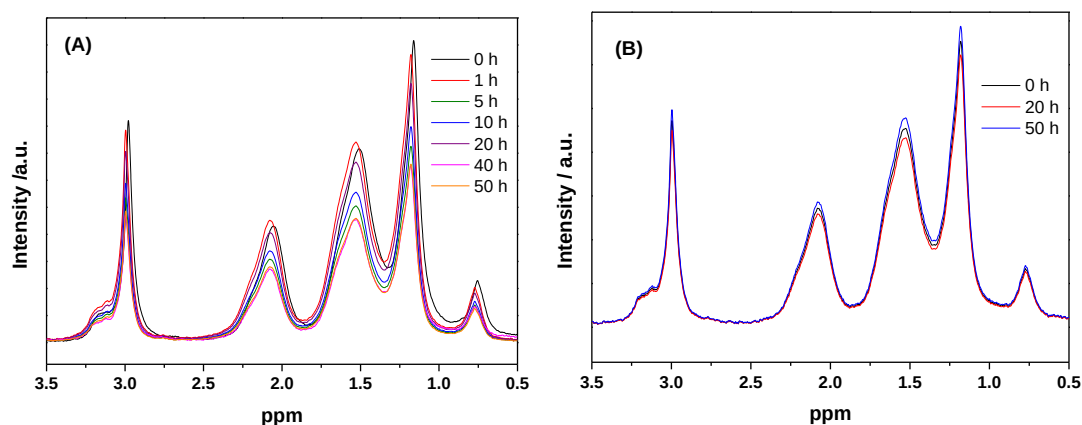


Figure S4. Low resolution ^1H NMR spectra for an *intact* 1.0 wt. % C_{12}S sample as a function of time of sample preparation in (A) D_2O ; (B) 30:70 $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixture.

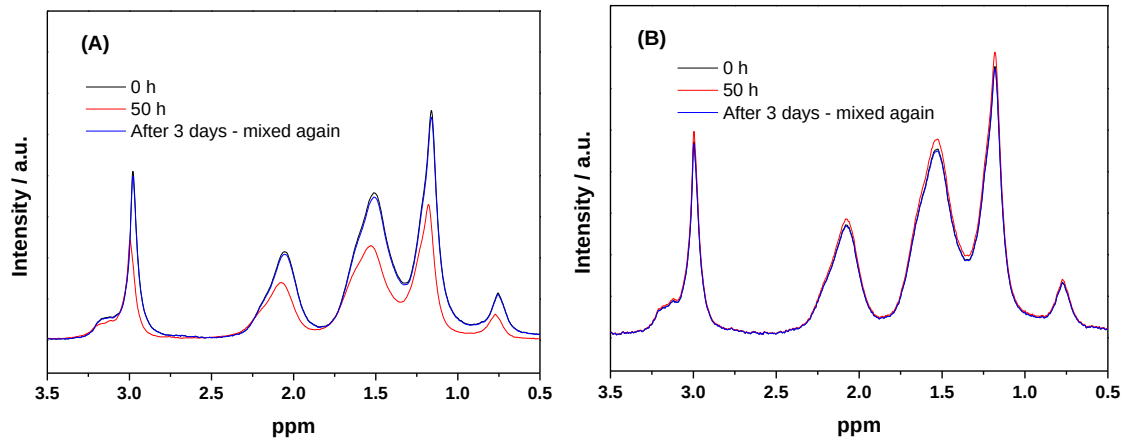


Figure S5. Low resolution ^1H NMR spectra for a 1.0 wt. % C_{12}S *intact* dispersion after 3 days after sample preparation, followed by redispersion, in (A) D_2O ; (B) 30:70 $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixture. For comparison purposes, spectra obtained at 0 h and 50 h are presented again for both samples.

Table S1. Self-diffusion coefficients obtained for surfactant ion (D_{surf}), polyion (D_{pol}) in a 1 wt% C_{12}S *intact* sample prepared in D_2O and in a mixture of $\text{H}_2\text{O}:\text{D}_2\text{O}$ at different time intervals (t).

t / h	$D_{surf} / \text{m}^2.\text{s}^{-1}$		$D_{pol} / \text{m}^2.\text{s}^{-1}$	
	D_2O	$\text{H}_2\text{O}:\text{D}_2\text{O}$	D_2O	$\text{H}_2\text{O}:\text{D}_2\text{O}$
0	0.51×10^{-10}	0.50×10^{-10}	2.10×10^{-12}	2.00×10^{-12}
50	1.04×10^{-10}	0.85×10^{-10}	3.30×10^{-12}	2.60×10^{-12}
3 days – mixed again	0.52×10^{-10}	0.50×10^{-10}	2.30×10^{-12}	2.20×10^{-12}

C₁₂S and C₁₂L nanoparticle dispersions prepared by the conventional protocol of mixing

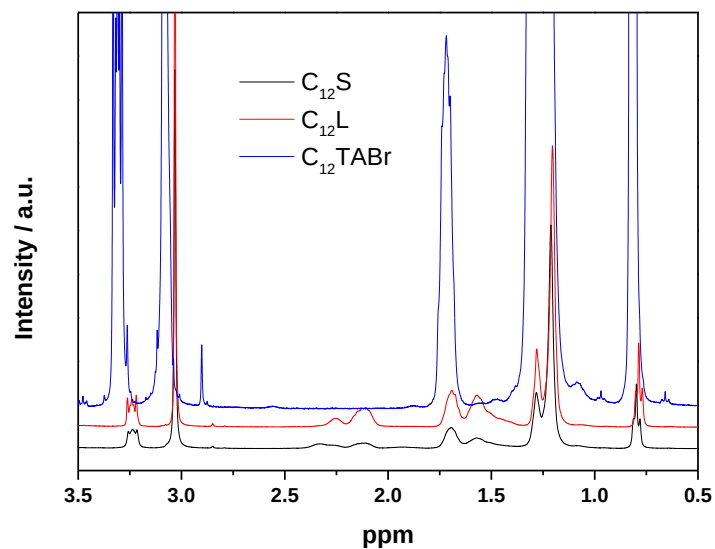


Figure S6. High resolution ¹H NMR spectra obtained for C₁₂S and C₁₂L nanoparticle dispersions prepared by the conventional protocol of mixing of aqueous solutions of surfactant salt and sodium salt of BCP at a charge ratio of 1. Spectrum for C₁₂TABr solution is also shown. Molar charge concentration for each specie equal to 25 mM.