ASSOCIATED SUPPORTING CONTENT

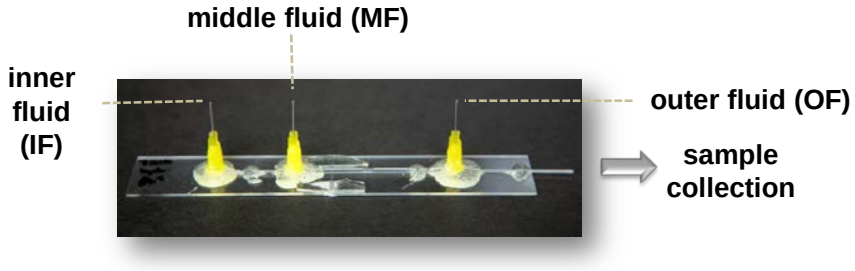

Figure S1. Photograph of the microcapillary glass device and verification of the outer fluid (OF), middle fluid (MF) and inner fluid (IF) flow streams.

SEM IMAGES OF THE PUMCS

Electron microscopy images of the W/O-PUMCs by changing the isocyanate are given in supporting Figure S2. The preparation of the polyurea microcapsules was done in toluene at 3 wt.% isocyanate, 3 wt. % Abil EM 90 and 5 wt.% of polyethyleneimine. The flow rates were Q_{OF} = 13,000 µL·h^{-1}, Q_{MF} = 12,000 µL·h^{-1}, Q_{IF} = 400 µL·h^{-1}.

In supporting Figure S3 the SEM micrographs of O/W-PUMCs using different isocyanates and polyethyleneimine are shown. The inner fluid consists of a toluene / isocyanate solution (5 wt. %) whereby the surfactant is SDS (5 wt.%); the PEI concentration in the outer fluid is 3 wt.%. The flow rates are Q_{OF} = 10,000 µL·h^{-1}, Q_{MF} = 9,000 µL·h^{-1}, Q_{IF} = 600 µL·h^{-1}, respectively. Thin-walled PUMCs used for this investigation had a diameter of 75±3 µm which was measured by optical microscopy directly after production. The molar amount of amine and isocyanate in each of the experiments was equal. The capsules have been freeze dried (–70 °C, 10^{-5} mbar, 12 h) prior to the SEM analysis to guarantee a spherical shape. However, as it can be seen in the SEM images S2 and S3, partially, thin-walled capsules inflated or collapsed (S2b,c; S3b) during

this procedure. Thus, the capsules in the SEM appear bigger than they have been measured *via* optical microscopy. The average capsule shell thickness of PEI/TDI O/W-PUMCs is 79±24 nm and 156±40 nm for W/O-PUMCs.

The effect of the amine partitioning on the shell morphology can be seen using the PEI/isocyanate system. In supporting Figure S4, SEM images of O/W and W/O-PUMC shells with the composition PEI/TDI are given that indicate the increased amine migration tendency when working with chloroform instead of toluene; thicker shells result (compare Fig. S2 and S3). Consequently, the average shell thicknesses of PEI/TDI PUMCs at the binary mixture water/chloroform jump to 890±108 nm (O/W) and 2500±219 nm (W/O).

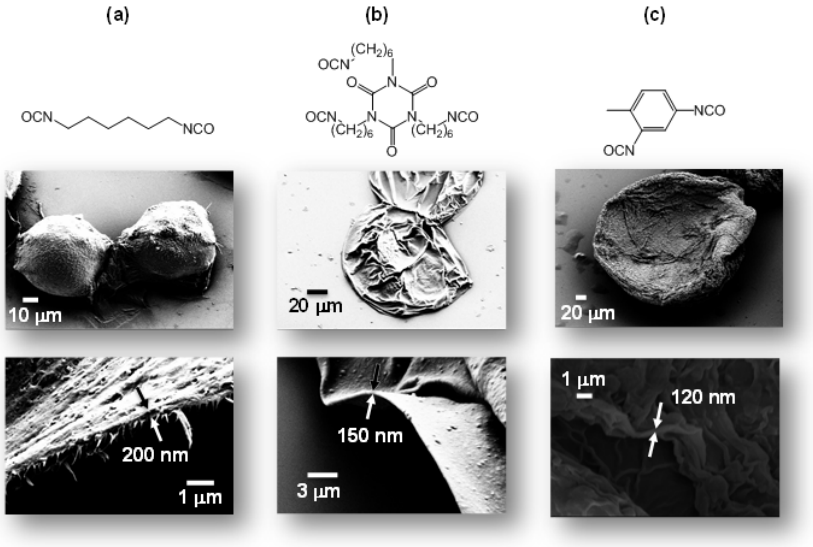

Figure S2. W/O-PUMCs with the composition PEI/HDI (a), PEI/Basonat H100 (b) and PEI/TDI (c).

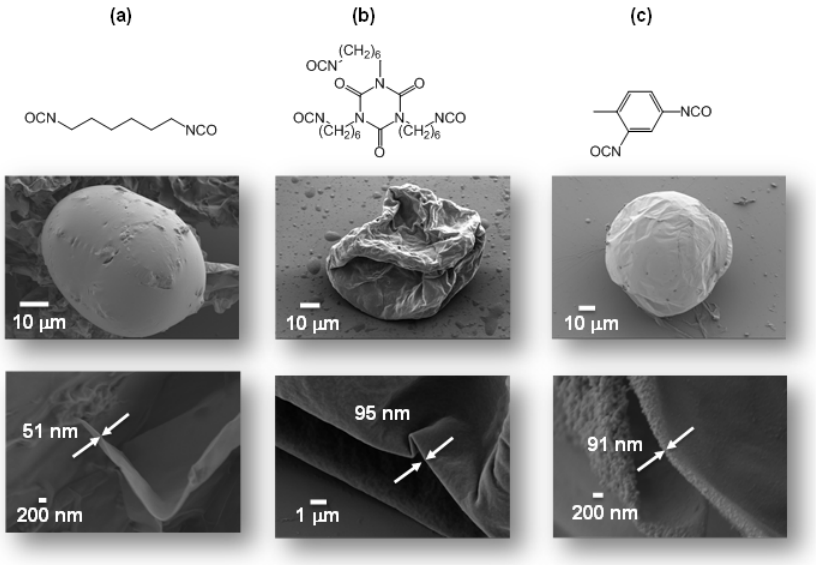

Figure S3. O/W-PUMC with the composition HDI/PEI (a), Basonat H100/PEI (b) and TDI/PEI (c).

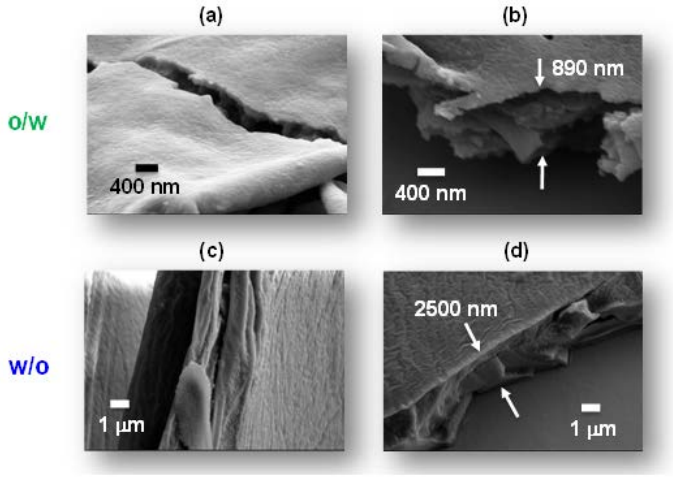

Figure S4. O/W- and W/O-PUMC with the shell composition PEI/TDI using chloroform as oil.

The partitioning coefficient of PEI at a water/chloroform mixture was measured to be $4.8 \cdot 10^{-3}$.

Determination of K_{OW}:

The amine was dissolved in the aqueous phase to the concentration $[amine]_{w,0}$. Oil was added to the solution in an amount equal to water. The emulsion was agitated for 72 h at room temperature. An aliquot volume of the oil phase was removed and the equilibrium molecular amount of amine in the oil phase $[amine]_{o,eq}$ was quantified by liquid ^1H NMR spectroscopy (calibration by internal standard tetrahydrofuran). The partitioning coefficient was then calculated by the following equation:

$$K_{OW} = \frac{[amine]_{o,eq}}{[amine]_{w,0} - [amine]_{o,eq}} \qquad \text{Eq. S1}$$

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