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Supporting Info

A Nondestructive, Statistical Method for Determination of Initiation Efficiency: Dipentaerythritol-Aided Synthesis of Ternary ABC_3 Miktoarm Stars using a Combined "Arm-First" and "Core-First" Approach

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Experimental

Materials

Poly(propylene glycol) (M_n = 4000 g/mol according to the manufacturer's data; $Đ_{M,SEC}$ = 1.1 and $M_{n,MALDI}$ = 4170 g/mol, $Đ_{M,MALDI}$ = 1.01) was delivered by Polysciences, Warrington, PA, USA. *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA; purified by filtration over basic alumina), silica and *N*,*N*-dimethyl-4-pyridinamine (DMAP) were purchased from Acros Organics, Geel, Belgium. Poly(ethylene glycol) monomethyl ether (M_n = 5000 g/mol according to the manufacturer's data; $Đ_{M,SEC}$ = 1.1 and $M_{n,MALDI}$ = 4950 g/mol, $Đ_{M,MALDI}$ = 1.01; dried in vacuo after precipitation twice in anhydrous diethylether and then hexane respectively), methanesulfonyl chloride, anhydrous tetrahydrofuran (THF; destabilized; for anionic polymerization destilled over Na/benzophenone before use), bromoisobutyryl bromide, trans-2-[3-(4-tert-butylophenyl)-2-methyl-2-propenylidene)]malononitrile (DCTB), α-cyano-4-hydroxycinnamic acid (CHCA), trimethylsilyldiazomethane (2M in diethylether), *N*,*N*,*N*´,*N*´´,*N*´´´,*N*´´´-hexamethyltriethyltriamine (HMTETA) and the phosphazene base t-BuP_4 in solution (1.0 M in n-hexane) was delivered by Sigma Aldrich. Ethyl glycidyl ether was delivered by ABCR and dried by distillation over calcium hydride. Chloroform, *n*-hexane, 1,4-dioxane (HPLC-grade), ethyl acetate, methanol, anhydrous diethylether and anisole were obtained by VWR. Triethylamine, butanol, n-heptanes, formic acid, sodium and alumina were obtained from Merck (Darmstadt, Germany). Sodium hydride (50% in paraffin oil) and molecular sieves (4Å) were delivered by Fluka. CuCl and $CuCl_2$ were obtained from Alfa Aesar. Acetone and THF for the preparation was bought by AppliChem (Darmstadt, Germany). Sodium chloride was obtained by KMF (Lohmar, Germany). Acetic acid was purchased from Riedel de-Haën. Dichloromethane was bought from Promochem (Wesel, Germany). Basic alumina (Alumina B-Super 1) was obtained from MP Biomedicals (Enschede, Germany). Dipentaerythritoldiacetonketal was synthesized according to reference.[1] For purification, column chromatography was followed by thin layer chromatography (TLC) on silica TLC plates (Merck, Darmstadt), using the same solvent mixture (ethyl acetate/acetone 100 : 1) as mobile phase. After TLC, the plates were immersed into concentrated HNO_3 and then dried with help of a heat gun for staining the dipentaerythritoldiacetonketal spots brownish (R_f = 0.4). Monomesylated poly(ethylene oxide) (M_n = 5000 g/mol; $Đ_{M,SEC}$ = 1.1) was prepared according to reference from above-mentioned poly(ethylene glycol) monomethyl ether.[2] Regenerated cellulose dialysis membranes (Cellu Sep H1, MWCO 3500; Cellu Sep T2, MWCO 12000) were purchased from Interchin. For reagents, the highest purities available were acquired and used as delivered (except where otherwise stated).

Syntheses

Monotelechelic Poly(ethylene oxide) with dipentaerythritoldiacetal-endgroup (PEO_{114}-(OH)) *A*

The monomesylated poly(ethylene glycol) (4.55 g, $9 \cdot 10^{-4}$ mol) was dissolved in 35 mL THF under nitrogen counterflow by carefully heating with a fan. The dipentaerythritoldiacetonketal (1.51 g; $4.52 \cdot 10^{-3}$ mol) and sodium hydride (100 mg 50% NaH, $2.08 \cdot 10^{-3}$ mol) were suspended in 15 ml THF under nitrogen-counterflow and refluxed at 75°C. Then, the PEO solution was slowly added with a syringe under nitrogen counterflow and refluxed at 75°C over night. The next day, further NaH (450 mg 50% NaH, $9.4 \cdot 10^{-3}$ mol) was added under N_2-counterflow and stirring was allowed for another 5 h. The mixture was centrifuged and the supernatant was acidified by addition of acetic acid until wet pH paper shows neutral pH. The mixture was centrifuged and the supernatant was reconcentrated and precipitated in diethylether and the precipitated polymer was dissolved in methanol and dialyzed against methanol over night. Then it was again precipitated in diethylether, filtrated, washed with heptanes and hexane and dried in vacuo to yield 2.8 g (60%) PEO-block-dipentaerythritoldiketal with a conversion of more than 92 % according to NMR (comparing methyl signal at 3.38 ppm and methyl signal at 1.4 ppm). SEC (DMF, 1 g/L LiBr; PMMA calibration): M_n= 11700 g/mol, $Đ_M$ = 1.05; MALDI-ToF MS (DCTB): M_n = 5290 g/mol, $Đ_M$ = 1.01; δ_H(400 MHz; $CDCl_3$; Me_4Si) 3.85-3.4 (s, PEO-H; 16H, overlapping peaks of dipentaerythritol unit -R-CH_2-OR), 3.38 (3H, s, CH_3-O-PEO), 1.4 (12H, s, ketal-R-CH_3).

Bismesylated Mes-PPO_{69}-Mes *B*

Hydroxy-telechelic PPO with one OH-group on each terminus (60 g, M_n = 4000 g/mol, 0.015 mol) was dissolved in dichloromethane (200 g) and triethylamine (11g, 0.11 mol) and mixed with 20 grains of molecular sieve. After 3h, the grains were removed and the solution was cooled with ice before methansulfonylchloride (6 g, 5 mL, 0.052 mol) was added dropwise with help of syringe through a septum (30 min). Then, the solution was allowed to warm up overnight under stirring.

The mixture was filtered over silica and concentrated, before the polymer was dissolved in dioxane (~100 mL) and dialyzed against dioxane for 10 days (MWCO 3500). Then, the solution was again concentrated by freeze-drying and vacuum (30 g). SEC (DMF, 1 g/L LiBr; PMMA calibration): M_n = 6200 g/mol, $Đ_M$ = 1.13; δ_H(400 MHz; $CDCl_3$; Me_4Si): 4.79 (2H, m, CH_3SO_3-C*H*CH_3-CH_2-O), 3.6-3.45 (m, O-C*H*$_2$-$CHCH_3$-O), 3.45-3.3 (m, O-CH_2-C*H*CH_3-O), 3.04, 3.02 (6H, ds, C*H*$_3SO_3$-), 1.34 (6H, dd, CH_3SO_3-CHC*H*$_3$-CH_2-O), 1.2-1.0 (m, O-CH_2-CHC*H*$_3$-O).

Poly(ethylene oxide)-block-poly(propylene oxide) with inner dipentaerythritol (PEO_{114}-$(OH)_4$-PPO_{69}) *D*, prepared with bismesylated poly(propylene oxide) (Mes-PPO_{69}-Mes)

The mesylated poly(propylene oxide) (*B*, 3.0 g, $1.1 \cdot 10^{-4}$ mol) was dissolved in 5 mL dry, inhibitor-free THF and dried over molecular sieves. The solution was added with a syringe into the setup that was equipped with a nitrogen-flushed condenser / water trap ($CaCl_2$) and heated at 65°C. A mixture of PEO-dipentaerythritoldiketal (*A*, freshly precipitated in anhydrous diethyl ether and hexane from dichloromethane solution; dried in vacuum; 0.5 g, $9.4 \cdot 10^{-5}$ mol) and NaH (100 mg, 50% NaH, $2.1 \cdot 10^{-3}$ mol) in 5 mL dry THF was slowly added with a syringe under nitrogen counterflow and stirring, before it was refluxed for 2 h at 75°C. Then, the left-over precipitate of non-reacted NaH was washed with 5 mL dry THF and added to the reaction mixture, before it was refluxed under stirring at 65°C over the weekend. Then it was refluxed at 75°C. After 1 h, 400 mg NaH were added under N_2-counterflow, stirring and reflux. After another hour, sodium butanolat (1 g butanol was mixed with 0.6 g of 50% NaH in 10 mL dry THF) was added under N_2-counterflow, stirring and the mixture was refluxed for further 2 h. Then, the mixture was acidified by addition of acetic acid until wet pH paper shows neutral pH. The mixture was centrifuged at 40°C and 5000 rpm in order to remove non-dissolved sodium salts and the supernatant was concentrated. It was dissolved in 10 mL hot THF and precipitated in the freezer overnight. The next day, hexane was added and the suspension was centrifuged at 5°C and 5000 rpm in order to remove non-bound PPO. The precipitate was dried in vacuo before it was dissolved in water and dialyzed for 16 h against water (MWCO 3500) and freeze dried to yield 0.54 g (60 %) with 50% conversion to diblock according to NMR. The polymer was dissolved in 10 mL of a concentrated NaCl solution and dialyzed for 4 days at 40°C against a 3 M NaCl solution (MWCO 12000) in order to reduce the amount of non-reacted PEO (no full removal of PEO possible in that way). Then, 1.5 g acetic acid and 0.15 g formic acid were added to 30 mL of the polymer solution (pH 3). The mixture was stirred for 20 h at RT. Then it was dialyzed for 8 h against water. When a pH of 6 was reached, it was freeze dried to get 0.47 g PEO/PPO mixture with 95 % conversion in deprotection of the ketal and a conversion to diblock of ~ 50 mol % according to NMR. One part of this mixture was directly used for the synthesis of the macroinitiator. Another part was used for the full removal of non-bound PEO. This was achieved by dissolution of 210 mg of the polymer mixture in ~ 10 mL acetone and a successive fractionated precipitation by a careful and dropwise addition of diethyl ether. When the solution turned hazy, the addition was stopped. After removal of the precipitated PEO by filtration with a syringe filter (0.45 µm, PTFE membrane), the dissolved fraction was dried in vacuo and analyzed by NMR in order to assess the block ratio. This precipitation procedure was repeated, until the block ratio did not change anymore and the pure diblock copolymer was obtained (75 mg). SEC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 15800 g/mol, $Đ_M$ = 1.12; MALDI-ToF MS (DCTB): M_n = 9400 g/mol, $Đ_M$ = 1.01; δ_H(400 MHz; $CDCl_3$; Me_4Si) 3.64 (s, PEO-*H*), 3.6-3.48 (m, O-C*H*$_2$-$CHCH_3$-O), 3.48-3.3 (m, O-CH_2-C*H*CH_3-O), 1.2-1.05 (m, O-CH_2-CHC*H*$_3$-O).

Macroinitiator with four ATRP initiation sites PEO_{114}-Br_4-PPO_{69} {poly(ethylene oxide) - block - 2,2,6,6-tetrakis[methyl-(2´-bromo-2´-methylpropionate)]-4-oxa-1,7-heptandiol - block - poly(propylene oxide)} *E*

1.6 g chloroform and triethylamine (0.8 g, $7.9 \cdot 10^{-3}$ mol) have been dried for one hour over molecular sieves and were added to the deprotected diblock PEO-*block*-PPO mixture (*D*, 100 mg, ~ 50 mol. % diblock) with inner dipentaerythritol moiety (< $6 \cdot 10^{-5}$ mol OH Groups) and 1.3 mg *N*,*N*-dimethyl-4-pyridinamine (DMAP) and then cooled with ice under stirring. Then 2-bromo-2-methylpropanoyl bromide (26 mg; $1.1 \cdot 10^{-4}$mol) was added and the mixture was stirred for 2.5 h, before another 80 mg of bromide ($3.5 \cdot 10^{-4}$ mol) were added. The temperature was allowed to slowly increase to RT overnight under stirring. The next day, the flask was equipped with a condenser and the mixture was refluxed at 75°C for 2 h. When the mixture was cooled down, chloroform was added and the mixture was filtrated. The mixture was concentrated, before it was dissolved in hot THF and centrifuged. The solution was cooled in the freezer. At the next day, after adding hexane, the mixture was centrifuged and the precipitate was dried in vacuo. The precipitate was dissolved in methanol and dialyzed for 3 days against methanol (MWCO 3500) and then for 10 h against water before it was freeze dried. It was dissolved in 5 mL acetone and the side product PEO(-Br_5) was precipitated. This was achieved by a careful and dropwise addition of diethyl ether. When the solution turned hazy, the addition was stopped. After removal of the precipitated PEO by filtration with a syringe filter (0.45 µm, PTFE membrane), the dissolved fraction was dried in vacuo and analyzed by NMR in order to assess the block ratio. This precipitation procedure was repeated, until the block ratio did not change anymore. Finally, the supernatant was concentrated, dissolved in water and freeze dried in order to obtain pure macroinitiator (22 mg, 33 % yield relative to pure diblock). SEC (DMF, 1 g/L LiBr; PMMA calibration): M_n = 18100 g/mol, $Đ_M$ = 1.07; MALDI-ToF MS (DCTB): M_n = 9670 g/mol, $Đ_M$ = 1.01; δ_H(400 MHz; $CDCl_3$; Me_4Si): 4.22 (8H, s, -C*H*$_2$-O-C=O-), 3.64 (s, PEO-*H*,), 3.6-3.45 (m, O-C*H*$_2$-$CHCH_3$-O), 3.45-3.25 (m, O-CH_2-C*H*CH_3-O), 1.92 (24H, s, -O-C=O-(C*H*$_3$)$_2$-Br), 1.18-1.07 (m, O-CH_2-CHC*H*$_3$-O).

Miktoarm star with 1 PEO arm, 1 PPO arm and ~ 4 PDMAEMA arms (PEO_{114}-$(PDMAEMA_{90})_{3.1}$-PPO_{69}) *F*

A mixture of the macroinitiator PEO_{114}-Br_4-PPO_{69} (*E*, 15 mg; M_n ~ 10200 g/mol; $5.88 \cdot 10^{-6}$ mol Br groups), copper(I)chloride (CuCl; 0.7 mg; $7.1 \cdot 10^{-6}$ mol) and copper(II)chloride ($CuCl_2$; 0.2 mg; $1.5 \cdot 10^{-6}$ mol) were mixed in anisole (filtrated over basic alumina; 0.57 g) and deoxygenated by purging with nitrogen.

Then, the ligand *N,N,N´,N´´,N´´´,N´´´*-hexamethyltriethyltriamine (HMTETA; 20.8 mg; $9.0 \cdot 10^{-5}$ mol) and the monomer *N,N*-dimethylaminoethyl methacrylate (DMAEMA; 1.256 g; $8.0 \cdot 10^{-3}$ mol; filtrated over basic alumina) were also mixed and deoxygenated. 134 mg of this solution (0.132 g DMAEMA, $8.4 \cdot 10^{-4}$ mol; 2.1 mg HMTETA, $9.1 \cdot 10^{-6}$ mol) was introduced to the macroinitiator mixture at 80°C under stirring and nitrogen counterflow. After 3 h, the reaction was terminated by injection of chloroform and contact with air. The conversion was 49 % according to NMR ($P_{n,theo}$(arm) = 70; $M_{n,theo}$(total) = 55000 g/mol; theoretical formula: PEO_{114}-$(PDMAEMA_{70})_4$-PPO_{69}). Then the polymer solution was filtrated through silica and then concentrated, before it was dissolved in dioxane and precipitated from hexane. Then the precipitate was dissolved in dioxane and dialyzed against dioxane for several days (MWCO 3500) before it was freeze dried to yield 70 mg of miktoarm star. SEC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 58900 g/mol, $Đ_M$ = 1.39; MALDI-ToF MS (CHCA): M_n = 60000 g/mol, $Đ_M$ = 1.19; δ_H(400 MHz; $CDCl_3$; Me_4Si): 4.2 - 3.9 (O-CH_2CH$_2$-N, PDMAEMA), 3.64 (s, PEO-H), 3.6-3.45 (m, O-CH_2-CHCH$_3$-O, PPO), 3.45-3.25 (m, O-CH$_2$-CHCH$_3$-O, PPO), 2.65-2.5 (O-CH$_2$CH_2-N, PDMAEMA), 2.35 - 2.25 (-N(CH_3)$_2$, PDMAEMA), 2.0 - 1.7 (PDMAEMA backbone CH_2); 1.17-1.1 (m, O-CH$_2$-CHCH_3-O, PPO), 1.1 – 0.85 (PDMAEMA backbone CH_3).

Cleavage of the arms: Different samples of the miktoarm star, which were used for the investigation of the solution properties,[3] were collected after the respective experiment in order to gain about 10 mg of miktoarm star. For this reason, the crude mixture of the miktoarm stars was freeze-dried (~ 200 mg of solid content), redissolved in water, dialyzed against water (MWCO 1000; 2 d), methanol (1d) and water (1d) in order to freeze-dry the sample (16 mg of miktoarm star). The lyophilized polymer was dissolved in 0.7 g acetone for addition of 25 mg of methyliodide. After 1 h of stirring at RT (gelation took place), the mixture was dialyzed against acetone (MWCO 1000; 1d) and then 1d against water, in order to obtain the quaternized product after freeze-drying (13 mg). This product was then mixed with 0.25 g concentrated, aqueous NaOH in a plastic vial. Water was dropwise added until the mixture turns clear. This mixture was left for 14 d at 80°C in order to cleave off the former PDMAEMA arms from the diblock copolymer PEO-*b*-PPO. Then, the pH of the mixture was carefully set to pH 10. After freeze-drying, the mixture was dialyzed against water in order to remove residual salt (MWCO 1000; 2d) and in order to obtain 8 mg of crude poly(sodium methacrylate) (contains PEO-*b*-PPO) after lyophilization. The powder was dispersed in 5 mL methanol (containing 1 g/L NaOH) and left for PEO-*b*-PPO extraction for 4 days (with daily exchange of supernatant against 1g/L NaOH in methanol). Then, the precipitate was dissolved in water, acidified to pH 2, dialyzed against water and freeze-dried in order to obtain 3 mg of protonated poly(methacrylic acid) (PMAA). The PMAA was dissolved in 0.1 ml water and 1 mL THF before 3 drops of 2 M trimethylsilyldiazomethane in diethylether were added, until the solution remains yellowish for more than an hour under stirring at RT. Then, the solution was dialyzed against dioxane (MWCO 1000) for 1 day and freeze-dried in order to obtain 2 mg of poly(methyl methacrylate) (PMMA). SEC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 9200 g/mol, $Đ_M$ = 1.15; => P_n(arm) ≈ 90 => final formula: PEO_{114}-$(PDMAEMA_{90})_{3.1}$-PPO_{69}

Poly(ethylene oxide)-block-poly(ethyl glycidyl ether) with inner protected dipentaerythritol (PEO_{114}-$(OR)_4$-$PEGE_{17}$), prepared by anionic polymerization *G*

For the anionic polymerization, it is important to polymerize under anhydrous conditions. Therefore, all flasks were heated under high vacuum (10^{-3} mbar) several times and flushed with nitrogen before use in anionic polymerization. Further, the macroinitiator (telechelic, dipentaerythritoldiketal-modified PEO with one unprotected hydroxyl group) is dried before use by several steps. First, the macroinitiator was dissolved in anhydrous DCM and precipitated in anhydrous diethyl ether to remove excess of water. This step is repeated three times. The second step is to dry the macroinitiator over high vacuum for several days. In the last step, it is dissolved (with a concentration of 50 g/L) in dried and degassed THF (distilled over Na/benzophenone) with addition of fresh molecular sieves to remove the remaining water.

A solution of PEO-dipentaerythritoldiketal (*A*, 100 mg, $2 \cdot 10^{-5}$ mol) in THF (2 mL, distilled over Na/benzophenone) was dried over molecular sieves under stirring and slight heating. The solution was transferred under nitrogen counterflow with a syringe through a septum into the sealed reaction flask. 50 µL of the t-BuP_4 base solution (1M in hexane, $4 \cdot 10^{-5}$ mol, 2 eq.) were added under nitrogen counter flow and the mixture was stirred for 30 min at 55 °C. The reaction was started by adding the monomer ethyl glycidyl ether (0.15 mL, 150 mg, $1.5 \cdot 10^{-3}$ mol, 70 eq.). The reaction was stopped after 90 h (100 % conversion according NMR) by adding excess of methyl iodide (0.1 mL, 0.2 g, $1.6 \cdot 10^{-3}$ mol ~80 eq.). The solvent was removed in vacuum. The product was dissolved in hot THF and precipitated upon cooling in the freezer over night. The next day, the precipitate was separated by centrifugation at -10 °C and 5000 rpm from the supernatant. Finally the precipitate was dissolved in 1,4 dioxane and the product was recovered by freeze-drying (yield 109 mg).

SEC (THF, 1 g/L; PMMA calibration): M_n = 9400 g/mol, $Đ_M$ = 1.09; δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.8-3.6 (PEO-H, s), 3.53-3.33 (PEGE R-O-CH_2-CHCH$_2$OCH_2CH$_3$-O-R, m), 3,31 (3H, PEO-CH$_3$, s), 3,30 (3H, PEGE-CH$_3$, bs), 1.33 (12H, acetal -R-CH_3, s), 1.16-1.08 (PEGE R-O-CH$_2$-CH_3, m).

Poly(ethylene oxide)-block-poly(ethyl glycidyl ether) with inner dipentaerythritol (PEO_{114}-$(OH)_4$-$PEGE_{17}$) *H*

Acetic acid was added to an aqueous polymer solution (*G*, 0.09 g in 10 mL) until a pH of 3 was reached. Then it was dialyzed for 16 h against water with acetic acid (pH 3). Finally it was dialyzed for 3 days against millipore water and freeze dried to yield 0.08 g with 96 % conversion in deprotection.

SEC (THF, 1 g/L; PMMA calibration): M_n = 12800 g/mol, $Đ_M$ = 1.10, MALDI-ToF MS (DCTB): M_n = 6700 g/mol, $Đ_M$ = 1.02; δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.8-3.6 (PEO-H, s), 3.53-3.33 (PEGE R-O-CH_2-CHCH$_2$OCH_2CH$_3$-O-R, m), 3,31 (3H, PEO-CH$_3$, s), 3,30 (3H, PEGE-CH$_3$, bs), 1.2-1.1 (PEGE R-O-CH$_2$-CH_3, m).

Macroinitiator with four ATRP initiation sites PEO_{114}-Br_4-$PEGE_{17}$ {poly(ethylene oxide) - block - 2,2,6,6-tetrakis[methyl-(2´-bromo-2´-methylpropionate)]-4-oxa-1,7-heptandiol - block - poly(ethyl glycidyl ether)} *I*

1.8 g chloroform and triethylamine (0.9 g, $8.9 \cdot 10^{-3}$ mol) have been dried for one hour over molecular sieves and were added to the deprotected diblock PEO-*b*-PEGE mixture (*H*, PEO_{114}-$(OH)_4$-$PEGE_{17}$, 48 mg, $7 \cdot 10^{-6}$ mol) with inner dipentaerythritol moiety ($3 \cdot 10^{-5}$ mol OH Groups) and 3 mg *N*,*N*-dimethyl-4-pyridinamine (DMAP) and then cooled with ice under stirring. Then 2-bromo-2-methylpropanoyl bromide (50 mg; $2.2 \cdot 10^{-4}$ mol) was added under nitrogen counterflow and temperature was allowed to slowly increase to RT overnight under stirring. After 18 h, the mixture was heated to 55 °C. After another 5 h, the mixture was cooled down, chloroform was added and the mixture was filtrated. The mixture was reconcentrated before it was dissolved in hot THF and dialyzed for 1 week against THF (MWCO 1000) and then for 16 h against 1,4-dioxane before it was freeze dried to yield 42 mg product.

δ_H (400 MHz; $CDCl_3$; Me_4Si) 4.25-4.20 (8H, s, C-CH_2-CH_2-OOC-), 3.8-3.6 (PEO-*H*, s), 3.6-3.4 (m, R-O-CH_2-C*H*CH_2OC$H_2$$CH_3$-O-R), 3.39 (3H, s, PEO-CH_3), 3.30 (3H, s, PEGE-CH_3), 1.95-1.90 (24H, s, -O-C=O-$(CH_3)_2$-Br), 1.16-1.08 (m R-O-CH_2-CH_3)

Miktoarm star with 1 PEO arm, 1 PEGE arm and ~ 4 PDMAEMA arms (PEO_{114}-$(PDMAEMA_{74})_{3.1}$-$PEGE_{17}$) *J*

A mixture of the macroinitiator PEO_{114}-Br_4-$PEGE_{17}$ (*I*, 9.6 mg; M_n ~ 7600 g/mol; $5.1 \cdot 10^{-6}$ mol Br groups), copper(I)chloride (CuCl; 0.7 mg; $7.1 \cdot 10^{-6}$ mol) and copper(II)chloride ($CuCl_2$; 0.1 mg; $7 \cdot 10^{-7}$ mol) were mixed in anisole (filtrated over basic alumina; 0.555 g) and deoxygenated by purging with nitrogen. Then, the ligand *N*,*N*,*N*´,*N*´´,*N*´´´,*N*´´´- hexamethyltriethylentriamine (HMTETA; 25.5 mg; $1.1 \cdot 10^{-4}$ mol) and the monomer *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA; 2.232 g; $1.42 \cdot 10^{-2}$ mol; filtrated over basic alumina) were also mixed and deoxygenated. 150 mg of this solution (0.148 g DMAEMA, $9.4 \cdot 10^{-4}$ mol; 1.7 mg HMTETA, $7.4 \cdot 10^{-6}$ mol) was introduced to the macroinitiator mixture at 80°C under stirring and nitrogen counterflow. After 3 h 50 min, the reaction was terminated by injection of chloroform and contact with air. The conversion was 31 % according to NMR ($P_{n,theo}$(arm) = 58; $M_{n,theo}$(total) = 43000 g/mol; theoretical formula: PEO_{114}-$(PDMAEMA_{58})_4$-$PEGE_{17}$; formula after estimation of initiation site efficiency by mass spectrometry: PEO_{114}-$(PDMAEMA_{74})_{3.1}$-$PEGE_{17}$). Then the polymer solution was filtrated through silica and precipitated from hexane. The precipitate was dissolved in dioxane and dialyzed against dioxane for 2 days (MWCO 1000) before it was freeze dried to yield 50 mg of miktoarm star. SEC (DMF, 1 g/L LiBr, PMMA calibration): M_n = 39500 g/mol, $Đ_M$ = 1.19; SEC (DMF, 1 g/L LiBr, universal calibration): M_n = 42500 g/mol, $Đ_M$ = 1.49; MALDI-ToF MS (CHCA): M_n = 63000 g/mol, $Đ_M$ = 1.32; δ_H(400 MHz; $CDCl_3$; Me_4Si): 4.15 - 4.0 (O-C$H_2$$CH_2$-N, PDMAEMA), 3.64 (s, PEO-H), 3.6-3.4 (PEGE R-O-CH_2-C*H*CH_2OC$H_2$$CH_3$-O-R, m), 3.38 (3H, PEO-$CH_3$, s), 3,30 (3H, PEGE-$CH_3$, bs), 2.56 (O-$CH_2CH_2$-N, PDMAEMA), 2.28 (-N($CH_3$)$_2$, PDMAEMA), 2.1 - 1.7 (PDMAEMA backbone CH_2), 1.2-1.14 (PEGE R-O-CH_2-CH_3, m), 1.14 – 0.85 (PDMAEMA backbone CH_3).

Polymer characterization

NMR

The NMR spectra were measured with a 400-MHz Bruker DRX 400 NMR spectrometer at 23 °C. Unless otherwise stated, $CDCl_3$ was used as solvent (usually 10 mg·mL^{-1}). The chemical shifts are presented in parts per million downfield from the TMS standard. As reference the proton signal of residual $CHCl_3$ was used.

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.

Size exclusion chromatography (SEC)

SEC analyses were performed at room temperature using a high-pressure liquid chromatography pump (Bischoff 2250) and a refractive index detector (Jasco 2031plus) and in some cases with a PSS viscosity detector. The eluting solvent was dimethylformamide (DMF) with 1 g/L LiBr and a flow rate of 1.0 mL/min (polymer concentration 1 g/L). Five columns with PSS GRAM material were applied. The length of the precolumn was 50 mm and the diameter 8 mm (30 Å). The remaining four columns had a length of 300 mm, diameter of 8 mm, particle size of 10 µm, and the nominal pore widths were 30, 100, 1000 and 3000 Å. Narrow-dispersed poly(methyl methacrylate) samples (PSS, Mainz, Germany) were used for (universal) calibration and the software package PSS WinGPC Unity (PSS, Mainz, Germany) was used for the evaluation.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF) Mass Spectrometry

MALDI-TOF mass spectrometry was performed on a Bruker ultrafleXtreme equipped with a 337 nm smartbeam laser in the reflective and linear mode. THF solutions of trans-2-[3-(4-tert-butylophenyl)-2-methyl-2-propenylidene)]malononitrile (DCTB) (5 µL of 20 mg/ mL), sodium trifluoroacetate (0.1 µL of 10 mg/ mL) and analyte (5 µL of 10 mg/ mL linear polymers) were mixed and 0.5 µL thereof were applied on the 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).[4] This mixture was applied on a sample plate and dried in vacuo (1 µL; measurement in linear mode). The spectra acquisition and spectra handling was performed with software Bruker Daltronics flexControl and Bruker Daltronics flexAnalysis (both vers. 3.3), before the spectra were exported to the program OriginPro 9.0 for further analysis. For determination of the molar mass obtained by

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MALDI-ToF, the spectra were directly evaluated by integration in order to obtain M_n and M_w. In case of overlapping peaks, Gaussian fitting in the region above $3 \cdot 10^4$ g/mol was performed for the miktoarm stars, taking then the whole Gaussian distribution above 0 g/mol for integration. In Origin, the spectra were compared with simulated ones. The detailed procedure for extraction of the arm number (/initiation site efficiency) is presented in the Results and Discussion section.

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