

Shear-induced gelation of soft strawberry-like particles in the presence of polymeric P(BA-b-AA) surfactants

—Electronic Supplementary Information

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A. Synthesis procedure of the surfactants

ATRP of n-butyl acrylate to form block polymeric surfactant (together with t-butyl acrylate/tBA for a random polymeric surfactant) was initiated by methyl α -chloropropionate employing Cu(I)Br and 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) as catalyst in 25% ethyl acetate solution at 70 °C (or acetone at 60 °C for the random surfactant). The obtained PnBA chains were reinitiated in 25% acetone solution at 60 °C to grow a PtBA block. The resulting block or random polymeric surfactants (PnBA-b/co-PtBA) were treated with trifluoroacetic acid (TFA) in dichloromethane in order to de-protect the t-butyl groups towards acrylic acid (AA) units.

B. Molecular characterization

Gel Permeation Chromatography (GPC) was performed at 30 °C through an Agilent OligoPore (300×7.5mm) column calibrated against polystyrene standards and mounted on an Agilent 1100 Series HPLC, equipped with UV and RI detector, as well as an isocratic pump,

operated with chloroform as the mobile phase at 1 L/L. The chromatograms were recorded and analyzed using the commercial WinGPC software to obtain molecular weights and polydispersity indices.

^1H NMR spectra were recorded in CDCl_3 or MeOD on a Bruker UltraShield 500 MHz spectrometer and were treated with the commercial Bruker Topspin software.

Atomic Absorption Spectroscopy measurements were carried out on a Varian SpectrAA 220FS Spectrometer equipped with an acetylene flame nebulizer, to determine the residual copper in the synthesized surfactants. A defined amount of a surfactant was dissolved in 0.1M aqueous NaOH and the atomic copper concentration was determined at 324.8 nm on the basis of a 6-point calibration curve ranging from 0 to 5 ppm. Five analyses were performed for each surfactant and averaged, and the results are reported in Table S1. It is seen that even for the product with the highest residual Cu amount, there correspond less than 4 moles of Cu per 1000 carboxylate moles. Therefore, any irreversible complexation of copper cations with PAA should be negligible.

Table S1. Detailed molecular characteristics of the synthesized surfactants. Res Cu: residual ppm of Copper in the final product reported on the basis of dry polymer.

Surf. #	PnBA			PnBA-b/co-PtBA			PnBA-b/co-PAA		
	$M_{n,\text{NMR}}$	$M_{n,\text{GPC}}$	PDI	$M_{n,\text{NMR}}$	$M_{n,\text{GPC}}$	$\text{DP}_{n,\text{tot}}$	$M_{n,\text{NMR}}$	PDI	Res Cu
B ₁₅₋₅	2045	2402	1.36	2686	3188	20	2405	1.31	1072
B ₁₄₋₁₂	1917	2105	1.30	3455	3454	26	2782	1.39	523
B ₁₃₋₉	1789	2071	1.34	2942	2820	22	2437	1.35	460
R ₁₂₋₁₂	-	-	-	3199	3689	24	2525	1.29	1172
R ₁₃₋₁₄	-	-	-	3583	3927	27	2798	1.22	358

C. Characterization of the primary particles using dynamic (DLS) and static (SLS)
light scattering:

