Electronic Supplementary Information

Core-shell nanoparticle monolayers at planar liquid-liquid interfaces: effects of polymer architecture on the interface microstructure

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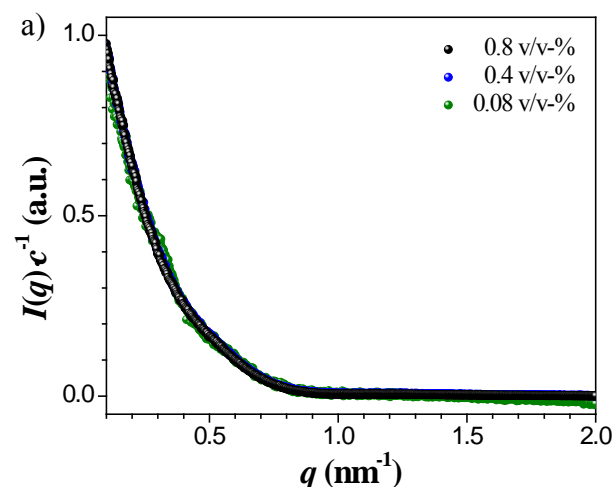[c] *University of Natural Resources and Life Sciences Vienna, Institute for Biologically inspired materials, Department of Nanobiotechnology, Muthgasse 11-II, 1190 Vienna, Austria*
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1 SAXS measurements

In order to get information about the size and distribution of the core-shell NPs, small-angle X-ray (SAXS) experiments were performed on aqueous suspensions of L2.5 at three different concentrations (0.8, 0.4 and 0.08 v/v-%). First, the curves expressing the concentration-normalized intensities ($I(q) \cdot c^{-1}$) were verified to fall on the same master curve, indicating that the concentrations are sufficiently diluted to leave only the form factor $P(q)$ visible in the curves, with the structure factor $S(q)$ independent from concentration and $S(q) = 1$ (Figure ESI 1a). Then, the form factors $P(q)$ were calculated from the corresponding scattering patterns from the highest concentration by following two models for polydisperse spherical particles with a core-shell structure: i) keeping constant the thickness (t_{shell}) of the PEG shell and estimating the radius of the core (r_{core}) and its polydispersity ($p_{core} = \sigma r_{core}$), or ii) keeping a constant ratio between both the radius of the core (r_{core}) and the total radius of the nanoparticle ($r_{core-shell} = r_{core} + t_{shell}$) and calculating an overall polydispersity factor ($p_{core-shell} = \sigma r_{core-shell}$). The scattering length densities used for the magnetite core and the solvent (water) were $\rho_{core} = 4.22 \cdot 10^{-3}$ nm^{-2} and $\rho_{solvent} = 9.51 \cdot 10^{-4}$ nm^{-2}, respectively. Figures ESI 1b and 1c show the scattering patterns together with the corresponding fitting curves for the three studied concentrations, where the estimated core radius and shell thickness were $r_{core} = 4.2\text{-}4.3$ nm and $t_{shell} = 9.0\text{-}10.0$ nm, respectively. The corresponding polydispersity values were $p_{core} = 0.16$ and $p_{core-shell} = 0.14$ from the two scattering models, and the obtained scattering length density for the shell was $\rho_{shell} = 9.84\text{-}9.90 \cdot 10^{-4}$ nm^{-2} which is lower than the scattering length density for pure PEG ($\rho_{PEG} = 1.02 \cdot 10^{-3}$ nm^{-2}) due to the swelling of the shell with water molecules and roughly 3% higher than pure water. These data refer to L2.5, but the core size distribution is the same for all PEG architectures.
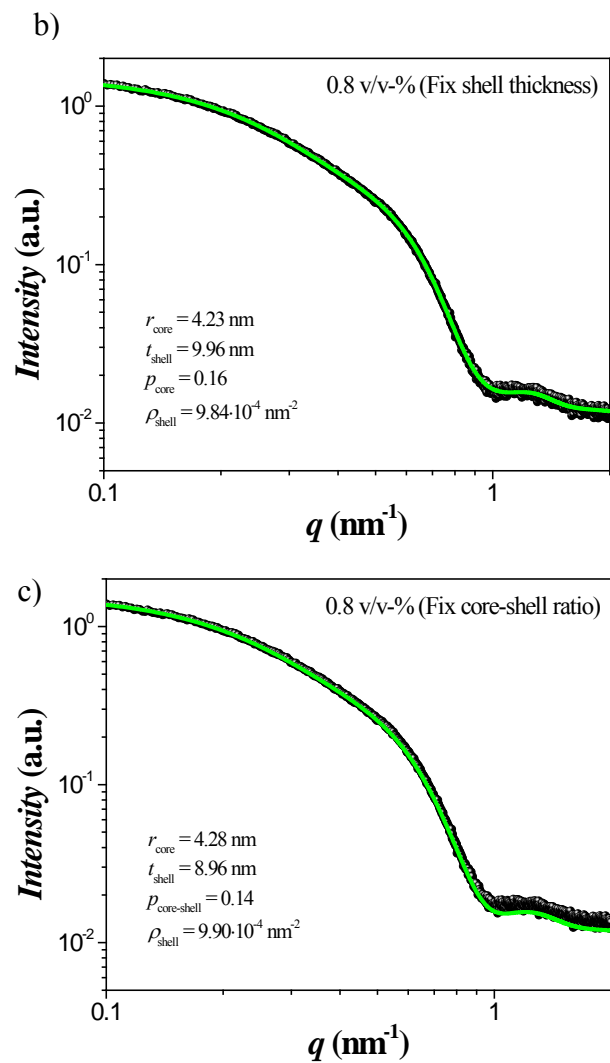
b)

0.8 v/v-% (Fix shell thickness)

$r_{core} = 4.23$ nm
$t_{shell} = 9.96$ nm
$p_{core} = 0.16$
$\rho_{shell} = 9.84 \cdot 10^{-4}$ nm^{-2}

Intensity (a.u.)

q (nm^{-1})

c)

0.8 v/v-% (Fix core-shell ratio)

$r_{core} = 4.28$ nm
$t_{shell} = 8.96$ nm
$p_{core-shell} = 0.14$
$\rho_{shell} = 9.90 \cdot 10^{-4}$ nm^{-2}

Intensity (a.u.)

q (nm^{-1})

Figure ESI 1. a) Concentration-normalized scattering intensity profiles for the aqueous suspensions of the L2.5 nanoparticles at three different concentrations. Scattering intensity profile and the form factor fitting curve following the polydisperse spherical particles with a core-shell structure model with b) fixed shell thickness, and c) fixed core-shell ratio.

2 HE-XR cell

polyoxymethylene (POM) cell for liquid-liquid measurements

lid

X-ray entrance window

X-ray entrance window

X-ray exit window

Water trough

Trough's raised rim

Lowered floor around the water trough

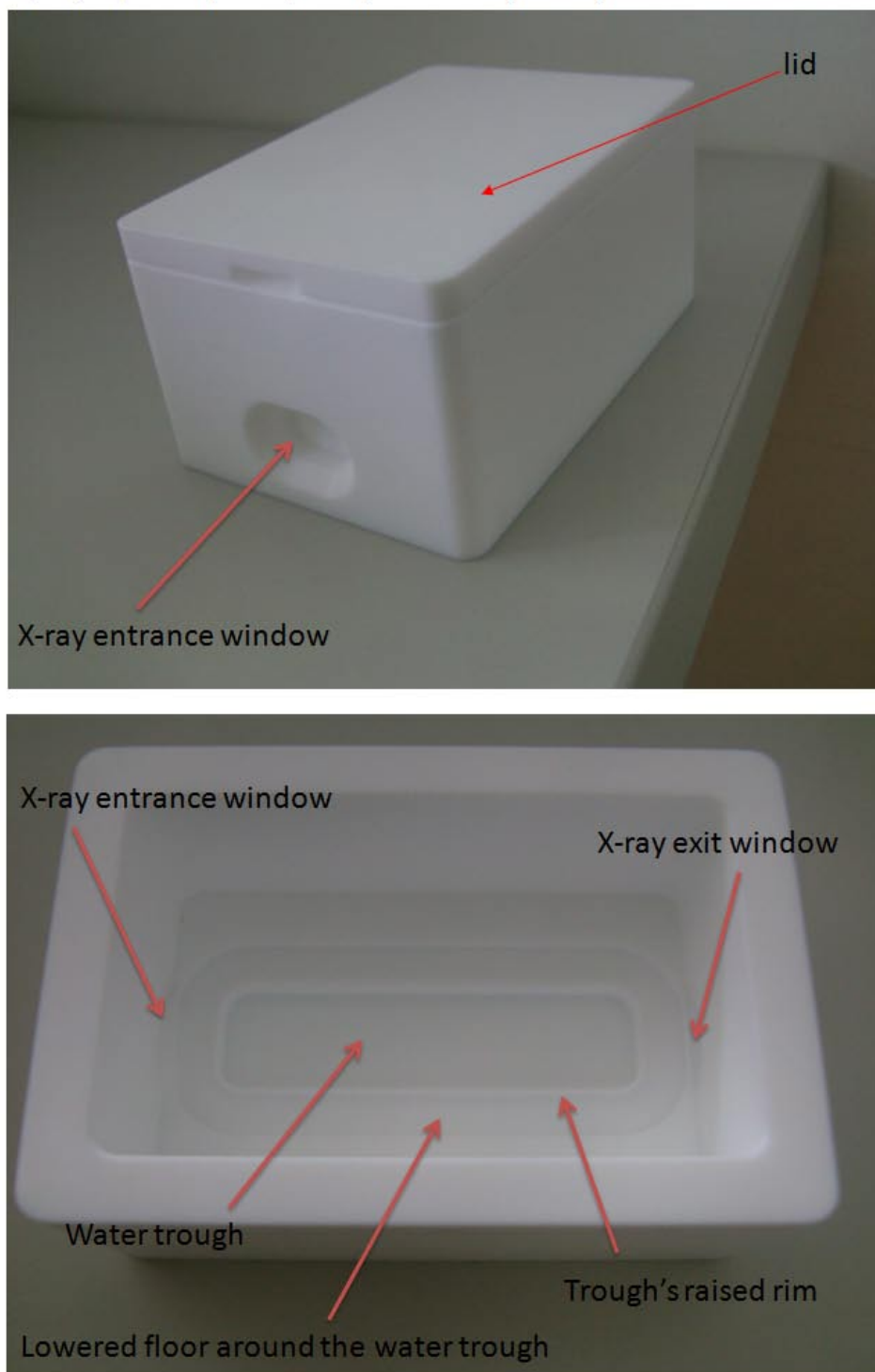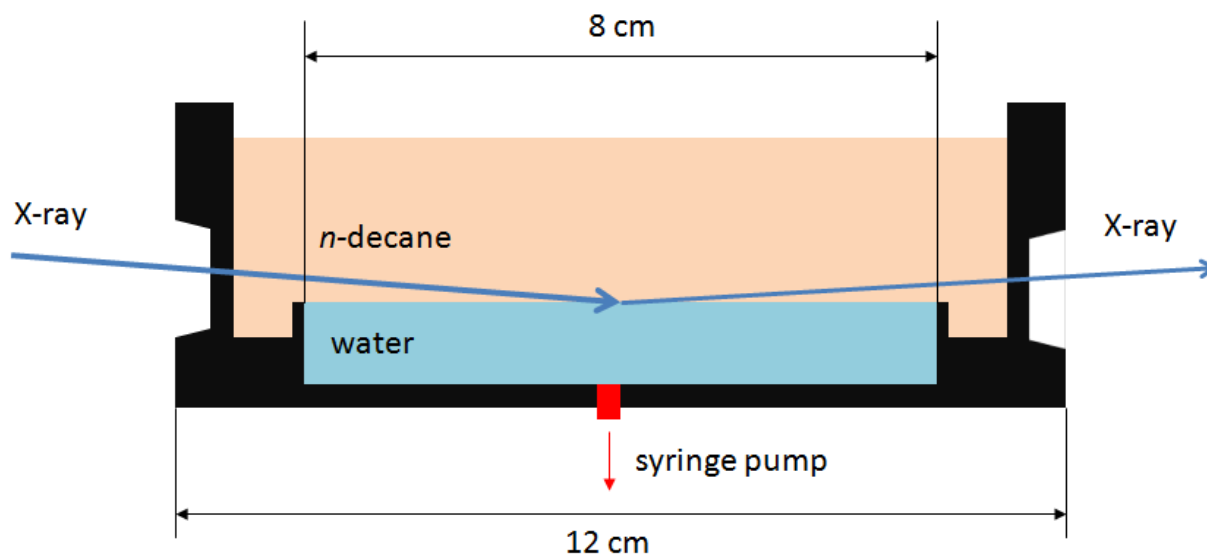**Figure ESI 2.** Photographs of the sample cell used for HE-XR.

Figure ESI 3. Schematics of the sample cell used for HE-XR.