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An easy accessible homologous set of first to fifth generation dendritic methacrylic macromonomers and their polymerizations

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Synthetic Procedures and Characterization of all Compounds

3,5-Bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzyl alcohol 3a

N-Hydroxybenzotriazole (1.86 g, 13.77 mmol) was added to a solution of 4-*tert*-butoxy-4-oxobutanoic acid **2** (2 g, 11.48 mmol) in dry DCM (150 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (2.90 g, 15.14 mmol) was added at -20°C and the reaction mixture was stirred until the hydrochloride had dissolved completely (ca. 4 h). Then a solution of TEA (6.19 g, 61.19 mmol) and **1a** (4.91 g, 10.19 mmol) in DCM/methanol (50 mL, 1/1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature, stirred for 16

h and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Chromatographic separation (silica gel, ethyl acetate/methanol 15/1) yielded **3a** as a colorless liquid (4.15 g, 72%); R_f = 0.51 (ethyl acetate/MeOH 20/1); ^{1}H NMR: δ = 1.39 (s, 18 H; ^{t}Bu), 1.96 (m, 7 H; C*H*$_2$), 2.38 (t, 4 H; $CH_2CO_2{}^tBu$), 2.54 (t, 4 H; NHCOC*H*$_2$), 3.41 (m, 4 H; C*H*$_2$NH), 3.50 (br, 1 H; OH), 3.90 (t, 4 H; $PhOCH_2$), 4.55 (s, 2 H; OCH_2Ph), 6.28 (t, 1 H, Ph), 6.45 (t, 2 H, Ph), 6.55 (t, 2 H, NH); ^{13}C NMR: δ = 28.27 ($C(\underline{C}H_3)_3$), 29.00 ($OCH_2\underline{C}H_2CH_2N$), 30..80 ($\underline{C}H_2COC^tBu$), 31.08 ($\underline{C}H_2CH_2COC^tBu$), 36.90 ($OCH_2CH_2\underline{C}H_2N$), 64.69 ($O\underline{C}H_2CH_2CH_2N$), 65.75 ($CO_2\underline{C}H_2$), 80.70 ($\underline{C}(CH_3)_3$), 100.34, 105.14, 144.0, 159.92 (Ar), 172.02 (CO), 172.37 (NHCOO); HR-ESI MS: *m/z* (rel-%): 589.3 (100) $[M + Na]^+$; elemental analysis (%) calcd. for $C_{29}H_{46}N_2O_9$ (566.69): C 61.47, H 8.18, N 4.94; found: C 61.46, H 7.97, N 4.91.

3,5-Bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzyl methacrylate MG1

A solution of MAC (1.4 g, 13.14 mmol) in THF (10 mL) was added dropwise to a mixture of **3a** (3.80 g, 6.71 mmol), triethylamine (TEA; 2.02 g, 20.10 mmol), and DMAP (80 mg) in dry THF (100 mL) at 0°C over 30 min. The mixture was stirred for 16 h at room temperature, then washed with aqueous $NaHCO_3$ and brine, and dried with magnesium sulfate. After evaporation of the solvent under vacuum and two successive chromatographic separations (silica gel, ethyl acetate/methanol 30/1), **MG1** was obtained as colorless foam (3.62 g, 85%). R_f = 0. 68 (10:1 DCM/MeOH); M.p.: 75 – 77 °C; ^{1}H NMR: δ = 1.39 (s,

18 H; ^{t}Bu), 1.96 (m, 7 H; CH_2 and C=CCH_3), 2.38 (t, 4 H; $CH_2CO_2{}^t$Bu), 2.54 (t, 4 H; NHCOCH_2), 3.41 (m, 4 H; CH_2NH), 4.00 (t, 4 H; $PhOCH_2$), 5.09 (s, 2 H; OCH_2Ph), 5.56 (m, 1 H; C=CH_2), 6.12 (m, 1 H; C=CH_2), 6.23 (br, 4 H; NH), 6.38 (t, 1 H; Ph), 6.48 (t, 2 H; Ph); ^{13}C NMR: δ = 18.36 (C=C$\underline{C}H_3$), 28.05 (C($\underline{C}H_3)_3$), 29.01 ($OCH_2\underline{C}H_2CH_2N$), 30.84 ($\underline{C}H_2COC{}^t$Bu), 31.28 ($\underline{C}H_2CH_2COC{}^t$Bu), 37.05 ($OCH_2CH_2\underline{C}H_2N$), 65.98 ($O\underline{C}H_2CH_2CH_2N$), 66.17 ($CO_2\underline{C}H_2$), 80.72 ($\underline{C}(CH_3)_3$), 100.94, 106.45, 138.44, 159.99 (Ar), 136.10 ($\underline{C}H_2$=C), 167.14 (CO) , 171.85 ($\underline{C}O_2C(CH_3)_3$) 172.33 (NHCOO); HR-ESI: *m/z* (rel-%): 657.3 (100) $[M + Na]^+$; elemental analysis (%) calcd. for $C_{33}H_{50}N_2O_{10}$ (634.77): C 62.44, H 7.94, N 4.41; found: C 62.15, H 7.79, N 5.34.

3,5-Bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy) benzamido)propoxy) allyl benzoate 4a

N-Hydroxybenzotriazole (2.50 g, 18.50 mmol) was added to a solution of acid **3c** (9.10 g, 15.67 mmol) in dry DCM (250 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (3.8 g, 19.82 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (3.25 g, 60.58 mmol) and **1b** (3.24 g, 6.05 mmol) in methanol/DCM (70 mL, 1/ 1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature, stirred for 16 h, and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Two successive chromatographic separations [silica gel, DCM/methanol (20/1)] yielded **4b** as a colorless foam (6.4 g, 73%); R_f = 0.48 (10:1 DCM/MeOH); M.p.: 94-96 °C; ^{1}H NMR: δ = 1.38 (s, 36 H; ^{t}Bu), 1.85 (m,

8 H; CH_2), 2.05 (m, 4 H; CH_2), 2.38 (t, 8 H; $CH_2CO_2{}^tBu$), 2.48 (t, 8 H; NHCOCH_2), 3.36 (m, 8 H; CH_2NH), 3.57 (m, 4 H; CH_2NH), 3.87 (m, 8 H; $PhOCH_2$), 4.03 (m, 4 H; $PhOCH_2$), 4.75 (d, 2 H; CO_2CH_2), 5.28 (dd, 2 H; CH=CH_2), 5.98 (ddd, 1 H; *H*=CH_2), 6.38 (t, 2 H; Ph), 6.55 (t, 1 H; Ph), 6.63 (br, 4 H; NH), 6.85 (d, 4 H; Ph), 7.08 (d, 2 H; Ph), 7.48 (t, 2 H; NH); ^{13}C NMR: δ = 27.97 (C($\underline{C}H_3)_3$), 28.97 ($OCH_2\underline{C}H_2CH_2N$), 30.75 ($\underline{C}H_2COC{}^tBu$), 31.04 ($\underline{C}H_2CH_2COC{}^tBu$), 36.66, 37.63 ($OCH_2CH_2\underline{C}H_2N$), 65.76 ($O\underline{C}H_2CH_2CH_2N$), 66.30 ($OCH_2$), 80.57 ($\underline{C}(CH_3)_3$), 104.28, 105.65, 106.71, 107.82, 131.99, 136.54, 159.69, 159.76 (Ar), 117.89 ($\underline{C}H_2$=C), 136.54 (CH_2=$\underline{C}$), 165.80, 167.34 (CO) , 171.94, 172.23 (NHCOO); FAB-MS (2 kV): *m/z* (rel-%): 1455.7 (78) $[M + Na]^+$, 1432.7 (23) $[M + H]^+$; elemental analysis (%) calcd. for $C_{74}H_{108}N_6O_{22}$ (1432.75): C 61.99, H 7.59, N 5.86; found: C 61.70, H 7.32, N 5.34.

3,5-Bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzamido) propoxy)benzoic acid 4b

A solution of *p*-toluenesulfinic acid hydrate (1.01 g, 6.14 mmol) in methanol (10 mL) was added dropwise at RT to a mixture of **4a** (7.35 g, 5.12 mmol) and $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) in DCM (100 mL). The reaction was monitored with TLC and stopped after 4 h. The solvent was removed under vacuum at RT and chromatographic separation (silica gel, DCM/methanol 10/1) and ethyl acetate/methanol 15/1) yielded **4c** as colorless foam (6.1 g, 85%).; R_f = 0. 24 (10:1 DCM/MeOH).; M.p. = 78-80 ° C; ^{1}H NMR: δ = 1.30 (s, 36 H; ^{t}Bu), 1.83 (m, 8 H; CH_2), 2.02 (m, 4 H; CH_2), 2.35 (t, 8 H; $CH_2CO_2{}^tBu$), 2.46 (t, 8 H;

NHCOCH_2), 3.25 (m, 8 H; CH_2NH), 3.53 (m, 4 H; CH_2NH), 3.85 (m, 8 H; PhOCH_2), 3.97 (m, 4 H; PhOCH_2),6.35 (t, 2 H; Ph), 6.45 (t, 1 H; Ph), 6.82 (d, 4 H; Ph), 7.02 (d, 2 H; Ph), 7.50 (br, 4 H; NH); ^{13}C NMR : δ = 27.95 (C(<u>C</u>H_3)$_3$), 28.89, 28.95 (OCH_2<u>C</u>H_2CH_2N), 30.78 (<u>C</u>H_2COC^{t}Bu), 31.99 (<u>C</u>H_2CH_2COC^{t}Bu), 36.83, 37.71 (OCH_2CH_2<u>C</u>H_2N), 65.90, 66.43 (O<u>C</u>H_2CH_2CH_2N), 80.60 (<u>C</u>(CH_3)$_3$), 104.60, 105.78, 108.22, 136.10, 159.73, 159.94 (Ar), 167.67 (CO) , 177.33, 177.43 (NHCOO); FAB-MS (2 kV): *m/z* (rel-%): 1415.17 (85) [M + Na]$^+$, 1393.8 (28) [M + H]$^+$; elemental analysis (%) calcd. for $C_{71}H_{104}N_6O_{22}$ (1393.63): C 61.19, H 7.52, N 6.03; found: C 61.20, H 7.01, N 5.81.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy) benzamido)propoxy)benzamido)propoxy)benzyl alcohol 5a

N-Hydroxybenzotriazole (1.25 g, 9.3 mmol) was added to a solution of acid **4b** (10.8 g, 7.74 mmol) in dry DMF (150 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (1.96 g, 10.23 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (1.95 g, 19.32 mmol) and **1a** (1.56 g, 3.25 mmol) in methanol/DMF (10 mL, 1/ 1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature and stirred for 16 h. Solvent was removed in vacuo and residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Two successive chromatographic separations [silica gel, DCM/methanol (20/1) and ethyl acetate/methanol (15/1)] yielded **5a** as a

colorless foam (7.40 g, 75 %); R_f = 0.44 (10:1 DCM/MeOH); M.p.: 84 – 86 °C.; ^{1}H NMR ($CDCl_3/CD_3OD$): δ = 1.41 (s, 72 H; ^{t}Bu), 1.93 (m, 16 H; CH_2), 2.07 (m, 12 H; CH_2), 2.41 (t, 16 H; $CH_2CO_2{}^t$Bu), 2.53 (t, 16 H; NHCOCH_2), 3.35 (m, 16 H; CH_2NH), 3.55 (m, 12 H; CH_2NH), 3.96 (m, 16 H; $PhOCH_2$), 4.02 (m, 12 H; $PhOCH_2$), 4.54 (s, 2 H; OCH_2Ph), 6.30 (t, 1 H; Ph), 6.49 (d, 2 H; Ph), 6.52 (t, 4 H, Ph), 6.91 (d, 12 H; Ph), 7.37, 7.82, 7.92 (br, 14 H; NH); ^{13}C NMR ($CDCl_3/CD_3OD$): δ = 28.04 ($C(\underline{C}H_3)_3$), 28.84, 28.96, 29.03 ($OCH_2\underline{C}H_2CH_2N$), 30.92 ($\underline{C}H_2COC(CH_3)_3$), 31.00 ($\underline{C}H_2CH_2COC{}^t$Bu), 36.65, 37.79, 37.52, 37.91 ($OCH_2CH_2\underline{C}H_2N$), 65.94, 66.35 ($O\underline{C}H_2CH_2CH_2N$), 66.47 ($OCH_2$), 81.08 ($\underline{C}(CH_3)_3$), 100.48, 104.81, 105.44, 105.85, 136.44, 136.59 144.15, 160.02, 160.05 (Ar), 168.12, 168.25, 168.33 (CO) , 172.70, 172.75 (NHCOO); HRMS-MALDI MS: *m/z* (rel-%): 1778 (100) [M – 8 x ($C_8H_{13}O_3$) + Na]$^+$, 3028 (45) [M + Na]$^+$; elemental analysis (%) calcd. for $C_{155}H_{226}N_{14}O_{45}$ (3003.57): C 61.94, H 7.59, N 6.52; found: C 61.77, H 7.62, N 6.35.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy) benzamido)propoxy)benzamido)propoxy) allyl benzoate 5b

N-Hydroxybenzotriazole (1.86 g, 13.77 mmol) was added to a solution of acid **4b** (16 g, 11.48 mmol) in dry DCM (500 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (2.90 g, 15.14 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (3.02 g, 29.88 mmol) and **1b** (2.67 g, 4.98 mmol) in methanol/DCM (30 mL, 1/ 1) was added dropwise at -10°C. The resulting mixture was warmed to room

temperature, stirred for 16 h and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Two successive chromatographic separations [silica gel, DCM/methanol (25/1 and 10/1)] yielded **5b** as a colorless foam (9.57 g, 63 %); R_f = 0.34 (DCM/methanol 10/1); M.p.: 85–87 ° C; GPC: Monomodal peak at 3,100 with PDI = 1.01; ^{1}H NMR (CD_3OD): δ = 1.34 (s, 72 H; ^{t}Bu), 1.86 (m, 16 H; CH_2), 2.01 (m, 12 H; CH_2), 2.34 (t, 16 H; $CH_2CO_2{}^t$Bu), 2.46 (t, 16 H; NHCOC*H*$_2$), 3.28 (m, 16 H; C*H*$_2$NH), 3.48 (m, 12 H; C*H*$_2$NH), 3.89 (m, 16 H; $PhOCH_2$), 3.95 (m, 8 H; $PhOCH_2$), 4.00 (m, 4 H; $PhOCH_2$), 4.70 (d, 2 H; $PhCO_2CH_2$), 5.25 (dd, 2 H; CH=C*H*$_2$), 5.93 (ddd, 1 H; C*H*=CH_2), 6.45 (t, 2 H; Ph), 6.55 (t, 1 H; Ph), 6.83 (d, 12 H, Ph), 6.85 (d, 4 H; Ph); ^{13}C NMR (CD_3OD): δ = 27.94 (C(*C*H$_3$)$_3$), 28.83, 28.89, 28.96 ($OCH_2CH_2CH_2N$), 30.84 (*C*H$_2$COC(CH$_3$)$_3$), 30.92 (*C*H$_2$CH$_2$COC^{t}Bu), 36.57, 36.70, 37.42, ($OCH_2CH_2CH_2N$), 53.45 (OCH_2), 65.90, 66.3, 66.52 (O*C*H$_2$CH$_2$CH$_2$N), 81.93 (*C*(CH$_3$)$_3$), 104.72, 105.80, 136.43, 136.56, 159.85, 159.97 (Ar), 118.43 (*C*H$_2$=C), 132.01 (CH_2=*C*), 167.98, 168.05 (CO) , 172.56, 172.63 (NHCOO); MALDI–TOF MS: *m/z* 3083.1 $[M + Na]^+$, 3098 $[M + K]^+$; elemental analysis (%) calcd. for $C_{158}H_{228}N_{14}O_{46}$ (3059.61): C 62.03, H 7.51, N 6.42; found: C 61.74, H 7.69, N 6.53.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy) benzamido)propoxy)benzamido)propoxy)benzoic acid 5c

A solution of *p*-toluenesulfinic acid hydrate (0.60 g, 3.39 mmol) in methanol (10 mL) was added dropwise at RT to a mixture of **5b** (8.66 g, 2.83 mmol) and $Pd(PPh_3)_4$ (0.164 g, 0.141 mmol) in DCM (100 mL). The reaction was monitored with TLC and stopped after 4 h. The solvent was removed under vacuum at RT and chromatographic separation performed twice (silica gel, DCM/methanol 20/1 and 10/1) yielded **5c** as colorless foam (6.85 g, 80%); R_f = 0.42 (DCM/Methanol 10/1); M.p.: 85–90 ° C; GPC: Monomodal peak at 3019 with PDI = 1.05; ^{1}H NMR (CD_3OD): δ = 1.24 (s, 72 H; ^{t}Bu), 1.76 (m, 16 H; CH_2), 1.87 (m, 12 H; CH_2), 2.24 (t, 16 H; $CH_2CO_2{}^t$Bu), 2.35 (t, 16 H; NHCOCH_2), 3.17 (m, 16 H; CH_2NH), 3.37 (m, 12 H; CH_2NH), 3.80 (m, 16 H; $PhOCH_2$), 3.96 (m, 12 H; $PhOCH_2$), 6.367 (br, 4 H; Ph), 6.42 (br, 1 H; Ph), 6.76 (br, 12 H, Ph), 6.97 (br, 4 H; Ph); ^{13}C NMR (CD_3OD): δ = 27.69 ($C(\underline{C}H_3)_3$), 28.63, 28.89 ($OCH_2\underline{C}H_2CH_2N$), 30.84 ($\underline{C}H_2COC(CH_3)_3$), 30.92 ($\underline{C}H_2CH_2COC{}^t$Bu), 36.57, 36.70, 37.42, ($OCH_2CH_2\underline{C}H_2N$), 65.90, 66.3, 66.52 ($O\underline{C}H_2CH_2CH_2N$), 81.93 ($\underline{C}(CH_3)_3$), 104.72, 105.80, 136.43, 136.56, 159.85, 159.97 (Ar), 167.98, 168.05 (CO) , 172.56, 172.63 (NHCOO); MALDI – TOF MS: *m/z* 3040.4 $[M + Na]^+$, 3056.2 $[M + K]^+$; elemental analysis (%) calcd. for $C_{155}H_{224}N_{14}O_{46}$ (3017.56): C 61.65, H 7.48, N 6.49; found: C 61.61, H 7.28, N 5.96.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy) benzamido)propoxy)benzamido)propoxy)benzyl methacrylate MG3

A solution of MAC (0.21 g, 2.05 mmol) in DMF (10 mL) was added dropwise to a mixture of **5a** (3.83 g, 1.27 mmol), triethylamine (TEA; 0.51 g, 8.08

mmol), and DMAP (100 mg) in dry DMF (100 mL) at 0°C over 30 min. The resulting mixture was warmed to room temperature and stirred for 16 h. The solvent was removed in vacuo and the residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Three successive chromatographic separations (silica gel, DCM/methanol 10/1 and ethyl acetate/methanol 10/1) yielded **MG3** as colorless foam (2.95 g, 75 %); R_f = 0.40 (DCM/methanol 10/1); M.p.: 87 – 90 ° C.; GPC: Monomodal peak at 3019 with PDI = 1.10; ^{1}H NMR ($CDCl_3$/CD_3OD): δ = 1.41 (s, 72 H; ^{t}Bu), 1.97 (m, 19 H; C*H*$_2$+C=CC*H*$_3$), 2.10 (m, 12 H; CH_2), 2.41 (t, 16 H; $CH_2CO_2{}^t$Bu), 2.52 (t, 16 H; NHCOC*H*$_2$), 3.33 (m, 16 H; C*H*$_2$NH), 3.55 (m, 12 H; C*H*$_2$NH), 4.00 (m, 16 H; $PhOCH_2$), 4.05 (m, 12 H; $PhOCH_2$), 5.07 (s, 2 H; OCH_2Ph), 5.59 (m, 1 H; C=CH_2), 6.13 (s, 1 H; C=CH_2), 6.40 (t, 1 H; Ph), 6.50 (d, 2 H; Ph), 6.56 (t, 4 H, Ph), 6.93 (d, 12 H; Ph);^{13}C NMR ($CDCl_3$/CD_3OD): δ =1 8.33 (C=C*C*H$_3$), 27.95 (C(*C*H$_3$)$_3$), 28.79, 28.94, 29.58 (OCH_2*C*H_2CH_2N), 30.70 (*C*H$_2$COC(CH$_3$)$_3$), 30.89 (*C*H$_2$CH$_2$COC^{t}Bu), 36.51, 37.24, 37.56 (OCH_2CH_2*C*H_2N), 65.54, 66.80 (O*C*H$_2$CH$_2$CH$_2$N), 66.08 (OCH_2), 80.53 (*C*(CH$_3$)$_3$), 101.06, 104.17, 105.60, 106.15, 136.32, 138.28, 159.69, 159.89 (Ar), 126.03 (*C*H$_2$=C), 135.91 (CH_2=*C*), 167.10, 167.39, 167.47 (CO) , 172.07, 172.72 (NHCOO); HRMS-MALDI MS: *m/z* (rel-%) 3095.4 [M + Na]$^+$; elemental analysis (%) calcd. for $C_{159}H_{230}N_{14}O_{46}$ (3073.63): C 62.21, H 7.54, N 6.38; found: C 62.08, H 7.39, N 6.24.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido) propoxy)benzamido)propoxy)benzamido)propoxy)benzamido)propoxy) benzyl alcohol 6a

N-Hydroxybenzotriazole (0.31 g, 2.28 mmol) was added to a solution of acid **5c** (5.75 g, 1.90 mmol) in dry DMF (150 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (0.48 g, 2.50 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (0.51 g, 5.10 mmol) and **1a** (0.41 g, 0.85 mmol) in methanol/DMF (5 mL, 1/ 1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature and stirred for 48 h. The solvent was removed in vacuo and the residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Three successive chromatographic separations [silica gel, DCM/methanol (10/1) and ethyl acetate/methanol (7/1)] yielded **6a** as a colorless foam (3.50 g, 66 %); R_f = 0.28 (DCM/methanol 10/1); GPC: Monomodal peak at 9,100 with PDI = 1.10; M.p.: 90 - 92 °C; ^{1}H NMR: δ = 1.38 (s, 144 H; ^{t}Bu), 1.84 (br, 48 H; CH_2), 1.94 (br, 12 H; CH_2), 2.41 (t, 32 H; $CH_2CO_2{}^t$Bu), 2.50 (t, 32 H; NHCOCH_2), 3.30 (br, 48 H; CH_2NH), 3.46 (br, 12 H; CH_2NH), 3.84 (br, 60 H; $PhOCH_2$), 4.48 (br, 2 H; OCH_2Ph), 6.20, 6.40, 6.86, 7.02 (br, 45 H; Ph), 7.97 (br, 30 H; NH); ^{13}C NMR: δ = 28.21 (C($\underline{C}H_3)_3$), 29.20, 29.34 ($OCH_2\underline{C}H_2CH_2N$), 31.11 ($\underline{C}H_2COC(CH_3)_3$), 31.35 ($\underline{C}H_2CH_2COC{}^t$Bu), 36.92, 37.65 $OCH_2CH_2\underline{C}H_2N$), 66.25, 66.51, 66.52 ($O\underline{C}H_2CH_2CH_2N$), 66.71 ($OCH_2$), 80.69 ($\underline{C}(CH_3)_3$), 91.83, 104.90, 106.24,

136.91, 136.59, 160.14,167.60 (Ar), 167.60, 167.68 (CO) , 172.14, 172.30 (NHCOO); MALDI-TOF MS: *m/z* (%): 6253.3 (100) $[M]^+$; elemental analysis (%) calcd. for $C_{323}H_{466}N_{30}O_{93}$ (6253.27): C 62.00, H 7.51, N 6.72; found: C 61.74, H 7.30, N 6.70.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido) propoxy)benzamido)propoxy)benzamido)propoxy)benzamido)propoxy) allyl benzoate 6b

N-Hydroxybenzotriazole (0.41 g, 3.05 mmol) was added to a solution of acid **5c** (7.67 g, 2.54 mmol) in dry DMF (200 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (0.65 g, 3.35 mmol) was added at -20°C and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (1 g, 10 mmol) and **1b** (0.536 g, 1 mmol) in methanol/DMF (20 mL, 1/1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature and stirred for 48 h. The solvent was removed in vacuo and the residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Three successive chromatographic separations [silica gel, DCM/methanol (10/1) and ethyl acetate/methanol (10/1)] yielded **6b** as a colorless foam (3.50 g, 65 %); R_f = 0.37 (DCM/methanol 10/1); GPC: Monomodal peak at 9,300 with PDI = 1.10; M.p.: 97 – 99 °C; ^{1}H NMR: δ = 1.41 (s, 144 H; ^{t}Bu), 1.93 (br, 48 H; CH_2), 2.05 (br, 12 H; CH_2), 2.41 (t, 32 H; $CH_2CO_2{}^t$Bu), 2.53 (t, 32 H; NHCOCH_2), 3.36 (br, 48 H; CH_2NH), 3.54 (br, 12

H; C*H*$_2$NH), 3.98 (br, 48 H; PhOCH_2), 4.02 (br, 12 H; PhOCH_2), 4.70 (d, 2 H; PhCO$_2$CH_2), 5.32 (dd, 2 H; CH=C*H*$_2$), 5.98 (ddd, 1 H; C*H*=CH_2), 6.54, 6.62, 6.92, 7.13, 7.35 (br, 45 H; Ph), 7.98 (br, 30 H; NH); ^{13}C NMR: δ = 28.07 (C(*C*H$_3$)$_3$), 29.13 (OCH$_2$*C*H$_2$CH$_2$N), 31.03 (*C*H$_2$*C*H$_2$COC(CH$_3$)$_3$), 36.73, 36.86, 37.57 37.67 (OCH$_2$CH$_2$*C*H$_2$N), 66.06, 66.40 (O*C*H$_2$CH$_2$CH$_2$N), 66.51 (OCH$_2$), 81.17 (*C*(CH$_3$)$_3$), 104.91, 106.01,106.85, 108.14, 136.56, 136.55, 136.63, 160.18 (Ar), 118.57 (*C*H$_2$=C), 132.18 (CH$_2$=*C*),166.45, 168.37, 168.42, 168.49 (CO) , 172.79, 172.92, 173.01 (NHCOO); MALDI - TOF: *m/z* (rel-%): 6331.97 (100) [M + Na$^+$]; elemental analysis (%) calcd. for $C_{326}H_{468}N_{30}O_{94}$ (6311.4): C 62.04, H 7.47, N 6.66; found: C 61.28, H 7.39, N 6.75.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido) propoxy)benzamido)propoxy)benzamido)propoxy)benzamido)propoxy) benzoic acid 6c

A solution of *p*-toluenesulfinic acid hydrate (0.162 g, 0.912 mmol) in methanol (10 mL) was added dropwise at RT to a mixture of **6b** (4.8 g, 0.76 mmol) and Pd(PPh$_3$)$_4$ (0.05 g, 0.038 mmol) in DCM/MeOH (150 mL , 1:1 v/v). The reaction was monitored with TLC and stopped after 4 h. The solvent was removed under vacuum at RT and chromatographic separation performed twice (silica gel, DCM/methanol 20/1 and 10/1) yielded **6c** as colorless foam (3.30 g, 70%); R_f = 0.33 (DCM/methanol 10/1) .; GPC: Monomodal peak at 9682 with PDI = 1.05; M.p.: 93 – 95 °C.; ^{1}H NMR: δ = 1.41 (s, 144 H; ^{t}Bu), 1.94 (m, 48 H; CH$_2$), 2.06 (m, 12 H; CH$_2$), 2.43 (t, 32 H; CH$_2$CO$_2$^{t}Bu), 2.54 (t,32 H; NHCOC*H*$_2$), 3.35 (m, 48 H; C*H*$_2$NH), 3.54 (m, 12 H; C*H*$_2$NH), 3.98 (m,

48 H; $PhOCH_2$), 4.02 (m, 12 H; $PhOCH_2$), 6.54, 6.59, 6.92, 7.12, 7.16, 7.40 (br, 45 H; Ph), 7.71, 7.86, 8.00 (br, 30 H; NH); ^{13}C NMR: δ = 28.10 ($C(\underline{C}H_3)_3$), 29.18 ($OCH_2\underline{C}H_2CH_2N$), 31.07 ($\underline{C}H_2\underline{C}H_2COC(CH_3)_3$), 36.78, 37.62 ($OCH_2CH_2\underline{C}H_2N$), 66.11, 66.45 ($O\underline{C}H_2CH_2CH_2N$), 81.20 ($\underline{C}(CH_3)_3$), 104.99, 106.07,130.47, 130.57, 130.88, 130.98, 133.82, 133.91, 133.93, 134.01, 135.31, 131.33, 136.60, 136.67 (Ar), 160.25, 168.46, 168.51 (CO) , 172.82, 173.01 (NHCOO); MALDI–TOF MS: *m/z* (rel-%): 6310.17 (100) $[M+Na]^+$; elemental analysis (%) calcd. for $C_{323}H_{464}N_{30}O_{94}$ (6271.36): C 61.86, H 7.46, N 6.70; found: C 61.60, H 7.58, N 6.19.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido) propoxy)benzamido)propoxy)benzamido)propoxy)benzamido)propoxy) benzyl methacrylate MG4

A solution of MAC (0.164 g, 1.56 mmol) in DMF (5 mL) was added dropwise to a mixture of **6a** (4.90 g, 0.78 mmol), triethylamine (TEA; 0.24 g, 2.34 mmol), and DMAP (300 mg) in dry DMF (100 mL) at 0°C over 30 min. The resulting mixture was warmed to room temperature and stirred for 16 h. The solvent was removed in vacuo and the residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Three successive chromatographic separations [silica gel, DCM/methanol (20/1, 10/1)] and ethyl acetate/methanol 10/1) yielded **MG4** as colorless foam (4.15 g, 85 %); R_f = 0.31 (DCM/methanol 10/1); GPC: Monomodal peak at 10,300 with PDI = 1.10; M.p.: 93 – 95 °C.; ^1H NMR ($CDCl_3/CD_3OD$): δ = 1.42 (s, 144

H; ^{t}Bu), 1.95 (m, 48 H; CH_2), 2.05 (m, 15 H; C*H*$_2$+C=CC*H*$_3$), 2.41 (t, 32 H; $CH_2CO_2{}^{t}Bu$), 2.53 (t, 32 H; NHCOC*H*$_2$), 3.34 (m, 48 H; C*H*$_2$NH), 3.54 (m, 12 H; C*H*$_2$NH), 3.98 (m, 48 H; $PhOCH_2$), 4.09 (m, 12 H; $PhOCH_2$), 5.06 (s, 2 H; OCH_2Ph), 5.60 (m, 1 H; C=CH_2), 6.12 (s, 1 H; C=CH_2), 6.38, 6.48, 6.56, 6.95, 7.02, 7.63 (br, 45 H; Ph), 7.82, 8.32 (br, 30 H; NH); ^{13}C NMR ($CDCl_3$/CD_3OD): δ = 18.44 (C=C<u>*C*</u>H$_3$), 28.21 (C(<u>*C*</u>H$_3$)$_3$), 29.51, 29.78 (OCH_2<u>*C*</u>H_2CH_2N), 31.22 (<u>*C*</u>$H_2COC(CH_3)_3$), 31.31 (<u>*C*</u>$H_2CH_2COC{}^{t}Bu$), 37.00, 37.84, 37.91, 38.01 (OCH_2CH_2<u>*C*</u>H_2N), 66.29, 66.61, 66.71, 66.85 (O<u>*C*</u>$H_2CH_2CH_2N$), 69.08 (OCH_2), 81.36 (<u>*C*</u>$(CH_3)_3$), 101.59, 105.19, 106.37, 106.96, 136.90, 136.96, 138.90, 160.65, 160.74 (Ar), 126.58 (<u>*C*</u>H_2=C), 136.65 (CH_2=<u>*C*</u>), 168.06 (CH_2=CH<u>*C*</u>O) , 168.95, 169.04, 169.06, 173.04 (CO), 173.58 (NHCOO); MALDI - TOF: *m/z* (rel-%): 6350.7 (100) $[M + Na]^+$; elemental analysis (%) calcd. for $C_{327}H_{470}N_{30}O_{94}$ (6325.45): C 62.09, H 7.49, N 6.64; found: C 61.82, H 7.61, N 6.56.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzamido)propoxy)benzamido)propoxy)benzamido)propoxy) benzamido)propoxy) benzyl alcohol 7a

N-Hydroxybenzotriazole (0.085 g, 0.63 mmol) was added to a solution of acid **6c** (3.3 g, 0.53 mmol) in dry DMF (150 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (0.135 g, 0.69 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride had dissolved completely (ca. 4 h). Then a solution of TEA (0.20 g, 2 mmol) and **1a** (0.105 g, 0.21 mmol) in methanol/DMF (5 mL, 1/1)

was added dropwise at -10°C. The resulting mixture was warmed to room temperature and stirred for 48 h. The solvent was removed in vacuo and the residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Three successive chromatographic separations (silica gel, DCM/methanol 7/1) and ethyl acetate/methanol 5/1) yielded **7a** as colorless foam (2.12 g, 80%); R_f = 0.35 (DCM/methanol 7/1); GPC: Monomodal peak at 21,750 with PDI = 1.10; M.p: 105 - 107 °C; ^{1}H NMR: δ = 1.38 (s, 288 H; ^{t}Bu), 1.94, 2.05 (m, 124 H; CH_2), 2.42 (t, 64 H; $CH_2CO_2{}^t$Bu), 2.53 (t, 64 H; NHCOCH_2), 3.36, 3.53 (m, 124 H; CH_2NH), 3.95, 4.01 (m , 124 H; $PhOCH_2$), 4.46 (br, 2 H; OCH_2Ph), 6.30, 6.47, 6.54, 6.93 (br, 93 H; Ph), 7.58, 8.15 (br, 62 H; NH); ^{13}C NMR: δ = 28.13 (C($\underline{C}H_3)_3$), 29.26 ($OCH_2\underline{C}H_2CH_2N$), 31.07 ($\underline{C}H_2COC(CH_3)_3$), 31.12 ($\underline{C}H_2CH_2COC{}^t$Bu), 36.82, 37.66, 37.73 $OCH_2CH_2\underline{C}H_2N$), 66.10, 66.29, 66.41 ($O\underline{C}H_2CH_2CH_2N$), 60.97 ($OCH_2$), 81.25 ($\underline{C}(CH_3)_3$), 104.90, 106.13, 136.64, 136.71, 160.33 (Ar), 168.61, 168.66 (CO) , 172.88, 173.17 (NHCOO); MALDI - TOF: *m/z* (rel-%): 12784.84 (90) $[M+Na]^+$; elemental analysis (%) calcd. for $C_{659}H_{946}N_{62}O_{189}$ (12761.02): C 62.03, H 7.47, N 6.81; found: C 61.20, H 7.56, N 6.73.

3,5-Bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzamido)propoxy)benzamido)propoxy)benzamido)propoxy) benzamido)propoxy) benzyl methacrylate MG5

A solution of MAC (0.04 g, 0.37 mmol) in DMF (5 mL) was added dropwise to a mixture of **7a** (2.37 g, 0.185 mmol), triethylamine (TEA; 0.06 g, 0.55 mmol)

and DMAP (200 mg) in dry DMF (150 mL) at 0 °C over 30 min. The resulting mixture was warmed to room temperature and stirred for 16 h. The solvent was removed in vacuo and the residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Five successive chromatographic separations [silica gel, DCM/methanol (8/1, 5/1) and ethyl acetate/methanol (5/1)] yielded **MG5** as colorless foam (1.45 g, 60 %); R_f = 0.41 (DCM/methanol 10/1); GPC: Monomodal peak at 22852 with PDI = 1.10; M.p.= 107 – 109 °C; ^{1}H NMR ($CDCl_3/CD_3OD$): δ = 1.41 (s, 288 H; ^{t}Bu), 1.94, 2.05 (m, 127 H; CH_2 and C=CCH_3), 2.42 (t, 64 H; $CH_2CO_2{}^t$Bu), 2.51 (t, 64 H; NHCOCH_2), 3.35, 3.53 (m, 124 H; CH_2NH), 3.97, 4.01 (m , 124 H; $PhOCH_2$), 5.05 (br, 2 H; OCH_2Ph), 5.58 (m, 1 H; C=CH_2), 6.12 (s, 1 H; C=CH_2), 6.38, 6.47, 6.54, 6.93, 7.01, (br, 93 H; Ph), 7.57, 8.14 (br, 62 H; NH); ^{13}C NMR ($CDCl_3/CD_3OD$): δ = 21.06 (C=C$\underline{C}H_3$), 28.13 (C($\underline{C}H_3)_3$), 29.25 ($OCH_2\underline{C}H_2CH_2N$), 31.08 ($\underline{C}H_2COC(CH_3)_3$), 31.12 ($\underline{C}H_2CH_2COC{}^t$Bu), 36.83, 36.96.37.50, 37.68 ($OCH_2CH_2\underline{C}H_2N$), 66.11, 66.43 ($O\underline{C}H_2CH_2CH_2N$), 60.97 ($OCH_2$), 81.25 ($\underline{C}(CH_3)_3$), 104.97, 105.19, 106.13, 136.65, 136.72, 160.34 (Ar), 136.65 ($\underline{C}H_2$=C), 136.72 (CH_2=$\underline{C}$), 168.06 (CH_2=CH$\underline{C}$O), 168.60, 168.65, 172.88 (CO), 173.16 (NHCOO); MALDI - TOF: *m/z* (rel-%) 12850.69 (90) [M + Na]$^+$; elemental analysis (%) calcd. for $C_{663}H_{950}N_{62}O_{190}$ (12829.10): C 62.07, H 7.46, N 6.77; found: C 61.28, H 7.64, N 6.66.

Poly(3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzyl methacrylate) PG1

To monomer **MG1** (1.68 g, 2.64 mmol) and AIBN (1.3 mg, 0.0079 mmol) in a Schlenk Tube was added DMF (1.75 g, 1.85 mL) and the mixture stirred for 30 min until everything had dissolved. Then the tube was weighed and vacuum of 2 mbar applied until 869 mg of DMF had been removed. This was typically the case after 3 h at RT. The obtained highly concentrated solution was still homogenous. Then the tube was placed into a 65°C preheated oil bath. After 4-5 h the viscosity had increased to the point that magnetic stirring was not possible anymore but the heating was continued for another 12 h. After cooling, DCM (3 mL) was added and the resulting solution precipitated into CH_3OH/H_2O (3/1). This procedure was repeated four times to give **PG1** as colorless precipitate (1.47 g, 90%) which was collected and dried under high vacuum; ^{1}H NMR: δ = 0.72 (br, 2 H, CH_2), 0.93 (br, 3 H, CH_3), 1.43 (br, 18 H; ^{t}Bu), 1.90 (br, 4 H; PhOC*H*$_2$), 2.46 (br, 4 H; $CH_2CO_2{}^t$Bu), 2.54 (br, 4 H; NHCOC*H*$_2$), 3.35 (br, 4 H; C*H*$_2$NH), 3.88 (br, 4 H; $PhOCH_2$), 4.75 (br, 2 H; OCH_2), 6.35 (br, 1 H; Ph); ^{13}C NMR : δ = 28.07, 29.10, 30.89, 36.59, 65.46, 80.39, 128.31, 172.13; elemental analysis (%) calcd. for $(C_{33}H_{50}N_2O_{10})_n$ $(634.77)_n$: C 62.44, H 7.94, N 4.41; found: C 62.59, H 7.80, N 4.56.

Poly(3,5-Bis(3-(4-*tert*-butoxy-4-oxobutanaoicacid)propoxy)benzyl methacrylate) PG1a

To neat **PG1** (0.5 g, 0.78 mmol) TFA (2.5 mL, 3.7 g, 32 mmol) was added. After stirring for 12 h, methanol (1 mL) and TFA (1 mL) were added and the mixture was left stirring for 12 h. Precipitation into DCM gave **PG1a** as

colorless solid (0.4 g, 95 %); ^{1}H NMR: δ = 0.72 (br, 2 H, CH_2), 0.93 (br, 3 H, CH_3), 1.90 (br, 4 H; PhOC*H*$_2$), 2.46 (br, 4 H; CH_2CO_2), 2.54 (br, 4 H; NHCOC*H*$_2$), 3.35 (br, 4 H; C*H*$_2$NH), 3.88 (br, 4 H; $PhOCH_2$), 4.75 (br, 2 H; OCH_2), 6.35 (br, 1 H; Ph); ^{13}C NMR: δ = 29.10, 30.89, 36.59, 65.46, 80.39, 128.31, 172.13.

Poly(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-tert-butoxy-4-oxobutanamido) propoxy) benzamido)propoxy)benzamido)propoxy)benzyl methacrylate) PG3

To monomer **5d** (1.16 g, 0.377 mmol) and AIBN (1 mg, 0.0069 mmol) in a Schlenk Tube was added DMF (0.85 g, 0.90 mL) and the mixture stirred for 30 min until everything had dissolved. Then the tube was weighed and vacuum of 2 mbar applied until 400 mg of DMF had been removed. This was typically the case after 3 h at RT. The obtained highly concentrated solution was still homogenous. Then the tube was put into a 75°C preheated oil bath. After 24 h the viscosity had increased to the point that magnetic stirring was not possible anymore but reaction mixture was continued to be heated for another 12 h. The polymer formed was dissolved in DCM and then purified by column chromatography (silica gel, DCM as eluent) which yielded **PG3** as colorless foam (0.97 g, 85%); ^{1}H NMR ($CDCl_3$/CD_3OD): δ = 0.67 (br, 2 H, CH_2), 0.85 (br, 3 H, CH_3), 1.39 (br, 72 H; ^{t}Bu), 1.85 (br, 28 H; PhOC*H*$_2$), 2.41 (br, 16 H; C*H*$_2$CO$_2$^{t}Bu), 2.47 (br, 16 H; NHCOC*H*$_2$), 3.27 (br, 28 H; C*H*$_2$NH), 3.72 (br, 28 H; OCH_2C*H*$_2$$CH_2$N), 4.65 (br, 2 H; OCH_2Ph), 6.43 (br, 6 H; Ph), 7.02 (br, 12 H, Ph) 7.65 (br, 12 H; NH); ^{13}C NMR: δ = 28.13, 30.85, 30.89,

31.05, 36.72, 67.29, 80.85, 104.18, 106.17, 160.21, 172.47, 172.99; elemental analysis (%) calcd. for $(C_{159}H_{230}N_{14}O_{46})_n$ $(3073.63)_n$: C 62.13, H 7.54, N 6.38; found: C 61.88, H 7.53, N 6.26.

Poly(3,5-bis(3-(3,5-bis(3-(3,5-bis(3-(4-tert-butoxy-4-oxobutanoicacid) propoxy)benzamido)propoxy)benzamido)propoxy)benzyl ethacrylate) PG3a

To neat **PG3** (0.33 g, 0.11 mmol) TFA (5 mL, 7.4 g, 65 mmol) was added. After stirring for 36 h, 1 mL of methanol and 2 mL of TFA were added and mixture was left stirring for 3 d. Evaporation of the solvent under high vacuum **PG3b** as colorless solid (0.265 g, 95 %); ^{1}H NMR ($CDCl_3$/CD_3OD): δ = 0.67 (br, 2 H, CH_2), 0.85 (br, 3 H, CH_3), 2.24 (br, 28 H; PhOC*H*$_2$), 2.44 (br, 16 H; C*H*$_2$C$O_2{}^t$Bu), 2.54 (br, 16 H; NHCOC*H*$_2$), 3.27 (br, 28 H; C*H*$_2$NH), 3.86 (br, 28 H; OCH_2C*H*$_2$$CH_2$N), 4.65 (br, 2 H; OCH_2Ph), 6.45 (br, 6 H; Ph), 6.86 (br, 12 H, Ph) 7.66 – 8.23 (br, 12 H; NH); ^{13}C NMR ($CDCl_3$/CD_3OD): δ = 29.24, 29.56, 30.75, 36.73, 66.01, 104.66, 106.14, 136.60,160.27, 168.32, 172.79, 173.86, 178.43.

Poly(3,5-bis (3-(3,5-bis (3-(3,5-bis(3-(3,5-bis(3-(4-tert-butoxy-4-oxobutan amido) propoxy) benzamido) propoxy) benzamido) propoxy) benzamido) propoxy) benzyl methacrylate) PG4

To monomer **MG4** (2.26 g, 0.357 mmol) and AIBN (1.2 mg, 0.0073 mmol) in a Schlenk Tube was added DMF (1.69 g, 1.8 mL) and the mixture stirred for 30

min. until everything had dissolved. Then the tube was weighed and vacuum of 2 mbar applied until 890 mg of DMF had been removed. This was typically the case after 5 h at RT. The obtained highly concentrated solution was still homogenous. Then the tube was put into a 75°C preheated oil bath. After 36 h the viscosity had increased to the point that magnetic stirring was not possible anymore, but the reaction mixture was continued to be heated for another 12 h at 85°C. The polymer formed was dissolved in DCM and then purified by column chromatography (silica gel, DCM eluent) which yielded **PG4** as colorless foam (1.86 g, 82%); ^{1}H NMR: δ = 0.67 (br, 2 H, CH_2), 0.85 (br, 3 H, CH_3), 1.32 (br, 144 H; ^{t}Bu), 1.81 (br, 60 H; PhOCH_2), 2.39 (br, 32 H; CH_2CO$_2{}^{t}$Bu), 2.45 (br, 32 H; NHCOCH_2), 3.27 (br, 60 H; CH_2NH), 3.80 (br, 60 H; OCH$_2$CH_2CH$_2$N), 4.65 (br, 2 H; OCH$_2$Ph), 6.36 (br, 15 H; Ph), 6.85 (br, 30 H, Ph) 7.44 – 8.17 (br, 30 H; NH); ^{13}C NMR: δ = 27.99, 28.96, 30.79, 36.61, 65.62, 80.51, 104.55, 105.38, 108.69, 136.21, 136.21, 159.77, 167.69, 172.13, 172.39; elemental analysis (%) calcd. for $(C_{327}H_{470}N_{30}O_{94})_n$ $(6325.45)_n$: C 62.09, H 7.49, N 6.64; found: C 61.48, H 7.60, N 6.70.

Poly(3,5-bis (3-(3,5-bis (3-(3,5-bis(3-(3,5-bis(3-(4-*tert*-butoxy-4-oxo butanoic acid) propoxy) benzamido) propoxy) benzamido) propoxy) benzamido) propoxy) benzyl methacrylate) PG4a

To neat **PG4a** (0.516 g, 0.082 mmol) TFA (10 mL, 14.8 g, 130 mmol) was added. After stirring for 36 h, methanol (1 mL) and TFA (2 mL) were added and the mixture was left stirring for 3 d. Evaporation of the solvent under high

vacuum gave **PG4b** as colorless solid (0.420 g, 95 %); ^{1}H NMR ($CDCl_3/CD_3OD$): δ = 0.69 (br, 2 H, CH_2), 0.88 (br, 3 H, CH_3), 1.89, 1.99 (br, 60 H; PhOC*H*$_2$), 2.45 (br, 32 H; C*H*$_2$CO$_2$^{t}Bu), 2.56 (br, 32 H; NHCOC*H*$_2$), 3.30, 3.48 (br, 60 H; C*H*$_2$NH), 3.91 (br, 60 H; $OCH_2CH_2CH_2N$), 4.68 (br, 2 H; OCH_2Ph), 6.49 (br, 15 H; Ph), 6.90 (br, 30 H, Ph) 7.68 – 8.20 (br, 30 H; NH); ^{13}C NMR ($CDCl_3/CD_3OD$) : δ = 29.25, 29.59, 30.78, 36.77, 66.02, 106.12, 136.64, 159.16, 160.33, 172.88, 173.99.

General procedure for the deprotonation of the polymers PG1b-PG4b

The respective polymer was dissolved in methanol at an initial pH = 5-6 (Litmus paper). A solution of KOH pellets in MeOH was added dropwise until precipitation set in which happened at pH = 7-8. The precipitate was recovered by filtration and dried under vacuo. The anionized polymers **PG1c**-**PG4c** were fully soluble at pH = 9, as was verified by shining laser light through the solutions.