Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Amine-containing diblock terpolymers *via* AROP: A versatile method for the generation of multifunctional micelles

*Johanna K. Elter[a,b], Jonas Eichhorn[a,b], Michael Ringleb[a], and Felix H. Schacher[a,b,]**

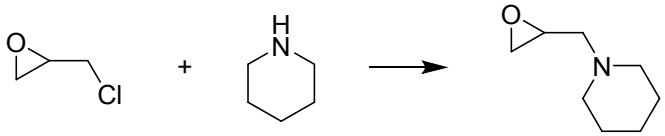
[a] Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University Jena, Humboldtstraße 10, D-07743 Jena, Germany

[b] Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, D-07743 Jena, Germany

*felix.schacher@uni-jena.de

Synthetic procedures

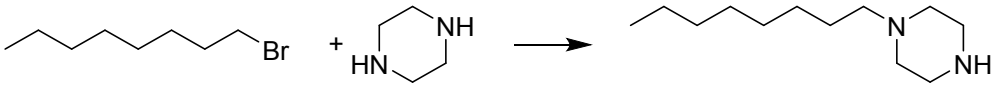
Synthesis of 1-(oxiran-2-ylmethyl)piperidine (PiGA).[1]



Piperidine (15.39 mL, 155.8 mmol) was cooled to 0 °C in a round-bottom flask under stirring, and deionized water (477 µL, 26.5 mmol) was added. Then, epichlorohydrin (1 eq, 12.22 mL, 155.8 mmol) was added dropwise over a time range of 20 minutes. After that, stirring was continued for one hour while keeping the temperature below 10 °C, followed by stirring for one hour at room temperature. Subsequently, the reaction mixture was cooled to 0 °C, and cooled aqueous NaOH (30%, 31.2 mL, 234 mmol) was added dropwise over a time range of 10 min. The mixture was allowed to reach room temperature under stirring for 18 hours. Then, the mixture was diluted with 50 mL of deionized water and extracted with diethyl ether (3x 90 mL). The combined organic phases were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The product was purified *via* vacuum distillation (0.39 mbar, bp 46-48 °C) to yield 15.27 g (69%) of the pure product as colorless liquid.

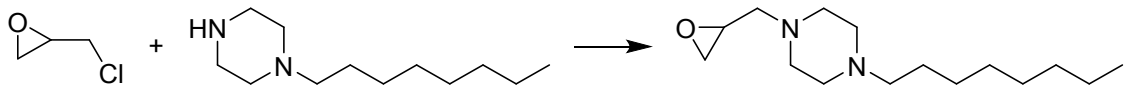
^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.05 (td, J = 6.8, 3.6 Hz, 1H, C*H*-O), 2.72 (t, J = 4.5 Hz, 1H, CH_2-O), 2.61 (dd, J = 13.3, 3.6 Hz, 1H, CH-CH_2-N), 2.57 – 2.30 (m, 5H, CH_2-CH_2-N and CH_2-O (1H)), 2.22 (dd, J = 13.3, 6.6 Hz, 1H, CH-CH_2-N), 1.66 – 1.48 (p, J = 5.4 Hz, 4H, CH_2-CH_2-N), 1.40 (p, J = 5.4 Hz, 2H, CH_2 -CH_2-CH_2).

Synthesis of 1-octyl-4-(oxiran-2-ylmethyl)piperazine (OPGA).[1-2]



Piperazine (11 g, 110 mmol) and K_2CO_3 (17.65 g, 128 mmol) were dissolved in 240 mL of dry acetonitrile. Then, the solution was heated to 50 °C and 1-bromoctane (3.8 mL, 22 mmol) was added slowly *via* syringe. The mixture was stirred for 24 hours at 50 °C before K_2CO_3 was filtered off, the solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (200 mL). The organic phase was washed with water several times to remove residual piperazine and K_2CO_3. Afterwards, the organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. Drying of the product under vacuum yielded 4.40 g (22 mmol, 100%) of *N*-octylpiperazine as white, crystalline solid.

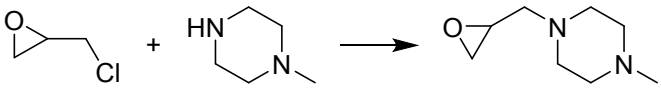
^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.96 – 2.81 (t, J = 4.8 Hz, 4H, C*H*$_2$-NH-C*H*$_2$), 2.39 (s, br, 4H, C*H*$_2$-N-C*H*$_2$), 2.33 – 2.24 (m, 2H, N-C*H*$_2$-CH$_2$), 1.90 (s, 1H, N*H*), 1.46 (p, J = 6.6 Hz, 2H, N-CH$_2$-C*H*$_2$), 1.26 (m, 10H, -C*H*$_2$-), 0.86 (t, J = 6.7 Hz, 3H, C*H*$_3$).



In a second step, 500 mg (2.50 mmol) of *N*-octylpiperazine were dissolved in 1 mL of deionized water in a pressure tube. Then, epichlorohydrin (200 µL, 2.55 mmol) was added and the mixture was stirred at room temperature for 2 hours. After that, the reaction vessel was sealed and the mixture was heated to 75 °C. Aqueous NaOH (30%, 1mL) was added and the mixture was stirred at 75 °C for 15 more minutes before it was cooled to room temperature. The solution was then diluted with 15 mL of deionized water and extracted with ethyl acetate (3x 25 mL). The organic phases were combined, washed with brine (1x 25 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield 478 mg of the crude product as pale yellow oil. The crude product was purified *via* column chromatography (Hexane/EtOAc/MeOH 12:8:1) to yield 255 mg (1.00 mmol, 40%) as pale orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.10 (td, J = 6.7, 3.6 Hz, 1H, C*H*-O), 2.83 – 2.23 (m, 14H, overlap of signals C*H*$_2$-O, CH-C*H*$_2$-N, N-C*H*$_2$-C*H*$_2$-N), 1.50 (p, J = 6.6 Hz, 2H, N-CH$_2$-C*H*$_2$), 1.38 – 1.18 (m, 10H, -C*H*$_2$-), 0.88 (t, J = 6.7 Hz, 3H, C*H*$_3$).

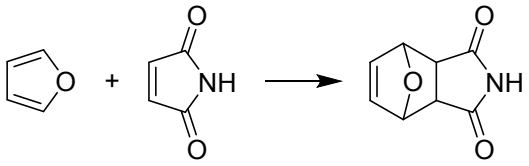
Synthesis of 1-methyl-4-(oxiran-2-ylmethyl)piperazine (MPGA).[3]



N-Methylpiperazine (556 µL, 5 mmol) was dissolved in 30 mL of diethyl ether and epichlorohydrin (392 µL, 5 mmol) was added dropwise, keeping the temperature below 35 °C by partial cooling using an ice bath. After the addition, the reaction mixture was refluxed for two hours before powdered NaOH (200 mg, 5 mmol) was added. Stirring under reflux was continued for 15 hours. The solid was removed *via* filtration and the filtrate was extracted with deionized water (2x 15 mL). Water was removed under vacuum to yield the crude product, which can be purified *via* distillation. In our case, only small amounts of the product (54 mg, 7%) of the pure product were obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.01 (td, J = 6.8, 3.4 Hz, 1H, C*H*-O), 2.73 – 2.63 (m, 2H, C*H*$_2$-O (1H), CH-C*H*$_2$-N (1H)), 2.63 – 2.26 (m, 10H, C*H*$_2$-O (1H), CH-C*H*$_2$-N (1H), N-C*H*$_2$-C*H*$_2$-N (8H)), 2.22 (s, 3H, C*H*$_3$), 2.25 – 2.14 (m, 1H, CH-C*H*$_2$-N (1H)).

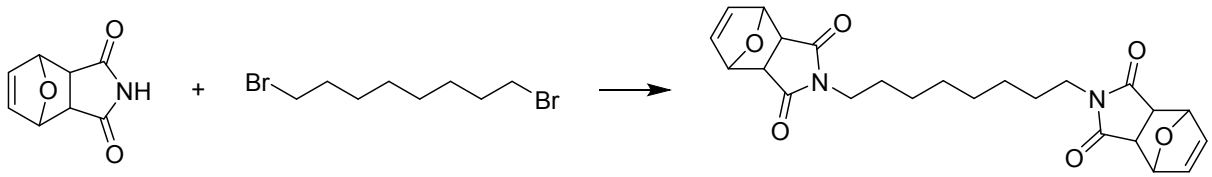
Synthesis of furan-protected maleimide.[4]



Maleimide (1g, 10.3 mmol) was dissolved in 10 mL of redistilled Toluene in a microwave vial. Then, furan (1.5 mL, 22.0 mmol) was added and the reaction vessel was sealed. The mixture was stirred at 90 °C for 24 hours. The product precipitated from the solution upon cooling to 4 °C for several hours. The precipitate was filtered off, washed with diethyl ether (2 x 30 mL), and dried under high vacuum to yield 1.51 g (9.2 mmol, 89%) of the product as white crystals. The material was directly used in the next step without further purification.

^{1}H NMR (300 MHz, DMSO-d_6) δ = 11.16 (s, 1H, N*H*), 6.53 (s, 2H, C*H*=C*H*), 5.11 (s, 2H, C*H*-O-C*H*), 2.85 (s, 2H, C*H*-C*H*).

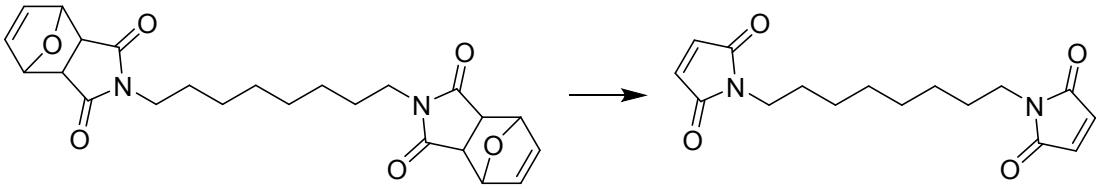
Synthesis of furan-protected 1,8-bismaleimidooctane.[5]



Protected maleimide (1.5 g 9.1 mmol), 1,8-dibromoctane (1.2 mL, 6.5 mmol), K_2CO_3 (1.23 g, 8.9 mmol) and 30 mL of dry acetonitrile were mixed in a microwave vial. The vial was sealed and the mixture was stirred at 90 °C for 18 hours. Then, the solution was cooled to room temperature and the solvent was removed under reduced pressure. Ethyl acetate (50 mL) was added and the solution was filtered to remove residual solids. The organic phase was washed with brine (3x 30 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure to yield the crude product as red, amorphous solid. The substance was then purified *via* column chromatography (solvent gradient, ethyl acetate/hexane 1:1 → ethyl acetate) to yield 603 mg of the product (1.4 mmol, 22 %) as well as 772 mg of monosubstituted product (2.2 mmol, 33 %), both as white solids. The monosubstituted product can be converted to this bismaleimide in a similar reaction.

^{1}H NMR (300 MHz, Acetone-d_6, Product) δ = 6.58 (s, 4H, C*H*=C*H*), 5.14 (s, 4H, C*H*-O-C*H*), 3.40 (t, *J* = 7.1 Hz, 4H, N-CH_2), 2.90 (s, 4H, C*H*-C*H*), 1.51 (p, *J* = 6.0 Hz, 4H, N-CH_2-CH_2), 1.43 – 1.13 (m, 8H, CH_2 (alkyl chain)).

Deprotection of 1,8-bismaleimidooctane.[6]

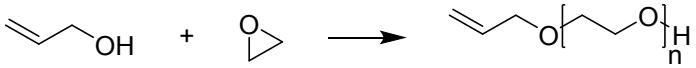


Furan-protected 1,8-bismaleimidooctane (1.6 g, 3.6 mmol) was dissolved in dry toluene in a round-bottom flask equipped with a reflux condenser. The mixture was stirred under reflux while conversion was controlled regularly *via* TLC analysis. After 24 hours, conversion was complete and the mixture was allowed to cool to room temperature. The insoluble residue formed was removed via filtration and the filtrate was concentrated under reduced pressure. Subsequent drying under high vacuum yielded 520 mg (1.7 mmol, 47 %) of the pure product as white, amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.69 (s, 4H, C*H*=C*H*), 3.50 (t, *J* = 7.2 Hz, 4H, N-CH_2), 1.58 (p, J = 6.6 Hz, 4H, N-CH_2-CH_2), 1.28 (m, 8H, CH_2 (alkyl chain)).

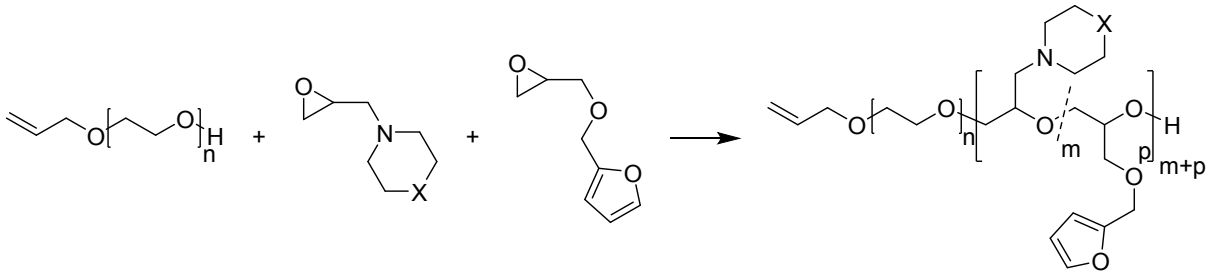
^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.88 (*C*=O), 134.03 (*C*H=*C*H), 37.83 (N-*C*H_2), 28.90 (N-CH_2-CH_2-CH_2-*C*H_2), 28.44 (N-CH_2-*C*H_2), 26.57 (N-CH_2-CH_2-*C*H_2).

Synthesis of the allyl-PEO-OH macroinitiator.[7]



The synthesis of the allyl-PEO-OH macroinitiator was described in our previous publication.

Synthesis of the diblock terpolymers.[7]



In a typical reaction, dry polyethylene oxide (allyl-PEO-OH, 5.000 g mol^{-1}) was dissolved in THF in a microwave vial in a glove box at a concentration of 30 mg mL^{-1}. Subsequently, a small excess of dried, solid potassium hydride was added, the vial was sealed and the suspension was stirred at 70 °C for one hour. Then, a 90:10 wt% mixture of the chosen glycidyl amine and FGE was added. The mixture was

allowed to stir at 70 °C for 24 hours. The polymerization was then quenched by adding 0.1 mL of ethanol. The solvent was evaporated under reduced pressure and the resulting diblock terpolymers were dried under vacuum. To remove residual potassium species, the polymers were again dissolved in $CHCl_3$, filtered through a 1 µm glass fibre filter, and dried under high vacuum.

allyl-PEO-*b*-P(PiGA-*co*-FGE): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38 (s, O-C*H*=CH-CH=C (FGE)), 6.31 (s, O-CH=C*H*-C*H*=C (FGE)), 6.10 – 5.84 (m, CH_2=C*H*-CH_2-O (allyl)), 5.23 (dd, J = 27.5, 13.4 Hz, C*H*$_2$=CH-CH_2-O (allyl)), 4.45 (s, C-C*H*$_2$-O (FGE)), 4.03 (d, J = 5.7 Hz, CH_2=CH-C*H*$_2$-O (allyl)), 3.84 – 3.44 (m, Polymer backbone), 2.59 – 2.27 (m, C*H*$_2$-N (PiGA)), 1.67 – 1.47 (m, N-CH_2-C*H*$_2$ (PiGA)), 1.41 (m, CH_2-C*H*$_2$-CH_2 (PiGA)).

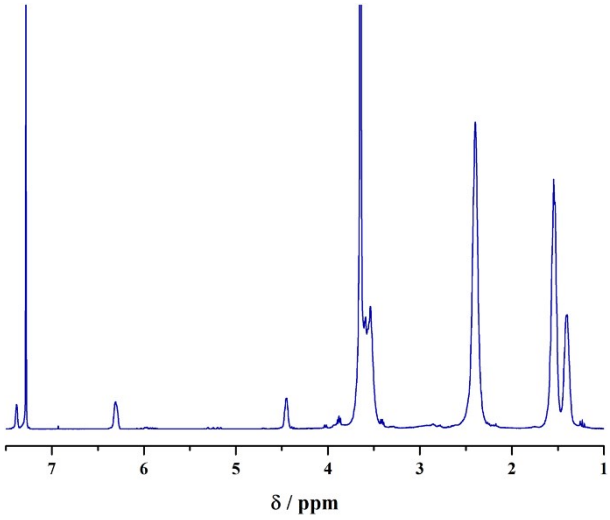


Figure S1 ^{1}H NMR spectrum of allyl-PEO_{90}-*b*-P($PiGA_{39}$-*co*-FGE_6)

allyl-PEO-*b*-P(OPGA-*co*-FGE): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 (s, O-C*H*=CH-CH=C (FGE)), 6.33 (s, O-CH=C*H*-C*H*=C (FGE)), 6.05 – 5.83 (m, CH_2=C*H*-CH_2-O (allyl)), 5.25 (dd, J = 28.6, 13.7 Hz, C*H*$_2$=CH-CH_2-O (allyl)), 4.46 (s, C-C*H*$_2$-O (FGE)), 4.04 (d, J = 5.7 Hz, CH_2=CH-C*H*$_2$-O (allyl)), 3.79 – 3.39 (m, Polymer backbone), 2.86 – 2.22 (m, CH-C*H*$_2$-N-C*H*$_2$-C*H*$_2$-N (OPGA)), 1.63 – 1.41 (m, N-CH_2-C*H*$_2$ (OPGA)), 1.41 – 1.15 (m, -C*H*$_2$- (OPGA)), 0.89 (t, J = 6.5 Hz, C*H*$_3$ (OPGA)).

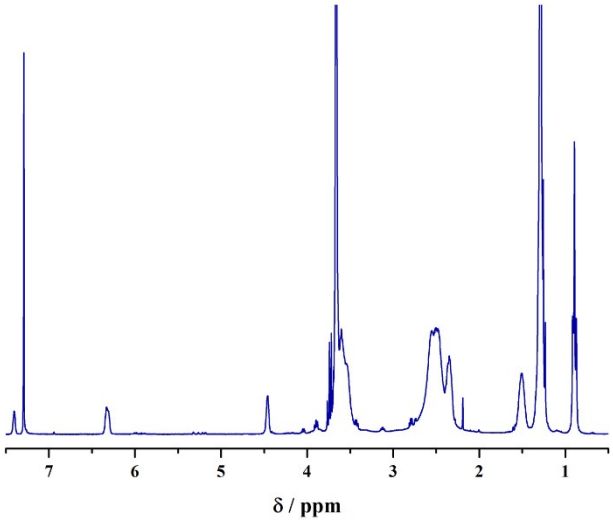


Figure S2 ^{1}H NMR spectrum of allyl-PEO_{90}-*b*-P($OPGA_{21}$-*co*-FGE_6).

allyl-PEO-*b*-P(MPGA-*co*-FGE): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 (s, O-C*H*=CH-CH=C (FGE)), 6.31 (d, J = 8.3 Hz, O-CH=C*H*-C*H*=C (FGE)), 6.06 – 5.82 (m, CH_2=C*H*-CH_2-O (allyl)), 5.27 (dd, J = 28.6, 14.2 Hz, CH_2=CH-CH_2-O (allyl)), 4.44 (d, J = 11.3 Hz, C-CH_2-O (FGE)), 4.03 (d, J = 5.6 Hz, CH_2=CH-CH_2-O (allyl)), 3.95 – 3.40 (s, Polymer backbone), 2.80 – 2.34 (m, N-CH_2 (MPGA)), 2.30 (s, N-CH_3 (MPGA)).

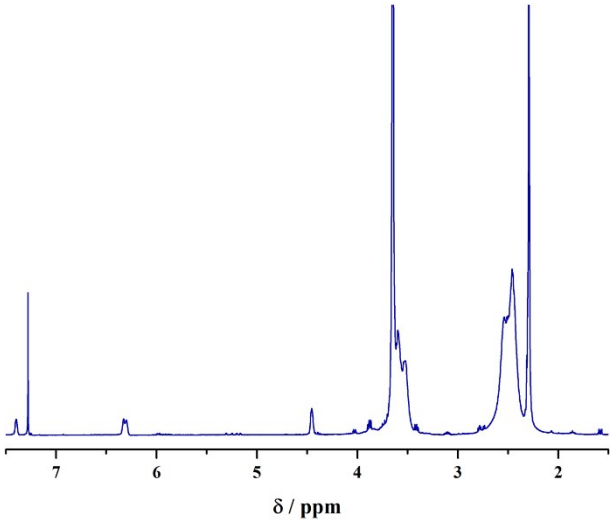


Figure S3 ^{1}H NMR spectrum of allyl-PEO_{90}-*b*-P($MPGA_{37}$-*co*-FGE_5).

Formation and investigation of micelles

Micellization

For micelle formation, 5 mg of the desired diblock terpolymer was dissolved in dichloromethane in a glass vial. The solvent was evaporated slowly under reduced pressure in order to form a diblock terpolymer film in the vial. Then, the diblock terpolymer film was directly dissolved in 5 mL of micropure water under stirring for 24 hours.

Stimulus-triggered disassembly of the micelles

For stimulus-triggered disassembly studies of the micelles, 15 mL of micellar solution with a concentration of 1 mg polymer per mL micropure water were prepared for each individual diblock terpolymer. For the pH-triggered disassembly, the solutions were adjusted to a pH of 11 with 0.1N NaOH (aq) using a ScienceLine pH combination electrode attached to a TitroLine® 7000 titrator with digital output and a TM235 magnetic stirrer from ScienceLine Analytics GmbH (Mainz, Germany). Subsequently, the solutions were stirred for 24 hours for equilibration. Afterwards, the pH was controlled again. Then, DLS measurements were carried out, and the next pH value was adjusted using 0.1N HCl (aq). This process was continued for all data points. The experiment for H_2O_2-triggered disassembly was carried out similarly. In this case, 5 mL of micellar solution were generated for each individual diblock terpolymer. Then, the desired amount of H_2O_2 was added as a 35% aqueous solution, equilibration was allowed to take place for 24 hours, and DLS measurements were carried out. Afterwards, the next concentration of H_2O_2 was adjusted, repeating all steps as described before.

Dye encapsulation and release

For dye release experiments, diblock terpolymer films containing the hydrophobic dye Sudan I (0.05 mg per mg of polymer) and, in case of the crosslinked micelles, also 1,8-bismaleimidooctane (0.75 eq compared to the amount of furfuryl units present in the polymer), were generated by slow evaporation of a solution of all components in $CHCl_3$ in a glass vial. Then, the film was rehydrated in micropure water. The final polymer concentration in micropure water was 1 mg mL^{-1}. For crosslinked micelles, the micellar solutions were stirred at 65 °C for 24 hours in the dark, while the samples without crosslinker were stirred at room temperature.

For pH-dependent dye release experiments, the micellar solution was adjusted to a pH of 11 using 0.1N NaOH (aq). All other pH values were adjusted subsequently using 0.1N HCl (aq). The samples with different pH values were allowed to equilibrate under stirring for 24 hours in the dark. Afterwards, the pH value was controlled. In all cases, the BIOTRODE (Deutsche METROHM Prozessanalytik GmbH

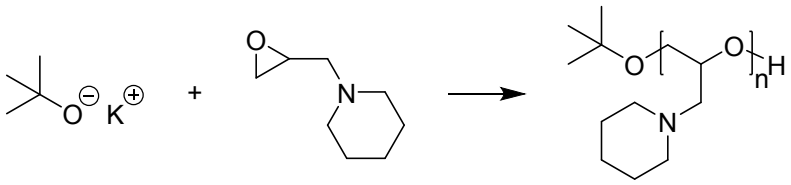
& Co. KG, Filderstadt, Germany) electrode was used. Before DLS and UV/vis measurements were carried out, samples based on allyl-PEO_{90}-*b*-P($PiGA_{26}$-*co*-FGE_4) were filtered through a 1 µm nylon filter (SimplePure), and allyl-PEO_{90}-*b*-P($OPGA_9$-*co*-FGE_3)-based samples were centrifuged at 5000 rpm for 2 minutes to remove small aggregates of released dye.

For H_2O_2-dependent release experiments, crosslinked and non-crosslinked, dye-loaded micelles were prepared as described. The samples were distributed to different glass vials, the desired concentrations of H_2O_2 were added as 35% aqueous solution, and the solutions were stirred for 24 hours. Before DLS and UV/vis measurements were carried out, samples based on allyl-PEO_{90}-*b*-P($PiGA_{26}$-*co*-FGE_4) were filtered through a 1 µm nylon filter (SimplePure), and allyl-PEO_{90}-*b*-P($OPGA_9$-*co*-FGE_3)-based samples were centrifuged at 5000 rpm for 2 minutes to remove small aggregates of released dye.

Dye complexation and transfer to $CHCl_3$

For dye complexation studies, a thin film of allyl-PEO_{90}-*b*-P($MPGA_{24}$-*co*-FGE_3) and the hydrophilic dye Orange G (1.39 mg per mg of polymer to target an equal ratio of positive and negative charges, assuming that all *N*-methylpiperazine units are fully protonated) was formed by dissolving both components in a mixture of EtOH and micropure water (1:1) and slow evaporation of the solvent. Subsequently, the film was rehydrated using micropure water. The final concentration of the diblock terpolymer/dye solution was 1 mg of polymer per mL. Then, the sample was split to different vials and the desired pH values were adjusted using the BIOTRODE (Deutsche METROHM Prozessanalytik GmbH & Co. KG, Filderstadt, Germany) electrode. The samples were stirred for 24 hours in the dark for equilibration. Subsequently, UV/vis- and DLS measurements were carried out. For dye transfer, 1 mL of each solution was added to 1 mL of $CHCl_3$, and the two-phase system was stirred in the dark for 48 hours. Afterwards, DLS and UV/vis measurements were carried out. In all cases, the solutions were diluted 1:80 with micropure water to avoid saturation of the UV/vis detector.

Homopolymerization of PiGA.[8]



For the polymerization of PiGA, the necessary amount of a stock solution of KOtBu (0.09 mol L^{-1}) in dry THF was diluted in 2 mL of dry THF in a microwave vial in a glovebox. Subsequently, 1 mL (7.1 mmol) of PiGA were added, the vial was sealed, and the solution was stirred at 45 °C for four days. Then, 1 mL of methanol was added, the solvent was evaporated under reduced pressure, and the polymers were dried under high vacuum. No further purification was carried out before analysis.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.78 – 3.45 (m, O-CH_2-CH-O), 2.66 – 2.31 (m, N-CH_2), 1.76 – 1.47 (m, N-CH_2-CH_2), 1.51 – 1.34 (m, N-CH_2-CH_2-CH_2), 1.19 (s, CH_3).

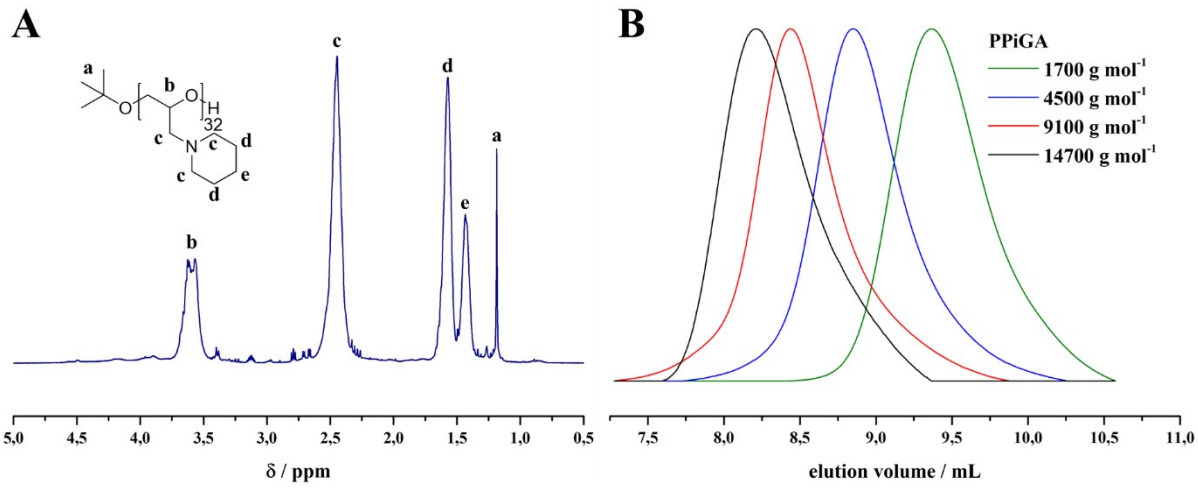


Figure S4 ^{1}H NMR spectrum of $PPiGA_{32}$ (A) and SEC traces (B) of PPiGA of different molecular weights.

Table S1 Targeted and experimental DP, molar masses and dispersities of synthesized PPiGA homopolymers.

DP (targeted)	DP (^{1}H NMR)	M_n (^{1}H NMR)	M_n (SEC)	Đ (SEC)
14	13	1700	1000	1.16
35	32	4500	2000	1.19
71	65	9100	3300	1.23
213	105	14700	4300	1.17

[a] $CHCl_3$/NEt_3/iPrOH 94:4:2, PEO-Calibration

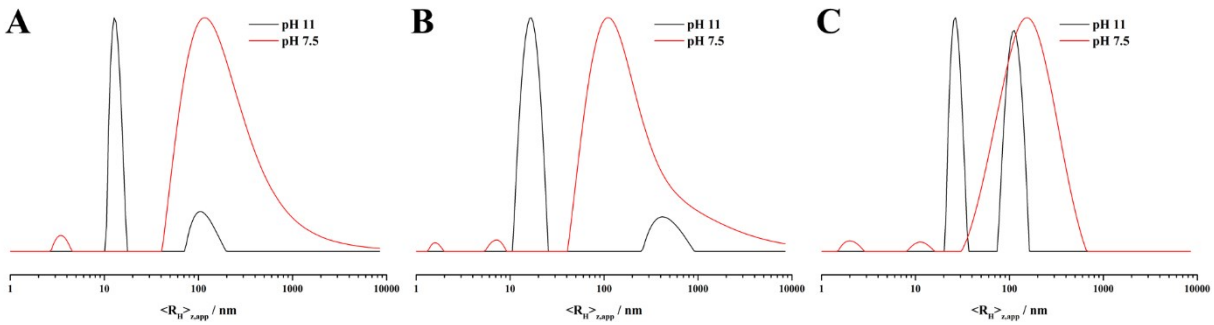


Figure S5 Intensity-weighted CONTIN plots of allyl-PEO_{90}-*b*-P($PiGA_{18}$-*co*-FGE_3) (A), allyl-PEO_{90}-*b*-P($PiGA_{26}$-*co*-FGE_4) (B), and allyl-PEO_{90}-*b*-P($PiGA_{39}$-*co*-FGE_6) (C) at pH 11 and pH 7.5. The micelles, exhibiting a hydrodynamic radius in the range of 10 – 20 nm at pH 11, disassemble into unimers ($<R_H>_{z,app}$ < 10 nm), which also form loose aggregates ($<R_H>_{z,app}$ ≈ 100 nm), at pH 7.5.

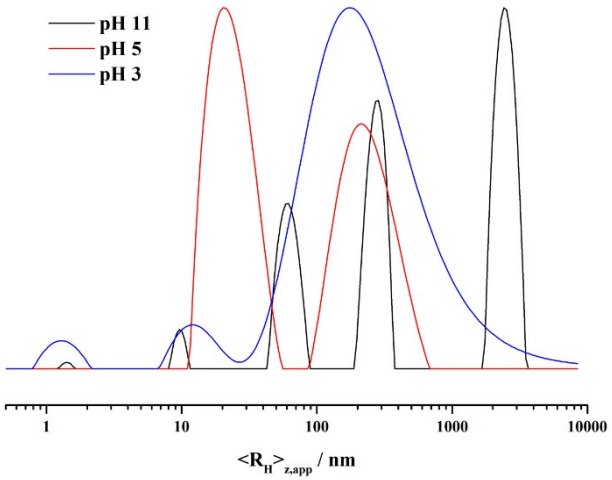


Figure S6 Intensity-weighted DLS CONTIN plots of allyl-PEO_{90}-*b*-P($OPGA_9$-*co*-FGE_3) at different pH values. At pH 11, a multimodal distribution of the hydrodynamic radii is observable, which hints towards the presence of non-spherical morphologies with multiple diffusion coefficients. At pH 5, a bimodal distribution of hydrodynamic radii is present. The larger distribution at $<R_H>_{z,app}$ = 20 nm may be attributed to the swollen, spherical micelles visible in the cryo-TEM micrograph at pH 5 in Figure 6.

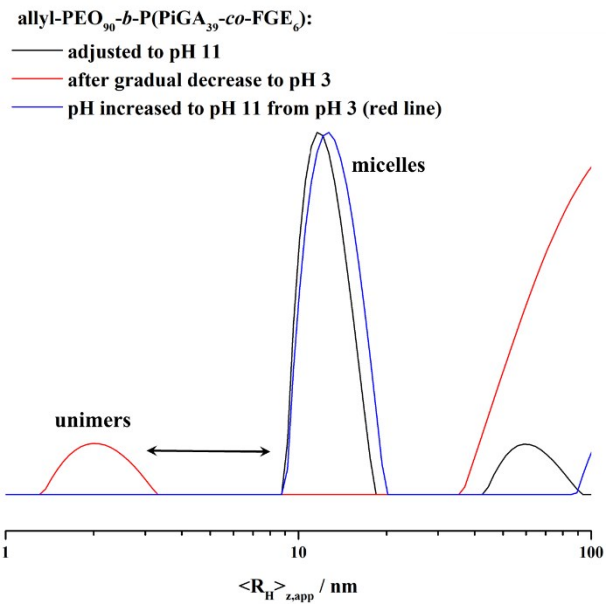


Figure S7 pH-Induced disassembly and subsequent re-assembly of micelles formed from allyl-PEO_{90}-*b*-P($PiGA_{39}$-*co*-FGE_6), shown *via* DLS measurements (intensity weighted DLS CONTIN plots).

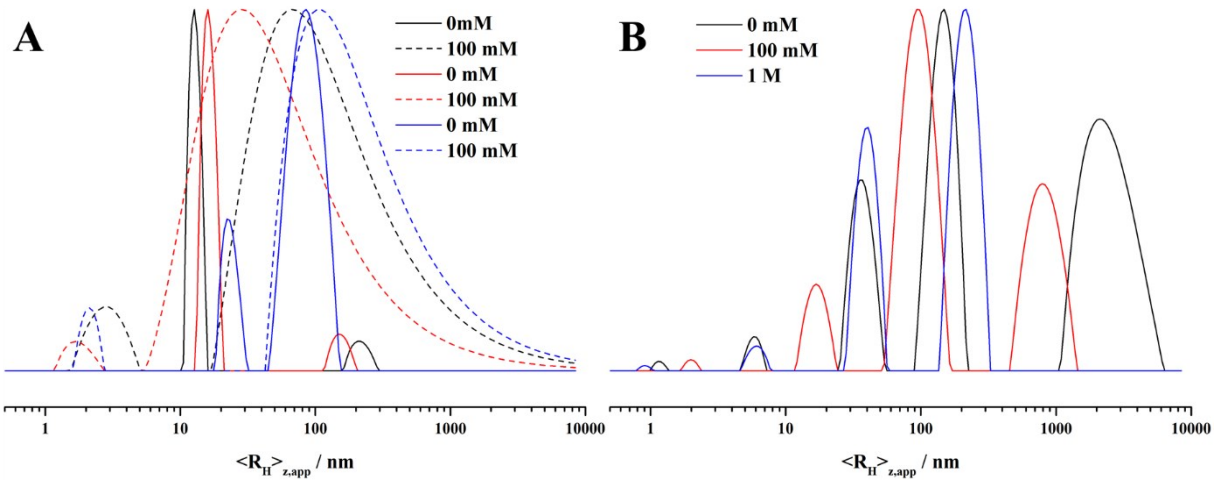


Figure S8 Intensity-weighted DLS CONTIN plots of micelles formed from allyl-PEO_{90}-*b*-P($PiGA_{18}$-*co*-FGE_3) (black lines), allyl-PEO_{90}-*b*-P($PiGA_{26}$-*co*-FGE_4) (red lines), and allyl-PEO_{90}-*b*-P($PiGA_{39}$-*co*-FGE_6) (blue lines) before H_2O_2 addition, and one day after adjustment of a H_2O_2 concentration of 100 mM. It is visible that the micelles disassemble into unimers and loose aggregates thereof. In contrast, intensity-weighted CONTIN plots of micelles formed from allyl-PEO_{90}-*b*-P($OPGA_9$-*co*-FGE_3) (B) do not reveal morphological changes with increasing H_2O_2 concentration.

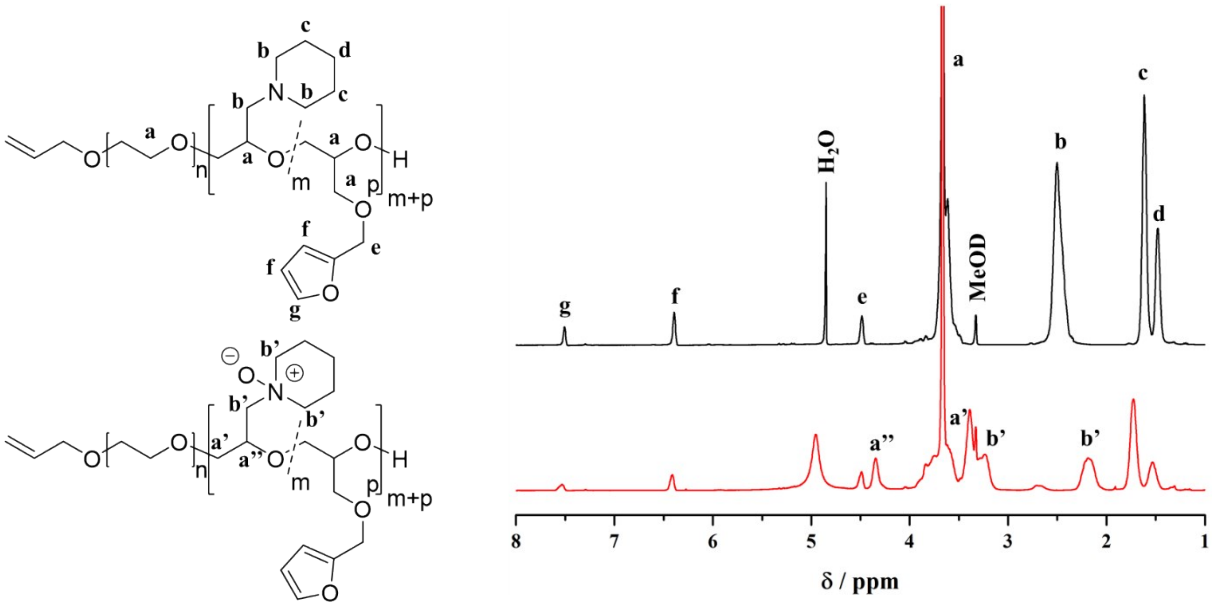


Figure S9 ^{1}H NMR spectra from freeze-dried micelles of allyl- PEO_{90}-*b*-P($PiGA_{39}$-*co*-FGE_6) before and after *N*-oxidation with H_2O_2 in aqueous solution. Deuterated solvent: MeOD.

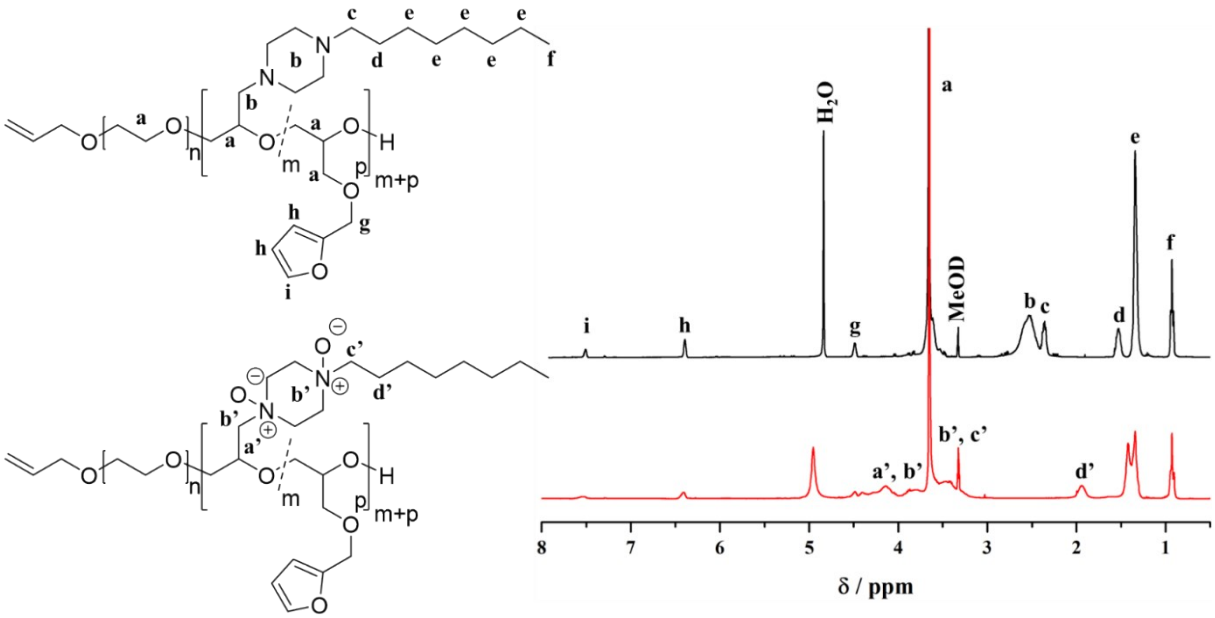


Figure S10 ^{1}H NMR spectra from freeze-dried micelles of allyl- PEO_{90}-*b*-P($OPGA_{21}$-*co*-FGE_6) before and after *N*-oxidation with H_2O_2 in aqueous solution. Deuterated solvent: MeOD.

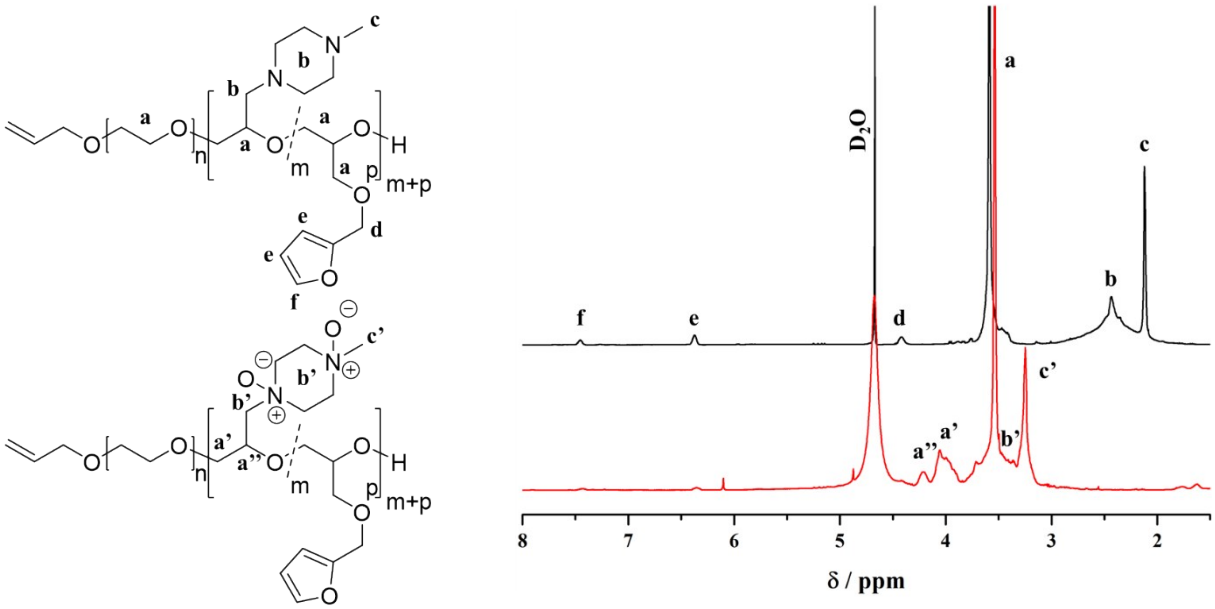


Figure S11 ^{1}H NMR spectra from freeze-dried micelles of allyl- PEO_{90}-*b*-P($MPGA_{37}$-*co*-FGE_5) before and after *N*-oxidation with H_2O_2 in aqueous solution. Deuterated solvent: D_2O.

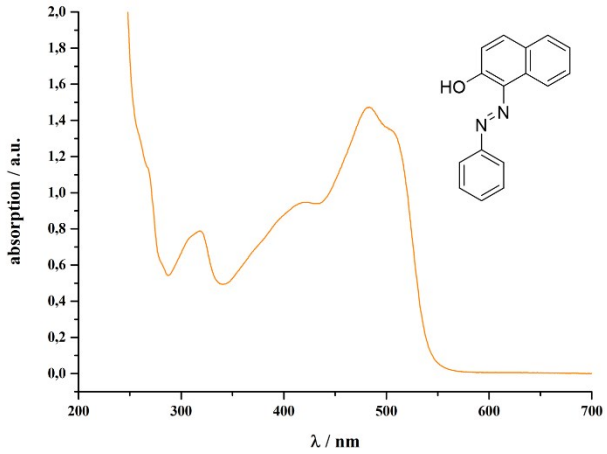


Figure S12 Structure and UV/vis absorption spectrum of the hydrophobic dye Sudan I (c = 0.025 mg mL^{-1} in $CHCl_3$) which was used as model compound for encapsulation and release experiments.

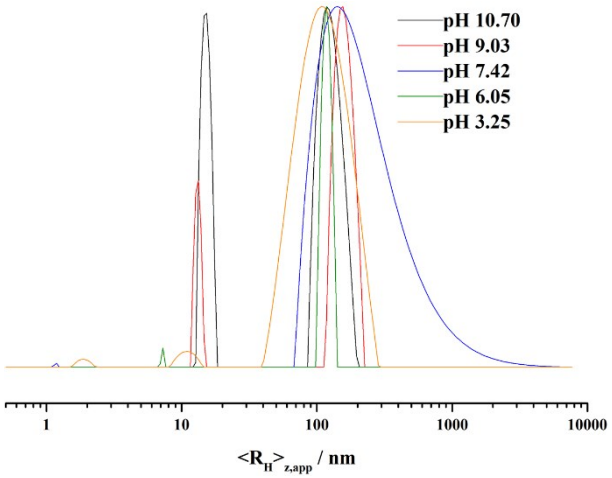


Figure S13 Intensity-weighted DLS CONTIN plots of non-crosslinked micelles formed from allyl-PEO_{90}-*b*-P($PiGA_{26}$-*co*-FGE_4) with Sudan I as encapsulated dye. It is visible that the micellar structures are stable at pH 11 and pH 9, while they disassemble at lower pH values.

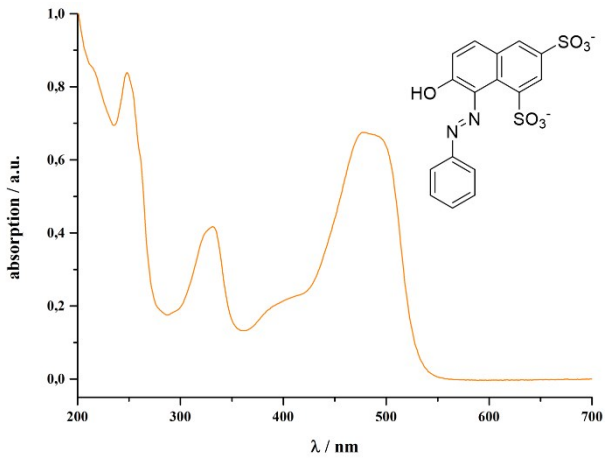


Figure S14 Structure and UV/vis absorption spectrum of the hydrophilic dye Orange G (c = 0.0125 mg mL^{-1} in H_2O) which was used as model compound for complexation and transfer experiments.

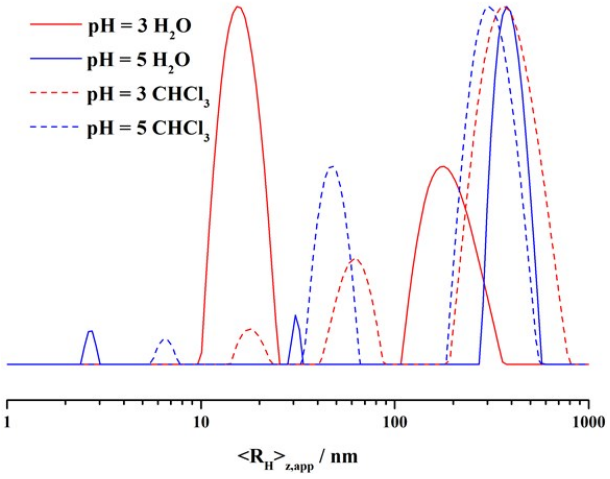


Figure S15 Intensity-weighted DLS CONTIN plots of aggregates of allyl-PEO_{90}-*b*-P(MPG24-*co*-FGE_3) and Orange G at pH 3 and pH 5 in H_2O and $CHCl_3$, respectively.

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