

Microfluidic fabrication of polyethylene glycol microgel capsules with tailored properties for the delivery of biomolecules

Additional experimental section

Synthesis of star-PEG-acrylate

The synthesis of star-PEG-acrylate is performed according to the literature.¹ Hydroxyl-terminated sP(EO-*stat*-PO) (3kDa) (105.0 g, 0.21 mol OH groups) is dried at 80°C for 20 h. Subsequently, toluene (600 mL) and pyridine (24.9 g, 0.315 mol, 1.5 eq) are added to the solution. Acrylic acid anhydride (34.43 g, 0.273 mol, 1.3 eq) is added dropwise to the solution at room temperature. After stirring for 24 h, toluene is removed under reduced pressure and the residue is taken up in dichloromethane, after which the polymer is purified by repeated precipitation in cold diethyl ether (3 times). Yield: 73.03 g (63%).

Analysis of star-PEG-acrylate

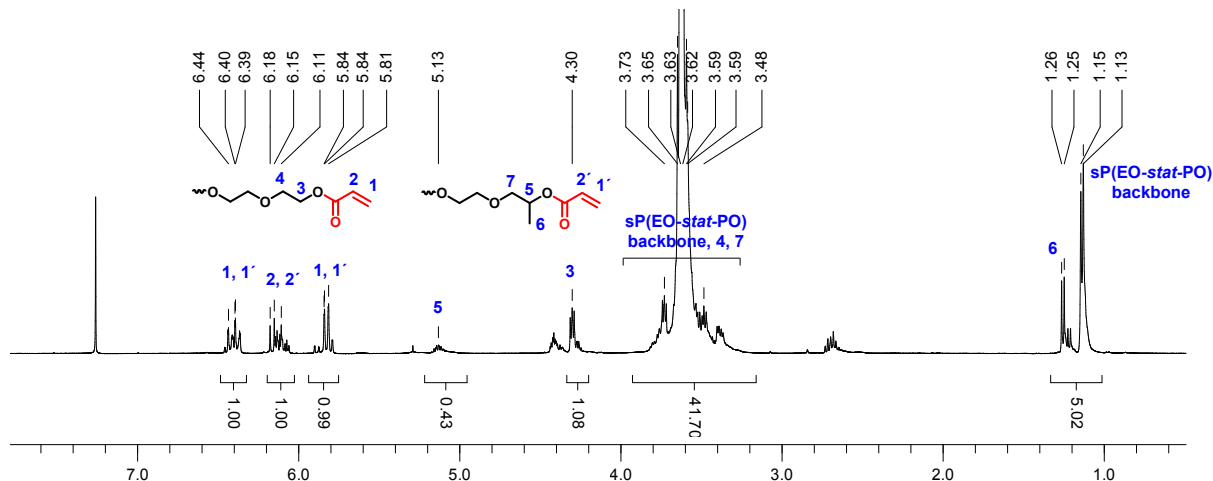


Figure S.1 - ¹H NMR and SEC analysis of acrylate-terminated sP(EO-*stat*-PO) (3kDa)

Results are reported as follows: chemical shift δ (ppm) (multiplicity, number of protons, assignment). TMS (δ=0.0 ppm) was used as internal standard. Chemical shifts are reported to the nearest 0.01 ppm. Degree of functionalization: 97 %.

¹H NMR (CDCl₃): δ (ppm) = 1.14 (d, 3H, -CH₃ sP(EO-*stat*-PO) backbone), 1.25 (d, 3H, H-6), 3.20-3.80 (m, sP(EO-*stat*-PO) backbone, H-4,7), 4.25-4.30 (m, 2H, H-3), 5.00-5.20 (m, 1H, H-5), 5.74-5.82 and 6.32-6.48 (m, 2H, H-1,1'), 6.02-6.20 (m, 1H, H-2,2').

Molecular weights (M_n and M_w) and dispersity values ($\mathcal{D} = M_w/M_n$) are determined by size exclusion chromatography (SEC) as $M_n = 2800$ g/mol; $M_w = 3200$ g/mol; $\mathcal{D} = 1.2$.

SEC analysis is carried out with dimethylformamide (DMF, HPLC grade, VWR). DMF-SEC is performed using an Agilent 1100 system equipped with a dual RI-/Visco detector (ETA-2020, WGE). The eluent contains 1g/L LiBr ($\geq 99\%$, Sigma Aldrich). The sample solvent contains traces of water (HPLC grade, VWR) as internal standard. One pre-column (8x50 mm) and four PSS Gram gel columns (8x300 mm) are applied at a flow rate of 1.0 mL/min at 40°C. The average diameter of the gel particles is 10 μm and the nominal pore widths 30, 10^2 , 10^3 and 3000 Å. Calibration is achieved using narrowly distributed PEG standards (PSS Mainz). Results are evaluated using the PSS WinGPC UniChrom software (version 8.1).

Movie 1 – Production of W/O/W double emulsions that are crosslinked downstream

Movie 2 – Swelling of the dried microgel capsules in water

1. M. C. Lensen, P. Mela, A. Mourran, J. Groll, J. Heuts, H. Rong and M. Möller, *Langmuir*, 2007, **23**, 7841-7846.