

## Electronic Supplementary Information

### A simple one-step sonochemical route towards functional hairy polymer nanoparticles

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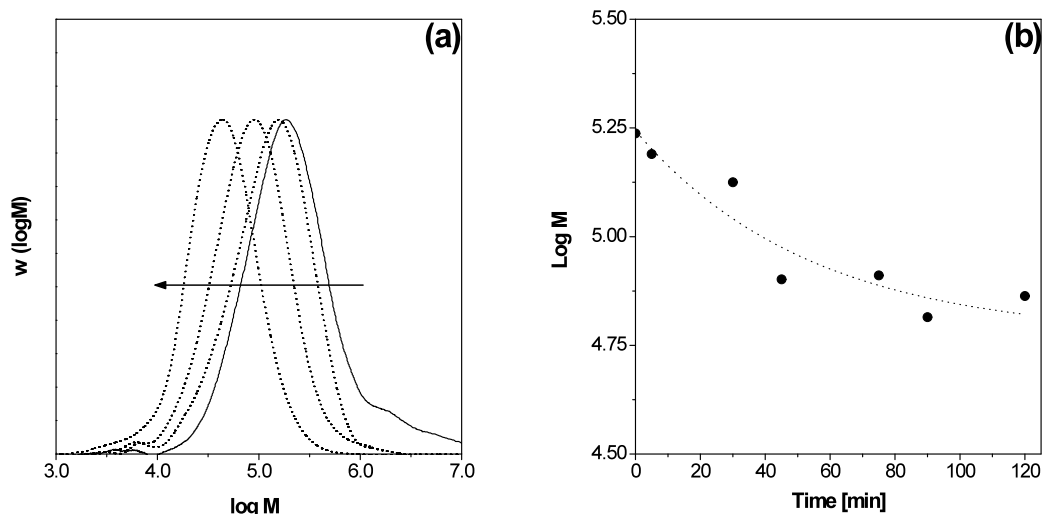
#### Experimental

##### *Materials*

The monomers, methyl methacrylate (MMA) (Aldrich, 99%), methyl acrylate (MA) (Across, 99%), ethyl methacrylate (EMA) (Aldrich, 99%), ethyl acrylate (EA) (Aldrich, 99%), butyl methacrylate (BMA) (Aldrich, 99%), butyl acrylate (BA) (Aldrich,  $\geq 99\%$ ), hydroxyethyl methacrylate (HEMA) (Aldrich,  $>97\%$ ) were purified by passing it over a column of activated basic alumina (Aldrich) to remove the methyl hydroquinone inhibitor and stored at  $-24^{\circ}\text{C}$ . The polymers poly(vinyl alcohol) (pVOH) (Celanese, Celvol 840), poly(acrylic acid) (pAA) (Aldrich, 35 w/w% in water,  $M_w \approx 250,000$  g/mol), poly(ethylene imine) (pEI) (Aldrich, 50 w/w% in water,  $M \approx 800,000$  g/mol), poly(ethylene oxide) (pEO) (Aldrich,  $M_v \approx 600,000$  g/mol) and hydroxyethyl cellulose (HEC) (Aqualon) were used as received. For all experiments distilled deionized water (DDW) was used.

##### *Sonochemical Degradation of PVOH*

The batch of pVOH used in all the reported experiments had an approximate number-average molecular weight ( $M_n$ ) of  $150 \cdot 10^3$  g $\cdot$ mol $^{-1}$ . An amount of 0.5 g of PVOH was dissolved in 100 g of water under vigorous stirring at  $50^{\circ}\text{C}$ . The PVOH solution was placed inside the glass reactor and hydroquinone (30 mg; 0.27 mmol) added. Subsequently, the solution was subjected to ultrasound for 2h. Samples for molecular weight analysis were withdrawn periodically and analyzed by SEC using HFIP as an eluent and relative to PMMA standards. The course of the number-average molecular weight as a function of the sonication time is shown in Figure 1 and it is clear from this figure that a lower critical molecular weight is reached at about  $75 \cdot 10^3$  g $\cdot$ mol $^{-1}$ .



**Fig. S1** Ultrasonic degradation of pVOH. (a) Evolution of the molecular weight distribution with increasing sonication time, and (b) Evolution of  $M_n$  with sonication time. The used pVOH is Celvol 840, all SEC measurements in hexafluoro isopropanol (HFIP) against poly(methyl methacrylate) standards.

#### *Sonochemical Polymerization Procedure*

All polymerizations were performed in a 250 mL double-walled glass reactor, equipped with baffles, a temperature sensor, magnetic stirrer bar and a Hielscher US200S ultrasonic processor (200 W, 24 kHz) combined with a S14 titanium sonotrode (diameter = 14 mm, length = 100 mm).

A PVOH solution was prepared by dissolving an accurate amount of PVOH in water, overnight at 50°C under vigorous stirring. Prior to the polymerization, the PVOH solution was placed inside the reactor and the temperature adjusted to the desired reaction temperature. The PVOH solution and the monomer were purged separately for 1 hour with argon. The required amount of monomer was added drop wise to the PVOH solution under vigorous stirring. Subsequently, the argon purge was removed from the liquid and the ultrasonication started at an amplitude of 80%. It should be noted here that the use of argon serves two purposes: (1) the removal of oxygen and (2) it is required for creating cavitations. Hence a continuous argon flow would in principle be beneficial for the polymerization, but excessive foaming occurred; the procedure that we followed here avoided this problem and was sufficient for an efficient polymerization. Samples were withdrawn periodically to monitor conversion by gravimetry, molecular weight distributions and/or particle size distributions. The properties of the resulting dispersions are reported in the manuscript. Additionally, the properties of the dispersions resulting from mixtures of pVOH and pEO are shown in Table S1.

**Table S1** Properties of the self-stabilizing nanoparticle dispersions prepared with different ratios of PVOH and PEO under optimal reaction conditions

PVOH:PEO	polymer	BA	x <sup>b</sup>	d <sub>p</sub> <sup>c</sup>	N <sub>p</sub> <sup>d</sup>
	[g]	[g]	[-]	[10 <sup>-9</sup> m]	[10 <sup>15</sup> dm <sup>-3</sup> ]
1:0	0.50	5.0	0.90	376	1.4
0:1	1.00	5.0	0.64	425	3.1
1:1	1.00	5.0	0.84	365	3.6
1:4	1.00	5.0	0.91	1849	0.7

#### *Solubility of the PVOH-co-PMMA and the PVOH-co-PBA polymers*

For detailed chemical analysis of the block-copolymers, their solubility was tested in a range of solvents. No detectable solubility was observed in acetone, dimethylformamide (DMF), chloroform, methanol, ethanol, dimethylacetamide (DMA), tetrahydrofuran (THF) and DMF with lithium bromide. The solubility in toluene and dimethyl sulfoxide (DMSO) was too low to allow for SEC or gradient polymer elution chromatography (GPEC). Only hexafluoro isopropanol (HFIP) was found to be a sufficiently good solvent to allow SEC analysis.

#### *Molecular weight analysis*

Size exclusion chromatography analysis using HFIP (Biosolve, AR-S from supplier or redistilled) as eluent measurements were carried using a Shimadzu LC-10AD pump (flow rate 0.8 ml/min) and a WATERS 2414, differential refractive index detector (at 35 °C). Injections were done by a Spark Holland, MIDAS injector, a 50 µL injection volume was used. The column is a PSS, 2\* PFG-lin-XL (7 µm, 8\*300 mm) column at 40°C. Calibration has been done using narrow molecular weight poly(methyl methacrylate) standards. Size exclusion chromatography analysis using THF (Biosolve) as eluent measurements were carried out using a Waters GPC equipped with a Waters model 510 pump and a Waters model 410 differential refractometer. A set of two mixed bed columns (Mixed-C, Polymer Laboratories, 30 cm, 40 8C) were used. Calibration was done using narrow polystyrene standards ranging from 600 to 7·10<sup>6</sup> g.mol<sup>-1</sup>.

#### *Particle size analysis*

Particle size distributions were measured in triplicate on a Malvern Zetasizer Nano Series (Nano ZS). All nanoparticle dispersions were diluted with distilled deionized water prior to the measurement. The averages of the measurements are reported.

#### *TEM imaging*

Transmission electron microscopy images were made using a FEI Tecnai 20 (type Sphera) TEM, operated with a 200 kV LaB6 filament and a bottom mounted 1024 x 1024 Gatan CCD camera.

#### *Serum analysis*

A Centrikon T-2060 ultracentrifuge (Kontron Instruments) was used to separate the aqueous and polymer phase. The remaining residual content in the separated aqueous phase was determined gravimetrically after ultracentrifugation at 40.000 rpm for 1h.