Supporting Information: Polymer nanocomposite capsules formed by droplet extraction: spontaneous stratification and tailored dissolution

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Optical microscopy movies: droplet extraction kinetics and nanoparticle release

The following four videos detail the extraction droplet process for 1.0 w/v% NaPSS + 10 w/v% SiO_2 droplets immersed in methyl ethyl ketone (MEK), ethyl acetate (EA), butyl acetate (BA) and Toluene (T):

- Movie S1: Capsule formation in MEK over a timescale of 100 s (video 4× faster)
- Movie S2: Capsule formation in EA over a timescale of 200 s (video 4× faster)
- Movie S3: Capsule formation in BA over a timescale of 1,500 s (video 150× faster)
- Movie S4: Capsule formation in T over a timescale of 30,600 s (video 3000× faster)

The following two videos depict the single and multiple burst release of nanoparticle clusters from capsules prepared in EA and BA. For MEK and T, only marginal release of nanoparticle is observed, over considerably long timescales.

- Movie S5: Immersion of bicontinuous capsule, obtained from EA, in deionized water (pH 5 to 6), depicting the pulsed release of nanoparticle clusters, over a time scale of 1800 s (video 300× faster)
- Movie S6: Immersion of core-shell capsule, obtained from BA, in deionized water (pH 5 to 6), depicting the single burst release of nanoparticle clusters, over a time scale of 2200 s (video 30× faster)

Characterisation of NaPSS: Small Angle Neutron Scattering (SANS), and viscosity measurements

SANS and viscosity measurements were carried out to characterise the commercial NaPSS polymer employed in this study. Polymer solutions of 0.025 and 0.05 g/ml NaPSS/D_2O were investigated at the D22 spectrometer of the Institut Laue-Langevin (Grenoble, France), with incident wavelength $\lambda = 6$ Å, sample-detector distance of 1.4 m and 5.0 m, and collimation 2.8 m and 5.6 m. The accessible q range (where $q = (4\pi/\lambda)\sin(\theta/2)$) is therefore 0.013-0.608 Å^{-1}. Total measurement time per sample was 600 s. All data were reduced and calibrated using GRASP.

Figure 1A shows the coherent scattering for the semi-dilute solutions investigated. Typical features for salt-free polyelectrolyte such as the presence of a pronounced correlation peak at finite wavevectors, whose position q^* increases with concentration, and a low q upturn are not observed. The origin of the correlation peak,[1,2] has been attributed to repulsion generated by the cloud of counterions surrounding the polyion, which prevent the overlap of correlation blobs[3] and suppress long range fluctuations. The absence of a peak in our data is in agreement with expected results for neutral polymers and for polyelectrolyte solutions in the presence of salt ions;[4,5] the presence of mono- as well as multivalent electrolyte solutions have been shown to screen the intra-chain Coulombic interactions between charged monomers.[6–8] We estimate the salt to monomer ratio to be ≈ 1:3 to 1:4 in our commercial NaPSS system. Fits of the static SANS data to the Ornstein-Zernike model with an exponent of 2 gives a poor fit, suggesting the polymer conformation cannot be approximated by a Gaussian chain in a θ-solvent. Instead, we observe a high q scaling exponent of approximately 5/3, corresponding to a polymer in a good solvent,[9] and a subtle polyelectrolyte shoulder for the highest polymer concentration.

Viscosity measurements were also carried out over a wide range of NaPSS concentrations, 0.01 - 0.4 g/mL, to further characterize the sample as shown in Figure 1B. The expected scaling of the specific viscosity ($n_{sp} = \eta - \eta_{H_2O}/\eta_{H_2O}$) as described by a Fuoss scaling for salt-free polyelectrolyte solutions in the semidilute regime: $\eta_{sp} = N(b^3c_p)^{0.5}B^{-3/2}$ where N is the degree of polymerization, b is the monomer size and B is the solvent quality parameter, is not observed;[10,11] instead, a linear dependence of viscosity on polymer concentration as described by the Huggins relation, $\eta_{sp} = [\eta]c_p + k_H[\eta c]^2$ where k_H is the Huggins constant, is observed - as reported for neutral polymers as well as polyelectrolytes with added salt.[5,12]

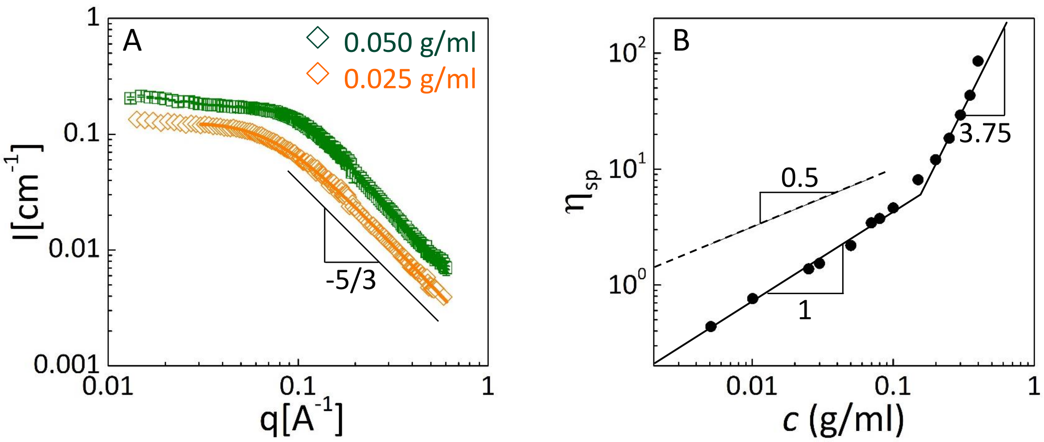

Figure 1: (A) Static 1-D coherent SANS profile of NaPSS/D_2O solutions with 2.5 and 5 wt % polymer mass fraction. (B) Specific viscosity of as a function polymer concentration for NaPSS. Broken lines indicate expected $\eta_s \approx c^{0.5}$scaling for salt free polyelectrolytes. Black lines are power law fits to the semidilute non-entangled,and concentrated regimes, exponents indicated below the lines

Miscibility of H_2O, extraction solvents (Methyl ethyl ketone, Ethyl acetate, Butyl acetate, Toluene) and carrier phase (Hexadecane)

Table 1: Solvent properties[13]

Property	Water	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Toluene	Hexadecane
Dispersion (δ_D), MPa$^{1/2}$	15.5	16.0	15.8	15.8	18.0	16.3
Polarity (δ_P), MPa$^{1/2}$	16.0	19.0	5.3	3.7	1.4	0
Hydrogen (δ_H), MPa$^{1/2}$	42.3	5.1	7.2	6.3	2.0	0
Solubility of H_2O in solvent, v/v %	-	11.1	2.72	1.36	0.038	-
Solubility of solvent in H_2O, v/v %	-	31.01	9.09	0.7	0.06	-

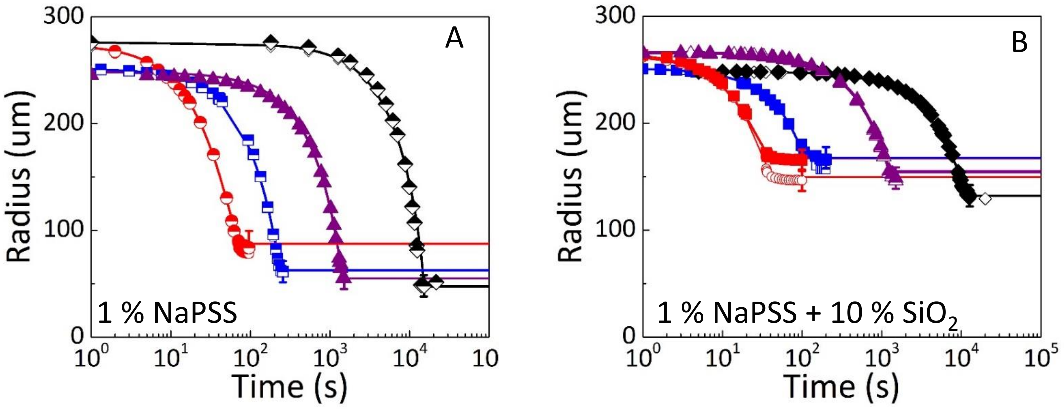

Figure 2: Droplet extraction kinetics in selected non-solvents, for data shown in Figure 4B-C of the main paper. Evolution of radius with time for (A) pure H_2O, (B) 1 %(w/v) NaPSS, and (C) 1 w/v% NaPSS + 10 w/v%SiO_2, droplets immersed in MEK, EA, BA, Toluene [L-R]. Initial droplet radius for data shown ranges between 250 - 270 μm. Lines shown are empirical fits to the extraction data.

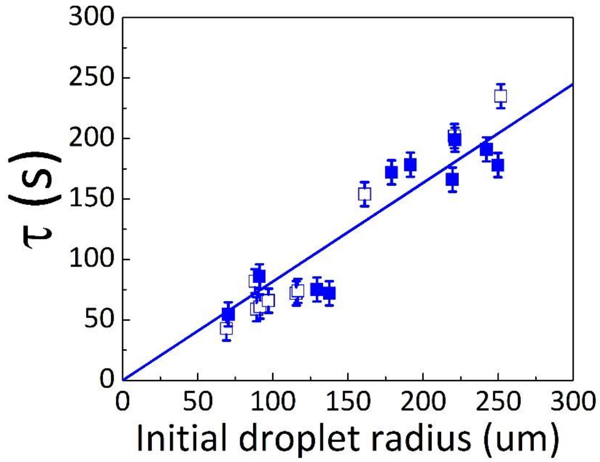

Figure 3: Linear dependence of extraction time τ on initial droplet radius R_O for neat 1 w/v% NaPSS (open squares) and composite 1 w/v% NaPSS + 10 w/v% SiO_2 (filled squares) droplets shown for non-solvent EA.

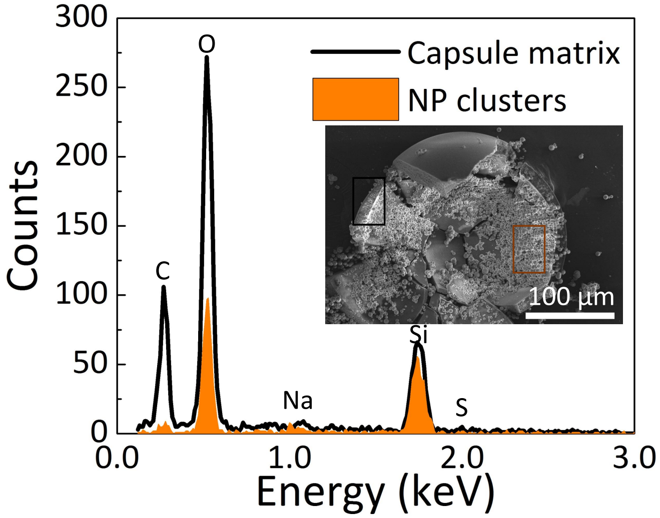

Figure 4: Energy dispersive x-ray spectroscopy (EDX) analysis of polymer-nanoparticle capsules showing the atomic components of the capsule matrix and the nanoparticle clusters. Inset is a core-shell capsule obtained from a droplet with initial composition 1 w/v% NaPSS + 10 w/v% SiO_2, extracted in butyl acetate (BA)

Estimation of Péclet number

A comparison between the rates of droplet volume reduction and solute diffusion is provided by the dimensionless Péclet number, which we write as $Pe = \frac{dR}{dt}\frac{R_0}{D}$; where $\frac{dR}{dt}$ is the linear drying rate, R_0 is the initial droplet radius and D is the diffusion coefficient. We estimate D of the silica nanoparticle in the droplet using the Stokes-Einstein relation: $D = k_{\mathrm{B}}T/6\pi\eta R_{\mathrm{NP}}$, taking the silica nanoparticle radius $R_{\mathrm{NP}} = 11$ nm, and the viscosity, η, to be that of the ternary polymer/silica/H_2O mixture at temperature T; k_{B} is the Boltzmann constant. We find initial values of Pe between 0.9 - 60, from Toluene to MEK in qualitative agreement with observed formation of dense compact, and crumpled capsule morphologies with Toluene with MEK respectively. Upon extraction, we expect η to rise, further increasing Pe; however, the estimations presented above are not expected to hold as the solute concentration increases, and upon nanoparticle agglomeration and demixing.

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