7. Experimental section (Experimenteller Teil)

7.1. General remarks

All chemicals were purchased from Aldrich, Acros, Fluka and Avocado and used without further purification if not described different. The solvents were dried and purified using standard procedures.[89]

Experiments under a protective atmosphere were carried out using Schlenk-technique with nitrogen in a purity of 4.7 (Messner-Griesheim).

All reactions were monitored with thin layer chromatography (TLC) on silica gel on an aluminium foil (Merck). For column chromatography silica gel from Merck („Kieselgel 60“, 230-400mesh) was used.

All ^{1}H- and ^{13}C-NMR-spektra were recorded with a Bruker spektrometer AC 259 (250 MHz), AM 270 (270 MHz) or AC 500 (500 MHz). Tetramethylsilane was used as an external standard. For the description of the signals the following abreviations were used: s-singulett, d-dublett, dd-dublett of a dublett, t-triplett, q-quartett, m-multiplett, br-broad signal.

Mass spectra were recorded on a Varian spectrometer CH 5 DF 7711 and 112 S. Ionisation by Electron Bombardement was used (EI, ionisation energy 70 eV) or for substances with higher masses Fast Atom Bombardement (FAB). For some samples MALDI-Tof-MS (Matrix Assisted Laser Desorption Ionisation Time of Flight) were recorded on a Shimadzu Kraos MALDI 3 using a dithranol matrix.

GPC measurements were carried out with a Waters 150-C ALC/GPC (UV detection at 254 nm) with a toluene standard (calibration: polystyrene).

CHN-analysis were measured with a Perkin-Elmer EA 240. The melting points were measured with a Büchi SMP 510 and are uncorrected. For the thermogravimetric measurements (TGA) a Netzsch TGA-209-apparatus was used.

The molecular dynamics calculation of oligomer **48** was done with *CS Chem 3D Pro*[92] (MM2, 300K, 10fs).

Only CHN-analysis results which differ less than 0.4 from the calculated values are given in this section. For polymers a difference of 1.0 was accepted. For several acids and substances with free amines it was impossible to remove all traces of water and no correct data could be obtained.

7.2. Synthesis of Z-protected dendrons

Ethyl-3,5-bis-(2-cyanoehtenyl)benzoate (**18**):

A solution of 78.0 g ester **17** (0.25 mol), 82.0 ml acrylnitrile (66.25 mg) and 2.62 g triphenylphosphine (0.01 mol) in 120 ml triethylamine is degased. After degasing to the reaction mixture 1.12 g palladium-II-acetat (5 mmol) are added under nitrogen. The solution is heated to 120 °C for 7 days. After complete reaction (TLC) the precipitated solid is collected by filtration of the hot solution. The catalyst is removed by dissolving the colourless solid in dichloromethane and filtration over celite. After the dichloromethane is removed in vacuo the solid is washed with hot ethanol three times to yield 35.3 g (0.14 mol, 56.0%) of **18** as colourless solid.

m.p. 227-228 °C

^{1}H NMR ($CDCl_3$): δ = 1.41 (t, 3 H, CH_3), 4.41 (q, 2 H, CH_2), 6.02 (d, 2 H, =CH), 7.45 (d, 2 H, =CH), 7.62 (m, 1 H, ArH), 8.16 (m, 2 H, ArH).

^{13}C NMR ([D_6]DMSO): δ = 13.9 (CH_3), 61.2 (CH_2), 99.3 (=C), 129.4 (=C), 130.3 (Ar), 131.4 (Ar), 134.9 (Ar), 148.6 (Ar), 164.5 (CO).

MS (EI); *m/z* (%): 252 (39.95) [M^+].

$C_{15}H_{12}N_2O_2$ (252.2): calcd. C 71.42, H 4.79, N 11.10; found C 70.27, H 4.88, N 10.89.

Ethyl-3,5-bis-(2-cyanoethyl)benzoate (**19**):

2.14 g (8.5 mmol) of the ester **18** are hydrogenated at 2 bar over 435 mg palladium/C (20%) in 200 ml ethanol at room temperature for four hours. The catalyst is removed by filtration, cooling of the remaining solution gives 1.82 g (7.1 mmol, 83.6%) of the nitrile **19** as colourless crystals.

m.p. 92°C

^{1}H NMR ($CDCl_3$): δ = 1.38 (t, 3 H, CH_3), 2.64 (t, 4 H, $ArCH_2$), 3.0 (t, 4 H, CH_2CN), 4.35 (q, 2 H, CH_2), 7.31 (m, 1 H, ArH), 7.80 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 18.9 (CH_2), 30.9 (CH_2), 61.1 (CH_2), 118.6 (CN), 128.1 (Ar), 131.5 (Ar), 132.8 (Ar), 138.9 (Ar), 165.8 (CO).

MS (EI); *m/z* (%): 256 (28.58) [M^+].

$C_{15}H_{16}N_2O_2$ (256.1): calcd. C 70.29, H 6.29, N 10.93; found C 70.06, H 6.24, N 10.77.

Ethyl-3,5-bis-(3-aminopropyl)benzoate dihydrochloride (**20a**):

10.0 g (40 mmol) of **18** are hydrogenated in ethanol with hydrochloric acid (28.0 ml, 25% HCl, 198 mmol) at 3.6 bar over palladium/C (2.0 g, 20 mass%) for 14 hours. After removal of the catalyst by filtration the solvent is evaporated in vacuo and 12.9 g (38 mmol, 96.5%) of the hydrochloride **20a** are yielded by percipitation with diethylether as a colourless solid.

m.p. 241°C

^{1}H NMR ([D_4]methanol): δ = 1.37 (t, 3 H, CH_3), 1.99 (m, 4 H, -CH_2-), 2.77 (t, 4 H, $ArCH_2$), 2.96 (t, 4 H, $NHCH_2$), 4.35 (q, 4 H, CH_2), 7.42 (m, 1 H, ArH), 7.76 (m, 2 H, ArH).

^{13}C NMR ([D_4] methanol): δ = 14.6 (CH_3), 30.0 (CH_2), 33.1 (CH_2), 40.3 (CH_2), 62.1 (CH_2), 128.3 (Ar), 132.0 (Ar), 134.4 (Ar), 142.8 (Ar), 167.9 (CO).

MS (EI); *m/z* (%): 264 (7.7) [M^+].

$C_{15}H_{22}Cl_2N_2O_2$ (337.3): calcd. C 53.42, H 7.77, N 8.31; found C 52.15, H 7.54, N 8.21.

Ethyl-3,5-bis-[3(benzyloxycarbonylamino)propyl]benzoate (**20b**):

6.1 g (18 mmol) of the hydrochloride **20a** are suspended with 6.0 g potassium hydroxide in 100 ml THF and 20 ml of water at 0°C. 6.6 ml (7.7 g, 45 mmol) benzylchloroformate are slowly added, the reaction mixture is stirred for one more hour. After complete reaction (TLC) the layers are separated, the organic layer is washed with brine once, the inorganic layer is extracted with diethylether. The combined organic layers are dried with magnesium sulfate, the solvent is removed in vacuo. Crystallisation from ethanol/methanol (1:1) yields 8.9 g (17 mmol, 92.4%) of the protected **20b** as colourless solid.

m.p. 78-80°C

^{1}H NMR ($CDCl_3$): δ = 1.38 (t, 3 H, CH_3), 1.82 (m, 4 H, -CH_2-), 2.64 (t, 4 H, ArCH_2), 3.17 (q, 4 H, NHCH_2), 4.33 (q, 2 H, CH_2), 5.07 (s, 4 H, Z-CH_2), 7.16 (s, 1 H, ArH), 7.29 (m, 10 H, ArH), 7.66 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 31.3 (CH_2), 32.5 (CH_2), 40.3 (CH_2), 60.9 (CH_2), 66.6 (PhCH_2), 127.1 (Ar), 128.0 (Ar), 128.4 (Ar), 130.7 (Ar), 133.1 (Ar), 136.5 (Ar), 141.7 (Ar), 156.4 (CON), 166.7 (CO).

MS (EI); *m/z* (%): 532 (16.15) [M^+].

$C_{31}H_{36}N_2O_6$ (532.6): calcd. C 69.91, H 6.81, N 5.26; found C 69.59, H 6.52, N 5.10.

3,5-Bis-[3(benzyloxycarbonylamino)propyl]benzoic acid (**20c**):

1.2 g (2.3 mmol) of the ester **20b** are heated with 504 mg potassium hydroxide (9.0 mmol) in methanol to 60°C for 4 hours. The reaction is monitored with TLC. When the

reaction is finished, acetic acid is added to give a pH=5. The G1-acid is extracted with dichloromethane. The organic layer is dried with magnesium sulfate. After evaporation of the solvent 1.1 g (2.1 mmol, 93.8%) of the acid **20c** are received as a colourless solid.
m.p. 96°C

^{1}H NMR ($CDCl_3$): δ = 1.81 (m, 4 H, -CH_2-), 2.62 (m, 4 H, ArCH_2), 3.19 (m, 4 H, NHCH_2), 4.90 (s, br, 2 H, NH), 5.08 (s, 4 H, Z-CH_2), 7.18 (s, 1 H, ArH), 7.34 (m, 10 H, ArH), 7.93 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 31.2 (CH_2), 32.5 (CH_2), 40.4 (CH_2), 66.6 (PhCH_2), 127.6 (Ar), 127.9 (Ar), 128.4 (Ar), 130.0 (Ar), 133.7 (Ar), 136.4 (Ar), 141.8 (Ar), 156.5 (CON), 170.5 (CO).

MS (EI); *m/z* (%): 504 (0.1) [M^+].

$C_{29}H_{32}N_2O_6$ (504.6): calcd. C 69.03, H 6.39, N 5.55; found C 69.32, H 6.69, N 5.26.

Ethyl-3,5-[bis(3-{3,5-bis[3-(benzyloxycarbonylamino)propyl]benzoyl}amino)propyl] benzoate (**21a**):

4.40 g (8.7 mmol) of the acid **20c** are dissolved under nitrogen in dry dichloromethane at 0°C. 1.34 g (8.7 mmol) N-hydroxybenzotriazol (HOBt) are added. After 10 minutes 1.84 g (9.6 mmol) N-(3-dimethylaminopropyl)-N'-ethylcarbodiimid hydrochloride (EDC) are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 3.03 ml (2.25 mg, 12.4 mmol) diisopropylethylamine and 1.47 g (4.35 mmol) of the G1-hydrochloride **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Treatment of the crude reaction mixture with methanol in ultrasound yields 4.1g (3.3 mmol, 76.4%) of **21a** as a colourless solid.
m.p. 76°C

^{1}H NMR ($CDCl_3$): δ = 1.31 (t, 3 H, CH_3), 1.72 (m, 8 H, -CH_2-), 1.91 (m, 4 H, -CH_2-), 2.51 (t, 8 H, ArCH_2), 2.66 (t, 4 H, ArCH_2), 3.08 (q, 8 H, NHCH_2), 3.38 (q, 4 H, NHCH_2), 4.32 (q, 2 H, CH_2), 5.02 (s, 8 H, Z-CH_2), 5.12 (s, br, 4 H, NH), 7.02 (s, br, 2 H, ArH), 7.18 (s, 1 H, ArH), 7.35 (s, 22 H, ArH, NH), 7.38 (s, 4 H, ArH), 7.66 (s, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 30.6 (CH_2), 30.9 (CH_2), 32.2 (CH_2), 32.7 (CH_2), 39.3 (CH_2), 39.9 (CH_2), 60.8 (CH_2), 66.3 (PhCH_2), 124.7 (Ar), 127.0 (Ar), 127.6 (Ar), 127.8 (Ar), 128.3 (Ar), 130.5 (Ar), 131.4 (Ar), 133.1 (Ar), 134.7 (Ar), 136.4 (Ar), 141.5 (Ar), 141.8 (Ar), 156.5 (CON), 166.7 (CO), 167.8 (CO).

FAB-MS; *m/z* (%): 1237 (0.44) [M^++H].

$C_{73}H_{84}N_6O_{12}$ (1236.6): calcd. C 70.84, H 6.85, N 6.79; found C 70.44, H 6.63, N 6.70.

3,5-Bis(3-{3,5-bis[3-(benzyloxycarbonylamino)propyl]benzoyl}aminopropyl)benzoic acid (**21b**):

6.9 g (5.6 mmol) of the ester **21a** are stirred in 500 ml of a methanol/water/THF mixture (3:1:1) for 12 hours at 60 °C. After the reaction is finished (TLC), acetic acid is added to give a pH=5. The acid is extracted with dichloromethane. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. One receives 5.66 g (4.7 mmol, 84.1%) of the acid **21b** as colourless solid.

m.p. 91°C

^{1}H NMR ($CDCl_3$): δ = 1.79 (m, 12 H, -CH_2-), 2.50 (m, 8 H, ArCH_2), 2.59 (m, 4 H, ArCH_2), 3.03 (m, 8 H, NHCH_2), 3.25 (m, 4 H, NHCH_2), 5.09 (s, 8 H, Z-CH_2), 5.34 (s, br, 4 H, NH), 6.99 (s, 2 H, ArH), 7.25 (s, 20 H, ArH), 7.34 (s, 2 H, ArH), 7.39 (s, 4 H, ArH), 7.64 (s, 1 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 30.5 (CH_2), 31.0 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 39.2 (CH_2), 40.0 (CH_2), 66.4 (PhCH_2), 124.8 (Ar), 125.9 (Ar), 127.9 (Ar), 128.4 (Ar), 131.6 (Ar),

132.1 (Ar), 134.7 (Ar), 136.5 (Ar), 141.7 (Ar), 142.1 (Ar), 156.6 (CON), 165.5 (CO), 167.9 (CO).

FAB-MS; *m/z* (%): 1231 (0.25) [M^++Na], 1209 (0.59) [M^++H].

$C_{71}H_{80}N_6O_{12}$ (1208.6): calcd. C 70.50, H 6.67, N 6.95; found C 70.00, H 6.78, N 6.78.

Ethyl-3,5-bis-({3-[3,5-bis-(3-{3,5-bis-[3-(benzyloxycarbonylamino)-propyl]-benzoyl}-amino)-propyl]-benzoylamino}-propyl)-benzoate (**22a**):

2.0 g (1.66 mmol) of the G2-acid **21b** are dissolved under nitrogen in dry dichloromethane at 0°C. 253 mg (1.66 mmol) HOBt are added. After 10 minutes 349 mg (1.82 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 0.432 ml (342 mg, 2.65 mmol) diisopropylethylamine and 139 mg (0.41 mmol) of the G1-hydrochloride **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. A precipitating solid is collected and gives after chromatographic work up (silica gel, dichloromethane/2-4% methanol) 784 mg (0.30 mmol, 72.2 %) of the Z-protected G3 **22a** as a colourless solid.

^{1}H NMR ([D_7]DMF): δ = 1.32 (t, 3 H, CH_3), 1.81 (m, 16 H, -CH_2-), 1.94 (m, 12 H, -CH_2-), 2.66 (m, 28 H, ArCH_2), 3.15 (m, 16 H, NHCH_2), 3.41 (m, 12 H, NHCH_2), 4.32 (q, 3 H, CH_2), 5.07 (s, 16 H, Z-CH_2), 7.29 (m, 7 H, Ar), 7.35-7.45 (s, 48 H, Ar, NH), 7.64 (s, 14 H, Ar), 8.02 (s, 6 H, NH).

^{13}C NMR ([D_7]DMF): δ = 14.5 (CH_3), 31.9 (CH_2), 32.2 (CH_2), 33.3 (CH_2), 33.5 (CH_2), 33.6 (CH_2), 39.9 (CH_2), 40.9 (CH_2), 41.1 (CH_2), 61.4 (CH_2), 66.1 (PhCH_2), 125.5 (Ar), 127.4 (Ar), 128.4 (Ar), 129.1 (Ar), 131.2 (Ar), 131.9 (Ar), 135.9 (Ar), 138.4 (Ar), 142.8 (Ar), 142.9 (Ar), 143.5 (Ar), 157.2 (CO), 166.9 (CO), 167.4 (CO), 167.5 (CO).

MS (MALDI-Tof): *m/z* = 2670 [M^++Na], [M^++K].

$C_{157}H_{180}N_{14}O_{24}$ (2647.23): calcd. C 71.23, H 6.85, N 7.41; found C 70.30, H 6.89, N 7.06.

7.3. Synthesis of Boc-protected dendrons

Ethyl-3,5-bis-[3-(tert.butyloxycarbonylamino)propyl]benzoate (**20d**):

9.0 g (26.7 mmol) of the hydrochloride **20a** are suspended with 9.0 g potassium hydroxide in 100 ml THF and 20 ml of water at 0°C. 13.97 g (64.1 mmol) di-*tert.*butyl-dicarbonate are slowly added, the reaction mixture is stirred for one more hour. After complete reaction (TLC) the layers are separated, the organic layer is washed with brine once, the inorganic layer is extracted with diethylether. The combined organic layers are dried with magnesium sulfate, the solvent is removed in vacuo. 11.7 g (25.3 mmol, 94.6%) of the Boc protected **20d** are received as a colourless oil which becomes an amorphous solid.

^{1}H NMR ($CDCl_3$): δ = 1.34 (t, 3 H, CH_3), 1.39 (s, 18 H, CCH_3), 1.77 (m, 4 H, -CH_2-), 2.61 (t, 4 H, ArCH_2), 3.08 (m, 4 H, NHCH_2), 4.31 (q, 2 H, CH_2), 4.78 (s, br, 2 H, NH), 7.14 (m, 1 H, ArH), 7.63 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 28.3 (C*C*H_3), 31.5 (CH_2), 32.7 (CH_2), 39.9 (CH_2), 60.8 (CH_2), 79.0 (*C*CH_3), 127.1 (Ar), 130.6 (Ar), 133.1 (Ar), 141.8 (Ar), 155.9 (CON), 166.7 (CO).

MS (EI); *m/z* (%): 464 (0.52) [M^+].

$C_{25}H_{40}N_2O_6$ (464.3): calcd. C 64.63, H 8.68, N 6.03; found C 65.11, H 7.44, N 6.61.

3,5-Bis-[3-(tert.butyloxycarbonylamino)propyl]benzoic acid (**20e**):

1.37 g (3.0 mmol) of the ester **20d** are heated with 663 mg potassium hydroxide (11.8 mmol) in methanol/water (4:1) to 50°C for 6 hours. The reaction is monitored with TLC. When the reaction is finished, acetic acid is added to give a pH=5. The acid is extracted with dichloromethane, the organic layer is subsequently dried with magnesium

sulfate. After evaporation of the solvent 1.14 g (2.6 mmol, 88.2%) of the **20e** are received as a colourless foam.

^{1}H NMR ($CDCl_3$): δ = 1.41 (s, 18 H, CCH_3), 1.78 (m, 4 H, -CH_2-), 2.62 (t, 4 H, ArCH_2), 3.09 (q, 4 H, NHCH_2), 4.64 (s, br, 2 H, NH), 7.16 (m, 1 H, ArH), 7.64 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.4 (C*C*H_3), 31.5 (CH_2), 32.7 (CH_2), 39.9 (CH_2), 79.9 (*C*CH_3), 127.2 (Ar), 132.1 (Ar), 134.2 (Ar), 141.9 (Ar), 155.9 (CO), 167.4 (CO).

MS (EI); *m/z* (%): 436 (3.15) [M^+].

$C_{23}H_{36}N_2O_6$ (436.3): calcd. C 63.27, H 8.32, N 6.42; found C 62.36, H 8.11, N 6.15.

Ethyl-3,5-[bis(3-{3,5-bis[3-(tert.butyloxycarbonylamino)propyl]benzoyl}amino)propyl] benzoate (**21d**):

1.31 g (3.0 mmol) of the G1-acid **20e** are dissolved under nitrogen in dry dichloromethane at 0°C. 459 mg (3.0 mmol) HOBt are added. After 10 minutes 633 mg (3.3 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 1.044 ml (775 mg, 6.0 mmol) diisopropylethylamine and 506 mg (1.5 mmol) of the G1-hydrochloride **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/2% methanol) gives 1.18 g (1.1 mmol, 71%) of the G2 **21d** as colourless foam.

^{1}H NMR ($CDCl_3$): δ = 1.24 (t, 3 H, CH_3), 1.39 (s, 18 H, CCH_3), 1.72 (m, 8 H, -CH_2-), 1.95 (m, 4 H, -CH_2-), 2.56 (m, 8 H, ArCH_2), 2.69 (m, 4 H, ArCH_2), 3.04 (m, 8 H, NHCH_2), 3.40 (m, 4 H, NHCH_2), 4.31 (q, 2 H, CH_2), 4.73 (s, br, 4 H, NH), 7.04 (s, br, 5 H, ArH, NH), 7.39 (s, 4 H, ArH), 7.67 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 28.4 (C*C*H_3), 30.9 (CH_2), 31.3 (CH_2), 32.4 (CH_2), 32.9 (CH_2), 39.5 (CH_2), 60.9 (CH_2), 79.1 (*C*CH_3), 124.8 (Ar), 127.2 (Ar), 130.7 (Ar), 131.6 (Ar), 133.3 (Ar), 134.8 (Ar), 141.7 (Ar), 141.9 (Ar), 156.1 (CON), 166.8 (CO), 167.9 (CO).

FAB-MS; *m/z* (%): 1124 (0.12) [M^++Na].

$C_{61}H_{88}N_6O_{12}$ (1100.7): calcd. C 66.50, H 8.42, N 7.63; found C 64.73, H 8.05, N 7.10.

3,5-Bis(3-{3,5-bis[3-(tert.butyloxycarbonylamino)propyl]benzoylamino}propyl)benzoic acid (**21e**):

6.9 g (5.6 mmol) of the G2-acid **21d** are stirred in 500 ml of a methanol/water/THF mixture (3:1:1) for 12 hours at 50 °C. After the reaction is complete (TLC), acetic acid is added to give a pH=5. The acid is extracted with dichloromethane. The organic layer is dried with magnesium sulfate. Chromatographic work up (silica gel, dichloromethane/5% methanol) affords 5.4 g (5.1 mmol, 91%) of the acid **21c** as colourless oil.

^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 18 H, CCH_3), 1.71 (m, 8 H, -CH_2-), 1.91 (m, 4 H, -CH_2-), 2.54 (m, 8 H, ArCH_2), 2.65 (m, 4 H, ArCH_2), 3.02 (m, 8 H, NHCH_2), 3.35 (m, 4 H, NHCH_2), 4.82 (s, br, 4 H, NH), 7.02 (s, br, 4 H, ArH, NH), 7.19 (s, 1 H, ArH), 7.36 (s, 4 H, ArH), 7.69 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.4 (C*C*H_3), 30.9 (CH_2), 31.3 (CH_2), 32.5 (CH_2), 33.0 (CH_2), 39.6 (CH_2), 79.1 (*C*CH_3), 124.8 (Ar), 127.5 (Ar), 130.6 (Ar), 131.5 (Ar), 133.2 (Ar), 134.7 (Ar), 141.7 (Ar), 156.2 (CON), 166.8 (CO), 167.8 (CO).

FAB-MS; *m/z* (%): 1124 (0.12) [M^++Na].

$C_{59}H_{88}N_6O_{12}$ (1072.6): calcd. C 66.00, H 8.27, N 7.83; found C 66.35, H 8.07, N 7.78.

Ethyl-3,5-(bis{3-[3,5-bis(3-aminopropyl)benzoyl]aminopropyl})benzoate tetratrifluoroacetate (**21c**):

75 mg (0.07 mmol) of the protected G2 **21d** are dissolved in a little (1.5 ml) dichloromethane and the same amount of trifluoroacetic acid. After stirring for one hour the solvent is removed completely in vacuo to give 80 mg (0.07 mmol, 98.5%) of the deprotected **21c** as yellowish oil which can be lyophilised from water.

^{1}H NMR ([D_4]methanol): δ = 1.35 (t, 3 H, CH_3), 1.98 (m, 12 H, -CH_2-), 2.73 (m, 12 H, ArCH_2), 2.92 (m, 8 H, NHCH_2), 3.40 (m, 4 H, NHCH_2), 4.31 (q, 2 H, CH_2), 7.27 (s, 2 H, ArH), 7.34 (s, 1 H, ArH), 7.51 (s, 4 H, ArH), 7.69 (s, 2 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 14.6 (CH_3), 30.0 (CH_2), 31.9 (CH_2), 33.2 (CH_2), 34.1 (CH_2), 40.2 (CH_2), 40.7 (CH_2), 62.1 (CH_2), 118.2 (q, TFAA), 126.3 (Ar), 128.1 (Ar), 131.8 (Ar), 132.7 (Ar), 134.6 (Ar), 136.4 (Ar), 142.7 (Ar), 143.7 (Ar), 162.2 (q, TFAA), 168.4 (CO), 170.2 (CO).

FAB-MS; *m/z* (%): 701 (37.63) [M^++H].

Ethyl-3,5-bis-({3-[3,5-bis-(3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-amino)-propyl]-benzoylamino}-propyl)-benzoate (**22b**):

210 mg (0.20 mmol) of the G2-acid **21e** are dissolved under nitrogen in dry dichloromethane at 0°C. 30 mg (0.20 mmol) HOBt are added. After 10 minutes 38 mg (0.20 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 65 ml (48 mg, 0.35 mmol) diisopropylethylamine and 30 mg (0.09 mmol) of the G1-hydrochloride **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/2-4% methanol)

affords 165 mg (0.07 mmol, 78.7 %) of the G3 **22b** as a colourless oil which can be lyophilised from dioxane.

^{1}H NMR ($CDCl_3$): δ = 1.35 (t, 3 H, CH_3), 1.37 (s, 72 H, CCH_3), 1.67 (m, 16 H, -CH_2-), 1.82 (m, 8 H, -CH_2-), 1.94 (m, 4 H, -CH_2-), 2.52 (m, 24 H, ArCH_2), 2.66 (m, 4 H, ArCH_2), 3.01 (m, 16 H, NHCH_2), 3.29 (m, 8 H, NHCH_2), 3.36 (m, 4 H, NHCH_2), 4.28 (q, 2 H, CH_2), 4.90 (s, br, 8 H, NH), 7.02 (s, 7 H, Ar), 7.31-7.48 (m, 20 H, Ar, NH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 28.4 (C*C*H_3), 30.5 (CH_2), 30.6 (CH_2), 31.2 (CH_2), 32.1 (CH_2), 32.7 (CH_2), 32.8 (CH_2), 39.2 (CH_2), 39.3 (CH_2), 39.5 (CH_2), 60.9 (CH_2), 67.0, 79.1 (*C*CH_3), 124.7 (Ar), 127.8 (Ar), 130.5 (Ar), 131.5 (Ar), 131.6 (Ar), 133.4 (Ar), 134.6 (Ar), 134.6 (Ar), 141.7 (Ar), 141.8 (Ar), 141.9 (Ar), 156.1 (CON), 166.8 (CO), 167.9 (CO), 168.1 (CO).

FAB-MS: *m/z* (%) = 2397 (34.74) [M^++Na], 2375 (40.26) [M^++H].

$C_{133}H_{196}N_{14}O_{24}$ (2373.45): calcd. C 67.26, H 8.32, N 8.26; found C 67.04, H 8.05, N 7.99.

Ethyl-3,5-bis-({3-[3,5-bis-(3.{3,5-bis-[(3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-amino)-propylbenzoyl]amino}-propyl)-benzoate (**23**):

202 mg (0.19 mmol) of the G2-acid **21e** are dissolved under nitrogen in dry dichloromethane at 0°C. 29 mg (0.19 mmol) HOBt are added. After 10 minutes 36 mg (0.19 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 64 ml (48 mg, 0.37 mmol) diisopropylethylamine and 51 mg (0.05 mmol) of the G2-trifluoroacetate **21c** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/2-3% methanol)

and GPC separation affords 180 mg (0.04 mmol, 82.2 %) of the G4 **23** as a colourless oil which can be lyophilised from dioxane.

^{1}H NMR ($CDCl_3$): δ = 1.29 (t, 3 H, CH_3), 1.37 (s, 144 H, CCH_3), 1.59 (s, br, 32 H, -CH_2-), 1.80 (s, br, 28 H, -CH_2-), 2.50 (s, br, 60 H, $ArCH_2$), 3.00 (s, br, 32 H, $NHCH_2$), 3.30 (s, br, 28 H, $NHCH_2$), 4.27 (q, 2 H, CH_2), 4.97 (s, br, 16 H, NH), 7.0-7.2 (s, 15 H, ArH), 7.3-7.6 (m, 44 H, Ar, NH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 28.4 (C*C*H_3), 29.6 (CH_2), 30.5 (CH_2), 30.6 (CH_2), 31.2 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 39.2 (CH_2), 39.6 (CH_2), 41.3 (CH_2), 60.9 (CH_2), 67.0, 78.9 (*C*CH_3), 124.9 (Ar), 127.1 (Ar), 130.5 (Ar), 131.6 (Ar), 133.2 (Ar), 134.5 (Ar), 141.7 (Ar), 141.7 (Ar), 141.9 (Ar), 156.2 (CON), 166.9 (CO), 167.9 (CO), 168.1 (CO).

FAB-MS: *m/z* (%) = 4945 (36.45) [M^++Na], 4923 (30.51) [M^++H], 4821 (76.40) [M^+-$C_5H_9O_2$].

$C_{278}H_{406}N_{30}O_{47}$ (4917.03): calcd. C 67.86, H 8.32, N 8.54; found C 67.99, H 7.00, N 7.33.

7.4. Synthesis of mixed protected dendrons

Ethyl-3-[3-(benzyloxycarbonylamino)propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]benzoate (**24a**):

3.4 g (10 mmol) of the G-1 hydrochloride **20a** are suspended with 3.0 g potassium hydroxide in 250 ml THF and 20 ml of water at 0°C. 8.7 g (40 mmol) di-*tert.*butyl-dicarbonate and 1.42 ml (1.7 g, 10 mmol) benzyl chloroformate in THF are slowly added, the reaction mixture is stirred for one more hour. After complete reaction (TLC) the layers are separated, the organic layer is washed with brine once, the inorganic layer

is extracted with diethylether. The combined organic layers are dried with magnesium sulfate, the solvent is removed in vacuo. Chromatographic separation (silica gel, dichloromethane/1% methanol) yields 3.34 g (6.7 mmol, 67%) of the mixed-protected **24a** as a colourless oil.

^{1}H NMR ($CDCl_3$): δ = 1.37 (t, 3 H, CH_3), 1.42 (s, 9 H, CCH_3), 1.81 (m, 4 H, -CH_2-), 2.63 (t, 4 H, ArCH_2), 3.17 (m, 4 H, NHCH_2), 4.33 (q, 2 H, CH_2), 4.95 (s, br, 1 H, NH), 5.06 (s, 2 H, Z-CH_2), 7.16 (s, 1 H, ArH), 7.31 (m, 6 H, ArH, NH), 7.65 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 28.3 (C*C*H_3), 31.3 (CH_2), 31.5 (CH_2), 32.5 (CH_2), 37.3 (CH_2), 39.9 (CH_2), 40.3 (CH_2), 60.8 (CH_2), 66.5 (PhCH_2), 77.0 (*C*CH_3), 127.1 (Ar), 128.0 (Ar), 128.4 (Ar), 130.7 (Ar), 133.1 (Ar), 136.5 (Ar), 141.7 (Ar), 141.8 (Ar), 156.4 (CON), 166.7 (CO).

MS (EI); *m/z* (%): 498 (1.89) [M^+].

$C_{28}H_{38}N_2O_6$ (498.62): calcd. C 67.45, H 7.68, N 5.62; found C 67.30, H 7.23, N 5.92.

3-[3-(Benzyloxycarbonylamino)propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]benzoic acid (**24b**):

665 mg (1.3 mmol) of the ester **24a** are heated with 299 mg potassium hydroxide (5.3 mmol) in methanol/water (3:1) to 50°C for 14 hours. The reaction is monitored with TLC. When the reaction is finished, citric acid is added to give a pH=5. The G-1 acid is extracted with dichloromethane, the organic layer is dried over magnesium sulfate. After evaporation of the solvent 564 mg (1.2 mmol, 93 %) of the acid **24b** are received as a colourless solid.

^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 9 H, CCH_3), 1.83 (m, 4 H, -CH_2-), 2.66 (m, 4 H, ArCH_2), 3.15 (m, 4 H, NHCH_2), 4.94 (s, br, 1 H, NH), 5.07 (s, 2 H, Z-CH_2), 5.17 (s, br, 1 H, NH), 7.21 (s, 1 H, ArH), 7.32 (m, 5 H, ArH), 7.74 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.2 (C*C*H_3), 31.2 (CH_2), 31.3 (CH_2), 32.5 (CH_2), 32.6 (CH_2), 40.1 (CH_2), 66.6 ($PhCH_2$), 79.3 (*C*CH_3), 127.4 (Ar), 127.9 (Ar), 128.4 (Ar), 130.5 (Ar), 133.4 (Ar), 136.4 (Ar), 141.8 (Ar), 156.2 (CON), 156.9 (CON), 169.1(CO).

FAB-MS; *m/z* (%): 471 (0.61) [M^++H].

Ethyl-3-[3-(benzyloxycarbonylamino)propyl]-5-(3-aminopropyl)benzoate hydrochloride (**24c**):

462 mg (0.93 mmol) of the mixed-protected **24a** are stirred at room temperature with 0.265 ml 25% HCl solution (1.86 mmol) for 36 hours. The reaction is monitored with TLC. When the reaction is finished the solvent is evaporated in vacuo, the raw material becomes an amorphus solid, which can not be purified.

^{1}H NMR ([D_4]methanol): δ = 1.37 (t, 3 H, CH_3), 1.82 (m, 4 H, -CH_2-), 2.64 (t, 4 H, ArCH_2), 3.16 (m, 4 H, NHCH_2), 4.34 (q, 2 H, CH_2), 4.95 (s, br, 1 H, NH), 5.06 (s, 2 H, Z-CH_2), 7.16 (s, 1 H, ArH), 7.32 (m, 5 H, ArH), 7.66 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 14.3 (CH_3), 31.4 (CH_2), 32.5 (CH_2), 40.3 (CH_2), 60.9 (CH_2), 66.6 ($PhCH_2$), 127.1 (Ar), 128.1 (Ar), 128.4 (Ar), 130.9 (Ar), 133.1 (Ar), 136.5 (Ar), 141.7 (Ar), 156.4 (CON), 168.2 (CO).

FAB-MS; *m/z* (%): 399 (11.69) [M^+].

Ethyl-3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]benzoylamino}propyl-5-[3-(benzyloxycarbonylamino)-propyl]-benzoate (**25a**):

730 mg (1.67 mmol) of the G-1 acid **20e** are dissolved under nitrogen in dry dichloromethane at 0°C. 256 mg (1.67 mmol) N-hydroxybenzotriazole (HOBt) are added. After 10 minutes 320 mg (1.67 mmol) N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) are added, the reaction mixture is stirred until

the hydrochloride is dissolved completely. Then 0.484 ml (359 mg, 2.78 mmol) diisopropylethylamine and 480 mg (1.11 mmol) of the deprotected **24c** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Chromatographic work up (silica gel, dichloromethane/2-4% methanol) afforded **25a** (596 mg, 0.73 mmol, 66 %) as a colourless solidified oil.

^{1}H NMR ($CDCl_3$): δ = 1.33 (t, 3 H, CH_3), 1.38 (s, 18 H, CCH_3), 1.74 (m, 6 H, -CH_2-), 1.91 (m, 2 H, -CH_2-), 2.53-2.69 (m, 8 H, ArCH_2), 3.03-3.14 (m, 6 H, NHCH_2), 3.42 (m, 2 H, NHCH_2), 4.29 (q, 2 H, CH_2), 4.80 (s, br, 2 H, NH), 5.01 (s, 2 H, Z-CH_2), 5.27 (s, br, 1 H, NH), 7.03 (s, br, 2 H, ArH, NH), 7.16 (s, 1 H, ArH),7.25 (m, 5 H, ArH), 7.39 (s, 2 H, ArH), 7.62 (s, 1 H, ArH), 7.66 (s, 1 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 28.2 (C*C*H_3), 30.9 (CH_2), 31.1 (CH_2), 32.2 (CH_2), 32.5 (CH_2), 32.9 (CH_2), 39.4 (CH_2), 40.3 (CH_2), 60.7 (CH_2), 66.3 (PhCH_2), 78.9 (*C*CH_3), 124.6 (Ar), 126.9 (Ar), 127.8 (Ar), 128.3 (Ar), 130.5 (Ar), 131.4 (Ar), 133.0 (Ar), 134.6 (Ar), 141.6 (Ar), 141.9 (Ar), 156.0 (CON), 156.4 (CON), 166.3 (CO), 167.7 (CO).

MS (EI); *m/z* (%): 816 (1.81) [M^+].

$C_{46}H_{64}N_4O_9$ (816.47): calcd. C 67.62, H 7.90, N 6.86; found C 67.21, H 7.54, N 7.13.

Ethyl-3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]benzoylamino}propyl-5-(3-aminopropyl)-benzoate (**25b**):

111 mg (0.14 mmol) of **25a** are hydrogenated in ethanol at 3.0 bar over palladium/C (10 mg, 10 mass%) for 2 hours. After removal of the catalyst by filtration over celite the solvent is removed in vacuo and the free amine **25b** (88 mg, 0.13 mmol, 96.1 %) is yielded as a colourless oil which can be lyophilised from dioxane.

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.32 (t, 3 H, CH_3), 1.36 (s, 18 H, CCH_3), 1.72 (m, 6 H, -CH_2-), 1.92 (m, 2 H, -CH_2-), 2.64 (m, 8 H, $ArCH_2$), 3.10 (m, 6 H, $NHCH_2$), 3.40 (m, 2 H, $NHCH_2$), 4.28 (q, 2 H, CH_2), 7.03 (s, 1 H, ArH), 7.16 (s, 1 H, ArH), 7.38 (s, 2 H, ArH), 7.62 (s, 1 H, ArH), 7.64 (s, 1 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 14.2 (CH_3), 28.2 (CCH_3), 31.0 (CH_2), 31.1 (CH_2), 32.2 (CH_2), 32.7 (CH_2), 33.0 (CH_2), 39.3 (CH_2), 39.5 (CH_2), 41.2 (CH_2), 60.7 (CH_2), 78.9 (CCH_3), 124.7 (Ar), 126.9 (Ar), 127.0 (Ar), 130.4 (Ar), 131.4 (Ar), 133.0 (Ar), 134.6 (Ar), 141.6 (Ar), 141.9 (Ar), 142.2 (Ar), 156.0 (CON), 166.7 (CO), 167.8 (CO).

MS (EI); *m/z* (%): 682 (13.2) [M^+].

$C_{38}H_{58}N_4O_7$ (682.43): calcd. C 66.84, H 8.56, N 8.20; found C 66.74, H 7.87, N 7.54.

Ethyl-3-(3-{3-[3-(benzyloxycarbonylamino)-propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-amino)-propyl-5-(3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-amino)-propyl-benzoate (**26a**):

61 mg (0.13 mmol) of acid **24b** are dissolved under nitrogen in dry dichloromethane at 0°C. 20 mg (0.13 mmol) HOBt are added. After 10 minutes 25 mg (0.13 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 0.041 ml (30 mg, 0.24 mmol) diisopropylethylamine and 73 mg (0.11 mmol) of the deprotected **25b** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried over magnesium sulfate, the solvent is removed in vacuo. After chromatographic work up (silica gel, dichloromethane/1-3% methanol) **26a** (80 mg, 0.07 mmol, 63 %) is received as a colourless oil which can be lyophilised from dioxane.

^{1}H NMR ($CDCl_3$): δ = 1.34 (t, 3 H, CH_3), 1.38 (s, 27 H, CCH_3), 1.72 (m, 8 H, -CH_2-), 1.94 (m, 4 H, -CH_2-), 2.54 (m, 8 H, $ArCH_2$), 2.68 (m, 4 H, $ArCH_2$), 3.08 (m, 8 H, $NHCH_2$), 3.38 (m, 4 H, $NHCH_2$), 4.30 (q, 2 H, CH_2), 4.76 (s, br, 2 H, NH), 5.02 (s, 2

H, Z-CH_2), 5.18 (s, br, 1 H, NH), 7.03 (s, br, 5 H, ArH, NH), 7.21 (s, 1 H, ArH), 7.27 (m, 5 H, ArH), 7.38 (s, 4 H, ArH), 7.67 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.27 (CH_3), 28.34 (CCH_3), 30.79 (CH_2), 31.01 (CH_2), 31.22 (CH_2), 32.33 (CH_2), 32.90 (CH_2), 39.40 (CH_2), 39.97 (CH_2), 60.87 (CH_2), 66.50 ($PhCH_2$), 79.09 (CCH_3), 124.78 (Ar), 127.15 (Ar), 127.98 (Ar), 128.40 (Ar), 130.61 (Ar), 131.53 (Ar), 133.24 (Ar), 134.73 (Ar), 136.50 (Ar), 141.72 (Ar), 141.93 (Ar), 156.08 (CON), 156.52 (CON), 166.75 (CON), 167.86 (CO).

FAB-MS; *m/z* (%): 1136 (0.05) [M^++H].

$C_{64}H_{90}N_6O_{12}$ (1134.66): calcd. C 67.70, H 7.99, N 7.40; found C 67.38, H 6.91, N 7.29.

Ethyl-3,5-bis-(3-{3-[3-(benzyloxycarbonylamino)propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylamino}-propyl)-benzoate (**26b**):

742 mg (1.58 mmol) of the acid **24b** are dissolved under nitrogen in dry dichloromethane at 0°C. 242 mg (1.58 mmol) HOBt are added. After 10 minutes 303 mg (1.58 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 0.522 ml (388 mg, 3.0 mmol) diisopropylethylamine and 236 mg (0.7 mmol) of **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried over magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/2-4% methanol) affords **26b** (630 mg, 0.54 mmol, 77 %) as a colourless foam.

^{1}H NMR ($CDCl_3$): δ = 1.28 (t, 3 H, CH_3), 1.38 (s, 18 H, CCH_3), 1.69 (m, 8 H, -CH_2-), 1.88 (m, 4 H, -CH_2-), 2.50 (m, 8 H, $ArCH_2$), 2.61 (m, 4 H, $ArCH_2$), 3.04 (m, 8 H, $NHCH_2$), 3.36 (m, 4 H, $NHCH_2$), 4.28 (q, 2 H, CH_2), 4.91 (s, br, 2 H, NH), 5.00 (s, 4 H, Z-CH_2), 5.40 (s, br, 2 H, NH), 7.00 (s, br, 3 H, ArH, NH), 7.16 (s, 2 H, ArH), 7.24-7.32 (m, 10 H, ArH), 7.39 (s, 4 H, ArH), 7.64 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 28.3 (CCH_3), 30.8 (CH_2), 31.0 (CH_2), 31.2 (CH_2), 32.2 (CH_2), 32.9 (CH_2), 39.3 (CH_2), 39.9 (CH_2), 60.9 (CH_2), 66.6 ($PhCH_2$), 79.1 (CCH_3), 124.8 (Ar), 127.2 (Ar), 128.0 (Ar), 128.0 (Ar), 128.4 (Ar), 130.6 (Ar), 131.6 (Ar), 133.3 (Ar), 134.8 (Ar), 136.4 (Ar), 141.6 (Ar), 141.7 (Ar), 141.9 (Ar), 156.1 (CON), 156.5 (CON), 166.8 (CO), 167.9 (CO).

FAB-MS; *m/z* (%): 1169 (0.78) [M^++H].

$C_{67}H_{88}N_6O_{12}$ (1168.65): calcd. C 68.81, H 7.58, N 7.19; found C 68.54, H 7.11, N 7.17.

3,5-Bis-(3-{3-[3-(benzyloxycarbonylamino)propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylamino}-propyl)-benzoic acid (**26c**):

585 mg (0.49 mmol) of the G-2 ester **26b** are heated with 113 mg potassium hydroxide (2.01 mmol) in methanol/water/THF (3:1:1) to 50°C for 14 hours. The reaction is monitored with TLC. When the reaction is finished, citric acid is added to give a pH=5. The G1-acid is extracted with dichloromethane, the organic layer is dried over magnesium sulfate . After evaporation of the solvent acid **26c** (513 mg, 0.45 mmol, 91 %) is received as a colourless solidified foam.

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.39 (s, 18 H, CCH_3), 1.83 (m, 8 H, -CH_2-), 1.91 (m, 4 H, -CH_2-), 2.61 (m, 12 H, $ArCH_2$), 3.06 (m, 8 H, $NHCH_2$), 3.36 (m, 4 H, $NHCH_2$), 5.06 (s, 4 H, Z-CH_2), 7.02 (s, 2 H, ArH), 7.22 (s, 1 H, ArH), 7.24-7.46 (m, 14 H, ArH), 7.71 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 28.1 (CCH_3), 30.3 (CH_2), 30.8 (CH_2), 30.9 (CH_2), 32.2 (CH_2), 32.8 (CH_2), 39.4 (CH_2), 39.7 (CH_2), 66.3 ($PhCH_2$), 79.0 (CCH_3), 124.5 (Ar), 125.1 (Ar), 127.2 (Ar), 127.9 (Ar), 127.8 (Ar), 128.2 (Ar), 131.5 (Ar), 133.2 (Ar), 134.4 (Ar), 136.7 (Ar), 138.5 (Ar), 141.7 (Ar), 141.9 (Ar), 154.8 (CON), 168.3 (CO).

(-)FAB-MS; *m/z* (%): 1140 (4.73) [M^-].

$C_{65}H_{84}N_6O_{12}$ (1140.61): calcd. C 68.40, H 7.42, N 7.36; found C 68.52, H 6.94, N 7.18.

7.5. Synthesis of modified dendrons

Ethyl-3,5-bis-{3-[(2-carboxic acidethyl)carbonylamino]propyl}benzoate (**27**):

674 mg (2 mmol) of hydrochloride **20a** are suspended in THF at 0°C. 600 mg (12 mmol) potassium hydroxide in water and 600 mg (6 mmol) succinic anhydride in THF are added. After 18 hours hydrochloric acid is added to give a pH=2, the mixture is extracted carefully with dichloromethane. Evaporation of the solvent yields 621 mg (1.3 mmol, 65.0 %) of **27** as a colourless solid.

^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 3 H, CH_3), 1.74 (s, 4 H, CH_2), 2.42 (s, 4 H, CH_2), 2.54 (s, 8 H, CH_2), 3.18 (s, 4H, CH_2), 3.60 (s, br, 2H, NH), 4.28 (q, 2H, CH_2), 7.12 (s, 1 H, ArH), 7.56 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 13.5 (CH_3), 28.8 (CH_2), 29.9 (CH_2), 30.3 (CH_2), 32.2 (CH_2), 38.4 (CH_2), 60.6 (CH_2), 126.6 (Ar), 129.9 (Ar), 133.0 (Ar), 141.6 (Ar), 166.9 (CO), 172.1 (CO), 173.4 (CO).

MS (EI): *m/z* (%) = 446 (0.28) [M^+-H_2O], 428 (29.77) [M^+-$2H_2O$].

Ethyl-3,5-bis-[3-(tert.butyloxycarbonylphenylalanoylamino)propy]lbenzoate (**28a**):

430 mg (1.3 mmol) of the G1-hydrochloride **20a** are dissolved with 0.47 ml (346 mg, 3.2 mmol) of diisopropylethylamine in dry dichloromethane. 1.15 g N-Boc-Phenylalanin-N-hydroxysuccinimidester **58** (3.2 mmol) are added, the reaction mixture is stirred at room temperature for 14 hours. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is

removed in vacuo. Column chromatography (silica gel, dichloromethane/2% methanol) affords 796 mg (1.1 mmol, 82.0 %) of the ester **28a** as a colourless solid.

^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 21 H, CH_3, CCH_3), 1.68 (m, 4 H, -CH_2-), 2.47 (m, 4 H, ArCH_2), 2.99 (m, 8 H, NHCH_2, PhCH_2), 4.30 (q, 2 H, CH_2), 4.68 (d, br, 2 H, CH), 5.79 (d, br, 2 H, NH), 7.03 (s, 1 H, ArH), 7.14 (m, 12 H, ArH, NH), 7.58 (s, 2H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 28.2 (C*C*H_3), 30.3 (CH_2), 37.9 (CH_2), 38.9 (CH), 55.9 (PhCH_2), 60.8 (CH_2), 69.6 (*C*CH_3), 126.6 (Ar), 127.0 (Ar), 128.2 (Ar), 129.3 (Ar), 130.6 (Ar), 133.7 (Ar), 136.9 (Ar), 141.4 (Ar), 155.7 (CON), 166.6 (CO), 171.8 (CO).

MS (EI): *m/z* (%) = 758 (1.97) [M^+].

$C_{43}H_{58}N_4O_8$ (758.43): calcd. C 68.05, H 7.70, N 7.38; found C 67.96, H 6.63, N 6.98.

Ethyl-3,5-bis-[3-(phenylalanoylamino)propy]lbenzoate x2 tetrafluoroacetate (**28b**):

180 mg (0.24 mmol) of the protected **28a** are dissolved in a little (1.5 ml) dichloromethane and the same amount of trifluoroacetic acid. After stirring for one hour the solvent is removed completely in vacuo to give 180 mg (0.24 mmol, 98.5%) of the deprotected **28b** as yellowish oil which can be lyophilised from water.

^{1}H NMR ([D_4]methanol): δ = 1.37 (t, 3 H, CH_3), 1.67 (m, 4 H, -CH_2-), 2.49 (m, 4 H, ArCH_2), 3.10-3.30 (m, 8 H, NHCH_2, PhCH_2), 4.07 (m, 2 H, CH), 4.34 (q, 2 H, CH_2), 7.19 (s, 1 H, ArH), 7.29 (m, 10 H, ArH), 7.62 (s, 2 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 14.6 (CH_3), 31.7 (CH_2), 33.6 (CH_2), 38.7 (CH), 40.1 (CH_2), 55.9 (PhCH_2), 62.1 (CH_2), 118.2 (q, TFAA), 128.1 (Ar), 128.7 (Ar), 130.0 (Ar), 130.5 (Ar), 131.7 (Ar), 134.5 (Ar), 135.7 (Ar), 134.4 (Ar s), 161.3 (q, TFAA), 168.31(CO), 169.5 (CO).

FAB-MS: *m/z* (%) = 559 (52.65) [M^++H].

3,5-Bis-[3-(tert.butyloxycarbonylphenylalanoylamino)propyl]benzoic acid (**28c**):

270 mg (0.36 mmol) of the ester **28a** are heated with 79 mg (1.4 mmol) potassium hydroxide in methanol/water (5:1) to 50°C for 14 hours. The reaction is monitored with TLC. When the reaction is finished, citric acid is added till the pH is 5. The G1-acid is extracted with dichloromethane. The organic layer is dried with magnesium sulfate. After evaporation of the solvent 256 mg (0.35 mmol, 97.2%) of the acid **28c** are received as a colourless foam.

^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 18 H, CCH_3), 1.67 (m, 4 H, -CH_2-), 2.45 (m, 4 H, ArCH_2), 3.05 (m, 8 H, $NHCH_2$, $PhCH_2$), 4.44 (s, br, 2 H, CH), 5.76 (d, 2 H, NH), 6.04 (s, 2 H, NH), 7.06 (s, 1 H, ArH), 7.3-7.4 (m, 12 H, ArH, NH), 7.63 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.3 (C*C*H_3), 30.2 (CH_2), 31.9 (CH_2), 37.9 (CH_2), 38.6 (CH), 43.7 (CH_2), 56.5 ($PhCH_2$), 65.9, 80.1 (*C*CH_3), 125.1 (Ar), 126.8 (Ar), 128.4 (Ar), 128.6 (Ar), 129.3 (Ar), 131.2 (Ar), 136.8 (Ar), 139.3 (Ar), 141.3 (Ar), 158.2 (CON), 165.3 (CO), 171.5 (CO).

FAB-MS: *m/z* (%) = 731 (9.89) [M^++H].

Ethyl-3,5-bis-[3-(tert.butyloxycarbonylcysteinoylamino)propyl]benzoate (**29a**):

1.24 g (4.0 mmol) N-Boc-S-Benzyl-cystein are dissolved under nitrogen in dry dichloromethane at 0°C. 612 mg (4.0 mmol) HOBt are added. After 10 minutes 843 mg (4.4 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 1.40 ml (1.03 g, 8.0 mmol) diisopropylethylamine and 674 mg (2.0 mmol) of the hydrochloride **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/2% methanol) affords 1.46 g (1.72 mmol, 86.0 %) of the ester **29a** as a colourless foam.

^{1}H NMR ($CDCl_3$): δ = 1.35 (t, 3 H, CH_3), 1.40 (s, 18 H, CCH_3), 1.80 (m, 4 H, -CH_2-), 2.62 (m, 4 H, ArCH_2), 2.77 (m, 4 H, NHCH_2), 3.17 (s, 4 H, CH_2), 4.23 (m, br, 4 H, PhCH_2), 4.32 (q, 2 H, CH_2), 5.54 (m, br, 2 H, CH), 6.66 (s, br, 2 H, NH), 7.15 (s, 1 H, ArH), 7.27 (m, 10 H, ArH), 7.65 (s, 2H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 28.3 (C*C*H_3), 30.5 (CH_2), 32.2 (CH_2), 33.8 (CH_2), 36.5 (CH_2), 38.5 (CH), 55.9 (CH_2), 60.9 (CH_2), 80.2 (*C*CH_3), 127.1 (Ar), 128.5 (Ar), 128.9 (Ar), 130.8 (Ar), 133.5 (Ar), 137.9 (Ar), 141.5 (Ar), 158.2 (CON), 168.4 (CO), 170.8 (CO).

FAB-MS: *m/z* (%) = 851 (5.07) [M^++H].

$C_{45}H_{62}N_4O_8S_2$ (850.40): calcd. C 63.50, H 7.34, N 6.58; found C 62.57, H 7.90, N 7.15.

Ethyl-3,5-bis-[3-(cysteinoylamino)propyl]benzoate x2 tetrafluoroacetate (**29b**):

100 mg (0.12 mmol) of the protected **29a** are dissolved in a little (1.5 ml) dichloromethane and the same amount of trifluoroacetic acid. After stirring for one hour the solvent is removed completely in vacuo to give 98 mg (0.12 mmol, 98.5%) of the deprotected **29b** as yellowish oil which can be lyophilised from water.

^{1}H NMR ([D_4]methanol): δ = 1.34 (t, 3 H, CH_3), 1.84 (m, 4 H, -CH_2-), 2.70 (m, 4 H, ArCH_2), 2.94 (m, 4 H, NHCH_2), 3.26 (m, 4 H, CH_2), 3.79 (s, 3 H, CH_3), 4.02 (t, 2 H, CH), 4.30 (q, 2 H, CH_2), 7.29 (m, 11 H, ArH), 7.69 (s, 2 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 14.6 (CH_3), 31.9 (CH_2), 33.3 (CH_2), 33.7 (CH_2), 37.1 (CH), 40.3 (CH_2), 53.6 (CH_2), 62.1 (CH_2), 118.1 (q, TFAA), 128.4 (Ar), 129.6 (Ar), 130.1 (Ar), 131.9 (Ar), 134.5 (Ar), 138.7 (Ar), 134.5 (Ar), 160.3 (q, TFAA), 168.3 (CO), 168.9 (CO).

FAB-MS: *m/z* (%) = 651 (15.61) [M^++H], 673 (1.56) [M^++Na].

Ethyl-3,5-bis-[3-(tert.butyloxycarbonylmethionoylamino)propyl]benzoate (**30a**):

674 mg (2.0 mmol) of the G1-hydrochloride **20a** are dissolved with 0.695 ml (516 mg, 4.0 mmol) of diisopropylethylamine in dry dichloromethane. 1.592 g N-Boc-Methionin-N-hydroxysuccinimidester (4.6 mmol) are added, the reaction mixture is stirred at room temperature for 14 hours. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/3% methanol) affords 1.29 g (1.7 mmol, 85.5 %) of the ester **30a** as a colourless foam.

^{1}H NMR ($CDCl_3$): δ = 1.33 (m, 24 H, CH_3, CCH_3), 1.79 (m, 4 H, -CH_2-), 1.95 (m, br, 4 H, CH_2), 2.59 (m, 4 H, ArCH_2), 3.11 (m, 4 H, NHCH_2), 4.28 (q, br, 6 H, CH_2), 4.68 (d, br, 2 H, CH), 5.83 (d, br, 2 H, NH), 7.12 (s, 1 H, ArH), 7.30 (s, br, 2 H, NH), 7.61 (s, 2H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 28.3 (C*C*H_3), 30.4 (CH_2), 32.1 (CH_2), 38.1 (CH), 38.9 (CH_2), 53.6, 60.8 (CH_2), 79.8 (*C*CH_3), 127.1 (Ar), 130.7 (Ar), 133.6 (Ar), 141.4 (Ar), 155.9 (CON), 166.6 (CO), 172.1 (CO).

MS (EI): *m/z* (%) = 726 (0.41) [M^+].

Ethyl-3,5-bis-[3-(methionoylamino)propyl]benzoate x2 tetrafluoroacetate (**30b**):

90 mg (0.12 mmol) of the protected **30a** are dissolved in a little (1.5 ml) dichloromethane and the same amount of trifluoroacetic acid. After stirring for one hour the solvent is removed completely in vacuo to give 88 mg (0.12 mmol, 97.3%) of the deprotected **30b** as yellowish oil which can be lyophilised from water.

^{1}H NMR ([D_4]methanol): δ = 1.36 (t, 3 H, CH_3), 1.85 (m, 4 H, -CH_2-), 2.13 (m, 11 H, CH_2, CH_3), 2.57 (m, 4 H, NHCH_2), 2.69 (m, 4 H, CH_2), 3.94 (m, 2 H, CH), 4.30 (q, 2 H, CH_2), 7.31 (s, 1 H, ArH), 7.69 (s, 2 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 14.6 (CH_3), 15.1 (CH_3), 29.9 (CH_2), 31.9 (CH_2), 32.1 (CH_2), 33.8 (CH_2), 40.2 (CH), 53.7 (CH_2), 62.1 (CH_2), 118.1 (q, TFAA), 128.1,131.9, 133.5, 134.5, 143.5, 161.2 (q, TFAA), 168.3 (CO), 169.7 (CO).

FAB-MS: *m/z* (%) = 527 (100.00) [M^++H], 549 (7.95) [M^++Na].

Ethyl-3,5-bis-(3-{3,5-bis-[3-(tert.butyloxycarbonylphenylalanoylamino)-propyl]-benzoylamino}-propyl)benzoate (**31**):

1.0 g (1.37 mmol) of the acid **18c** are dissolved under nitrogen in dry dichloromethane at 0°C. 210 mg (1.37 mmol) HOBt are added. After 10 minutes 290 mg (1.51 mmol) EDC are added, the reaction mixture is stirred until the hydrochloride is dissolved completely. Then 0.477 ml (354 mg, 2.74 mmol) diisopropylethylamine and 229 mg (0.68 mmol) of the hydrochloride **20a** are added. The reaction mixture is stirred for 14 hours at room temperature. It is then washed with a sat. sodium hydrogencarbonate solution and brine. The organic layer is dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane/1-4% methanol) affords 929 mg (0.55 mmol, 80.9 %) of the G2 **31** as a colourless foam.

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.29 (s, 39 H, CCH_3), 1.63 (m, 8 H, -CH_2-), 1.91 (m, 4 H, -CH_2-), 2.40 (m, 8 H, ArCH_2), 2.64 (m, 4 H, ArCH_2), 2.88 (m, 8 H, NHCH_2), 2.98 (m, 9 H, NHCH_2), 3.36 (d, 8 H, PhCH_2), 4.26 (m, br, 6 H, CH_2, CH), 6.95 (s, 3 H, ArH), 7.2-7.6 (m, br, 26 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 14.0 (CH_3), 27.9 (C*C*H_3), 30.0 (CH_2), 30.6 (CH_2), 32.1 (CH_2), 32.7 (CH_2), 38.1 (CH_2), 38.6 (CH), 39.3 (CH_2), 55.7 (PhCH_2), 60.9 (CH_2), 79.9 (*C*CH_3), 124.7 (Ar), 126.6 (Ar), 128.2 (Ar), 129.1 (Ar), 130.3 (Ar), 131.6 (Ar), 134.4 (Ar), 136.6 (Ar), 141.5 (Ar), 141.9 (Ar), 155.6 (CON), 168.5 (CO), 171.9 (CO).

FAB-MS: *m/z* (%) = 1690 (1.29) [M^++H].

7.6. Synthesis of monomers

4-(tert.Butyloxycarbonylamino)-methylbenzoic acid (**35b**):

To a solution of 4-aminomethylbenzoic acid **35a** (30.0 g, 149 mmol) and potassium hydroxide (8.3 g, 149 mmol) in 600 ml THF and 100 ml water, di-*tert.*butyloxydicarbonate (39.0 g, 179 mmol) was added and stirred at room temperature for 1 h. The layers were separated, the organic layer was washed with brine, dried with magnesium sulfate and evaporated in vacuo. The raw material was dried in high vacuo to give **35** (35.1 g, 140 mmol, 94 %) as a colorless oil.

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.30 (s, 9 H, CCH_3), 4.10 (s, br, 1 H, OH), 4.17 (s, br, 1 H, NH), 4.60 (s, 2 H, CH_2), 7.17 (d, 2 H, ArH), 7.82 (d, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 27.9 (C*C*H_3), 43.7 (CH_2), 80.4 (*C*CH_3), 126.6 (Ar), 129.4 (Ar), 129.9 (Ar), 143.9 (Ar), 156.4 (CON), 169.2 (CO).

MS (EI); *m/z* (%): 251 (3.8) [M^+].

4-(tert.Butyloxycarbonylamino)-methylbenzylalcohol (**36**):

Lithiumaluminiumhydride (3.0 g, 80 mmol) is suspended in 250 ml of dry THF. After the protected benzoic acid **35b** (20.9 g, 80 mmol) was slowly added, the reaction mixture is heated to 40 °C for 16 h. The reaction is stopped by addition of water, acetic acid is added to give a pH=5. The layers were separated, the organic layer was washed with brine. Extraction of the aquous layer with ether was carried out carefully. The combined organic layers were dried with magnesium sulfate and evaporated in vacuo. The raw material was dried in high vacuo to give **36** (11.6 g, 50 mmol, 63 %) as a colorless oil which solidified.

^{1}H NMR ($CDCl_3$): δ = 1.41 (s, 9 H, CCH_3), 2.63 (s, br, 1 H, OH), 4.29 (d, 2 H, $ArCH_2N$), 4.63 (s, 2 H, $ArCH_2O$), 4.80 (s, br, 1 H, NH), 7.22 (d, 2 H, ArH), 7.33 (d, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.4 (CCH_3), 44.4 ($ArCH_2N$), 64.8 ($ArCH_2O$), 79.5 (CCH_3), 127.2 (Ar), 127.5 (Ar), 138.2 (Ar), 140.1 (Ar), 155.9 (CON).

MS (EI); *m/z* (%): 237 (0.24) [M^+].

$C_{13}H_{19}NO_3$ (237.30): calcd. C 65.80, H 8.07, N 5.90; found C 65.79, H 7.01, N 5.94.

4-(tert.Butyloxycarbonylamino)-methylbenzylacrylate (**37a**):

To a mixture of the alcohol **36** (2.87 g, 12 mmol), triethylamine (6.7 ml, 4.85 g, 48 mmol) and DMAP in dry THF, acrylic acid chloride (1.38 ml, 1.53 g, 17 mmol) was added dropwise. The reaction was stirred at room temperature for 16 h, then extracted with sat. sodium hydrogencarbonate solution and brine. The organic layer was dried with magnesium sulfate and evaporated in vacuo. Chromatographic separation (silica gel, dichloromethane) gave **37a** (2.68 g, 9 mmol, 76 %) as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 9 H, CCH_3), 4.27 (d, 2 H, CH_2NH), 4.95 (s, br, 1 H, NH), 5.14 (s, 2 H, CH_2O), 5.80 (dd, 1 H, $CH=CH_2$), 6.11 (dd, 1 H, $CH=CH_2$), 6.40 (dd, 1 H, $CH=CH_2$), 7.25 (d, 2 H, ArH), 7.31 (d, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.3 (CCH_3), 44.3 ($ArCH_2N$), 66.0 ($ArCH_2O$), 79.4 (CCH_3), 121.6 ($CH=CH_2$), 128.2 (Ar), 128.5 (Ar), 131.0 ($CH=CH_2$), 134.8 (Ar), 139.1 (Ar), 155.8 (CON), 165.9 (CO).

MS (EI); *m/z* (%): 237 (0.24) [M^+].

$C_{16}H_{21}NO_4$ (291.35): calcd. C 65.96, H 7.26, N 4.81; found C 65.29, H 6.96, N 4.54.

4-(Aminomethyl)benzylacrylate hydrochloride (**37b**):

Hydrochloric acid (6.5 ml 25%, 45 mmol) was added to a solution of the protected acrylate **37a** (6.6 g, 23 mmol) in THF. The reaction mixture was stirred at room temperature for 36 h. The solvent was evaporated, the crude product dissolved in ethanol. Precipitation with ether gave **37b** (5.4 g, 19 mmol, 83 %) as a colorless amorphous solid.

^{1}H NMR ([D_4]methanol): δ = 4.12 (s, 2 H, CH_2NH), 5.22 (s, 2 H, CH_2O), 5.90 (dd, 1 H, $CH=CH_2$), 6.19 (dd, 1 H, $CH=CH_2$), 6.40 (dd, 1 H, $CH=CH_2$), 7.47 (s, 4 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 43.9 (CH_2NH), 66.9 (CH_2O), 129.0 ($CH=CH_2$), 129.8 (Ar), 130.3 (Ar), 132.7 ($CH=CH_2$), 134.4 (Ar), 138.3 (Ar), 168.0 (CO).

MS (EI); *m/z* (%): 191 (16.9) [M^+].

$C_{11}H_{14}NO_2Cl$ (227.69): calcd. C 58.03, H 6.20, N 6.15; found C 57.47, H 6.17, N 5.89.

4-(tert.Butyloxycarbonylamino)-methylbenzylmethacrylate (**43a**):

To a mixture 6.5 g of the alcohol **36** (27 mmol), 15.3 ml (11.0 g, 110 mmol) triethylamine and DMAP in dry THF under nitrogen 3.7 ml (4.0 g, 38 mmol) methacrylic acid chlorid are added dropwise. The reaction is stirred for 48 hours at 50 °C. The mixture is extracted with a sat. solution sodium hydrogencarbonate and brine and then dried with magnesium sulfate, the solvent is removed in vacuo. Column chromatography (silica gel, dichloromethane) yields 6.7 g (22 mmol, 81.5%) of the methacrylate **43a** as colourless oil which can be lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 9 H, CCH_3), 1.92 (s, 3 H, CH_3), 4.27 (d, 2 H, CH_2NH), 5.02 (s, br, 1 H, NH), 5.13 (s, 2 H, CH_2OH), 5.54 (d, 1 H, $CMe=CH_2$), 6.11 (dd, 1 H, $CMe=CH_2$), 7.24 (m, 4 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_3), 28.3 (CCH_3), 44.3 (CH_2N), 66.6 (CH_2O), 79.8 (CCH_3), 127.5, 128.3, 135.4, 136.3, 138.9, 139.2, 155.8 (CON), 168.2 (CO).

FAB-MS: *m/z* (%) = 328 (1.56) [M^++Na], 306 (0.54) [M^++H].

$C_{17}H_{23}NO_4$ (305.16): calcd. C 66.86, H 7.59, N 4.59; found C 66.08, H 7.17, N 4.32.

4-(Aminomethyl)benzylmethacrylate hydrochloride (**43b**):

3.0 g (10 mmol) of the monomer **43a** are stirred in THF with 2.8 ml (20 mmol) HCl for 36 hours. The solvent is then evaporated, the crude mixture is dissolved in ethanol. Precipitation with ether gives 1.9 g (8 mmol, 79.0 %) of the hydrochloride **43b** as colourless solid.

^{1}H NMR ([D_4]methanol): δ = 1.93 (s, 3 H, CH_3),4.13 (s, 2 H, CH_2NH), 5.21 (s, 2 H, CH_2OH), 5.64 (d, 1 H, CMe=CH_2), 6.11 (dd, 1 H, CMe=CH_2), 7.48 (s, 4 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 18.4 (CH_3), 44.0 (CH_2N), 66.9 (CH_2O), 126.4, 129.7, 130.3, 133.1, 134.3, 137.6, 138.9, 168.2 (CO).

FAB-MS: *m/z* (%) = 447 (1.30) [$2M^+$-Cl], 206 (100.0) [M^+-Cl].

General procedure for Macromonomer Preparation (A). To a solution of 1.0 mmol protected dendron acid in dry dichloromethane at 0°C 1.0 mmol HOBt is added. After 10 minutes 1.1 mmol EDC is added, the mixture is stirred until the reactands are dissolved. Then 2.0 mmol diisopropylethylamine and 1.0 mmol of hydrochloride **37b** respectively **43b** are added. The mixture is stirred for 14 hours, then washed with sat. sodium hydrogencarbonate solution and brine, subsequently dried with magnesium sulfate.

4-({3,5-Bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-aminomethyl)-benzyl acrylate (**38**):

From 1.04 g (2.38 mmol) G-1 acid **24b** and 680 mg 4-aminomethylbenzyl acrylate hydrochloride **37b**. Chromatographic work up (silica gel, dichloromethane/2-4% methanol) gives **38** (109 mg, 1.79 mmol, 75 %) as a colourless solidified oil which is lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 18 H, CCH_3), 1.76 (m, 4 H, -CH_2-), 2.61 (m, 4 H, $ArCH_2$), 3.07 (m, 4 H, $NHCH_2$), 4.61 (d, 2 H, $ArCH_2N$), 5.14 (s, 2 H, $ArCH_2O$), 5.82 (dd, 1 H, CH=CH_2), 6.11 (dd, 1 H, CH=CH_2), 6.40 (dd, 1 H, CH=CH_2), 7.08 (s, 2 H, ArH), 7.17 (s, 1 H, ArH), 7.24 (m, 4 H, ArH), 7.46 (s, 3 H, ArH, NH).

^{13}C NMR ($CDCl_3$): δ = 28.3 (C*C*H_3), 31.2 (CH_2), 32.3 (CH_2), 39.3 (CH_2), 43.6 ($ArCH_2N$), 66.0 ($ArCH_2O$), 79.2 (*C*CH_3), 124.9, 128.0, 128.6, 131.1, 131.8, 134.2, 138.8, 141.7, 156.1 (CON), 165.5 (CON), 167.7 (CO).

FAB-MS; *m/z* (%): 610 (9.89) [M^++H].

$C_{34}H_{47}N_3O_7$ (609.34): calcd. C 66.97, H 7.77, N 6.89; found C 67.37, H 7.86, N 5.38.

4-{[3,5-Bis(3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylamino}-propyl)-benzoyl] aminomethyl}benzyl acrylate (**39**):

From 1.69 g (1.6 mmol) of G-2 acid **21c** and 450 mg of hydrochloride **37b**. Chromatographic separation (silica gel, dichloromethane/2% methanol) gives **39** (1.43 mg, 1.15 mmol, 72 %) as a colourless oil which is lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 36 H, CCH_3), 1.67 (m, 8 H, -CH_2-), 1.87 (m, 4 H, -CH_2-), 2.56 (m, 12 H, $ArCH_2$), 3.01 (m, 8 H, $NHCH_2$), 3.32 (m, 4 H, $NHCH_2$), 4.59 (d, 2 H, $ArCH_2N$), 4.83 (s, br, 2 H, NH), 5.11 (s, 2 H, $ArCH_2O$), 5.78 (dd, 1 H, CH=CH_2), 6.08 (dd, 1 H, CH=CH_2), 6.37 (dd, 1 H, CH=CH_2), 7.02 (s, br, 2 H, ArH, NH), 7.09 (s, br, 2 H, ArH), 7.27 (s, br, 2 H, ArH), 7.33-7.45 (m, br, 12 H, ArH, NH).

^{13}C NMR ($CDCl_3$): δ = 28.2 (C*C*H_3), 29.2 (CH_2), 30.4 (CH_2), 31.1 (CH_2), 32.2 (CH_2), 39.0 (CH_2), 39.4 (CH_2), 45.8 (ArCH_2N), 66.8 (ArCH_2O), 78.8 (*C*CH_3), 123.6, 124.7, 125.9, 127.8, 128.3, 131.5, 134.2, 134.4, 138.9, 141.6, 156.0 (CON), 165.8 (CO), 167.8 (CO).

FAB-MS; *m/z* (%)*:* 1246 (9.89) [M^++H].

4-({3,5-Bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-aminomethyl)-benzyl methacrylate (**45**):

From 1.45 g (3.35 mmol) of G-1 acid **20e** and 730 mg 4-aminomethylbenzyl methacrylate hydrochloride **43b**. Chromatographic separation (silica gel, dichloromethane/2-4% methanol) affords **45** (299 mg, 0.48 mmol, 79 %) as a colourless oil which is lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 18 H, CCH_3), 1.70 (m, 4 H, -CH_2-), 1.87 (s, 3 H, CH_3), 2.54 (m, 4 H, ArCH_2), 3.01 (m, 4 H, NHCH_2), 4.54 (d, 2 H, ArCH_2N), 4.84 (s, br, 1 H, NH), 5.07 (s, 2 H, ArCH_2O), 5.50 (s, 1 H, CMe=CH_2), 6.06 (s, 1 H,CMe=CH_2), 7.03 (s, 1 H, ArH), 7.25 (m, 4 H, ArH), 7.45 (s, 2 H, ArH), 7.52 (s, br, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_3), 28.2 (C*C*H_3), 31.1 (CH_2), 32.2 (CH_2), 39.3 (CH_2), 43.3 (ArCH_2N), 65.9 (ArCH_2O), 78.9 (*C*CH_3), 124.8, 125.6, 127.8, 128.1, 131.6, 134.3, 134.6, 135.9, 138.6, 141.6, 155.9 (CON), 167.0 (CO), 167.6 (CO).

FAB-MS; *m/z* (%): 624 (1.36) [M^++H].

4-{[3,5-Bis(3-{3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylamino}-propyl)-benzoyl] aminomethyl}benzyl methacrylate (**46**):

From 800 mg (0.74 mmol) of G-2 acid **21c** and 180 mg of hydrochloride **43b**. Chromatographic work up (silica gel, dichloromethane/1.5% methanol) gives monomer

46 (780 mg, 0.62 mmol, 84 %) as a colourless oil which can be lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 36 H, CCH_3), 1.71 (m, 8 H, -CH_2-), 1.91 (m, 7 H, -CH_2-, CH_3), 2.5-2.64 (m, 12 H, $ArCH_2$), 3.02 (m, 8 H, $NHCH_2$), 3.34 (m, 4 H, $NHCH_2$), 4.60 (d, 2 H, $ArCH_2N$), 4.81 (s, br, 3 H, NH), 5.11 (s, 2 H, $ArCH_2O$), 5.53 (s, 1 H, $CMe=CH_2$), 6.09 (s, 1 H, $CMe=CH_2$), 7.03 (s, 2 H, ArH), 7.10 (s, br, 3 H, ArH, NH), 7.24-7.46 (m, 12 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_3), 28.3 (CCH_3), 30.4 (CH_2), 31.2 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 39.1 (CH_2), 39.5 (CH_2), 43.5 ($ArCH_2N$), 66.0 ($ArCH_2O$), 79.1 (CCH_3), 124.7, 125.0, 125.8, 128.0, 128.2, 131.6, 134.4, 134.6, 134.9, 136.0, 138.7, 141.8, 156.1 (CON), 167.9 (CO).

FAB-MS; *m/z* (%): 1282 (0.22) [M^++Na], 1261 (0.08) [M^++H].

$C_{71}H_{101}N_7O_{13}$ (1260.62): calcd. C 67.65, H 8.08, N 7.78; found C 67.38, H 6.91, N 7.29.

4-{3-[3-(Benzyloxycarbonylamino)-propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylaminomethyl}benzyl methacrylate (**49**):

From 964 mg (2.05 mmol) of G-1 acid **24b** and 494 mg of **43b**. After chromatographic work up (silica gel, dichloromethane/1-3% methanol) **49** (1.077 g, 1.64 mmol, 80 %) is received as a colourless foam which is lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 9 H, CCH_3), 1.76 (m, 4 H, -CH_2-), 1.91 (s, 3 H, CH_3), 2.58 (m, 4 H, $ArCH_2$), 3.09 (m, 4 H, $NHCH_2$), 4.58 (d, 2 H, $ArCH_2N$), 4.88 (s, br, 1 H, NH), 4.96 (s, 2 H, Z-CH_2), 5.10 (s, br, 3 H, $ArCH_2O$, NH), 5.54 (s, 1 H,$CMe=CH_2$), 6.10 (s, 1 H,$CMe=CH_2$), 7.06 (s, br, 2 H, ArH, NH), 7.24-7.35 (m, 9 H, ArH), 7.44 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_3), 28.3 (CCH_3), 30.7 (CH_2), 30.9 (CH_2), 31.1 (CH_2), 32.2 (CH_2), 39.3 (CH_2), 39.8 (CH_2), 43.5 ($ArCH_2N$), 65.9 ($ArCH_2O$), 66.4 ($PhCH_2$),

80.0 (*C*CH_3), 124.9, 124.7, 127.9, 128.2, 128.3, 131.7, 134.5, 135.1, 136.1, 136.4, 138.5, 141.5, 156.0 (CON), 156.4 (CON), 167.1 (CO), 167.7 (CO).

FAB-MS; *m/z* (%): 658 (0.24) [M^++H].

$C_{38}H_{47}N_3O_7$ (657.34): calcd. C 69.38, H 7.20, N 6.39; found C 70.01, H 6.88, N 6.98.

4-{3,5-Bis-[(3-{3-[3-(benzyloxycarbonylamino)propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylamino}-propyl]-benzoyl]-aminomethyl}benzyl methacrylate (**50**):

From 1.143 g (0.33 mmol) of acid **26c** and 243 mg of hydrochloride **43b**. Column chromatography (silica gel, dichloromethane/2-4% methanol) gives **50** (1.074 g, 0.81 mmol, 82 %) as colourless foam which is lyophilised from benzene.

^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 18 H, CCH_3), 1.72 (m, 8 H, -CH_2-), 1.89 (m, 7 H, -CH_2-, CH_3), 2.53 (m, 12 H, ArCH_2), 3.10 (m, 8 H, NHCH_2), 3.31 (m, 4 H, NHCH_2), 4.58 (d, 2 H, ArCH_2N), 4.9 (s, br, 2 H, NH), 5.02 (s, 4 H, Z-CH_2), 5.10 (s, 2 H, ArCH_2O), 5.24 (s, br, 2 H, NH), 5.52 (s, 1 H, CMe=CH_2), 6.08 (s, 1 H, CMe=CH_2), 7.02 (s, 1 H, ArH), 7.08 (s, 3 H, ArH, NH), 7.24-7.36 (m, 20 H, ArH, NH), 7.45 (s, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.2 (CH_3), 28.3 (C*C*H_3), 30.4 (CH_2), 31.0 (CH_2), 31.2 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 39.1 (CH_2), 39.5 (CH_2), 40.0 (CH_2), 43.5 (ArCH_2N), 66.0 (ArCH_2O), 66.4 (PhCH_2), 79.1 (*C*CH_3), 124.8, 125.0, 125.3, 125.8, 127.9, 128.2, 128.4, 131.6, 132.1, 134.4, 134.6, 135.0, 136.0, 136.5, 138.7, 141.6, 141.8, 156.1 (CON), 156.5 (CON), 167.9 (br, CO).

FAB-MS; *m/z* (%): 1351 (0.25) [M^++Na], 1329 (0.12) [M^++H].

$C_{77}H_{97}N_7O_{13}$ (1328.66): calcd. C 69.61, H 7.36, N 7.38; found C 69.91, H 6.96, N 6.71.

4-{3,5-Bis-[3-(tert.butyloxycarbonylphenylalanoylamino)propyl]benzoyl-aminomethyl}benzyl acrylate (**53**):

From 1.0 g (1.37 mmol) of the acid **28c** and 391 mg of the 4-aminomethylbenzyl acrylate hydrochloride **37b**. Chromatographic separation (silica gel, dichloromethane/2-3% methanol) affords 948 mg (1.05 mmol, 76.6 %) of the monomer **53** which is lyophilised from dioxane.

^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 18 H, CCH_3), 1.63 (m, 4 H, -CH_2-), 2.44 (m, 4 H, $ArCH_2$), 2.93 (m, 4 H, $PhCH_2$), 3.03 (m, 4 H, $NHCH_2$), 4.30 (s, br, 2 H, CH), 4.62 (d, 2 H, $ArCH_2N$), 5.11 (d, br, 1 H, NH), 5.26 (s, br, 2 H, $ArCH_2O$), 5.80 (dd, 1 H, $CH=CH_2$), 6.10 (dd, 1 H, $CH=CH_2$), 6.36 (dd, 1 H, $CH=CH_2$), 6.97 (s, 1 H, ArH), 7.1-7.5 (m, br, 20 H, ArH, NH).

^{13}C NMR ($CDCl_3$): δ = 28.3 (CCH_3), 30.2 (CH_2), 31.9 (CH_2), 37.9 (CH_2), 38.6 (CH_2), 43.7 ($ArCH_2N$), 56.4 ($PhCH_2$), 58.1, 65.9 ($ArCH_2O$), 80.1 (CCH_3), 125.1, 126.8, 128.4, 128.6, 129.3, 131.2, 136.8, 139.1, 141.4, 158.2 (CON), 165.7 (CO), 171.5 (CO).

FAB-MS: *m/z* (%) = 904 (5.88) [M^+].

$C_{52}H_{65}N_5O_9$ (904.12): calcd. C 69.08, H 7.25, N 7.95; found C 68.69, H 6.82, N 7.70.

4-{3,5-Bis-[3-(tert.butyloxycarbonylphenylalanoylamino)propyl]benzoyl-aminomethyl}benzyl methacrylate (**55**):

From 660 mg (0.9 mmol) of the acid **28c** and 198 mg 4-aminomethylbenzyl methacrylate hydrochloride **43b**. Column chromatography (silica gel, dichloromethane/1-4% methanol) affords 615 mg (0.67 mmol, 81.7 %) of the monomer **55** which can be lyophilised from dioxane.

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.32 (s, 18 H, CCH_3), 1.65 (m, 4 H, -CH_2-), 1.88 (s, 3 H, CH_3), 2.44 (m, 4 H, $ArCH_2$), 2.88 (m, 4 H, $PhCH_2$), 3.04 (m, 4 H, $NHCH_2$), 4.30 (s, br, 2 H, CH), 4.57 (s, 2 H, $ArCH_2N$), 5.10 (s, 2 H, $ArCH_2O$), 5.52 (s, 1 H,

CMe=CH_2), 6.07 (s, 1 H, CMe=CH_2), 6.98 (s, 1 H, ArH), 7.14-7.26 (m, br, 10 H, ArH), 7.29-7.38 (m, br, 6 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 17.8 (CH_3), 27.8 (C*C*H_3), 29.9 (CH_2), 31.9 (CH_2), 37.9 (CH_2), 38.5 (CH), 43.1 (ArCH_2N), 55.5 (PhCH_2), 65.8 (ArCH_2O), 79.6 (*C*CH_3), 124.7, 125.6, 126.4, 128.1, 128.9, 131.6, 133.9, 134.7, 135.7, 136.5, 138.5, 141.3, 155.4 (CON), 167.7 (CO), 168.1 (CO), 171.8 (CO).

FAB-MS: *m/z* (%) = 919 (1.05) [M^++H].

7.7. Polymerisations

General Polymerisation Procedure (B). To a solution of the monomer (0.15 mmol) in 200 µl freshly degassed benzene under nitrogen 100 µl (1.5 mol-%) of a 0.022 M initiator solution in benzene are added. The mixture is stirred in a sealed tube at polymerisation temperature for the given time. The polymer is dissolved in THF, precipitated with hexane and lyophilised.

Poly-[4-(tert.butyloxycarbonylamino)-methylbenzyl acrylate] (**40**):

From monomer **37a** (Tabel 3.1., 48 h).

^{1}H NMR ($CDCl_3$): δ = 1.41 (s, br, 9 H, CCH_3), 1.6-1.8 (s, br, 2 H, CH_2), 2.32 (s, br, 1 H, CH), 4.15 (s, br, 2 H, ArCH_2N), 4.88 (s, br, 2 H, ArCH_2O), 5.48 (s, br, 1 H, NH), 7.12 (s, br, 4 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.4 (C*C*H_3), 35.2, 41.4, 44.1 (ArCH_2N), 66.2 (ArCH_2O), 79.3 (*C*CH_3), 127.4 (Ar), 128.1 (Ar), 134.4 (Ar), 139.2 (Ar), 156.0 (CON), 174.1 (CO).

TGA: 180°C (-40.8%, -Boc).

$(C_{16}H_{21}NO_4)_n$ $(291.35)_n$: calcd. C 65.92, H 7.26, N 4.81; found C 66.25, H 7.35, N 4.36.

Poly-[4-({3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-aminomethyl)-benzyl acrylate] (**41**):

From G-1 monomer **38** (Tabel 3.1., 48 h).

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.27 (s, br, 18 H, CCH_3), 1.56 (s, br, 6 H, -CH_2-), 1.78 (s, br, 1 H, CH), 2.39 (s, br, 4 H, ArCH_2), 2.85 (s, br, 4 H, NHCH_2), 4.27 (s, br, 2 H, ArCH_2N), 4.74 (s, br, 2 H, ArCH_2O), 6.96 (s, br, 5 H, ArH), 7.35 (s, br, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 28.4 (C*C*H_3), 31.3 (CH_2), 32.6 (CH_2), 35.4 (CH_2), 39.8 (CH_2), 41.6 (CH_2), 43.4 (ArCH_2N), 66.2 (ArCH_2O), 78.9 (*C*CH_3), 125.1 (Ar), 125.7 (Ar), 127.7 (Ar), 128.1 (Ar), 131.7 (Ar), 134.6 (Ar), 138.9 (Ar), 141.9 (Ar), 156.1 (CON), 167.9 (CO), 174.2 (CO).

TGA: 207°C (-30.3%, -2 Boc).

$(C_{34}H_{47}N_3O_7)_n$ $(609.34)_n$: calcd. C 66.97, H 7.77, N 6.89; found C 66.04, H 7.51, N 7.26.

Poly-[4-(tert.butyloxycarbonylamino)-methylbenzyl methacrylate] (**44**):

From monomer **43a** (Tabel 3.2., 48 h).

^{1}H NMR ($CDCl_3$): δ = 0.8-0.9 (s, br, 3 H, CH_3), 1.40 (s, br, 9 H, CCH_3), 1.5-1.6 (s, br, 2 H, CH_2), 4.21 (s, br, 2 H, ArCH_2N), 4.85 (s, br, 2 H, ArCH_2O), 5.50 (s, br, 1 H, NH), 7.16 (s, br, 4 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.6 (CH_3), 28.4 (C*C*H_3), 44.2 (ArCH_2N), 54.0, 66.5 (ArCH_2O), 79.3 (*C*CH_3), 127.5 (Ar), 128.4 (Ar), 133.8 (Ar), 139.4 (Ar), 156.0 (CON), 176.9 (CO).

TGA: 181°C (-36.8%, -Boc).

$(C_{17}H_{23}NO_4)_n$ $(305.16)_n$: calcd. C 66.86, H 7.59, N 4.59; found C 67.04, H 8.04, N 4.84.

Poly-[4-({3,5-bis-[3-(tert.butyloxycarbonylamino)-propyl]-benzoyl}-aminomethyl)-benzyl methacrylate] (**47**):

From G-1 monomer **45** (Tabel 3.2., 15 h).

^{1}H NMR ($CDCl_3$): δ = 0.80 (s, br, 3 H, CH_3), 1.35 (s, br, 18 H, CCH_3), 1.66 (s, br, 6 H, -CH_2-), 2.48 (s, br, 4 H, $ArCH_2$), 2.96 (s, br, 4 H, $NHCH_2$), 4.44 (s, br, 3 H, $ArCH_2N$, NH), 4.82 (s, br, 2 H, NH), 5.07 (s, br, 2 H, $ArCH_2O$), 7.02-7.20 (s, br, 5 H, ArH), 7.47 (s, br, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.8 (CH_3), 28.4 (C*C*H_3), 31.2 (CH_2), 32.4 (CH_2), 39.6 (CH_2), 43.3 (CH_2), 44.7 (Ar CH_2N), 54.4, 67.0 (Ar CH_2O), 78.9 (*C*CH_3), 124.0 (Ar), 127.8 (Ar), 131.8 (Ar), 134.3 (Ar), 139.0 (Ar), 141.8 (Ar), 156.1 (CON), 168.6 (CO), 178.3 (CO).

TGA: 199°C (-29.7%, -2 Boc).

$(C_{35}H_{49}N_3O_7)_n$ $(623.79)_n$: calcd. C 67.39, H 7.92, N 6.74; found C 68.33, H 6.92, N 7.47.

Poly-(4-{[3,5-bis(3-{3,5-bis-[3-(tertbutyloxycarbonylamino)-propyl]-benzoylamino}-propyl)-benzoyl]aminomethyl}benzyl methacrylate) (**48**):

From G-2 monomer **46**, 0.5 M solution in toluene, 3 mol-% BPB, 100°C, 16 hours (Tabel 3.2. and 3.4.)

^{1}H NMR ($CDCl_3$): δ = 0.5-0.8 (s, br, 3 H, CH_3), 1.3-1.4 (s, br, 36 H, CCH_3), 1.6-1.8 (s, br, 12 H, -CH_2-), 1.8-2.0 (s, br, 2 H, -CH_2-), 2.5 (s, br, 12 H, $ArCH_2$), 3.0 (s, br, 8 H,

$NHCH_2$), 3.2 (s, br, 4 H, $NHCH_2$), 4.5 (s, br, 2 H, $ArCH_2N$), 4.7-5.2 (s, br, 9 H, $ArCH_2O$, NH), 6.9-7.2 (s, br, 5 H, ArH), 7.4 (s, br, 8 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_3), 28.4 (CCH_3), 30.6 (CH_2), 31.2 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 39.6 (CH_2), 41.2 (CH_2), 43.4 (CH_2), 45.2 ($ArCH_2N$), 54.2, 66.6 ($ArCH_2O$), 78.9 (CCH_3), 124.9 (Ar), 127.1 (Ar), 128.6 (Ar), 131.6 (Ar), 134.5 (Ar), 139.2 (Ar), 141.8 (Ar), 156.1 (CO), 167.9 (CO).

Poly-(4-{3-[3-(benzyloxycarbonylamino)-propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylaminomethyl}benzyl methacrylate) (**51**):

From G-1 monomer **49** (Tabel 3.3., 12 h).

^{1}H NMR ($CDCl_3$): δ = 0.77 (s, br, 3 H, CH_3), 1.39 (s, br, 9 H, CCH_3), 1.63 (s, br, 5 H, -CH_2-), 2.01 (s, br, 1 H, -CH_2-), 2.43 (s, br, 4 H, $ArCH_2$), 2.94 (s, br, 4 H, $NHCH_2$), 4.41 (s, br, 2 H, $ArCH_2N$), 4.92 (s, br, 5 H, $ArCH_2O$, Z-CH_2, NH), 5.55 (s, br, 1 H, NH), 6.99-7.29 (s, br, 11 H, ArH), 7.45 (s, br, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_3), 28.3 (CCH_3), 32.2 (CH_2), 32.4 (CH_2), 39.6 (CH_2), 40.0 (CH_2), 43.3 (CH_2), 44.7 ($ArCH_2N$), 54.6, 66.3 ($ArCH_2O$), 78.9 (CCH_3), 125.0 (Ar), 127.9 (Ar), 128.3 (Ar), 131.8 (Ar), 134.3 (Ar), 136.5 (Ar), 139.0 (Ar), 141.7 (Ar), 156.1 (CON), 156.7 (CON), 168.0 (CO), 178.1 (CO).

TGA: 210°C (-35.8%, -Boc).

$(C_{38}H_{47}N_3O_7)_n$ $(657.34)_n$: calcd. C 69.38, H 7.20, N 6.39; found C 70.0, H 6.76, N 6.50.

Poly-(4-{3,5-bis-[(3-{3-[3-(benzyloxycarbonylamino)propyl]-5-[3-(tert.butyloxycarbonylamino)-propyl]-benzoylamino}-propyl]-benzoyl]-aminomethyl}benzyl methacrylate) (**52**):

From G-2 monomer **50**, 0.25 M solution in toluene, 3 mol-% BPB, 100°C, 5 hours (Tabel 3.3.).

^{1}H NMR ($CDCl_3$): δ = 0.5-0.8 (s, br, 3 H, CH_3), 1.3-1.4 (s, br, 18 H, CCH_3), 1.6-1.7 (s, br, 12 H, -CH_2-), 2.0 (s, br, 2 H, -CH_2-), 2.3-2.5 (s, br, 12 H, $ArCH_2$), 2.9-3.0 (s, br, 8 H, $NHCH_2$), 3.1 (s, br, 4 H, $NHCH_2$), 4.9-5.0 (s, br, 9 H, $ArCH_2N$, Z-CH_2), 5.1 (s, br, 2 H, $ArCH_2O$), 5.6-5.8 (s, br, 2 H, NH), 6.9-7.0 (s, br, 5 H, ArH, NH), 7.1-7.3 (s, br, 13 H, ArH), 7.4-7.5 (s, br, 7 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.3 (CH_3), 28.43 (C*C*H_3), 29.69 (CH_2), 31.12 (CH_2), 32.46 (CH_2), 39.66 (CH_2), 40.22 (CH_2), 42.1 (CH_2), 45.3 ($ArCH_2N$), 54.1, 66.45 ($ArCH_2O$), 78.93 (*C*CH_3), 124.88 (Ar), 127.83 (Ar), 128.40 (Ar), 131.67 (Ar), 134.68 (Ar), 136.69 (Ar), 141.82 (Ar), 156.01 (CON), 156.23 (CON), 156.72 (CON), 168.01 (CO).

Poly-(4-{3,5-bis-[3-(tert.butyloxycarbonylphenylalanoylamino)propyl]benzoyl-aminomethyl}benzyl acrylate) (**54**):

From monomer **53** (Tabel 3.5., 48 h).

^{1}H NMR ([D_7]DMF): δ =1.2-1.3 (s, br, 18 H, CCH_3), 1.5-1.6 (s, br, 4 H, -CH_2-), 1.8 (s, br, 3 H, CH, -CH_2-), 2.3-2.4 (s, br, 4 H, $ArCH_2$), 2.8 (s, br, 2 H, CH), 2.9 (s, br, 4 H, $NHCH_2$), 4.2-4.3 (s, br, 6 H, $ArCH_2N$, $PhCH_2$), 4.8-4.9 (s, br, 2 H, $ArCH_2O$), 6.9-7.3 (s, br, 15 H, ArH), 7.4 (s, br, 2 H, ArH).

^{13}C NMR ([D_7]DMF): δ = 28.4 (C*C*H_3), 29.9 (CH_2), 32.0 (CH_2), 38.1 (CH_2), 38.6 (CH), 43.0 ($ArCH_2N$), 54.1, 55.6 ($PhCH_2$), 65.8 ($ArCH_2O$), 79.5 (*C*CH_3), 124.8 (Ar), 126.4 (Ar), 127.7 (Ar), 128.0 (Ar), 129.0 (Ar), 134.6 (Ar), 138.3 (Ar), 141.4 (Ar), 155.6 (CON), 168.2 (CO), 172.1 (CO).

Poly-(4-{3,5-bis-[3-(tert.butyloxycarbonylphenylalanoylamino)propyl]benzoyl-aminomethyl}benzyl methacrylate) (**56**):

From monomer **55** (Tabel 3.5., 48 h).

^{1}H NMR ($CDCl_3$): δ = 0.5 (s, br, 3 H, CH_3), 1.35 (s, br, 18 H, CCH_3), 1.6 (s, br, 2H, CH_2), 1.9 (s, br, 4 H, CH_2), 2.4 (s, br, 4 H, CH_2), 2.9 (s, br, 4 H, CH_2), 3.1 (s, br, 2 H, CH), 4.3 (s, br, 6 H, CH_2), 4.6 (s, br, 2 H, CH_2), 5.35 (s, br, 2 H, NH), 6.8-7.0 (s, br, 7 H, ArH), 7.1-7.5 (s, br, 10 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 18.3 (CH_3), 28.3 (CCH_3), 30.2, 31.8, 37.8, 38.6 (CH), 43.7 ($ArCH_2N$), 45.7, 56.0 ($PhCH_2$), 66.0 ($ArCH_2O$), 80.1 (CCH_3), 125.1, 125.9, 126.8, 128.3, 128.4, 128.5, 129.3, 132.1, 134.5, 135.2, 136.1, 136.7, 138.6, 141.4, 155.6 (CON), 167.2 (CO), 167.8 (CO), 171.6 (CO).

TGA: 189°C (-20.8%, -2 Boc).

7.8. Reactions on the polymer

General Procedure for Deprotection of Amino Polymers (C). 100 mg of the protected amino polymer are dissolved in 5 ml of trifluoroacetic acid and strirred at room temperature for 24 hours. The trifluoroacetic acid is removed and the residue lyophilised from water.

General Procedure for Amide Coupling on the Polymer (D). 0.1 mmol of the deprotected polymer are dissolved in methanol. 0.4 mmol (70 µl) diisopropylethylamine are added, the solution is stirred for 1 hour, then 0.4 mmol of the hydroxysuccinimide ester are added, the reaction mixture is stirred for 24 hours. The solvent is partially removed, the polymer precipitated with diethyl ether, and lyophilised from dioxane.

Poly-(4-{[3,5-bis-(3-aminopropyl)-benzoyl]-aminomethyl}-benzyl acrylate) x 2 trifluoroacetic acid (**57**):

From polymer **41** according to general procedure (C).

^{1}H NMR ([D$_4$]methanol): δ = 1.59 (s, br, 2 H, -CH$_2$-), 1.91 (s, br, 4 H, -CH$_2$-), 2.34 (s, br, 1 H, CH), 2.64 (s, br, 4 H, ArCH$_2$), 2.86 (s, br, 4 H, NHCH$_2$), 4.50 (s, br, 2 H, ArCH$_2$N), 4.85 (s, br, 2 H, ArCH$_2$O), 7.17 (s, br, 5 H, ArH), 7.52 (s, br, 2 H, ArH).

^{13}C NMR ([D$_4$]methanol): δ = 30.0 (CH$_2$), 33.2 (CH$_2$), 35.9 (CH$_2$), 40.3 (CH$_2$), 42.8, 44.2 (ArCH$_2$N), 67.4 (ArCH$_2$O), 118.2 (q, TFAA), 125.9 (Ar), 127.2 (Ar), 128.2 (Ar), 129.5 (Ar), 133.0 (Ar), 135.9 (Ar), 140.3 (Ar), 142.8 (Ar), 162.1 (q, TFAA), 169.8 (CO), 175.8 (CO).

Poly-(4-{[3,5-bis-(3-aminopropyl)-benzoyl]-aminomethyl}-benzyl methacrylate) x 2 trifluoroacetic acid (**61**):

From polymer **47** according to general procedure (C).

^{1}H NMR ([D$_4$]methanol): δ = 0.72 (s, br, 3 H, CH$_3$), 1.92 (s, br, 6 H, -CH$_2$-), 2.65 (s, br, 4 H, ArCH$_2$), 2.87 (s, br, 4 H, NHCH$_2$), 4.47 (s, br, 2 H, ArCH$_2$N), 4.9-5.2 (H$_2$O), 7.23 (s, br, 5 H, ArH), 7.54 (s, br, 2 H, ArH).

^{13}C NMR ([D$_4$]methanol): δ = 16.1 (CH$_3$), 31.2 (CH$_2$), 33.2 (CH$_2$), 40.1 (CH$_2$), 44.3 (ArCH$_2$N), 46.2, 55.5, 67.8 (ArCH$_2$O), 118.1 (q, TFAA), 126.5 (Ar), 128.9 (Ar), 130.0 (Ar), 132.9 (Ar), 135.3 (Ar), 136.0 (Ar), 140.6 (Ar), 142.8 (Ar), 162.8 (q, TFAA), 170.0 (CO), 178.4 (CO).

Poly-{4-[(3,5-bis-{3-[(N-tert.butyloxycarbonylphenylalanoyl)amino]-propyl}-benzoyl)-aminomethyl]-benzyl acrylate} (**54a**):

From polymer **57** (80 mg) and N-*tert.*butyloxycarbonyl-phenylalanine hydroxysuccinimide ester (**58**) according to general procedure (D).

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ =1.2-1.3 (s, br, 18 H, CCH_3), 1.5-1.6 (s, br, 4 H, -CH_2-), 1.8 (s, br, 3 H, CH, -CH_2-), 2.3-2.4 (s, br, 4 H, $ArCH_2$), 2.8 (s, br, 2 H, CH), 2.9 (s, br, 4 H, $NHCH_2$), 4.2-4.3 (s, br, 6 H, $ArCH_2N$, $PhCH_2$), 4.8-4.9 (s, br, 2 H, $ArCH_2O$), 6.9-7.3 (s, br, 15 H, ArH), 7.4 (s, br, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 28.4 (CCH_3), 29.9 (CH_2), 32.0 (CH_2), 38.1 (CH_2), 38.6 (CH), 43.0 ($ArCH_2N$), 54.1, 55.6 ($PhCH_2$), 65.8 ($ArCH_2O$), 79.5 (CCH_3), 124.8 (Ar), 126.4 (Ar), 127.7 (Ar), 128.0 (Ar), 129.0 (Ar), 134.6 (Ar), 138.3 (Ar), 141.4 (Ar), 155.6 (CON), 168.2 (CO), 172.1 (CO).

Poly-{[4-[(3,5-bis-{3-[(2,2-dimethylacryl)amino]-propyl}-benzoyl)-aminomethyl]-benzyl acrylate} (**60**):

From polymer **57** (80 mg) and 2,2-dimethylacrylic acid hydroxysuccinimide ester (**59**) according to general procedure (D).

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 1.4-1.7 (s, br, 10 H, -CH_2-, CH_3), 2.0 (s, br, 6 H, CH_3), 2.4-2.5 (s, br, 7 H, $ArCH_2$, CH, -CH_2-), 3.0-3.1 (s, br, 4 H, $NHCH_2$), 4.1-4.2 (s, br, 2 H, $ArCH_2N$), 4.3-4.5 (s, br, 2 H, $ArCH_2O$), 5.6 (s, br, 2 H, =CH), 7.0-7.2 (s, br, 5 H, ArH), 7.4-7.5 (s, br, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 20.1 (CH_3), 32.1 (CH_2), 34.0 (CH_2), 39.5 (CH_2), 40.3 (CH_2), 42.6 (CH_2), 43.7, 44.2 ($ArCH_2N$), 52.2, 55.7, 67.3 ($ArCH_2O$), 119.7 (C=C), 126.2, 128.2, 128.8, 129.4, 133.1, 135.6, 140.3, 143.6, 151.4 (CO), 158.9 (CO), 169.4 (CO),175.3 (CO).

Poly-{4-[(3,5-bis-{3-[(2,2-dimethylacryl)amino]-propyl}-benzoyl)-aminomethyl]-benzyl methacrylate} (**62**):

From polymer **61** (90 mg) and **59** according to general procedure (D).

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 0.6-0.8 (s, br, 3 H, CH_3), 1.7 (s, br, 12 H, -CH_2-, CH_3), 2.0 (s, br, 6 H, CH_3), 2.4 (s, br, 4 H, ArCH_2), 3.1 (s, br, 4 H, NHCH_2), 4.4 (s, br, 2 H, ArCH_2N), 4.7-4.8 (s, br, 2 H, ArCH_2O), 5.6 (s, br, 2 H, =CH), 7.0-7.2 (s, br, 5 H, ArH), 7.4 (s, br, 2 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 18.3 (CH_3), 19.1 (CH_3), 30.3 (CH_2), 32.4 (CH_2), 37.9, 38.7 (CH_2), 42.9, 44.6 (ArCH_2N), 54.1, 66.6 (ArCH_2O), 68.7, 118.1 (C=C), 124.6, 127.4, 128.1, 131.5, 133.9, 138.6, 141.7, 149.9, 167.8 (CO), 174.2 (CO).

Poly-(4-{3-[3-(benzyloxycarbonylamino)-propyl]-5-(3-aminopropyl)-benzoylaminomethyl}benzyl methacrylate) x trifluoroacetic acid (**63**):

From polymer **51** according to general procedure (C).

^{1}H NMR ($CDCl_3$/[D_4]methanol): δ = 0.7-0.9 (s, br, 3 H, CH_3), 1.7 (s, br, 2 H, -CH_2-), 1.9 (s, br, 4 H, -CH_2-), 2.6 (s, br, 4 H, ArCH_2), 2.8 (s, br, 4 H, NHCH_2), 4.2 (s, br, 2 H, ArCH_2N), 4.3-4.4 (H_2O), 4.9 (s, br, 2 H, Z-CH_2), 7.1 (s, br, 8 H, ArH), 7.4 (s, br, 4 H, ArH).

^{13}C NMR ($CDCl_3$/[D_4]methanol): δ = 17.9 (CH_3), 29.0 (CH_2), 31.4 (CH_2), 38.2 (CH_2), 42.6, 44.2 (ArCH_2N), 56.7, 65.6 (ArCH_2O), 67.2 (PhCH_2), 124.5, 126.8, 127.4, 128.2, 131.6, 133.2, 134.0, 138.4, 140.6, 161.2 (CO), 168.0 (CO), 178.2 (CO).

Poly-(4-{3-[3-(benzyloxycarbonylamino)-propyl]-5-[3-(2,2-dimethylacrylamino)-propyl]- benzoylaminomethyl}benzyl methacrylate) (**64**):

From polymer **63** according to general procedure (D). 0.1 mmol of polymer **63** is dissolved in dichloromethane/methanol 1:1 and treated with 0.2 mmol of diisopropylamine and 0.2 mmol **59**.

^{1}H NMR ([D$_7$]DMF): δ = 1.3 (s, br, 3 H, CH_3), 1.7 (s, br, 7 H, -CH_2-, CH_3), 2.0-2.2 (s, br, 5 H, CH_3, -CH_2-), 2.6 (s, br, 4 H, ArCH_2), 3.1 (s, br, 4 H, NHCH_2), 4.6 (s, br, 2 H, ArCH_2N), 5.0 (s, br, 2 H, ArCH_2O), 5.7-5.8 (s, br, 3 H, Z-CH_2, =CH), 7.1-7.4 (s, br, 8 H, ArH), 7.5-7.6 (s, br, 4 H, ArH).

^{13}C NMR ([D$_7$]DMF): δ = 18.6 (CH_3), 31.7 (CH_2), 32.0 (CH_2), 39.9 (CH_2), 40.9 (CH_2), 43.6, 45.7 (ArCH_2N), 51.6, 54.5, 66.1 (ArCH_2O), 67.3 (PhCH_2), 112.3, 119.9 (C=C), 125.5, 128.3, 128.9, 132.0, 134.7, 138.3, 140.7, 142.8, 149.0, 157.1 (CO), 167.1 (CO).

Poly-[4-(3-[3-(benzyloxycarbonylamino)-propyl]-5-{3-[(N-tert.butyloxycarbonylphenylalanoyl) amino]-propyl}-benzoylaminomethyl)benzyl methacrylate] (**65**):

From polymer **63** according to general procedure (D). 0.1 mmol of polymer **63** is dissolved in dichloromethane/methanol 1:1 and treated with 0.2 mmol of diisopropylamine and 0.2 mmol **58**.

^{1}H NMR ([D$_7$]DMF): δ = 1.03 (s, br, 3 H, CH_3), 1.8-2.0 (s, br, 15 H, CCH_3, -CH_2-), 2.6 (s, br, 5 H, ArCH_2, CH), 3.1 (s, br, 4 H, NHCH_2), 4.3 (s, br, 4 H, ArCH_2N, PhCH_2), 4.4-4.5 (s, br, 2 H, ArCH_2O), 5.0 (s, br, 2 H, Z-CH_2), 6.7 (s, br, 3 H, ArH), 7.0-7.3 (s, br, 14 H, ArH, NH), 7.6 (s, br, 4 H, ArH).

^{13}C NMR ([D$_7$]DMF): δ = 20.1 (CH_3), 28.4 (C*C*H_3), 31.5 (CH_2), 32.0 (CH_2), 33.2 (CH_2), 39.0 (CH_2), 41.0, 43.6, 45.6 (ArCH_2N), 54.1, 56.8 (PhCH_2), 66.1 (ArCH_2O),

67.4 ($PhCH_2$), 78.8 (CCH_3), 125.6 (Ar), 126.9 (Ar), 128.3 (Ar), 128.7 (Ar), 128.9 (Ar), 129.9 (Ar), 135.5 (Ar), 138.8 (Ar), 142.7 (Ar), 156.1 (CO), 167.7 (CO), 172.3 (CO).

Poly-(4-{3-(3-aminopropyl)-5-[3-(phenylalanoylamino)-propyl]-benzoylaminomethyl}benzyl methacrylate} x 2 trifluoroacetic acid (**66**):

Polymer **65** (0.1 mmol) is dissolved in 5 ml trifluoroacetic acid; 94 µl thioanisole (99 mg, 0.8 mmol) are added. The mixture is stirred at room temperature for 24 hours. The solvents are evaporated and the residue is lyophilised from water.

^1H NMR ([D_4]methanol): δ = 0.7-0.9 (s, br, 2 H, CH_3), 1.5-1.6 (s, br, 6 H, $-CH_2-$), 2.4-2.6 (s, br, 5 H, $ArCH_2$, CH), 3.1 (s, br, 6 H, $NHCH_2$, $PhCH_2$), 4.1 (s, br, 2 H, $ArCH_2N$), 4.3-4.5 (s, br, 2 H, $ArCH_2O$), 7.0-7.5 (s, br, 12 H, ArH).

^{13}C NMR ([D_4]methanol): δ = 18.2 (CH_3), 30.0 (CH_2), 31.5 (CH_2), 33.7 (CH_2), 38.7 (CH_2), 40.0, 44.2 ($ArCH_2N$), 54.8, 55.8 ($PhCH_2$), 65.0 ($ArCH_2O$), 118.7 (q, TFAA), 126.4 (Ar), 127.4 (Ar), 128.8 (Ar), 130.0 (Ar), 130.5 (Ar), 135.7 (Ar), 140.5 (Ar), 142.4 (Ar), 143.4 (Ar), 162.7 (CO), 162.9 (q, TFAA), 169.5 (CO), 170.3 (CO).