Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information (ESI)

Compression of hard core-soft shell nanoparticles at liquid-liquid interfaces: influence of the shell thickness

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1 Supplementarv Data

1.1 SEM analysis of the silica particles

Figure S.1A represents a SEM image of the bare silica cores prior to encapsulation in cross-linked hydrogel shells. All particles show a spherical shape. Figure S.1B shows the corresponding histogram of the diameter distribution. The particle dimensions were measured using ImageJ 1.48v by analysing 200 particles. The particles show a narrow size distribution with an average diameter of 125±10 nm.

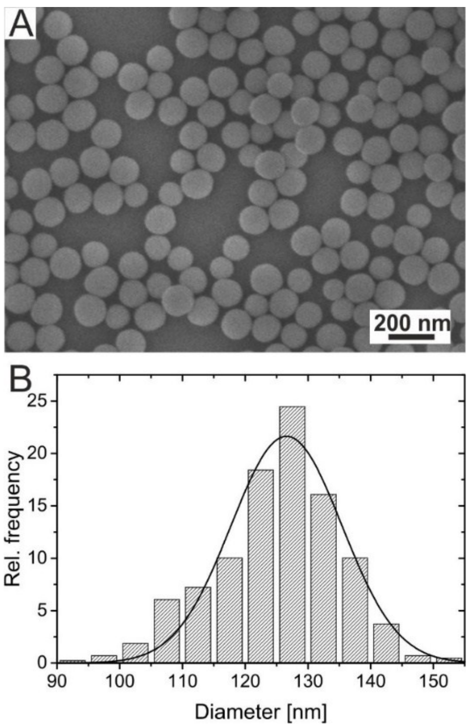

Figure S.1: A) Representative SEM image of the silica cores. B) Histogram of the diameter distribution. The black solid line indicates a Gaussian fit.

1.2 Probability distributions of nearest neighbours

Figures S.2 ($CS_{3.4}$), S.3 ($CS_{3.0}$) and S.4 ($CS_{2.2}$) show rendered AFM images and probability distributions of the nearest neighbours *P(d)* along the compression curve. The AFM images were binarised to identify the particle positions using a MATLAB particle-tracking algorithm (details in Section 3.2). The surface pressure increases from column A to column D. The upper image row shows a colour-coded Voronoi tasselation. The black dots in the images represent the particle centers, which were determined by the image analysis algorithm. The green tiles indicate particles with 6 neighbours, the blue ones particles with 5 neighbours and the red ones particles with 7 neighbours. In column A of the figures S.2-S.4 the systems have a slightly higher surface pressures compared to Figure 6 of the main manuscript. For all three systems we find a regular hexagonal lattice indicated by green tiles dominating the colour-coded Voronoi images. The probability distributions of the centre-to-centre distances *d* (image row at the bottom of each figure) all show one single peak indicating one preferential inter-particle distance at these low surface pressures. Upon compression, cluster formation begins, as inter-particle contacts fail and the particles aggregate (column B). This is well visible by the appearance of yellow triangles in the middle row of these figures. The yellow triangles indicate particles in the clusters, where belonging to the clusters is defined if the inter-particle distance is below a threshold value. Most of the particles are in a hexagonal lattice within the clusters. In this region, the probability distribution displays two peaks. One of them resembles the inter-particle distance at low surface pressures and the other one indicates the inter-particle distance within the clusters. In column C the number of clusters increases. The smaller center-to-center distance shows now a higher amplitude (probability) for all three core-shell systems. At high surface pressure (column D), mainly clusters separated by voids are found. Upon compression, several defects in the structure appear, as depicted in the Voronoi polygons. Increasing λ allows minimising the number of defects, as a thicker shell is more compliant. We also found that cluster formation sets in at much higher surface pressures with increasing λ. Additionally, the centre-to-centre distances are larger for particles with increasing shell-to-core ratios, as expected.

As a final remark, we point out that the nearest-neighbour distances extracted from this procedure coincide with the ones identified by the analysis of the radial distribution functions, but that this single-particle method makes it possible to assign directly the belonging of each particle to one of the two phases.

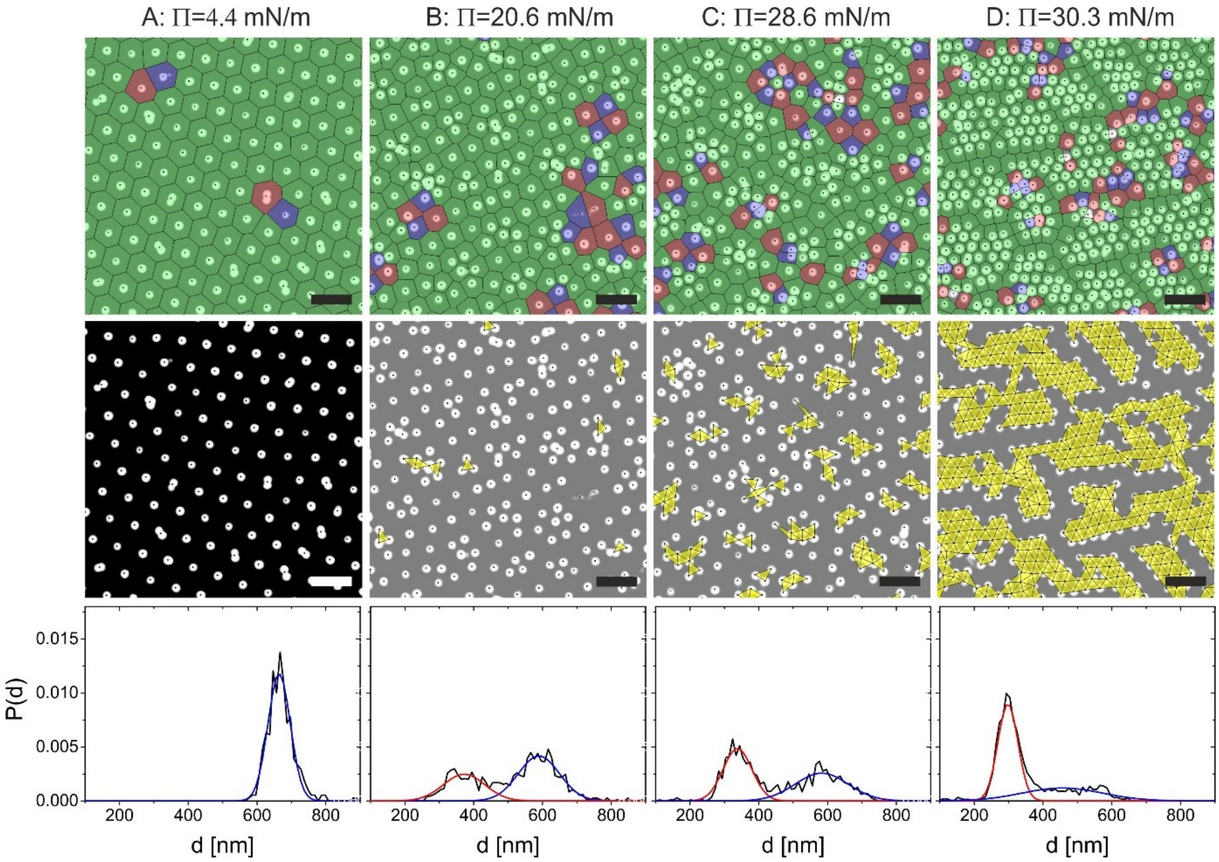

Figure S.2: Colour-coded Voronoi tasselations (upper row), depiction of the cluster formation using yellow triangles (middle row) and probability plots P(d) of the nearest neighbours (row at the bottom) for the particle monolayers consisting of $CS_{3.4}$ upon compression (from A to D). The black dots of the Voronoi polygons indicate the particle centers found by the image analysis algorithm. The polygons relate to particles with 6 neighbours (green), with 5 neighbours (blue) and with 7 neighbours (red). The yellow triangles in the middle row are used to label particles being in close contact and thus belonging to the cluster phase. The black lines in the P(d) are the data extracted from the images, whereas the coloured lines are Gaussian fits (blue for large inter-particle distance, red for smaller inter-particle distances). Scale bars: 1 µm.

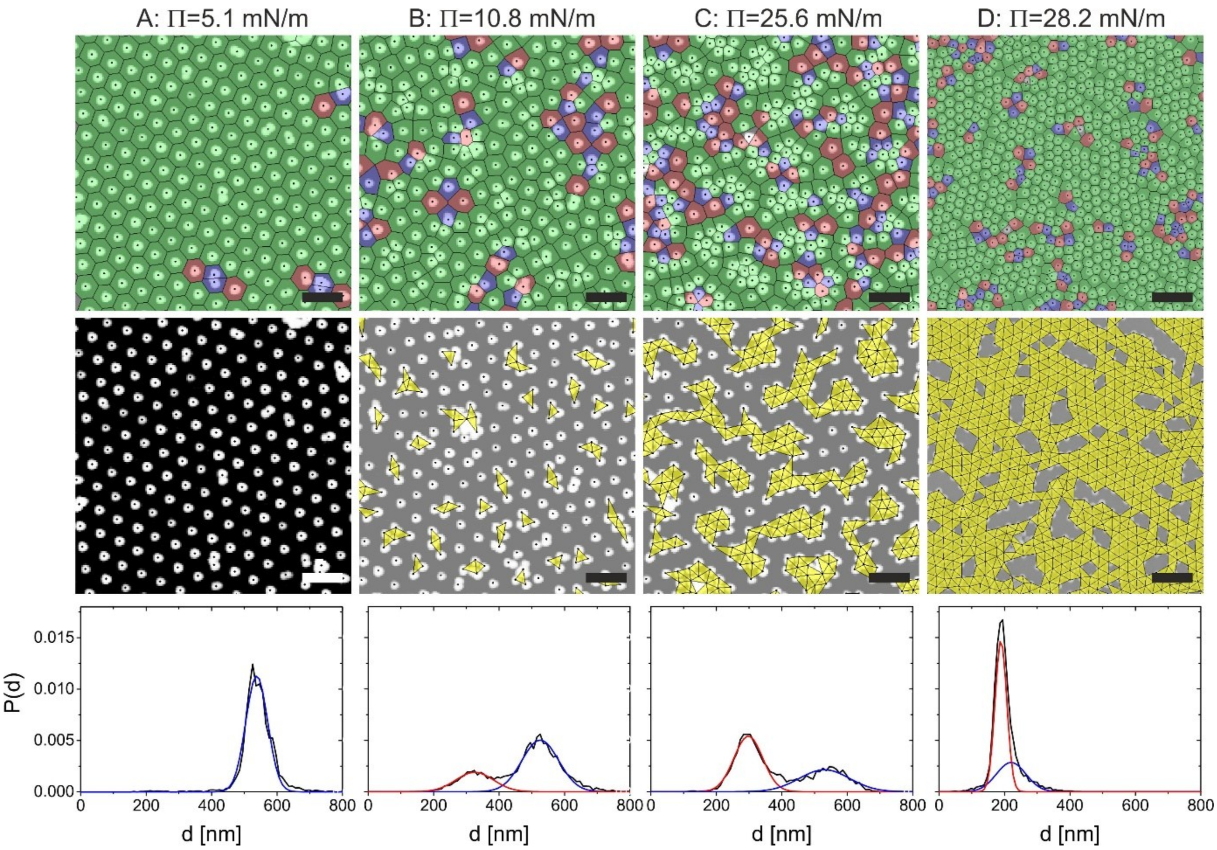

Figure S.3: Colour-coded Voronoi tasselations (upper row), depiction of the cluster formation using yellow triangles (middle row) and probability plots P(d) of the nearest neighbours (row at the bottom) for the particle monolayers consisting of $CS_{3.0}$ upon compression (from A to D). The black dots of the Voronoi polygons indicate the particle centers found by the image analysis algorithm. The polygons relate to particles with 6 neighbours (green), with 5 neighbours (blue) and with 7 neighbours (red). The yellow triangles in the middle row are used to label particles being in close contact and thus belonging to the cluster phase. The black lines in the P(d) are the data extracted from the images, whereas the coloured lines are Gaussian fits (blue for large inter-particle distance, red for smaller inter-particle distances). Scale bars: 1 μm.

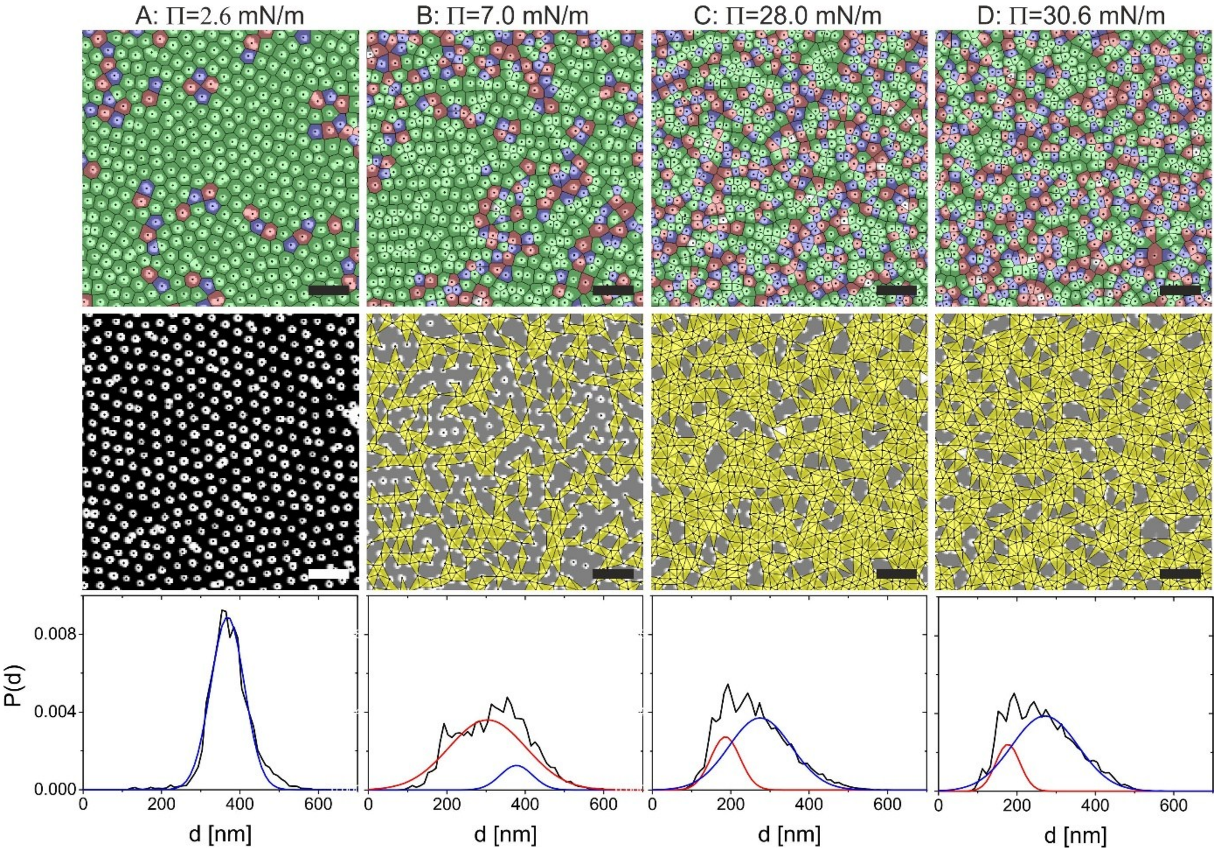

Figure S.4: Colour-coded Voronoi tasselations (upper row), depiction of the cluster formation using yellow triangles (middle row) and probability plots P(d) of the nearest neighbours (row at the bottom) for the particle monolayers consisting of $CS_{2.2}$ upon compression (from A to D). The black dots of the Voronoi polygons indicate the particle centers found by the image analysis algorithm. The polygons relate to particles with 6 neighbours (green), with 5 neighbours (blue) and with 7 neighbours (red). The yellow triangles in the middle row are used to label particles being in close contact and thus belonging to the cluster phase. The black lines in the P(d) are the data extracted from the images, whereas the coloured lines are Gaussian fits (blue for large inter-particle distance, red for smaller inter-particle distances). Scale bars: 1 µm.