Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Hollow Polymer Microrods of Tunable Flexibility from Dense Amphiphilic Block Copolymer Brushes

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Calculation of the PDMA content of the block copolymer brushes.

The PDMA content of the block copolymers was calculated from the GPC and TGA data. From the number average molecular weight of the P(MMA-*co*-GlyMA) block (M_n^1) and the number average molecular weight of the PDMA block (M_n^2), the PDMA content is[1]:

$$wt\%\ PDMA_{GPC} = \frac{M_n^2}{M_n^1 + M_n^2} \quad \text{(S1)}$$

It is worth noting that the PDMA content determined by equation S1 is accurate only if the chain extension efficiency of the polymer is close to 100%, and for polymers with narrow molecular weight distributions.

Alternatively, using the TGA weight loss for the rods grafted with the first P(MMA-*co*-GlyMA) block (ΔW_1) and the weight loss of the rods grafted with the P(MMA-*co*-GlyMA)-*b*-PDMA block copolymer (ΔW_2), the PDMA content is:

$$wt\%\ PDMA_{TGA} = 100\left(1 - \frac{\Delta W_1(100 - \Delta W_2)}{\Delta W_2(100 - \Delta W_1)}\right) \quad \text{(S2)}$$

Calculation of the grafting density of the block copolymer brushes.

The grafting density, σ, of the polymer on the silica rods was calculated using the following equation[2]:

$$\sigma\left(\frac{chains}{nm^2}\right) = \frac{m_{polymer}\,(g).N_A(mol^{-1})}{m_{silica}(g).S_{sp}(nm^2.g^{-1}).\,M_n(g.mol^{-1})} \quad \text{(S3)}$$

Where, M_n is the polymer molecular weight measured with GPC, S_{sp} is the BET specific surface and N_A is the Avogadro number. The ratio $\frac{m_{polymer}}{m_{silica}}$ was calculated from the respective weight losses, of the polymer functionalized particles (ΔW(Si-P)) and the initiator functionalized particles (ΔW(Si-I)), measured by TGA[3]:

$$\frac{m_{polymer}}{m_{silica}} = \frac{\Delta W(Si-P)}{100 - \Delta W(Si-P)} - \frac{\Delta W(Si-I)}{100 - \Delta W(Si-I)} \quad \text{(S4)}$$

Figures and Tables

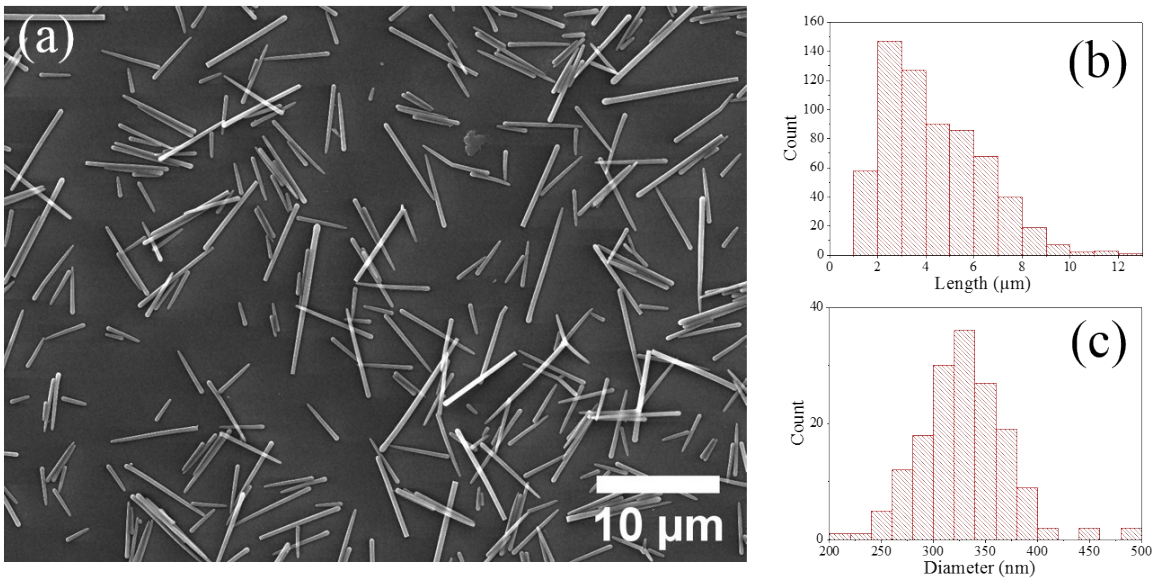

Figure S1. (a) SEM image, (b) length distribution and (c) diameter distribution of the silica rods. The dimensions of the silica rods were measured using ImageJ on at least 200 particles.

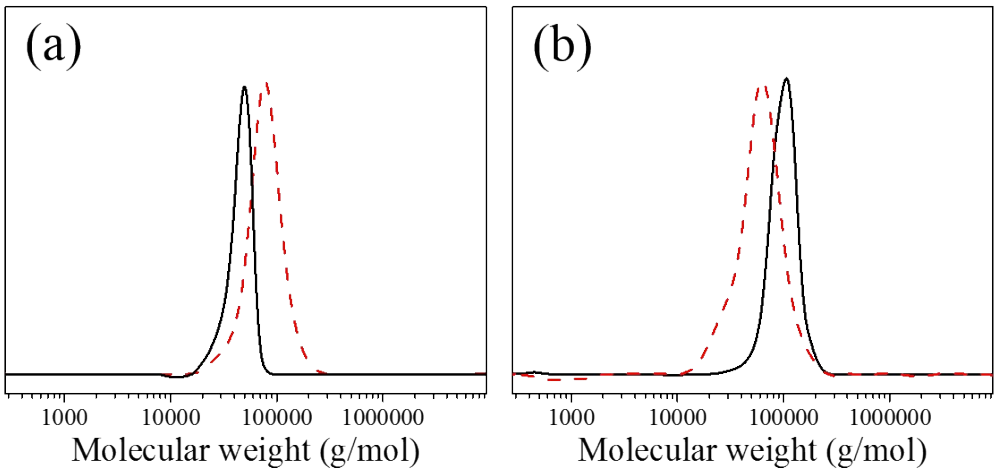

Figure S2. GPC traces of the "free" polymers, P(MMA-co-GlyMA) (black, solid line) and PDMA (red, dashed line), grown in solution at the same time as the grafted polymers, for (a) SiP-2 and (b) SiP-3.

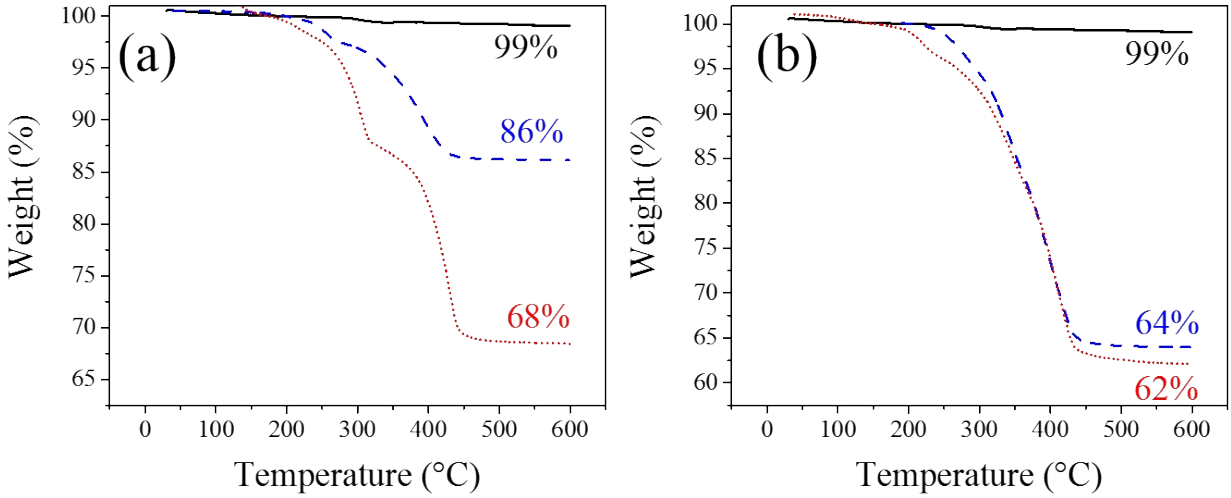

Figure S3. TGA analysis of the rods grafted with the initiator molecules (black, solid line), the P(MMA-*co*-GlyMA) block (blue, dashed line) and the P(MMA-*co*-GlyMA)-*b*-PDMA diblock copolymer (red, dotted line), for (a) SiP-2 (b) SiP-3.

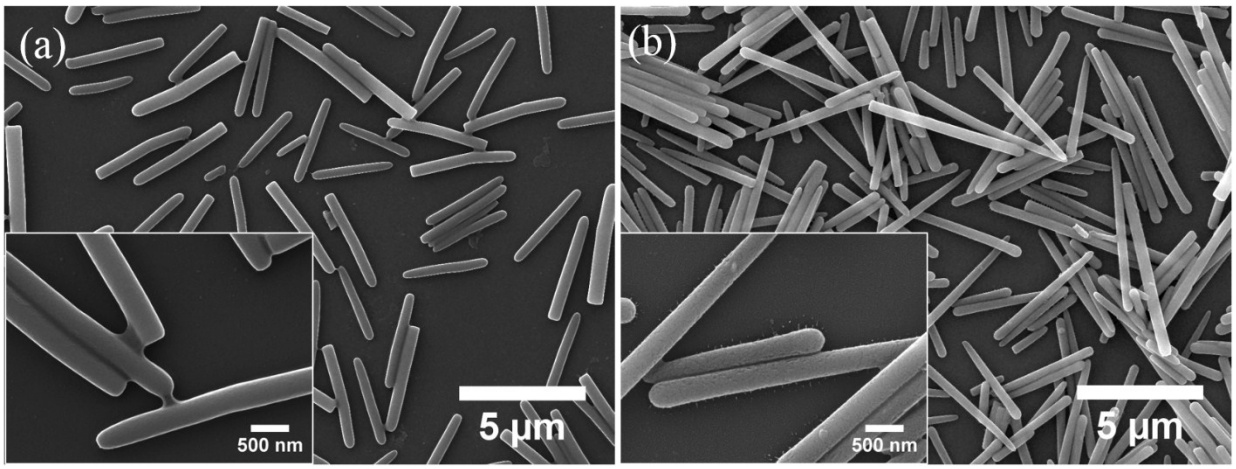

Figure S4. SEM images of the (a) SiP-0 and (b) SiP-2 core-shell rods. Insets show higher magnification images of the rods.

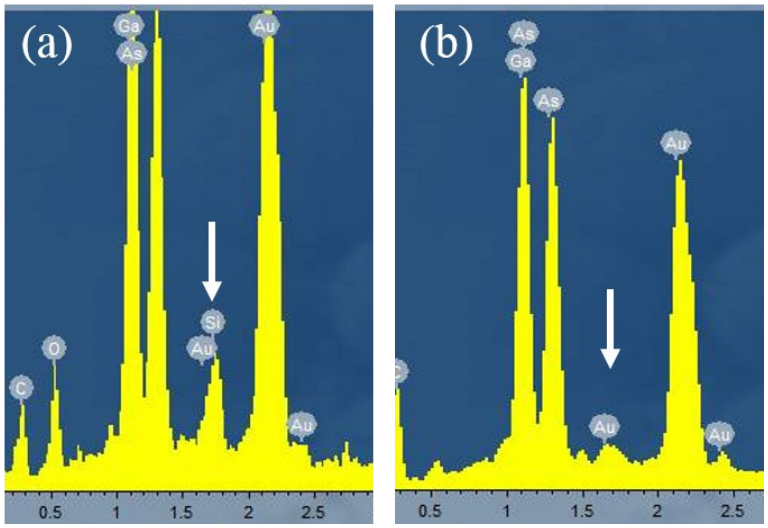

Figure S5. EDS analysis of (a) the SiP-2 core-shell rods and (b) the HR-2 hollow polymer rods deposited on GaAs substrates.

Table S1. Average dimensions of the bare silica rods, SiP-2 and SiP-3 core-shell rods and HR-2 and HR-3 hollow polymer rods.

	Bare silica rods	SiP-2	HR-2	SiP-3	HR-3
Diameter (nm)[a]	330 ± 40	390 ± 40	550 ± 80	410 ± 40	420 ± 110
Length (μm)[a]	4 ± 2	4 ± 2	5 ± 2	4 ± 2	4 ± 2
Polymer shell thickness by SEM (nm)[b]	-	30	-	40	-
Polymer shell thickness by TEM (nm)	-	23 ± 10	-	33 ± 10	80 ± 10

[a] Determined by SEM; [b] Polymer shell thickness determined as the difference of the diameter of the core-shell rods to the bare rods measured by SEM.

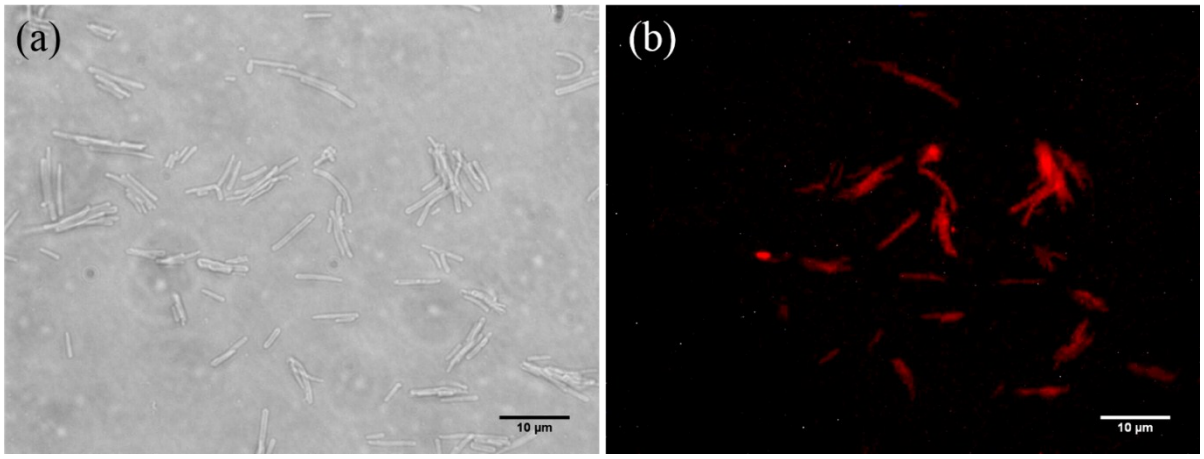

Figure S6. (a) Optical microscopy image in phase contrast mode and (b) fluorescence microscopy image of a dispersion of the HR-2 hollow polymer rods in water.

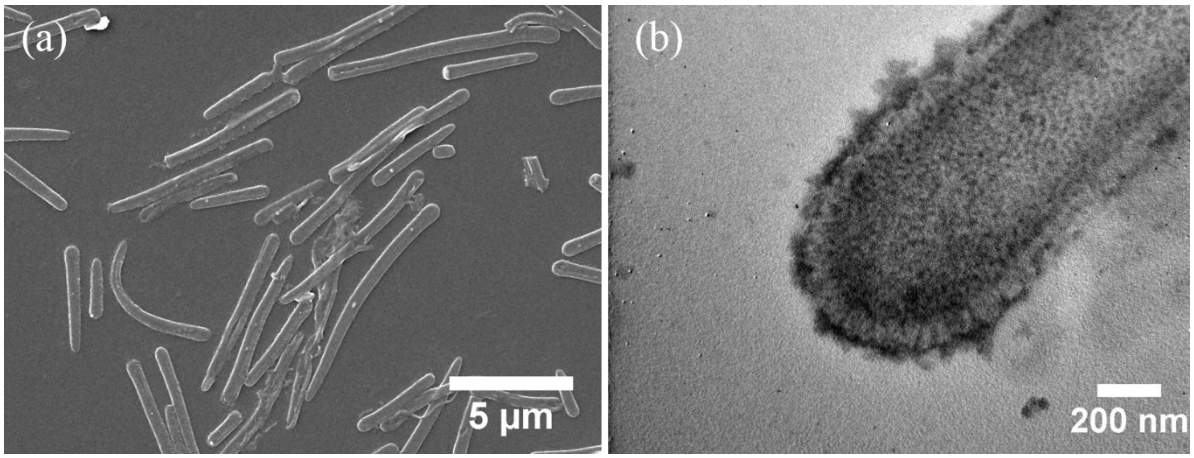

Figure S7. (a) SEM and (b) TEM image of the hollow polymer rods HR-2 after 7 months in water.

References

(1) Zhang, X.; Matyjaszewski, K. Synthesis of Well-Defined Amphiphilic Block Copolymers with 2-(Dimethylamino)Ethyl Methacrylate by Controlled Radical Polymerization. *Macromolecules* **1999**, *32* (6), 1763–1766. https://doi.org/10.1021/ma981332f.

(2) Ohno, K.; Akashi, T.; Huang, Y.; Tsujii, Y. Surface-Initiated Living Radical Polymerization from Narrowly Size-Distributed Silica Nanoparticles of Diameters Less Than 100 Nm. *Macromolecules* **2010**, *43* (21), 8805–8812. https://doi.org/10.1021/ma1018389.

(3) Pasetto, P.; Blas, H.; Audouin, F.; Boissière, C.; Sanchez, C.; Save, M.; Charleux, B. Mechanistic Insight into Surface-Initiated Polymerization of Methyl Methacrylate and Styrene via ATRP from Ordered Mesoporous Silica Particles. *Macromolecules* **2009**, *42* (16), 5983–5995. https://doi.org/10.1021/ma9003506.