Supporting Information for:

Triblock Terpolymer versus Blends of Diblock Copolymers for Nanocapsules Addressed by Three Independent Stimuli

Shahed Behzadi, a Markus Gallei, *b Johannes Elbert, b Michael Appold, b Gunnar Glasser, a Katharina Landfester, a and Daniel Crespy * a

a Max Planck Institute for Polymer Research, D-55128 Mainz, Germany

b Macromolecular Chemistry Department, Technische Universität Darmstadt, D-64287 Darmstadt, Germany

Email: crespy@mpip-mainz.mpg.de

Email: M.Gallei@mc.tu-darmstadt.de

Characterization methods: The morphology of the NCs was examined with a transmission electron microscope (TEM) (JEOL 1400) operating at an accelerating voltage of 120 kV and a LEO 1530 Gemini scanning electron microscope (SEM) operating at 350V. 10 μL of the diluted dispersions were placed on small silicon wafers for SEM and on copper grids with a carbon support film for TEM measurements. For the vapor staining of NCs, iodomethane (300 μL) was dropped into a glass container which is included with the TEM grids within a small open glass vial. The container was left sealed at room temperature overnight. The same protocol was applied for staining with chlorotrimethylsilane. The evaporation of chlorotrimethylsilane in the
sealed container was facilitated by using oil bath at 40 °C. All TEM samples were carbon coated by thermal evaporation in a BALZERS BAE 250 for 5 s to reduce beam damage during the TEM measurements. Dynamic light scattering (DLS) measurements were carried out on a commercially available instrument from ALV GmbH (Langen, Germany) consisting of a goniometer and an ALV-5000 multiple tau full-digital correlators with 320 channels. A helium-neon laser from JDS Uniphase (Milpitas, USA) with an operating intensity of 25 mW and a laser wavelength of $\lambda = 632.8$ nm was used as a light source. All solutions for the light scattering experiments were prepared in dust-free quartz cuvettes from Hellma (Müllheim, Germany) with an inner diameter of 18 mm, which were cleaned before with distilled acetone. For the measurements of NCs size, their dispersion was diluted against sodium hydroxide or hydrochloric solutions, which were prepared by dilution 1 mol L$^{-1}$ solutions to the desired pH value, with concentration of 0.05 mg mL$^{-1}$ of hexadecyltrimethylammonium chloride for 1 h before measurement. Hydrodynamic diameter and poly dispersity index (PDI) were an average of three times repetitions at an angle of 90°. Zeta potential of the NCs was measured on the dispersions were diluted in aqueous solutions at the desired pH value with concentration of 0.001 mol L$^{-1}$ of potassium chloride (KCl) for 1 h before measurement. In all release experiments, the fluorescence intensity at the emission wavelength of 620 nm of the treated dispersion was measured on a Tecan Plate Reader Infinite M1000 at an excitation wavelength of 520 nm. Standard SEC was performed with THF as the mobile phase (flow rate 1 mL min$^{-1}$) on a SDV column set from PSS, Mainz (SDV 1000, SDV 10$^5$, SDV 10$^6$) at 30 °C. The calibration was carried out using PS standards from PSS (Mainz). For the SEC-MALLS experiments, a system composed of a Waters 515 pump (Waters, Milford, CT), a TSP AS100 autosampler, a Waters
column oven, a Waters 486 UV-detector operating at 254 nm, a Waters 410 RI-detector, and a DAWN DSP light scattering detector (Wyatt Technology, Santa Barbara, CA) was used. The Astra version 4.73 (Wyatt Technology, Santa Barbara, CA) was used for data acquisition and the evaluation of the light-scattering experiments. The light scattering instrument was calibrated using pure toluene, assuming a Rayleigh ratio of $9.78 \times 10^{-6}$ cm$^{-1}$ at 690 nm. An injection volume of 118 $\mu$L, a sample concentration of 1 g L$^{-1}$ to 2 g L$^{-1}$, a column temperature of 35 °C, and a THF flow rate of 1 mL min$^{-1}$ were applied. Additional TEM images of the PVFc-b-PDMAEMA-b-PMMA bulk samples were performed on a Zeiss EM10 with an operating voltage of 60 kV. The block copolymer was diluted in methylene chloride and the solvent was allowed to evaporate at room temperature. Thin films were heated at 150 °C in vacuum for 24 h. Ultrathin sections of the block copolymer film were cut into slices of 50-80 nm by using an ultramicrotome Ultracut UTC (Leica) equipped with a diamond knife. TEM images were recorded with a slow-scan CCD camera TRS (Tröndle).
**Figure S1.** TEM images of ultrathin sections of sample PVFC_{11.4-b-PDMAEMA_{17.8-b-PMMA_{70.8}} in the bulk state. The images were recorded without further staining. Scale bars correspond to 500 nm (left) and 100 nm (right), respectively.
Figure S2. TEM images of NCs prepared from PVFc$_{20}$-b-PMMA$_{80}$ diblock copolymer (a) and from PDMAEMA$_{34}$-b-PMMA$_{66}$ diblock copolymer (b). In the case of PVFc$_{20}$-b-PMMA$_{80}$, the presence of the iron in PVFc caused an inherent contrast between the two building blocks.

Figure S3. TEM images of NCs prepared from PDMAEMA$_{34}$-b-PMMA$_{66}$ diblock copolymer (a) and from PVFc$_{20}$-b-PMMA$_{80}$ diblock copolymer (b) after selective staining experiment with iodomethane and chlorotrimethylsilane, respectively.