Electronic Supporting Information for:

pH-Responsive Nanocapsules from Silylated Copolymers

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Experimental details

Materials

Styrene S (Merck, 99%) was purified by passing through a column filled with alumina. Trimethylsilyl methacrylate TMSMA (Sigma Aldrich, 98%) was vacuum distilled and stored until use at -20 °C. 2,2′-Azobisisobutyronitrile AIBN (Aldrich), oleic acid (Alfa Aesar, 99%), SDS (Alfa Aesar, 99%), *n*-hexadecane HD (Sigma Aldrich, 99%), *n*-hexane (Fisher Scientific, 98.9%), 1 M NaOH in water (VWR), dry tetrahydrofuran THF (Acros Organics, 99.8%), and chloroform (VWR, 99.8%) were used as received. The non-ionic block copolymer surfactant Lutensol AT50, a poly(ethylene oxide)-hexadecyl ether (Figure S5) with an ethylene oxide block length of ~ 50 units, was a gift from BASF.

Synthesis of the copolymers

The copolymers were synthesized by free-radical polymerization in solution. Known amounts of styrene and TMSMA in dry THF were degassed and bubbled with argon three times. After heating the solution to 80 °C in a flask equipped with a reflux condenser, certain amounts of AIBN dissolved in 4 mL THF were added (Table S1). The mixture was stirred at 80 °C for 6 h under argon atmosphere. The polymerization was then stopped by cooling to 0 °C in an ice-bath. After precipitation in *n*-hexane (100:1 of *n*-hexane:solvent), the polymer was filtrated, washed with the precipitant, and dried at 80 °C under vacuum. The molecular weight and the composition of the copolymer were measured by GPC and NMR (Table S2).

Table S1. Composition for the polymerization reactions.

Entry	polymer	S [g·L^{-1}]	TMSMA [g·L^{-1}]	AIBN [mg]	dried THF [ml]	precipitating agent
SC42	P($S_{0.87}$-*stat*-$TMSMA_{0.13}$)	257.4	43.4	80.1	280	dried ice/*n*-hexane
SC43	P($S_{0.71}$-*stat*-$TMSMA_{0.29}$)	200.2	130.3	80.7	280	*n*-hexane
SC45	P($S_{0.52}$-*stat*-$TMSMA_{0.48}$)	145.5	217.5	37.0	130	dried ice/*n*-hexane

Table S2. Characteristics of the synthesized copolymers.

Entry	polymer	Yield * [%][a]	M_w [g·mol^{-1}]	M_n [g·mol^{-1}]	PDI
SC42	P($S_{0.87}$-*stat*-$TMSMA_{0.13}$)	10.7	54,250	29,350	1.85
SC43	P($S_{0.71}$-*stat*-$TMSMA_{0.29}$)	7.9	57,400	31,000	1.85
SC45	P($S_{0.52}$-*stat*-$TMSMA_{0.48}$)	7.4	76,650	45,950	1.67

* after precipitation and drying of the copolymers.

Preparation of the nanocapsules

300 mg of synthesized copolymers were dissolved in 5 g chloroform and 300 mg of HD (12.5 mg HD in the case of nanoparticles prepared without surfactant). Even in the cases of nanoparticles, HD is added in small amount since it is known to hinder Ostwald ripening in direct miniemulsions.[1] The solutions were mixed with 10 mL of a 0.02 mmol·mL^{-1} aqueous solution of NaOH (200 µL 1 M NaOH + 9.8 mL H_2O). Sonication was carried out under ice cooling for 120 s at 70% amplitude in a pulse regime (30 s sonification, 10 s pause) using a Branson 450 W sonifier and a 1/2" tip. To evaporate the chloroform the miniemulsions were then stirred overnight at RT at 700 rpm. The composition of the nanocapsules is summarized in Table S3.

For the encapsulation of the fluorescent dye, 3 mg of *N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (PMI) was dissolved in the solution polymer/hexadecane/chloroform.

Table S3. Characteristics of the colloids. Amount of polymer = 300 mg, $CHCl_3$= 5 g.

Entry	polymer	HD [mg]	NaOH [b] [mL]	D_h [c] [nm]	morphology
JF186-3	P($S_{0.87}$-*stat*-TMSMA$_{0.13}$)	12.5	10	110 ± 40	particles
JF184-5	P($S_{0.71}$-*stat*-TMSMA$_{0.29}$)	12.5	10	130 ± 40	particles
JF186-1	P($S_{0.87}$-*stat*-TMSMA$_{0.13}$)	300	10	160 ± 50	capsules
JF190-1	P($S_{0.71}$-*stat*-TMSMA$_{0.29}$)	300	10	190 ± 70	capsules
JF184-4	P($S_{0.52}$-*stat*-TMSMA$_{0.48}$)	300	10	130 ± 40	capsules
JF190-3 [a]	P($S_{0.71}$-*stat*-TMSMA$_{0.29}$)	300	10	190 ± 40	capsules

[a] 1 mg *N*-(2,6-diisopropylphenyl) perylene-3,4-dicarbonacidimide (PMI) added to the dispersed phase;
[b] 0.02 mmol·mL^{-1} aqueous solution of NaOH;
[c] determined by DLS.

Kinetics of desilylation

300 mg of P($S_{0.71}$-*stat*-TMSMA$_{0.29}$) were dissolved in 5 g $CHCl_3$ and 300 mg HD. The solution was mixed with a 0.02 mmol·mL^{-1} aqueous solution of NaOH and stirred at RT at 1000 rpm without evaporation of $CHCl_3$. Samples were taken at fixed time intervals and directly freeze-dried. Further, a sample of surfactant-free dispersion of nanocapsules with desilylated P($S_{0.71}$-*stat*-TMSMA$_{0.29}$) (JF190-1) was also frozen. After freeze-drying and treatment at 80 °C under vacuum, each sample was dissolved in d_8-THF and investigated by ^{1}H-NMR spectroscopy. For quantitative analysis the integrals of the aromatic signals (6-8 ppm) were compared with the integrals of the TMS-group (0.03 ppm).

Turbidity measurements

Turbidity measurements were carried out in transmission with a red light He-Ne laser (JDSU, model 1145P, 633 nm, 25mW) through the diluted samples under constant magnetic stirring (300 rpm) and detection of the light by a photodiode detector. 200 µL of the dispersion of nanocapsules with desilylated P($S_{0.71}$-*stat*-TMSMA$_{0.29}$) (JF190-1) were mixed with 30.1 mL H_2O and 100 µL of 1M HCl (for the aggregation). 100 µL of 1M NaOH was added for the redispersion.

Aggregation of the nanocapsules in the presence of a non-ionic block copolymer surfactant

Surfactant-free dispersion of nanocapsules from desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) (JF190-1) containing various concentrations of Lutensol AT50 were prepared and the pH was adjusted to 3 by adding 1M HCl. DLS measurements were performed on the dispersions at the different stages.

Encapsulation of DCPD

150 µL of 1M HCl were added to 6 g of the dispersion containing DCPD (JF195-1) to aggregate the nanocapsules and the dispersion was filtrated. For redispersion, 0.479 g of the wet solid was mixed with 50 µL 1M NaOH and 150 µL water, stirred and treated in an ultrasonic bath until complete redispersion. For determination of the DCPD amount, 50-200 mg of each samples were dissolved in d_8-THF in the presence of 2 mg maleic acid as external standard for ^{1}H-NMR spectroscopy.

Increase of the amount of dispersed phase

200 µL of a 1M HCl was added to 8.5 g of the nanocapsules dispersion with desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) shell (JF190-1). The dispersion was filtrated and the residue was then redispersed by addition of 200 µL 1 M NaOH under stirring and sonication in an ultrasound-bath. The procedure was repeated a second time, with the exception that the amount of added 1 M NaOH was changed to 150 µL. The amount of dispersed phase (core-shell) and the solid content (only the shell) of the dispersions were investigated by gravimetry (Table S4).

Table S4. Characteristics of the dispersion JF190-1 after aggregation, separation, and redispersion.

Entry	$f_{d\varphi}$ * [wt%]	solid content ** [wt%]	D_h [nm]
after synthesis	5.8	3.0	190 ± 70
after 2nd filtration	-	17.7	-
after 2nd redispersion	31.9	15.6	190 ± 80

* fraction of the dispersed phase measured by gravimetry with HD still inside the nanocapsules);

** measured after freeze-drying followed by drying under vacuum (only the material of the shell).

Nanocapsules with encapsulated oleic acid and release experiments

300 mg of synthesized copolymers were dissolved in 5 g chloroform, 50 mg of HD and 250 mg of oleic acid. The solutions were mixed with 10 mg SDS dissolved in 10 mL of a 0.002 mmol·mL^{-1} aqueous solution of HCl (20 µL 1 M HCl + 9.98 mL H_2O) resulting to a pH of 3. After stirring 1h at 1000 rpm, sonication was carried out under ice cooling for 120 s at 70% amplitude in a pulse regime (30 s sonification, 10 s pause) using a Branson 450 W sonifier and a 1/2" tip. To evaporate the chloroform the miniemulsions were then stirred overnight at RT at 700 rpm.

The resulting dispersion (~10.6 g) with encapsulated oleic acid was mixed with 1.5 mL of 1 N NaOH and stirred for 10 min resulting to a pH of 10 and a complete transparency of the dispersion. After addition of 1.5 mL of 1 N HCl (pH=3), the dispersion was turbid again.

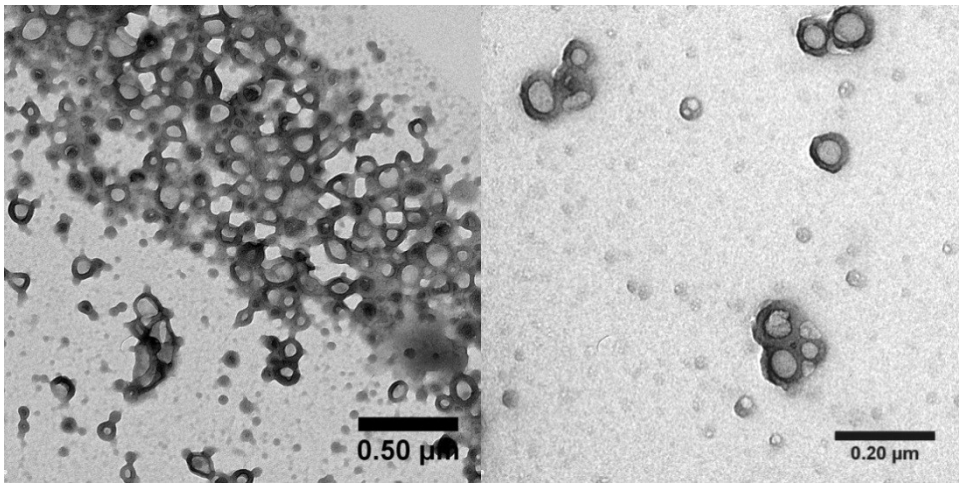
Table S5. Hydrodynamic diameter D_h of the dispersions of P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) containing oleic acid at different pH.

Entry		D_h [nm]
JF209-2	after synthesis	230 ± 80
JF209-2_pH10	after addition of 1.5 mL 1N NaOH	450 ± 320
JF209-2_pH3	after further addition of 1.5 mL 1N HCl	180 ± 80

Additional characterization

Morphology of the prepared nanoparticles and nanocapsules

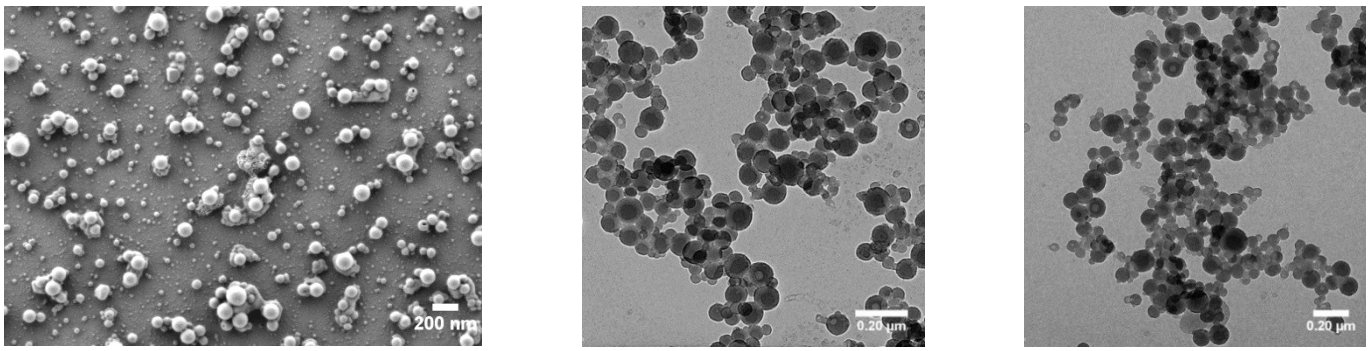
Surfactant-free preparation of nanocapsules



a. **b.**

Figure S1. TEM micrographs of desilylated P($S_{0.52}$-*stat*-$TMSMA_{0.48}$) nanocapsules (JF184-4).

Surfactant-free preparation of nanoparticles



a. **b.** **c.**

Figure S2. a: SEM micrograph of desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) nanoparticles (JF184-5). TEM micrographs of **b:** desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) nanoparticles (JF184-5), **c:** desilylated P($S_{0.87}$-*stat*-$TMSMA_{0.13}$) nanoparticles (JF186-3).

pH switchable aggregation and redispersion

Because of the limit of detection of DLS measurements, the size of the aggregates are represented as 1 μm in Figure 3.

Size of the aggregates

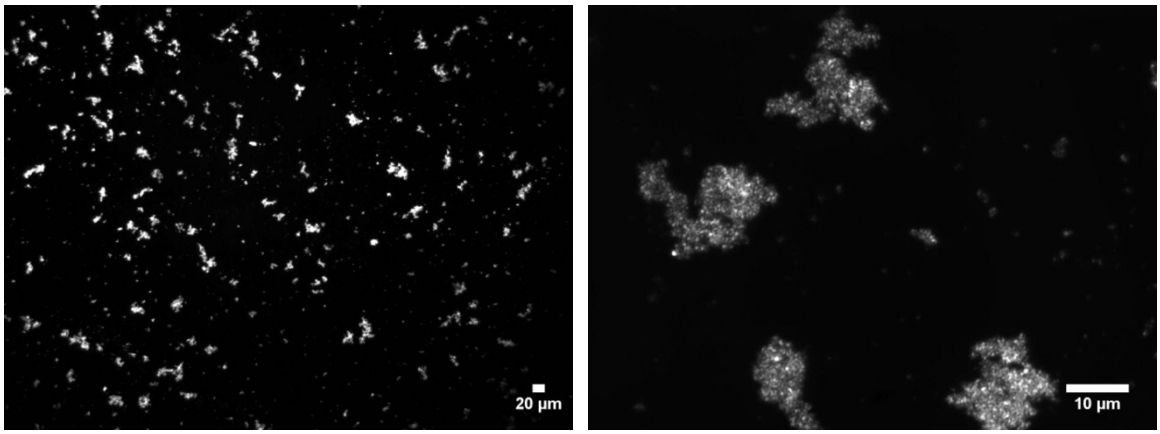
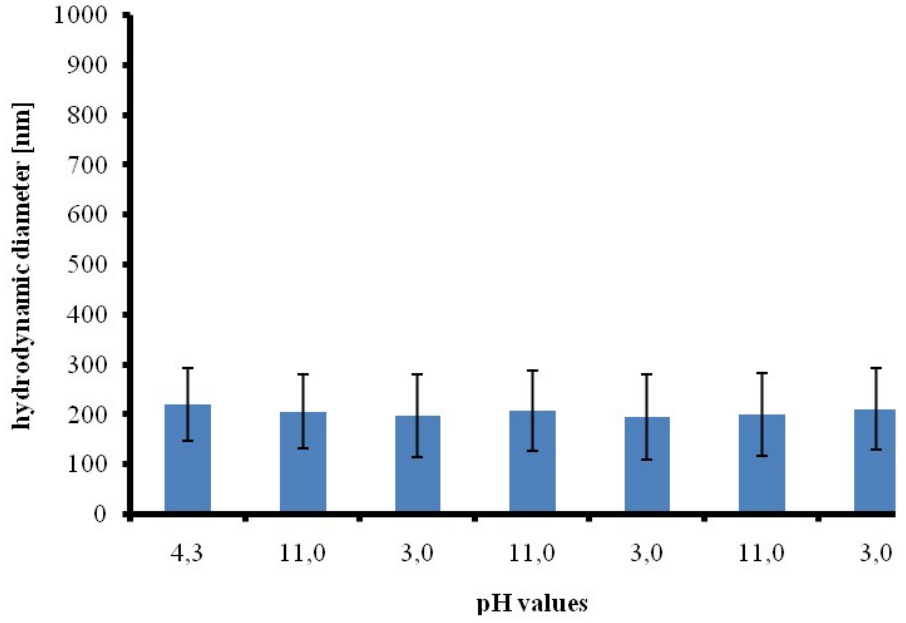
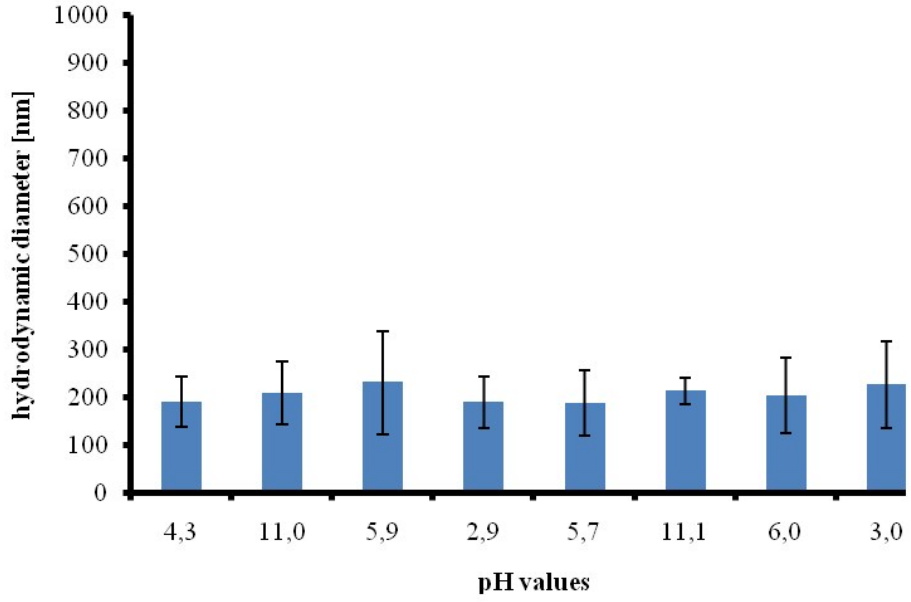


Figure S3. Optical microscope images of aggregated nanocapsules at pH < 3.5 (sample JF190-1). $D_{Aggregates}$ ~ 10.9 ± 8.0 μm (average of 200 measurements).



a.



b.

Figure S4. On the contrary to the desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) nanocapsules, nanocapsules from desilylated P($S_{0.87}$-*stat*-$TMSMA_{0.13}$) (a), or from P($S_{0.91}$-*stat*-$MAA_{0.09}$) (b), do not show a pH-dependent stability as measured by DLS.

Aggregation in the presence of a non-ionic block copolymer surfactant

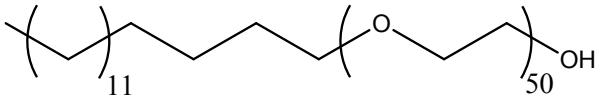


Figure S5. Chemical structure of the non-ionic block copolymer structure.

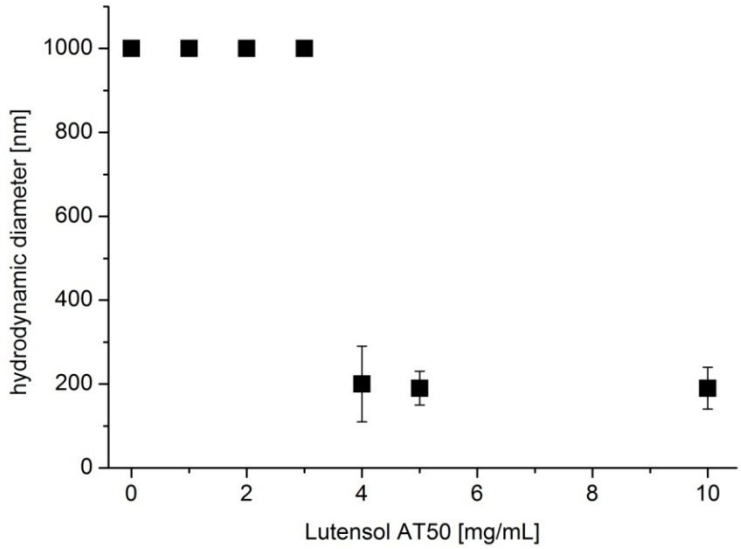


Figure S6. Plot of the hydrodynamic diameters of the surfactant-free dispersion of nanocapsules from desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) (JF190-1) versus concentration of Lutensol AT50 in the continuous phase at pH=3. Aggregates with sizes above 1 µm are counted as 1 µm in the diagram.

Encapsulation of the self-healing materials

Table S6. Composition of the nanocontainers for the encapsulation of healing agents.

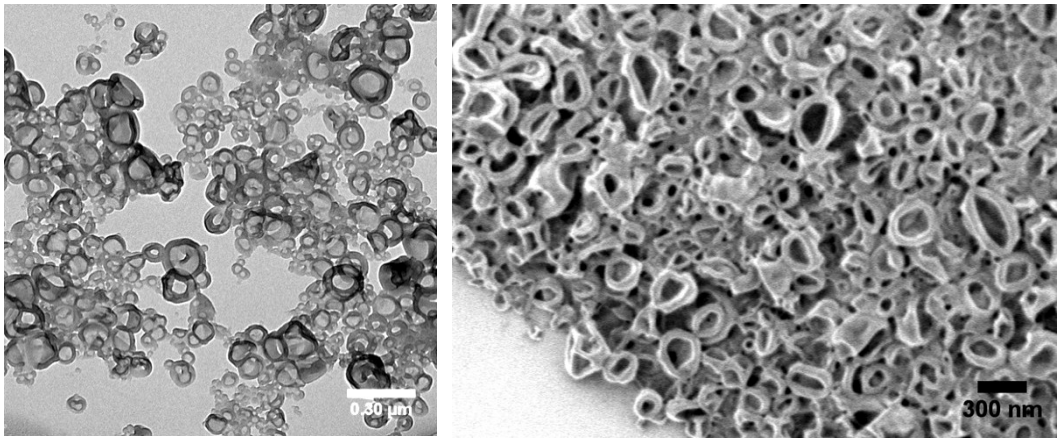
Entry	polymer	HD [mg]	DCPD [mg]	Grubbs catalyst [mg]	NaOH * [mL]	D_h [nm]	morphology
JF195-1	P($S_{0.71}$-*stat*-$TMSMA_{0.29}$)	100	200	0	10	160 ± 40	capsules
JF194-4	P($S_{0.71}$-*stat*-$TMSMA_{0.29}$)	300	0	15	10	210 ± 80	capsules

* 0.02 mmol·mL^{-1} aqueous solution

Table S7. Content of core and shell for P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) nanocapsules (sample 195-1).

Entry	solid content * [wt%]	$f_{d\varphi}$ ** [wt%]	encapsulated DCPD [wt%]
after synthesis	2.6	4.8	78
aggregated solid	10.6	19.4	76
after redispersion	9.3	17.2	78

* measured after freeze-drying and further drying the dispersions under vacuum at 80 °C;
** calculated with measured amount of encapsulated DCPD.



a. **b.**

Figure S7. a: TEM micrograph and **b:** SEM micrograph of the P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) nanocontainers for the encapsulation of DCPD.

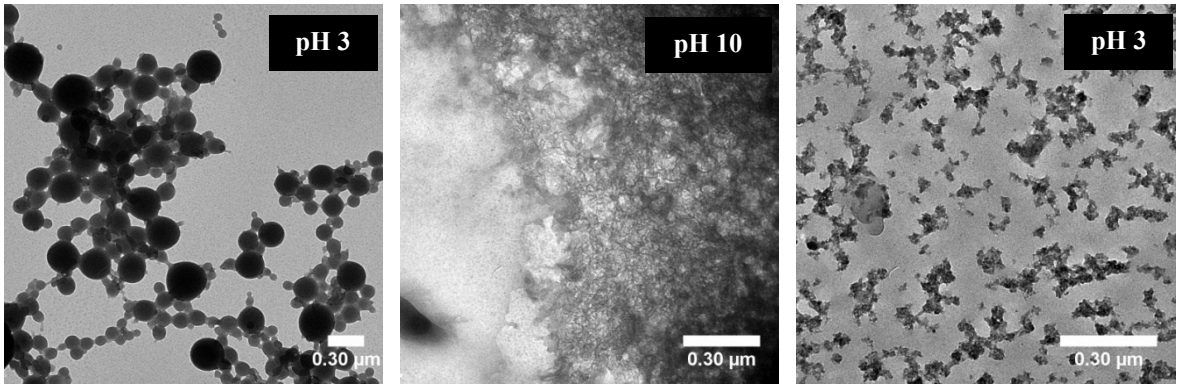
Nanocapsules with pH-responsive core and shell

Preparation of the nanocapsules with encapsulated oleic acid at pH=3

300 mg of the copolymer P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) was dissolved in 5 g chloroform, 50 mg of HD, and 250 mg of oleic acid. The solutions were mixed with 10 mg SDS dissolved in 10 mL of a 0.002 $mmol \cdot mL^{-1}$ aqueous solution of HCl (20 µL 1 M HCl + 9.98 mL H_2O) resulting to pH=3. After stirring 1h at 1000 rpm, sonication was carried out under ice cooling for 120 s at 70% amplitude in a pulse regime (30 s sonification, 10 s pause) using a Branson 450 W sonifier and a 1/2" tip. To evaporate the chloroform the miniemulsions were then stirred overnight at RT at 700 rpm.

Release experiments

The resulting dispersion (~10.6 g) with encapsulated oleic acid was mixed with 1.5 mL of 1 N NaOH and stirred for 10 min resulting to pH 10 and complete transparency of the dispersion. After addition of 1.5 mL of 1 N HCl (pH=3), the dispersion became turbid again.



a. **b.** **c.**

Figure S8. TEM micrographs of desilylated P($S_{0.71}$-*stat*-$TMSMA_{0.29}$) nanocapsules with encapsulated oleic acid **a:** after synthesis at pH=3; **b:** after addition of NaOH at pH=10; **c:** after further addition of HCl at pH=3 (collapsed aggregates).

References

(1) Landfester, K. *Macromol. Symp.* **2000**, *150*, 171-178.