Supplementary Information

Miktoarm Stars of Poly(ethylene oxide) and Poly(dimethylaminoethyl methacrylate): Manipulation of Micellization by Temperature and Light

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Experimental

Materials

Poly(ethylene glycol) monomethyl ether (M_n = 5000 g/mol; PDI = 1.1) was delivered by Polysciences, Warrington, PA, USA. *N,N*-dimethylaminoethyl methacrylate (DMAEMA; purified by filtration over basic alumina) and molecular sieves (3 Å, 8 to 12 mesh) was purchased from Acros Organics, Geel, Belgium. Methanesulfonyl chloride was delivered by Riedel de-Haën. Sodium hydride (50% in paraffin oil), formic acid and potassium hexacyanoferrate(III) were obtained from Merck (Darmstadt, Germany). Dichloromethane, chloroform, tetrahydrofuran (THF; distilled over sodium / benzophenone) and *n*-hexane were purchased from Lab-Scan (Poland) or VWR. Sodium hydroxide, sodium chloride, anhydrous diethylether, methanol and acetone were bought from J.T. Baker (Holland). Acetic acid was purchased from AppliChem (Darmstadt, Germany). Hydrochloric acid was obtained from FF-Chemicals Oy (Finland) or Merck (Germany). *N,N*-dimethyl-4-pyridinamine (DMAP), , 2-bromo-2-methylpropanoyl bromide, CuCl, $CuCl_2$, *N,N,N′,N′′,N′′′,N′′′*-hexamethyltriethyltriamine (HMTETA), anisole (purified by filtration over basic alumina), tributyltinhydride, trimethylsilyldiazomethane, methyliodide and potassium hexacyanocobaltate(III) were bought from Aldrich. Dipentaerythritoldiformal (2′,2′′:6′,6′′-di-*O*-methylene-2,2,6,6-tetrahydroxymethyl-4-oxa-1,7-heptandiol) was synthesized according to literature[1] and dried in desiccator under vacuum for 18 h. 2,2-Bis(2-bromoisobutyroyl-oxymethyl)propionic acid was synthesized according to literature.[2] Triethylamine, dicyclohexylcarbodiimide (DCC) and buffer solution pH 8.0 (20°C; 0.013 M sodium tetraborate / 0.021 M hydrochloric acid) was obtained from Fluka. Regenerated cellulose dialysis membranes (Cellu Sep H1, MWCO 1000; Cellu Sep T1, MWCO 3500; Cellu Sep T2, MWCO 6000 – 8000; Cellu Sep T4, MWCO 12000 - 14000) were purchased from Membrane Filtration Products, Inc., Texas, USA. For reagents highest purities available were used and used as delivered (except where otherwise stated).

Synthesis

Monomesylated poly(ethylene glycol) CH_3O-PEO_{114}-Mes [monomethyl poly(ethylene oxide) methanesulfonate].[3] Poly(ethylene glycol) monomethyl ether (50 g; 0.01 mol) was dissolved in 160 g dichloromethane and triethylamine (10 g; 0.1 mol), before 1g molecular sieves were added under stirring. After 1 h the sieves were removed and the mixture was cooled under stirring to 0°C. Then methanesulfonyl chloride (2g; 0.017 mol) was added dropwise under nitrogen counterflow and the mixture was slowly allowed to warm up to RT for 16 hours. Then the mixture was concentrated in vacuo and dissolved in 200 mL dichloromethane in order to filtrate the orange mixture through silica. Then the filtrate was precipitated in 800 mL anhydrous diethylether, separated from the supernatant and again dissolved in 200 mL dichloromethane to repeat the filtration and precipitation procedure. Then the precipitate was washed with *n*-hexane before the powder was dried in desiccator under vacuum (25 g, 50%). SEC (THF; PEO calibration): M_n = 4600 g/mol, *PDI* = 1.1; δ_H(200 MHz; $CDCl_3$; Me_4Si) 4.38 (2H, m), 3.98 (2H, m), 3.8-3.5 (m, PEO-H), 3.38 (3H, s, methoxy), 3.28 (2H, m), 3.09 (3H, s, mesylate); δ_C(50.3 MHz; $CDCl_3$; Me_4Si) 72.1, 70.9 (PEO), 69.6, 69.2, 59.2 (CH_3-O-), 37.9 (CH_3-SO_3-)

Poly(ethylene oxide)-*block*-dipentaerythritol-*block*-poly(ethylene oxide) (PEO_{114}-$(OH)_4$-PEO_{114}). The mesylated poly(ethylene glycol) (10 g; 1.9 10^{-3} mol) was dissolved in dry THF (distilled over Na / benzophenone; 100 mL) under nitrogen counterflow by carefully heating with a fan. The dipentaerythritoldiformal (200 mg; 7.2 10^{-4} mol) and sodium hydride (180 mg 50% NaH; 3.8 10^{-3} mol) were suspended in 20 ml dry THF under nitrogen-counterflow at RT. After 1.5 h of stirring, the PEO solution was slowly (over 10 min) added with a syringe under nitrogen counterflow. After 1.5 h of reaction, more NaH (900 mg 50% NaH; 19 · 10^{-3} mol) was added under N_2-counterflow and stirring was allowed for another 0.5 hours. Then the setup was equipped with a condenser (equipped with a water trap – $CaCl_2$; the condenser was flushed with nitrogen directly before use to avoid accumulation of water) and the mixture was refluxed for 18 h at 75°C. Finally more NaH (100 mg of raw 50% NaH; 4.1 10^{-3} mol) was added and the refluxing was conducted for another 3 h. Then the mixture was acidified by addition of acetic acid until wet *p*H paper shows neutral *p*H. The mixture was centrifuged in order to remove undissolved sodium salts and the supernatant was precipitated in diethylether and the precipitated polymer was dried after filtration in vacuo.

9 g of the dried polymer were dissolved in 1 M HCl (270 mL) and kept over night at 85°C in order to deprotect the acetals. After 16 h the mixture was filtrated, concentrated in vacuo to remove majority of HCl and dissolved in 50 mL water for dialysis against water (MWCO 6000-8000; 1 d). Then the polymer solution was freeze dried to obtain 8 g of crude diblock PEO.

Precipitation fractionation was used to purify the product. 7.5 g of deprotected crude product was dissolved in chloroform (1000 mL) and *n*-hexane (1000 mL), filtered and then fractions were collected by dropwise addition of *n*-hexane.

Each fraction was checked by SEC and finally all good fractions were combined to give the final product (0.5 g, 5 %). SEC (THF; PEO calibration): M_n = 8400 g/mol, *PDI* = 1.20; δ_H(200 MHz; $CDCl_3$; Me_4Si) 3.98 (4H, m, PEO), 3.8-3.5 (m, PEO-*H*; dipentaerythritol -CH_2-OR), 3.36 (6H, s, CH_3-O-), 3.28 (4H, m, PEO); δ_C(50.3 MHz; $CDCl_3$; Me_4Si) 72.2 (broad), 70.8 (predominantly PEO), 69.6, 68.7 (broad), 65.6 (-*C*H_2-OH), 59.3 (*C*H_3-O-), 45.7 (quaternary *C*)

Macroinitiator with four ATRP initiation sites PEO_{114}-Br_4-PEO_{114} (poly(ethylene oxide) - *block* - 2,2,6,6-tetrakis[methyl-(2´-bromo-2´-methylpropionate)]-4-oxa-1,7-heptandiol - *block* - poly(ethylene oxide)). Diblock PEO with inner dipentaerythritol moiety (0.12 g; $4.8 \cdot 10^{-5}$ mol OH-Groups) and *N,N*-dimethyl-4-pyridinamine (DMAP, 0.5 mg) were dissolved in 1.6 g chloroform and 0.8 g triethylamine, dried for one hour over molecular sieves and then cooled with ice under stirring. Then 2-bromo-2-methylpropanoyl bromide (20 mg; $8.7 \cdot 10^{-5}$ mol) was added and the mixture was stirred for 3 h before another 50 mg of bromide were added. The temperature was allowed to slowly increase to RT over night under stirring. The next day the flask was equipped with a condenser and the mixture was refluxed at 75°C for 2h. Then the mixture was cooled down, filtrated (precipitate washed with chloroform) and precipitated in diethylether. The precipitate was dissolved in chloroform and dialyzed for 3 h against THF (MWCO 6000 - 8000) and then over night against chloroform and then for 3 h against methanol and then it was precipitated from diethylether. The precipitate was dissolved in methanol and the solution was dialyzed against water for 4 h (MWCO 6000 - 8000), before it was freeze dried in order to obtain the macroinitiator (90 mg, 75%). SEC (DMF, 1 g/L LiBr; PEO calibration): M_n = 8100 g/mol, *PDI* = 1.18; δ_H(200 MHz; $CDCl_3$; Me_4Si) 4.22 (8H, s, dipentaerythritol -CH_2-O-C=O), 3.98 (4H, m, PEO), 3.8-3.5 (m, PEO-*H*; dipentaerythritol -CH_2-O-CH_2), 3.36 (6H, s, CH_3-O-), 3.28 (4H, m, PEO), 1.93 (24H, s, O=C-C(CH_3)$_2$Br); δ_C(50.3 MHz; $CDCl_3$; Me_4Si) 170.2 (weak signal, *C*=O), 72.2, 70.8 (predominantly PEO), 69.6, 68.7 (broad), 64.0 (-*C*H_2-OC=O-) 59.2 (*C*H_3-O-), 57.2 (weak signal, O=C-*C*(CH_3)$_2$Br), 43.9 (weak signal, quaternary *C*, dipentaerythritol), 31.2 (O=C-C(*C*H_3)$_2$Br)

Macroinitiator with 6 ATRP initiation sites PEO_{114}-Br_6-PEO_{114} (poly(ethylene oxide) - *block* - 2,2,6-tris{methyl-[2´,2´-bis(methyl-(2´´-bromoisobutyrate))propionate]}-6-hydroxmethyl-4-oxa-1,7-heptandiol - *block* - poly(ethylene oxide)). Diblock PEO with inner dipentaerythritol moiety (0.13 g; $5.2 \cdot 10^{-5}$ mol OH-Groups) was dissolved in 1 mL dry THF (distilled over Na / benzophenone) by careful warming under nitrogen. Additionally 10 beads of molecular sieves were added and the mixture was allowed to dry for 30 min. 2,2-bis-(2-bromoisobutyroyl-oxymethyl) propionic acid (77 mg; $1.8\ 10^{-4}$ mol), dicyclohexylcarbodiimide (DCC, 60 mg; $2.9\ 10^{-4}$ mol) and *p-N,N*-dimethylaminopyridin (DMAP; 0.5 mg) were also mixed with one mL THF under nitrogen before the polymer solution was added and stirred at RT. After 5 days additional DCC (35 mg) were added and stirred for another day. Then further 30 mg of initiator fragment in 1 mL THF was added and stirred for another 3 days. Then the mixture was diluted with 2 mL THF and filtrated. The THF solution was then dialyzed against THF for 6 days (MWCO 6000 – 8000) and then the dialysis was continued against water for 4 h, filtrated with syringe filter and freeze dried to obtain 100 mg of macroinitiator (100 mg, 80 %; ^{1}H NMR shows 70% esterification conversion - macroinitiator bears on average 6 initiation sites). δ_H(200 MHz; $CDCl_3$; Me_4Si) 4.39 (11H, m, -CH_2O-C=O-C(CH_3)$_2$Br), 3.98 (4H, m, PEO), 3.8-3.5 (m, PEO-*H*; dipentaerythritol -CH_2-OR), 3.37 (6H, s, CH_3-O-), 3.29 (4H, m, PEO), 1.92 (33H, s, O=C-C(CH_3)$_2$Br); 1.33 (8H, s, CH_3-C(CH_2-O-)$_2$(C=O))

Miktoarm star with 2 PEO arms and 4 PDMAEMA arms (PEO_{114}-($PDMAEMA_{40}$)$_4$-PEO_{114}). The macroinitiator PEO_{114}-Br_4-PEO_{114} (40 mg; M_n ~ 10800 g/mol; $1.48 \cdot 10^{-5}$ mol Br groups), copper(I)chloride (CuCl; 1.1 mg; $1.1 \cdot 10^{-5}$ mol) and copper(II)chloride ($CuCl_2$; 0.5 mg; $3.8 \cdot 10^{-6}$ mol) were mixed in anisole (0.5 g) and deoxygenated by purging with nitrogen. Then the ligand *N,N,N´,N´´,N´´´,N´´´*-hexamethyltriethyltriamine (HMTETA; 33 mg; $1.4 \cdot 10^{-4}$ mol) and the monomer *N,N*-dimethylaminoethyl methacrylate (DMAEMA; 2.33 g; $1.48 \cdot 10^{-2}$ mol) were also mixed and deoxygenated. 0.254 g of this solution (0.250 g DMAEMA - $1.59\ 10^{-3}$ mol; 3.5 mg HMTETA - $1.52\ 10^{-5}$ mol) was introduced to the macroinitiator mixture at 80°C under stirring and nitrogen counterflow. After 190 min the reaction was terminated by injection of tributyltinhydride (10 mg; $3.4 \cdot 10^{-5}$ mol; mixture turns brownish-black).[4] Reaction was stopped after one additional hour at 80 °C by dilution with chloroform (5 mL) and contact with air. The conversion was 37 % according to NMR ($P_{n,theo}$(arm) = 40; $M_{n,theo}$(total) = 35800 g/mol). Then the polymer solution was filtrated through silica and then reconcentrated before it was precipitated from *n*-hexane. Then the precipitate was dissolved in 4 mL THF and dialyzed against THF for 1 day (MWCO 12000 - 14000) to yield after drying in vacuo 80 mg of miktoarm star. SEC (DMF, 1 g/L LiBr; PEO calibration): $M_{n,app}$ = 10600 g/mol, PDI_{app} = 1.25; M_n(osmometry) = 44000 g/mol; δ_H(200 MHz; $CDCl_3$; Me_4Si) 4.2 - 3.9 (O-CH_2CH_2-N), 3.8 - 3.5 (PEO-*H*), 2.7-2.4 (O-CH_2CH_2-N), 2.4 - 2.1 (-N(CH_3)$_2$), 2.1 - 1.6 (PDMAEMA backbone CH_2); 1.2 - 0.7 (PDMAEMA backbone CH_3)

Cleaving of the arms. 5 mg of polymer PEO_{114}-($PDMAEMA_{40}$)$_4$-PEO_{114} was retained from solutions used for light scattering by repeated dialyses from salted solutions and final freeze drying. The polymer was dispersed in 0.5 mL concentrated NaOH and kept at 85 °C for 3 days. Then the solution was acidified by addition of 1 mL of concentrated HCl. Again the solution was kept at 85 °C for 3 days. Then the *p*H of the solution was set to *p*H 14 by careful addition of solid NaOH. This solution was kept at 85 °C for 3 days before the cooled solution (diluted to 5 mL) was extracted three times with 5 mL chloroform each. The aqueous phase was again kept for 1 day at 85 °C, before its *p*H was adjusted to *p*H 3 by HCl and then freeze dried. The dried salts were

dissolved in 3 mL water and were dialyzed against water (MWCO 1000) and after 1 day the dialysis tubing was opened to add 0.1 ml 1 M HCl. The dialysis was continued against pure water for 3 days before the solution was finally freeze dried (to get ~ 2 mg of PMAA). Then the dried poly(methacrylic acid) PMAA was dissolved in 0.2 ml water and 2 mL THF before 0.1 mL of 2 M trimethylsilyldiazomethane in diethylether was added. After one hour stirring at RT, the solution was dialyzed against THF (MWCO 1000) for 1 day, before the solution was dried (to obtain 2 mg of PMMA).

Synthesis of miktoarm star with 2 PEO arms and 3 PDMAEMA arms (PEO_{114}-($PDMAEMA_{55}$)$_3$-PEO_{114}). The macroinitiator PEO_{114}-Br_6-PEO_{114} (40.46 mg; M_n~11500 g/mol; 2.11 · 10^{-5} mol Br groups), copper(I)chloride (CuCl; 1.66 mg; 1.68 · 10^{-5} mol), copper(II)chloride ($CuCl_2$; 0.56 mg; 4.2 · 10^{-6} mol) and anisole (0.72 g) were mixed in a flask, equipped with septum and stirrer. The mixture was deoxygenated by purging with nitrogen. *N,N,N′,N′′,N′′′,N′′′*-hexamethyltriethyltriamine (HMTETA, 19.2 mg; 8.3 · 10^{-5} mol) was dissolved in *N,N*-dimethylaminoethyl methacrylate (DMAEMA; 1.321 g; 8.4 · 10^{-3} mol) and also deoxygenated by purging with nitrogen. Then 0.330 g of the monomer mixture (0.325 g DMAEMA - 2.09 10^{-3} mol; 4.7 mg HMTETA - 2.0 10^{-5} mol) was introduced to the macroinitiator mixture under nitrogen counterflow at 80 °C. After 60 min the polymerization was stopped by dilution with chloroform (5 mL), contact with air and cooling with ice water. The conversion was 25% according to NMR ($P_{n,theo}$(arm) = 26). Then the polymer solution was filtrated over silica and then reconcentrated before it was precipitated from hexane. Then the precipitate was taken upp in 4 mL THF and dialyzed against THF for 1 day (MWCO 12000 - 14000) to yield after drying in vacuo 110 mg of Polymer. SEC (DMF, 1 g/L LiBr; PEO calibration): $M_{n,app}$ = 9500 g/mol, PDI_{app} = 1.23; M_n(osmometry) = 31000 g/mol; δ_H(200 MHz; $CDCl_3$; Me_4Si) 4.3 - 3.9 (O-CH_2CH$_2$-N), 3.8 - 3.5 (PEO-*H*), 2.7-2.4 (O-CH$_2$CH_2-N), 2.4 - 2.1 (-N(CH$_3$)$_2$), 2.1 - 1.6 (PDMAEMA backbone CH_2); 1.2 - 0.7 (PDMAEMA backbone CH_3)

Quaternization. 10 mg of polymer PEO_{114}-($PDMAEMA_{55}$)$_3$-PEO_{114} was dissolved in 5 mL of THF and 1 ml of acetone before 0.1 mL of methyliodide was added. The solution was stirred light protected over night at RT. Then the solution was dialyzed against THF for 24 h (MWCO 6000 - 8000) and then against water for another 24 h before the solution was freeze dried (15 mg product).

Cleaving of the arms. 10 mg of quaternized miktoarmstar PEO_{114}-($PDMAEMA_{55}$)$_3$-PEO_{114} were dissolved in 1 mL of concentrated aqueous NaOH solution and kept at 85 °C for 5 days. The cooled solution was carefully brought to *p*H 3 with concentrated HCl and freeze dried. Then the residue was dialyzed against water for 1 day (MWCO 1000) and freeze dried in order to extract the dry residue with 10 mL methanol (containing 1 g/L NaOH) for 1 day at RT. The supernatant methanol was then rejected, whereas the residue was seen by ^{1}H-NMR as almost pure sodium salt of poly(methacrylic acid) PMAA. The PMAA was therefore dissolved in 2 mL *p*H 3 HCl and dialyzed for 1 day before 1 mL of 0.1 M HCl was added into the dialysis tube. The dialysis was continued for 6 h against water (MWCO 1000), before the mixture was finally freeze dried. Then the dried poly(methacrylic acid) PMAA was dissolved in 0.2 ml water and 2 mL THF before 0.1 mL of 2 M trimethylsilyldiazomethane in diethylether was added. After one hour stirring at RT the solution was dialyzed against THF (MWCO 1000) for 1 day and then dried (5 mg of PMMA).

Polymer Characterization

NMR Spectroscopy. The NMR spectra were measured with a 200-MHz Varian Gemini 2000 NMR spectrometer (operating at 200 MHz for ^{1}H and at 50.3 MHz for ^{13}C) using $CDCl_3$ as solvent (usually 10 mg/mL). The chemical shifts are presented in parts per million downfield from the internal TMS standard. Simulations were performed with ACD/HNMR and ACD/CNMR Predictor Ver.3.00.

Size Exclusion Chromatography (SEC). The SEC analyses were performed with a Waters instrument equipped with a Styragel guard column, 7.8 x 300 mm Styragel capillary column, and Waters 2487 UV and Waters 2410 RI detectors. Dimethylformamide with 1 g/L LiBr was used as an eluent at a flow rate of 0.8 mL/min (in some cases THF, where noted). PEO samples were carefully heated with a fan to accelerate the dissolution process. The conventional calibrations was performed with poly(ethylene oxide) (for samples containing PEO; Polymer Laboratories, Amherst, USA) or poly(methyl methacrylate) standards (for PMMA samples; Polymer Standards Service PSS, Mainz, Germany).

Matrix Assisted Laser Desorption Ionization – Time of Flight (MALDI-ToF) Mass Spectrometry. MALDI-ToF mass spectrometry was performed on a Bruker microflex equipped with 337 nm N_2 laser in the linear mode (accelerating voltage 20 kV, pressure 5 10^{-6} mbar) for determination of molecular weight of miktoarm stars and cleaved off and modified PDMAEMA arms (PMMA). THF solutions of dithranol (20 µL of 20 g/L), sodium trifluoroacetate (0.5 µL of 10 g/L) and analyte (5 µL of 10 g/L PMMA) were mixed and 0.5 µL were applied on sample plate. For miktoarm stars α-cyano-4-hydroxycinnamic acid (CHCA) was used as matrix (45 µL of 10 g/L in DMSO) mixed with polymer solution in THF (5 µL of 10 g/L).[5] This mixture was applied on a sample plate (1 µL). In case of overlapping peaks (e.g. double charged species / matrix related signals) Gaussian curve fitting was performed in order to calculate number average molar mass and polydispersity index.

Osmometry. A membrane osmometer (Osmomat 090, Gonotec GmbH, Berlin, Germany) with regenerated cellulose membrane (Gonotec two layer membrane 90.9.0010; cut off 20000 dalton) was used for the determination of the molecular weight of miktoarm stars. Solutions with different

concentrations in THF were injected to extrapolate to zero concentration. The cell was kept at 30 °C. To rinse the measurement cell with a new sample, approximately 0.7 mL of sample solution were injected three times.

Sample Preparation. The polymer concentrations were usually 0.12 g/L or below. 0.42 mg of miktoarm was dissolved in 3 mL of *p*H 8 buffer, containing additional 0.1 M NaCl. Then 0.54 mL of 0.0166 M $K_3[Co(CN)_6]$ were added, keeping the ionic strength basically constant (yielding 2.5 · 10^{-3} M $[Co(CN)_6]^{3-}$). For diluted samples, a 0.12 g/L solution was diluted with just solvent of *p*H 8 buffer, 0.1 M NaCl and 2.5 mM $[Co(CN)_6]^{3-}$.

Light Scattering. Some temperature-dependent static light scattering (SLS) and dynamic light scattering (DLS) measurements were obtained using Malvern Nano ZS instrument equipped with red laser (λ = 633 nm) and using backscattering optics (equilibration time 10 min between different temperatures; the measurements were performed with increasing temperature from 5 °C to 80 °C with 2.5 K intervals after first cooling to 5 °C with ~ 0.3 K/min). DLS and SLS measurements were otherwise conducted with Brookhaven Instruments BI-9000AT digital correlator and BI-200SM goniometer, which was equipped with a thermostat. Diode laser Mini-L30 (λ = 637.6 nm; 30 mW; Brookhaven Instruments) was used as a light source. The SLS data were analyzed by using relative scattered intensities compared to the scattering of toluene. In order to determine the molar mass of aggregates at 10 °C, we used Zimm's double extrapolation method. For PEO_{114}-$(PDMAEMA_{55})_3$-PEO_{114} each solution was first heated to 30 °C and cooled to 10 °C with 20 K/h to guarantee similar aggregation numbers and sizes for all solutions. The specific refractive index increments of the polymers (d*n*/d*c*) were determined from refractive indices measured by a Billingham & Stanley Abbe60 refractometer using the same light source as for the scattering experiments. E.g. 32 g/L solution of PEO_{114}-$(PDMAEMA_{40})_4$-PEO_{114} in 0.1 N NaCl, pH 8 buffer and 2.5 mmol/L $[Co(CN)_6]^{3-}$ was dialyzed against same solvent and diluted with dialyzed solvent to obtain different concentrations. The final polymer concentration was determined by NMR using formic acid as an internal standard. Therefore a 131 mg of mother solution (after dialysis) was freeze dried and redissolved in 0.702 g D_2O in presence of 2.18 mg formic acid. The integrals over formic acid peak at 8.2 ppm and PEO peak at 3.7 ppm was used to recalculate the concentration of polymer after dialysis (24.9 g/L; the integration over peak of formic acid was normalized to the methyl signal of methanol). d*n*/d*c* was then determined as 0.127 ± 0.002 mL/g. Prior to the light scattering measurements the sample solutions were filtered at 30 °C using Millipore Millex-HV filters (SLHV 013NK) with a pore size of 0.45 µm. The measured intensity correlation functions were subjected to the inverse Laplace transformation program (CONTIN; collection times approximately 300 s depending on signal strength). Apparent hydrodynamic radii of star-shaped polymers and their aggregates were calculated according to the Stokes-Einstein equation, using the viscosity of water.

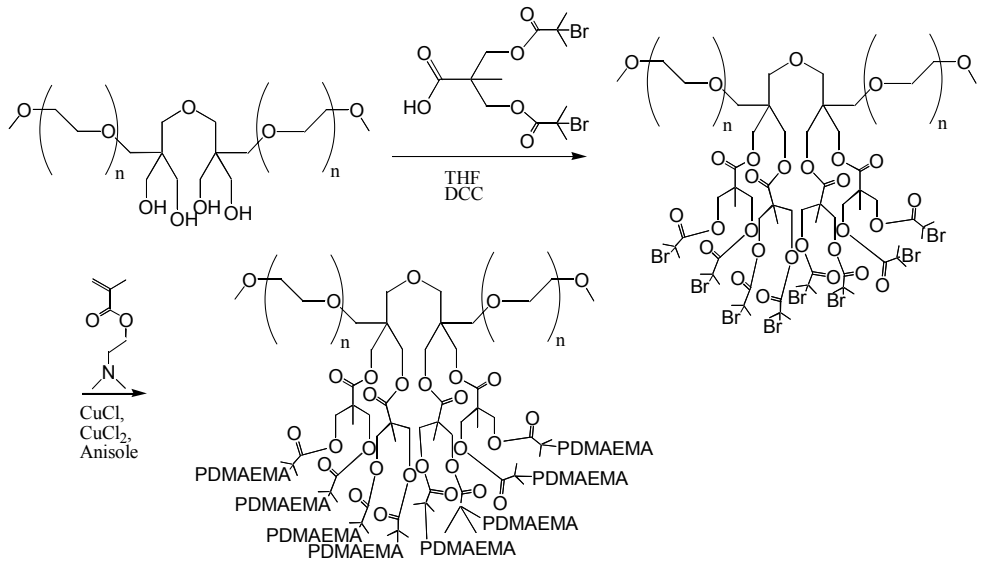
Cryo Transmission Electron Microscopy (cryo-TEM). The samples of PEO_{114}-$(PDMAEMA_{40})_4$-PEO_{114} were prepared by dissolving 0.42 mg of miktoarm star in 3 mL of buffered 1 M NaCl (*p*H 8) and 0.54 mL of 0.0166 M $K_3[Co(CN)_6]$. A drop of the sample (3 µL) was put on carbon coated copper grid R 2/2 (Quantifoil Micro Tools GmbH, Jena, Germany; hydrophilized by glow discharge unit Emitech KX100, 25 mA/min). The drop was kept at respective temperature (5 or 40 °C using Fei Vitrobot; 100 % humidity) for 15 min. For vitrification from 70 °C the sample was thermostated for 15 min in 70 °C water bath before applying one drop into the Vitrobot, which was kept at 60°C, instantly allowing the vitrification). Vitrification was performed by using a plot time of 1.5 or 3 s, zero off-set, no drain time, and liquid ethane / propane mixture (1:1 volume) as a coolant (cooled below -180 °C). PEO_{114}-$(PDMAEMA_{55})_3$-PEO_{114} samples were cooled down to 5 °C with 20 K/h and then applied into the thermostated Vitrobot (5 °C). Samples were maintained at -184 °C in a Gatan 910 cryoholder whilst images were recorded on a FEI Tecnai 12 transmission electron microscope operated at 120 kV under the low-dose conditions. All images were registered digitally by a bottom-mounted CCD camera system (Ultrascan 1000, Gatan) and processed with a digital imaging processing system (Gatan Digital Micrograph).

Steady-state Fluorescence Spectroscopy. Fluorescence probe 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (4HP; 0.5 mg) was dissolved in 0.1 ml THF und 0.1 ml methanol (~2.5 g/L) and 1 µL of this solution was added to 2 mL of sample (e.g. 0.12 g/L miktoarm dissolved in 0.1 M NaCl, *p*H8 buffer, 2.5 10^{-3} M $K_3[Co(CN)_6]$; other concentrations of polymer were achieved by dilution with saline solvent). Those solutions were kept over night at 4 °C for equilibration. Fluorescence spectra were recorded using PTI Photon Technology International spectrofluorometer (right-angle geometry, PTI 814 Photomultiplier Detection System; lamp unit PTI LPS-220B; ByteBox interface; FeliX32 processing software; half mikro quartz sample cell QS, 10.00 mm, 0.8 mL; University of Helsinki, Center for Drug Research) using the following conditions: excitation at 470 nm, recording range 500-680 nm, slit width 4 nm for excitation and emission. The spectrometer was equipped with a thermostat.

Irradiations. UV-lamp Omnicure Series 1000 (100 W; University of Helsinki, Center for Drug Research), equipped with 365 nm filter (output between 325 nm and 410 nm with maximum at 365 nm) was used for UV-illuminations. Illuminations were performed at 50 % opened iris. The light was directed to the sample by use of a light guide, equipped with collimating adaptor (EXFO 810-00042; S/N:0067), kept at 9 cm distance from sample (0.4 mW/cm^2).

Additional Comments to Synthesis

Two polymerizations of DMAEMA were conducted with two different macroinitiators, yielding allmost the same molecular weigth for both miktoarm stars. One pathway



Scheme S1 Alternative route to miktoarms stars

headed for stars with up to 8 PDMAEMA arms, the other limitied the PDMAEMA arm number to 4. Therefore the initiator fragment depicted in Scheme S1 was applied in addition to the initiator shown in Scheme 1 (main part of publication). The polymerization employing the initiator with 4 initiation sites (Scheme 1) was stopped with tributyltin hydride in order to replace the halogen with hydrogen.[4] This exchange prevents the possible substitution of the endgroup halogen with amino groups, causing intra- or intermolecular cross linking of polymers.[6] Since in the course of this exchange the conversion in monomer consumption is not totally controlled, the second polymerization with higher number of initiation sites per molecule (Scheme S1) was stopped just by cooling, dilution with chloroform and with contact with air. The 1H-NMR spectra of the intermediates for the preparation of miktoarm stars with up to 4 PDMAEMA arms are depicted in Figure S1.

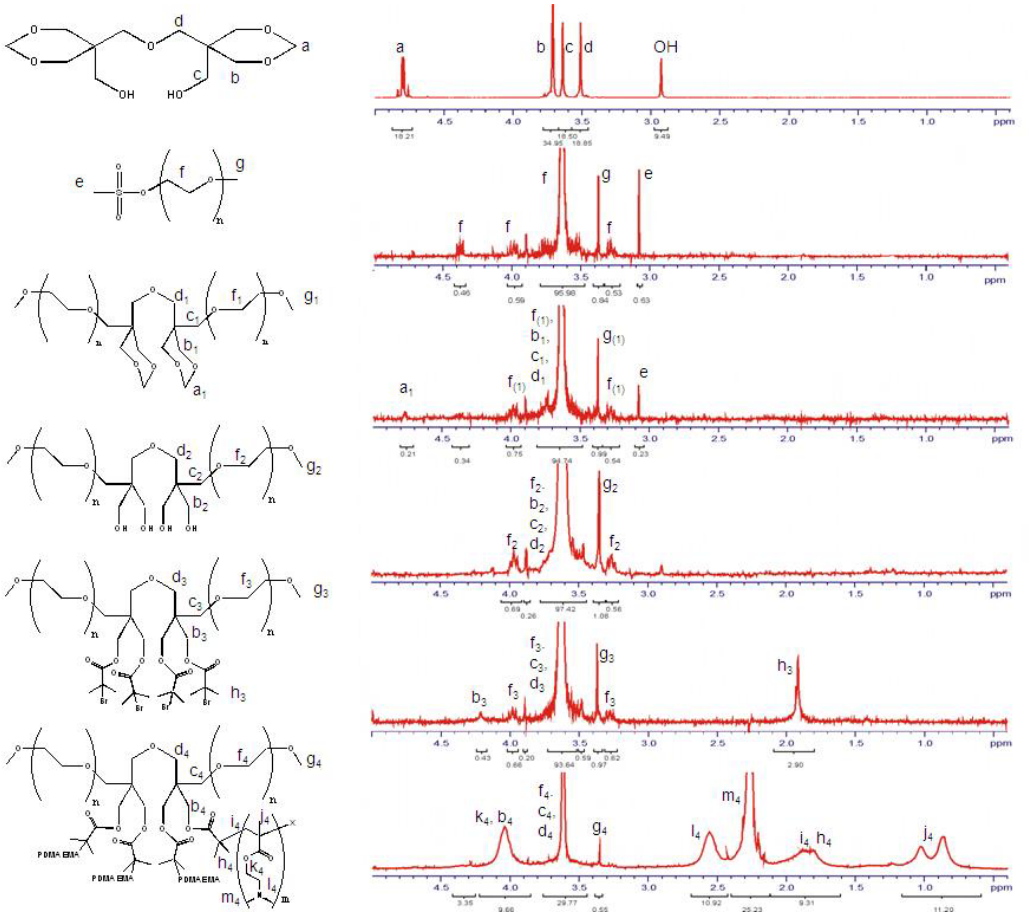


Fig. S1 NMR-Spectra of all intermediates for the synthesis of miktoarm stars with up to 4 PDMAEMA arms

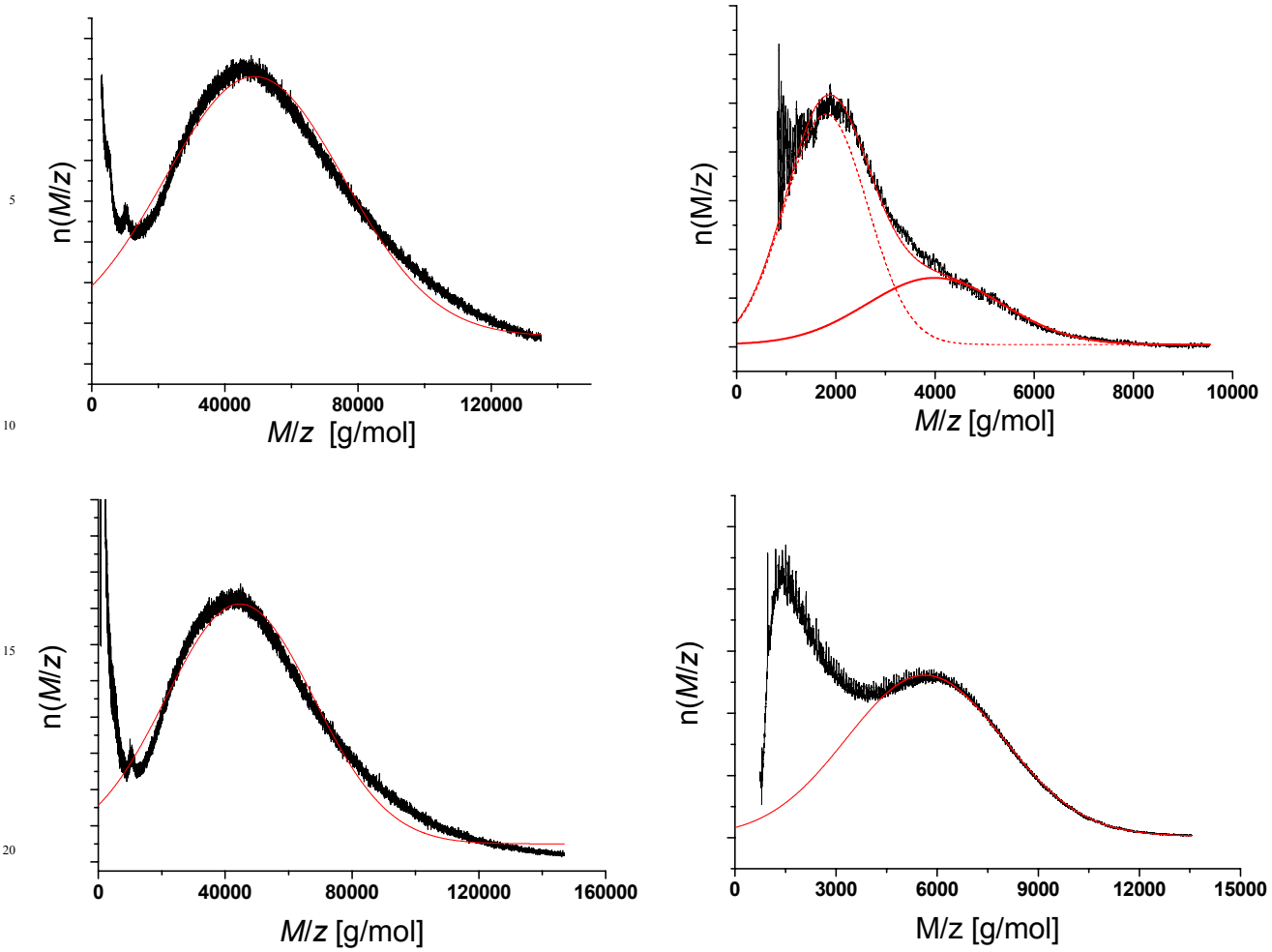


Fig. S2 MALDI-ToF mass spectra of miktoarm stars (left hand side) and their cleaved off arms (after transformation to PMMA, right hand side); top figures relate to PEO_{114}-$(PDMAEMA_{40})_4$-PEO_4, whereas the bottom row originates from PEO_{114}-$(PDMAEMA_{55})_3$-PEO_{114} (red curves are Gaussian fits, partly extracted by double Gaussian fitting)

However the cleavage of arms revealed, that especially the growth of arms from the dendritic initiation fragments is hindered probably due to increasing sterical demands. In order to determine the number of arms, we either prehydrolyzed the polymer by a treatment with hydrochloric acid or we quaternized the amino groups of the polymer.[6] Both procedures help to increase the solubility of the polymer in basic water. Then all the ester bonds were cleaved by alkaline treatment. The cleaved PEO was removed by extraction with alkaline MeOH (PMAA hardly dissolves) or by extraction with $CHCl_3$. The alkaline treatment works best for longer PMAA. The resulting poly(methacrylic acid) PMAA was methylated to obtain poly(methyl methacrylate) PMMA, which was analyzed by MALDI-ToF mass spectrometry.[6] The final MALDI-ToF mass spectra of cleaved off arms are depicted in Figure S2 (together with mass spectra of the whole mictoarm stars). The peaks were fitted by Gaussian functions, since always additional peaks from matrix or double charged species could be observed. For the smallest molecular weight, we needed even to apply a double Gaussian fit. The fitted functions were used to calculate number average molecular weight M_n and polydispersity (*PDI*).

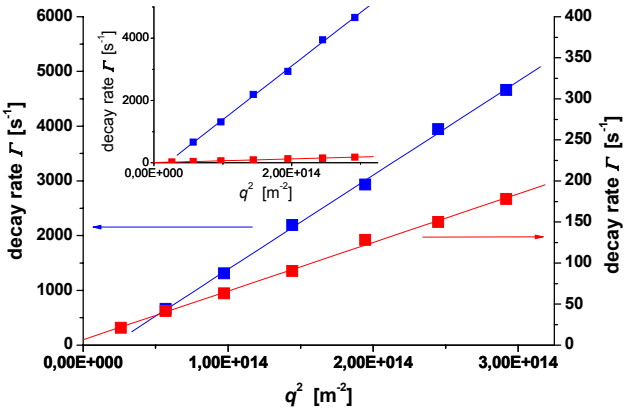


Figure S3: angular dependence of decay rate Γ obtained by CONTIN analysis of DLS data for 0.12 g/L PEO_{114}-$(PDMAEMA_{40})_4$-PEO_{114} (■) and PEO_{114}-$(PDMAEMA_{55})_3$-PEO_{114} (■) in 0.1 M NaCl, *p*H 8 buffer and 2.5 · 10^{-3} M of $[Co(CN)_6]^{3-}$ at 10 °C; inset shows plot with the same scale for both dependences

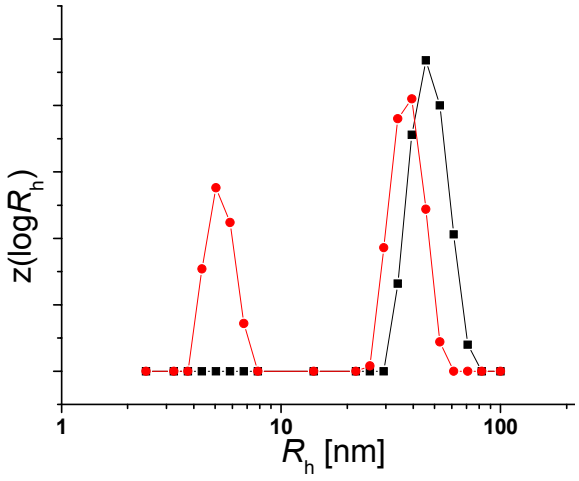


Figure S4: Exemplary intensity weighted size distributions at 80 °C (173°, Malvern Particle Sizer) for micelles of PEO_{114}-$(PDMAEMA_{40})_4$-PEO_{114} (red) and PEO_{114}-$(PDMAEMA_{55})_3$-PEO_{114} (black); 0.12 g/L polymer in 0.1 M NaCl with 2.5 mM $[Co(CN)_6]^{3-}$ in pH 8 buffer

Additional Comments to Self Assembly

The angular dependence of the Dynamic Light Scattering Data was investigated at 10 °C (Figure S3). The linear dependence of the decay rate against squared scattering vector emanating basically from the origin indicates low polydispersity of isotropic particles, which is consistent with the presence of spherical, star-shaped micelles as well as spherical vesicles.

Further, the size distributions of the micelles at 80°C were extracted by use of a particle sizer (Malvern Instruments), since our classical light scattering setup (Brookhaven Instruments) does not tolerate heating to such high temperatures. Though the backscattering optics prevents extraction of more detailed data, trends can be easily seen. Therefore we could detect monomodal size distribution for PEO_{114}-$(PDMAEMA_{55})_3$-PEO_{114} with hydrodynamic radius $\langle R_h \rangle_z$ close to 50 nm. This indicates that the aggregate size for is polymer is considerably smaller compared to the large vesicles obtained at low temperature. This is in accordance to collapsed, dense PDMAEMA domain instead of having a water-swollen PDMAEMA phase at low temperature. The gel-like PDMAEMA has much higher spacial demands, leading to the formation of large vesicles. At 80 °C, much smaller aggregates are obtained (most likely small vesicles; the hydrodynamic radius of 50 nm would however still allow the presence of spherical, star-shaped micelles). In contrast PEO_{114}-$(PDMAEMA_{40})_4$-PEO_{114} gives a bimodal distribution, resembling the situation present in the cryo-TEM images (Figure 4, main part). The smaller fraction, which is the major fraction in mass and number, gives only a $\langle R_h \rangle_z$ close to 5 nm. This is again considerably smaller compared to the size of the micelles at low temperatures. However the size is close to the core value seen in cryo-TEM, indicating good draining of the corona of the compact micelles.

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