

SUPPORTING INFORMATION

General Synthesis of the macro-CTAs(1). RAFT polymerizations of PFMA using 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid were performed in a Schlenk tube. The reaction vessel was loaded with AIBN, CTA (molar ratio of AIBN/CTA = 1:8) and 15 g of PFPMA in 20 mL of dioxane. Following three freeze–vacuum–thaw cycles, the tube was immersed in an oil bath at 70 °C. Afterwards the polymer poly(PFPMA) was 3 times precipitated into hexane, isolated by centrifugation and dried for 12 hours at 30 °C under vacuum. In the end a slightly red powder was obtained.

Table 1: Ratio of chemicals in homopolymer synthesis by RAFT polymerization

macro CTA	n(PFMA)	n(CTA)	n(AIBN)	V(dioxane)	Yield
R1	0.06 mol	0.55×10^{-3} mol	0.6×10^{-4} mol	40 ml	68 %
R2	0.06 mol	0.22×10^{-3} mol	0.3×10^{-4} mol	40 ml	65 %

General Synthesis of block copolymers(2). The macro CTA obtained in above mentioned polymerization was dissolved in dioxane and AIBN was added. Following three freeze–vacuum–thaw cycles, the tube was immersed in an oil bath at 70 °C. After 12 h polymerization time the solution was slightly concentrated and precipitated twice in EtOH and diethyl ether, removed by centrifugation and dried overnight at 30°C in vacuum. A slightly red powder was obtained.

Table 2: Ratio of chemicals in diblock copolymer synthesis by RAFT polymerization

block copolymer	n(PFMA in the macroCTA)	n(LMA)	n(AIBN)	V(solv.)	Yield
A1	11.9×10^{-3} mol	0.6×10^{-3} mol	0.6×10^{-4} mol	10 ml	87 %
A2	11.9×10^{-3} mol	1.2×10^{-3} mol	0.3×10^{-4} mol	10 ml	85 %

Dye incorporation. A solution of 1 mg of (HPMA)-*block*-poly(lauryl methacrylate) polymer and 2mg of bengal rosa b in 1 ml dioxane was prepared and added drop wise to 20ml of an aqueous solution of NaBr (1×10^{-3} M). In the control experiment 1ml of dye was dissolved in dioxane and dropped to the aqueous solution. Afterwards both solutions have been transferred to a molecular porous membrane tubing (Spectra/Por® Dialysis Membrane MWCO: 3,500) and dialysed against water for 4 days. The water was changed 3 times a day. The polymer containing solution was again dialysed for 4 days using Spectra/Por® Dialysis Membrane MWCO: 22,500 without any visible effect. A dark red solution was obtained.

Representative examples for static and dynamic light scattering curves

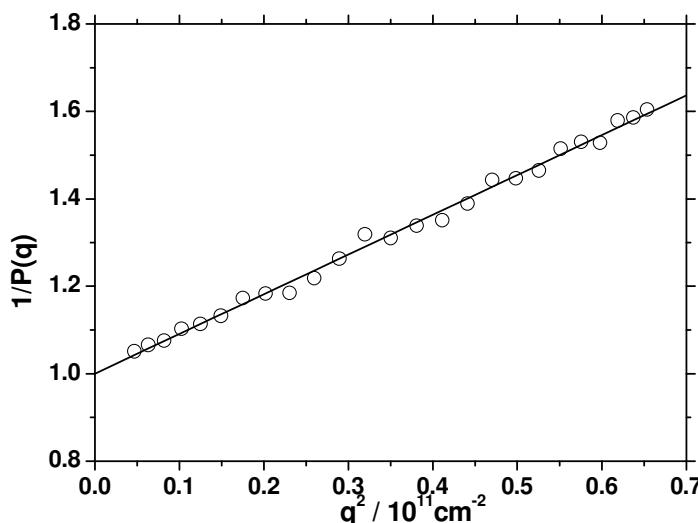


Figure S1: Reduced scattering intensity versus q^2 for sample P1, 18 hours after preparation yielding $R_g = 52.2$ nm.

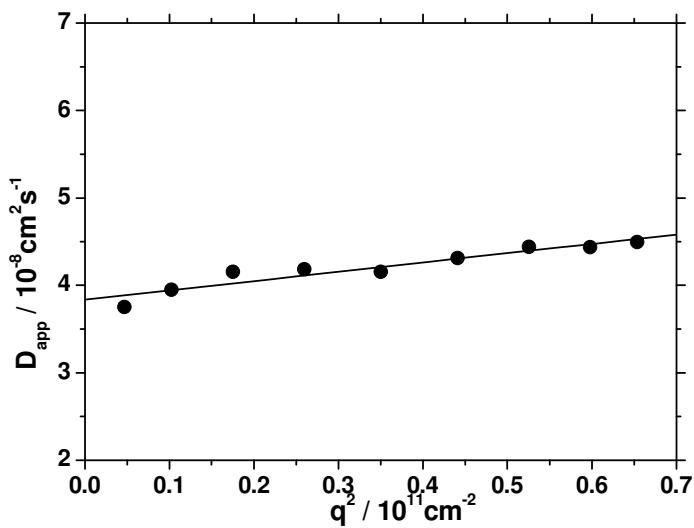


Figure S2: Apparent diffusion coefficient versus q^2 for sample P1, 18 hours after preparation yielding $R_h = 55.9 \text{ nm}$

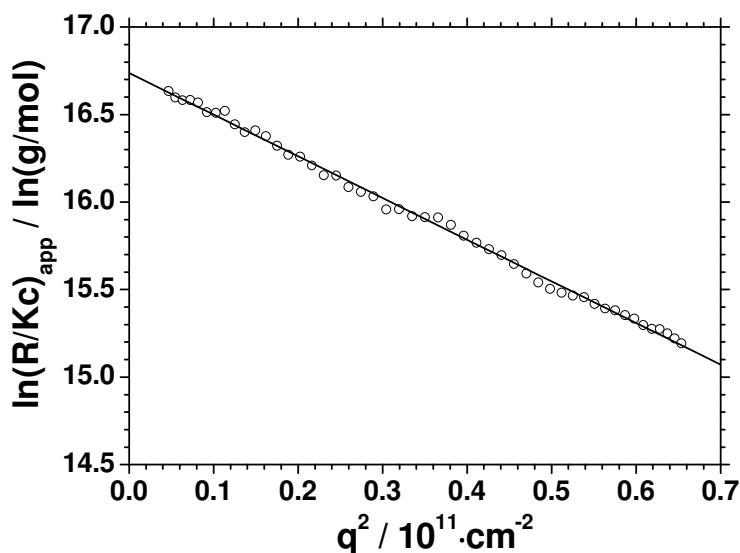


Figure S3: Guinier plot of sample P2 measured directly after preparation, yielding $R_g = 85 \text{ nm}$.

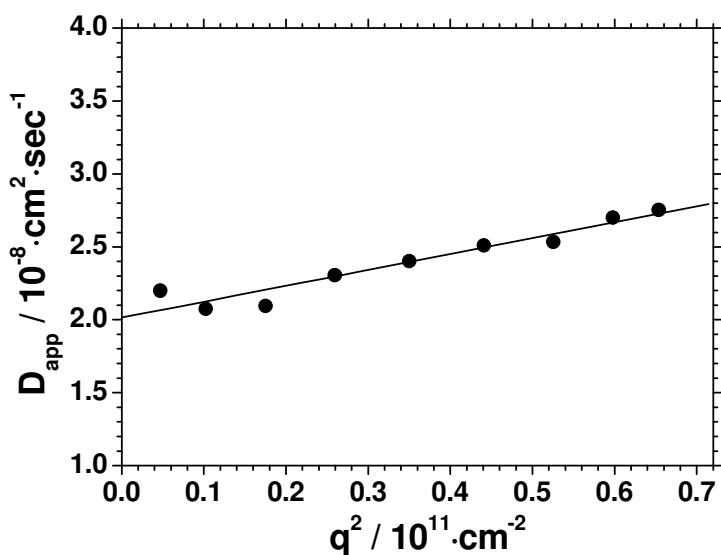
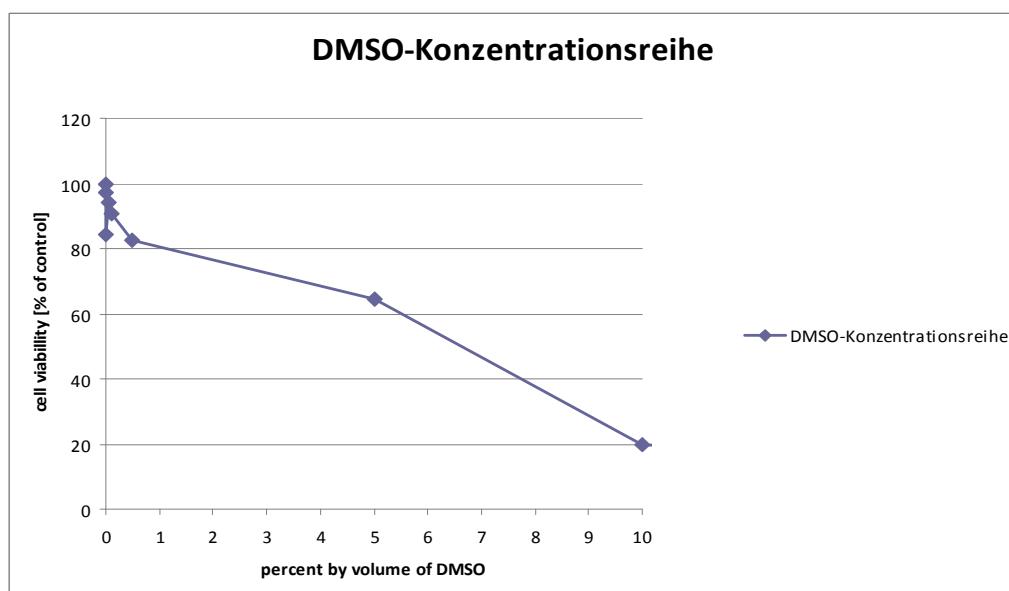


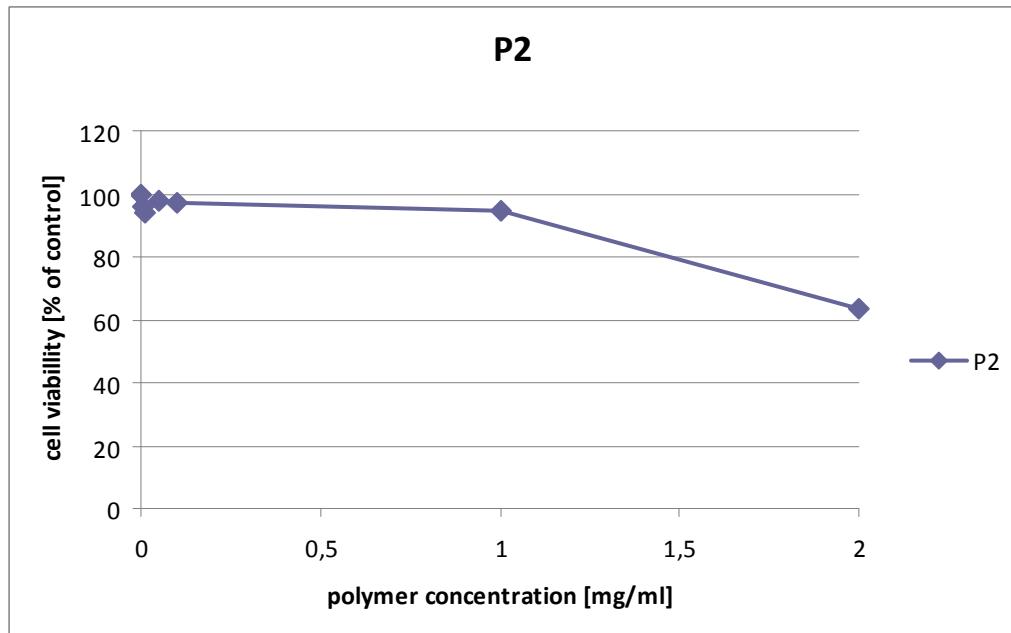
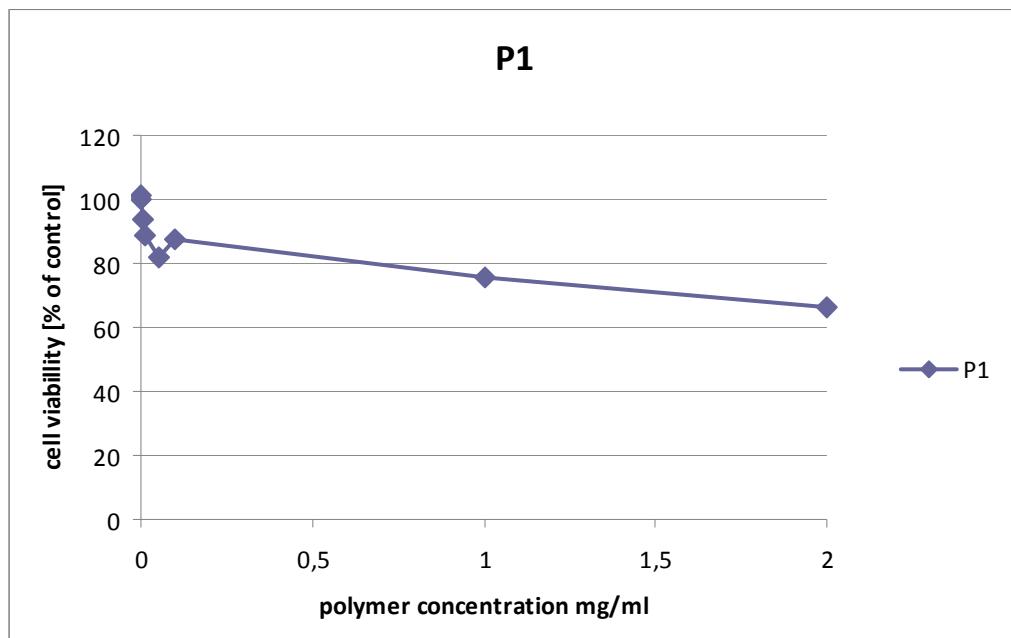
Figure S4: Apparent diffusion coefficient versus q^2 for sample P2, measured directly after preparation yielding $R_h = 106 \text{ nm}$

MTS Test:

The nano-aggregates have been prepared from a DMSO solution. There for the influence of DMSO itself has been evaluated.



In respect to the influence of DMSO we have investigated the cell toxicity of the polymeric particles up to a concentration of 2 mg/ml. At that concentration the DMSO percent of volume is 4 %. At that point there is already an influence of the DMSO, but no remarkable toxicity.



In this range we could detect any toxicity by the MTS test.

FACS measurements:

For flow cytometric analysis cells were plated in 24 well plates (5×10^4 cells/well). Subsequent incubation with 200 μ L of polymer solutions in media without FBS was performed for 1h at 37 °C. After washing thrice with ice-cold phosphate-buffered saline (PBS), cells were trypsinized and centrifuged. The pellet was resuspended in PBS containing bovine serum albumin (1 mg/mL). The mean fluorescence intensity was analyzed using a Becton Dickinson LSRII flow cytometer operating under FACSDiva software (San Jose, CA), equipped with an Coherent Sapphire Blue laser (488 nm) a 505 nm long pass filter and 530/30 bandpass filter. Data were acquired in linear mode and visualized in logarithmic mode. Data from 10,000 events were gated using forward and side scatter parameters to exclude debris and dead cells as well as control cells incubated with media alone as control for autofluorescence.

Concentration depended FACS measurement of **P1a** after 1 h incubation time:

