Dendronized polyacrylates with glucose units in the periphery

Andrea Zistler, Sabine Koch and A. Dieter Schlüter*

Institut für Organische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany. Fax.: Int. +49 30 838 3357. E-mail: adschlue@chemie.fu-berlin.de

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The synthesis of dendritic building blocks (dendrons) of the first (G-1) and second generation (G-2) with peripheral acetyl-protected glucose moieties is reported. The dendrons can be selectively deprotected at the focal point and the resulting carboxylic acids then attached to an acrylic acid derivative to furnish dendronized G-1 and G-2 macromonomers. Their radically initiated polymerization leads to dendronized polyacrylates with two and four surface glucose units per repeat unit.

Introduction

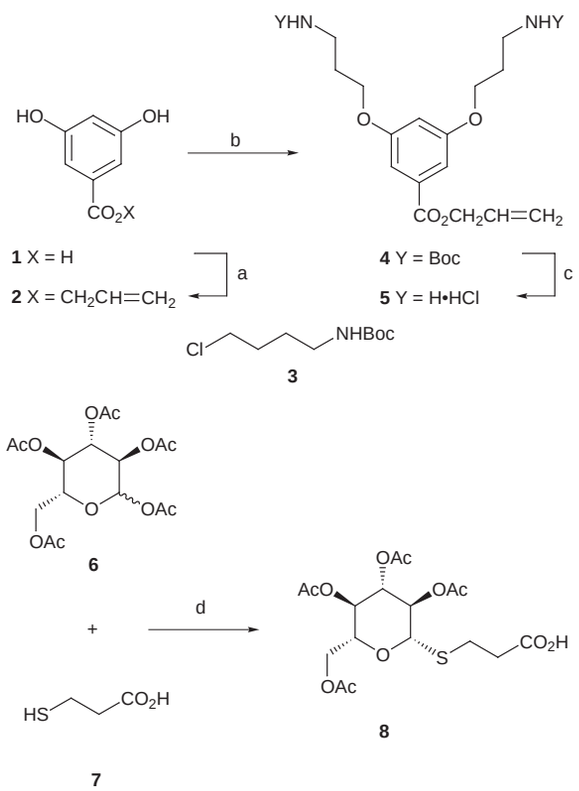
In recent years surface-functionalized dendrimers[1] have become particularly interesting because of their and the attached residues' unique properties. The dense packing of the residues on the dendrimers' surface has a cooperative effect upon these properties.[2–4] The multivalent effect of clustered saccharides[5] is well known for carbohydrate–protein interactions,[6] and a variety of carbohydrate-functionalized dendrimers have been prepared to obtain model compounds for the study of carbohydrate–protein interactions and new neoglycoconjugates.[7–10]

The goal of a long-term project in our group is to make organic molecular objects available which have a defined and predetermined shape and nanometer scale.[11] Dendronized polystyrenes and poly(*para*-phenylene)s were shown to have a cylindrical shape in the condensed phase as well as in solution.[12] Recently we described the synthesis of various dendronized polystyrenes with hydroxy and amino groups on the periphery.[13,14] This was the first step towards surface-functionalized cylinders carried out to engineer the properties of these unusual macromolecules. Here we present a next step toward this goal, which is the synthesis of new glucose-functionalized G-1 and G-2 dendronized acrylic monomers **14** and **16** and the results of their radically initiated polymerization. Glucose serves as a model for biologically more relevant carbohydrate derivatives which will be utilized at a later stage.

Results and discussion

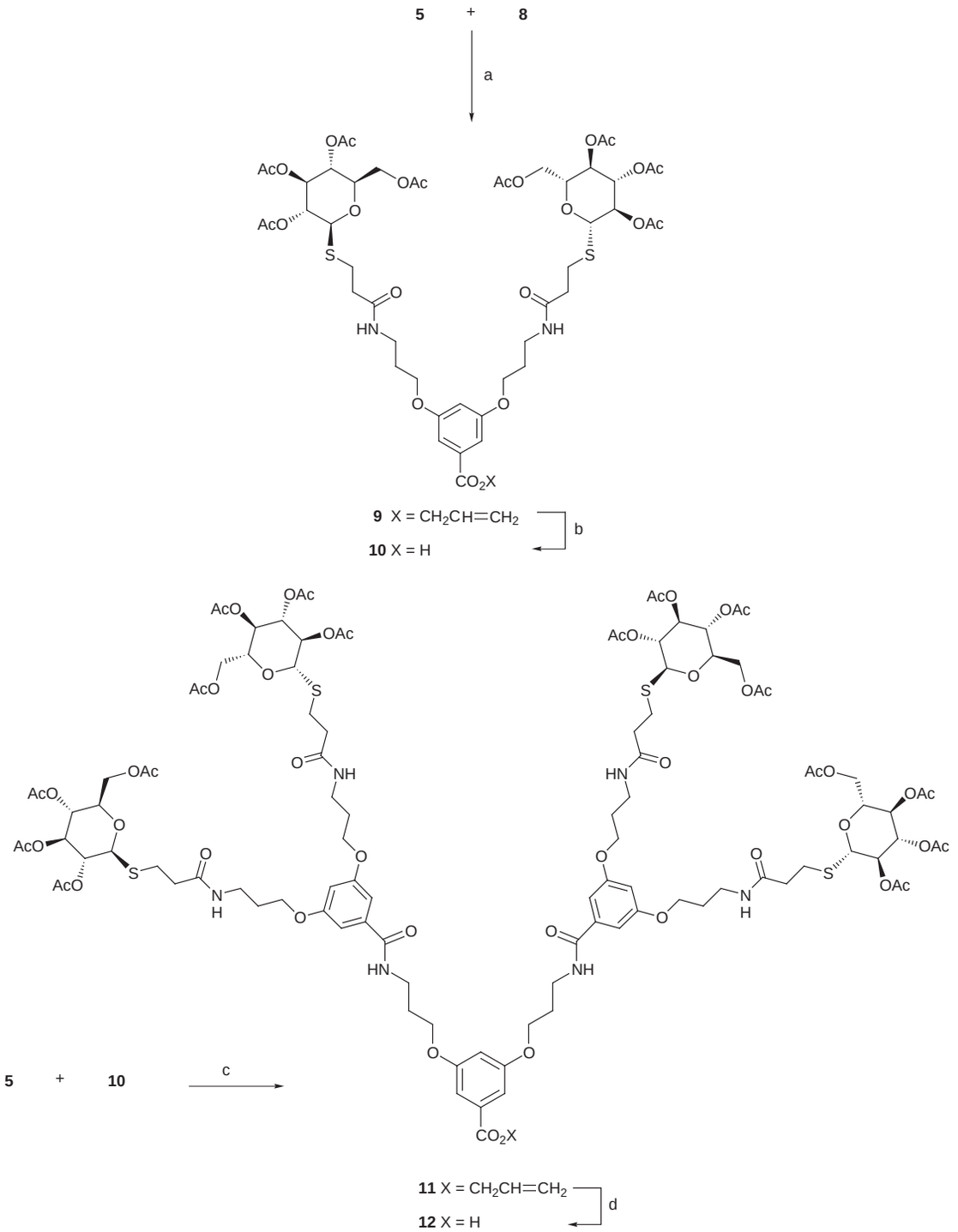
Recently we reported the convergent synthesis of a series of dendritic building blocks, which carry amino or hydroxy groups on the periphery and a carboxylic ester at the focal point.[15] Additionally, higher generation dendrons were synthesized according to a repetitive strategy from orthogonally protected G-1 building blocks. Amide formation proved a very successful growth step in many of these cases. It was therefore also applied in the present work to connect (a) G-1 dendrons to larger ones, (b) the glucose moieties to the amino-terminated dendrons, and (c) the sugar-coated dendrons to the polymerizable group in order to obtain the desired macromonomers **14** and **16**. The acetyl protective group on glucose was selected for cost reasons and because it can be easily and cleanly removed. The allylic carboxylates at the focal points of target molecules **9** and **11** have the advantage that they can be selectively cleaved in the presence of the peripheral acetates by a variety of transition-metal-catalyzed procedures.

The synthesis starts with esterification of cheap γ-resorcylic acid **1** to yield the allylic ester **2** (Scheme 1). The Boc-protected G-1 dendron **4** was obtained on the 20 gram scale in 81% yield



Scheme 1 Synthesis of G-1 aminodendron **5** and glucose unit **8**. *Reagents and conditions (yields)*: (a) prop-2-enol, H_2SO_4, reflux, 8 h (90%); (b) 1-(butoxycarbonylamino)-3-chloropropane **3**, K_2CO_3, 18-C-6, tetrabutylammonium iodide (TBAI), diethyl ketone, reflux, 18 h (81%); (c) THF, HCl, RT, 3 h (97%); (d) $BF_3{\cdot}Et_2O$, CH_2Cl_2, RT, 2 h (86%).

by a Williamson-type etherification of ester **2** with Boc-protected 3-chloropropylamine **3**. The peripherally deprotected G-1 dendron **5** was prepared by treatment of protected amine **4** with dil. hydrochloric acid in THF and isolated as the dihydrochloride in 97% yield. Compound **5** serves two purposes: the attachment of the carbohydrate moieties to give compound **9** and as an inner building block for the construction of the G-2 dendron **11** (Scheme 2). Acetyl-protected glucose was modified with a spacer according to an effective procedure[16] described by Stoddart and co-workers for galactose and lactose.[10c] The thioglycoside **8** was obtained as analytically pure material in 86% yield from penta-*O*-acetyl glucose **6** and 3-mercaptopropionic acid **7**. In the next step amino dendron **5** was derivatized by

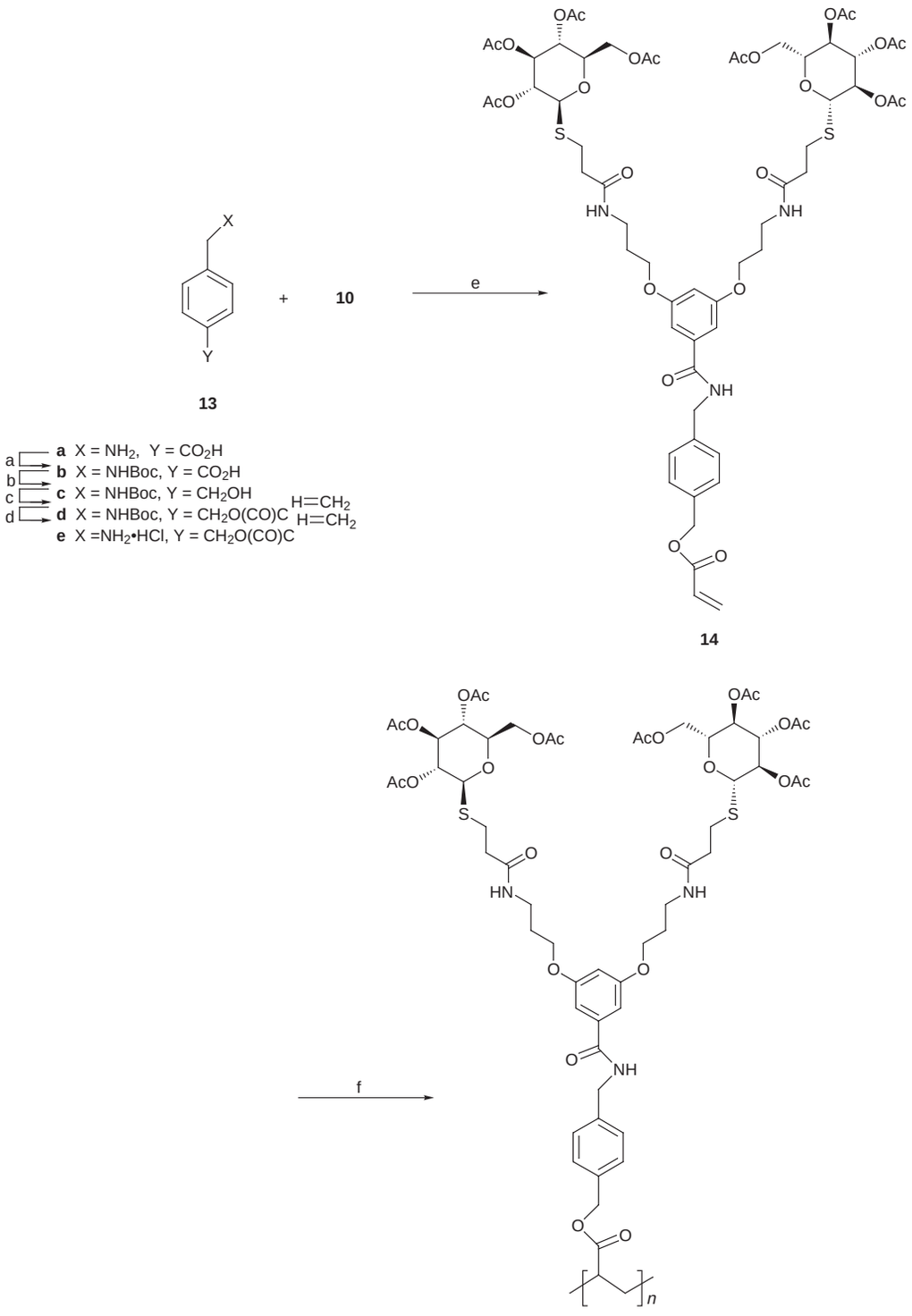


Scheme 2 Synthesis of glucose-modified dendrons **9** and **11**. *Reagents and conditions (yields)*: (a) (i) **8**, HOBT, CH_2Cl_2, RT, 10 min (ii) **5**, diisopropylethylamine (DIPEA), 30 min (iii) EDC, 18 h (91%); (b) $PdCl_2(PPh_3)_2$, TBTH, 0 °C, 2 h (94%); (c) (i) **10**, HOBT, CH_2Cl_2, RT, 10 min (ii) **5**, DBU, 30 min (iii) EDC, 18 h (68%); (d) $PdCl_2(PPh_3)_2$, TBTH, 0 °C, 2 h (60%).

attachment of two units of acid **8** (Scheme 2). Amide coupling was done by the convenient 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide (EDC)–HOBT method[17] and yielded the sugar G-1 dendron **9** on the 15 g scale in 91% yield. Selective deprotection of the allyl ester at the focal point did not affect the peripheral acetoxy groups and was best achieved with 2% $PdCl_2(PPh_3)_2$ and tributyltin hydride (TBTH). The reaction was performed on the 15 gram scale and gave the carboxylic acid **10** in excellent yields of 92–94%. The obtained product, however, contained some small quantities of tin impurities, which could not be entirely removed. To obtain analytically pure acid **10** the deprotection step was performed with 10% $Pd(PPh_3)_4$ and morpholine. This reaction was only carried out on the gram scale and gave the carboxylic acid **10** in 30% yield. Because of this unsatisfactory yield and the fact that the tin impurities did not interfere with the subsequent steps, the tin hydride method was preferred over the latter, and was the method we normally used.

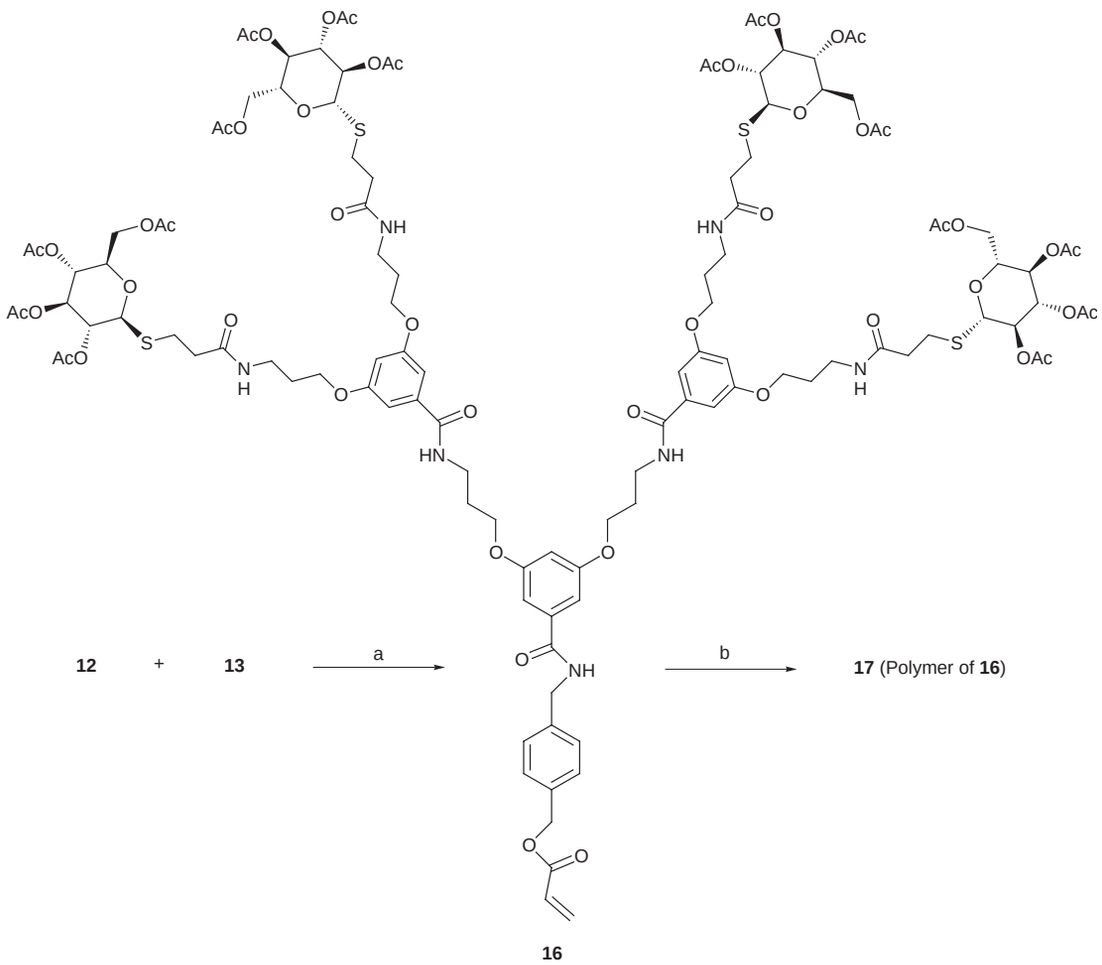
Combination of two equivalents of acid **10** with amino dendron **5** gave the G-2 dendron **11**. Amide coupling was performed analogously to the preparation of compound **9** and gave the sugar-functionalized second-generation dendron **11** in 68% yield. Cleavage of the allyl ester again was achieved with $PdCl_2(PPh_3)_2$–TBTH and yielded the G-2 carboxylic acid **12** in a clean and fast reaction (60%, losses during chromatography).

The obtained G-1 (**10**) and G-2 (**12**) carboxylic acids were used in the construction of dendronized macromonomers. Acrylate **13e**, easily obtained in four steps from acid **13a**, was



Scheme 3 Synthesis of G-1 macromonomer **14** and its polymerization. *Reagents and conditions (yields)*: (a) **13a**, di-*tert*-butyl dicarbonate, KOH, THF, RT, 1 h (94%); (b) **13b**, LAH, THF, 40 °C, 14 h (63%); (c) **13c**, NEt_3, DMAP, acryloyl chloride, THF, RT, 16 h (76%); (d) **13d**, HCl, THF, RT, 36 h (83%); (e) (i) **10**, HOBT, CH_2Cl_2, RT, 10 min (ii) **13e**, DIPEA, 30 min (iii) EDC, 24 h (88%); (f) AIBN, benzene, 55 °C, 16 h (92%).

chosen as the polymerizable unit (Schemes 3 and 4), as acrylates have been successfully used by various groups in the preparation of vinyl sugar polymers and copolymers.[18–20] The carbohydrate-functionalized dendrons were attached to compound **13e** again by the EDC–HOBT procedure. Macromonomers **14** (G-1) and **16** (G-2) were obtained as very viscous oils in yields of 88% and 76%, respectively. They could be lyophilized from 1,4-dioxane. Polymerizations were carried out in highly concentrated solutions using AIBN as starter at 55 °C for substrate **14** and *tert*-butyl perbenzoate (*t*BPB) at 90 °C for substrate **16**. The very small amounts of solvent required were added with a precision micropipette. The polymers were obtained in yields of 92% (**15**) and 46% (**17**).[21] The ^1H and ^{13}C NMR spectra of both monomers and polymers are rather complex. Nevertheless all signals could be assigned. The relative molecular masses of polymers **15** and **17** were determined by gel-permeation chromatography (GPC) *versus* a polystyrene standard as $M_n = 70\,860$ ($P_n = 55$), $M_w = 157\,100$ ($P_w = 123$) for **15** and $M_n = 11\,700$ ($P_n = 4.5$), $M_w = 12\,050$ ($P_w = 5$) for **17**. Whereas the values for polymer **15** were more or less as expected,[22] those for polymer **17** are unusual for two reasons. The degrees of polymerization are rather low and the relative molecular mass distribution ($M_w/M_n = 1.03$) is extremely narrow for a free-radical process. Obviously the polymerization self-terminates as soon as a certain



Scheme 4 Synthesis of G-2 macromonomer **16** and its polymerization. *Reagents and conditions (yields)*: (a) (i) **12**, HOBT, CH_2Cl_2, RT, 10 min (ii) **13e**, DBU, 30 min (iii) EDC, 24 h (76%); (b) ᵗBPB, toluene, 90 °C, 16 h (46%).

relative molecular mass is reached. This may indicate that the growing chain folds inward due to the steric demand of the dendrons, thus rendering the active chain inaccessible for further growth. Another explanation involves the assumption of a size-limited pre-aggregation of monomers to a 'molecular reactor' consisting of a defined number of constituents which then polymerizes.[23] Further work is required to differentiate these possibilities. It should also be noted at this point that GPC tends to underestimate the actual relative molecular masses of dendronized polymers by factors which easily can reach 2–3.[24]

Experimental

General procedures

All reagents were purchased from Fluka or Aldrich and used without further purification. All solvents were dried under standard conditions. All reactions were carried out under nitrogen. Analytical equipment: (a) NMR spectra: Bruker AMX 500 spectrometer (500 MHz) and Bruker AM 250 spectrometer (250 MHz); (b) mass spectra: Varian MAT 112S, Varian MAT 711; (c) elemental analyses: EA 240 Perkin Elmer; (d) GPC: Waters Ultra Styragel linear column [RI (refractive index) and UV (230 nm) detection; polystyrene standard; THF eluent].

Allyl 3,5-dihydroxybenzoate 2

A solution of 3,5-dihydroxybenzoic acid **1** (93.5 g, 607 mmol) and 9.0 ml of conc. H_2SO_4 in 250 ml of prop-2-enol was refluxed for 8 h. The solution was neutralized with saturated aq. sodium hydrogen carbonate and evaporated under vacuum. The residue was taken up in ethyl acetate, washed successively with saturated aq. sodium hydrogen carbonate (4 × 150 ml) and brine, dried with magnesium sulfate, and evaporated *in vacuo*. Chromatographic separation [silica gel; hexane–ethyl acetate (3 : 1 v/v)] afforded title ester **2** (106 g, 90%) as a viscous oil, ^{1}H-NMR δ($CDCl_3$–CD_3OD) 3.96 (br s, 2H, OH), 4.66 (d, 2H, CO_2CH_2), 5.20 (dd, 2H, CH=CH_2), 5.89 (ddd, 1H, CH=CH_2), 6.40 (t, 1H, ArH) and 6.89 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$–CD_3OD) 65.7 (CO_2CH_2), 107.7 (ArC-H), 108.4 (ArC-H), 118.9 (CH=CH_2), 131.5 (CH=CH_2), 131.6 (ArC-CO_2R), 157.5 (ArC-OH) and 166.8 (CO_2R); MS (80 eV) *m*/*z* (%) 194 (54) $[M]^+$, 138 (27) $[M - C_3H_4O]^+$ and 137 (100) $[M - C_3H_5O]^+$; HRMS (Found: 194.055 23 $[M]^+$. $C_{10}H_{10}O_4$ requires *M*, 194.057 91).

Allyl 3,5-bis-[3-(*tert*-butoxycarbonylamino)propoxy]benzoate 4

A solution of diol **2** (7.77 g, 40 mmol), 3-(*tert*-butyloxycarbonylamino)propyl chloride **3** (23.5 g, 121 mmol), potassium carbonate (16.6 g, 0.2 mol), 18-crown-6 (3.16 g), TBAI (4.94 g) and sodium iodide (1.32 g) in 500 ml of freshly distilled diethyl ketone was refluxed for 18 h. The solution was filtered, washed successively with saturated aq. sodium hydrogen carbonate and brine, dried with magnesium sulfate, and evaporated *in vacuo*. Chromatographic separation [silica gel; hexane–ethyl acetate (2 : 1 v/v)] gave title compound **4** (16.4 g, 81%) as a solid, ^{1}H-NMR δ($CDCl_3$) 1.35 (s, 18H, CH_3), 1.87 (quin, 4H, CH_2-C$H_2$$CH_2$), 3.20 (q, 4H, NHC$H_2$), 3.95 (t, 4H, ArOC$H_2$), 4.71 (d, 2H, CO_2CH_2), 4.90 (br s, 2H, NH), 5.26 (dd, 2H, CH=CH_2), 5.93 (ddd, 1H, CH=CH_2), 6.55 (t, 1H, ArH) and 7.13 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 28.3 ($CH_2CH_2CH_2$), 29.4 (CH_3), 37.7 ($NHCH_2$), 65.6 (CO_2CH_2), 65.9 (OCH_2), 79.0 [C(CH_3)$_3$], 106.4 (ArC-H), 107.8 (ArC-H), 118.2 (CH=CH_2), 131.8 (ArC-CO_2R), 132.0 (CH=CH_2), 155.9 ($NHCO_2$), 159.7 (ArC-O) and

165.8 (CO_2R); MS (80 eV) *m*/*z* (%) 508 (3.8) $[M]^+$; [$C_{26}H_{40}N_2O_8$ (508.6): Found: C, 61.0; H, 7.7; N, 5.35. Calc. C, 61.40; H, 7.93; N, 5.51%].

Allyl 3,5-bis-(3-aminopropoxy)benzoate dihydrochloride 5

A solution of compound **4** (2.6 g, 5.11 mmol) and hydrochloric acid (25%; 21 ml, 147 mmol) in 30 ml of dry THF was stirred for 3 h and then poured into 500 ml of acetone. After being cooled to 4 °C for 24 h the precipitate was filtered off by suction and dried *in vacuo* to give title compound **5** (1.89 g, 97%) as a solid, ^{1}H-NMR δ(CD_3OD) 2.05 (quin, 4H, CH_2-CH_2CH_2), 2.93 (t, 4H, NHCH_2), 4.10 (t, 4H, ArOCH_2), 4.78 (d, 2H, CO_2CH_2), 5.31 (dd, 2H, CH=CH_2), 6.05 (ddd, 1H, CH=CH_2), 6.82 (t, 1H, ArH), 7.08 (d, 2H, ArH) and 8.19 (s, br, 6H, NH); ^{13}C-NMR δ(CD_3OD) 28.3 ($CH_2CH_2CH_2$), 38.5 (NH_2CH_2), 66.7 (OCH_2), 66.8 (CO_2CH_2), 107.4 (ArC-H), 109.2 (ArC-H), 118.6 (CH=CH_2), 133.3 (Ar*C*-CO_2R), 133.6 (*C*H=CH_2), 161.2 (ArC-O) and 167.1 (CO_2R); EIMS (80 eV) *m*/*z* (%) 308 (32) $[M - 2HCl]^+$; HRMS (Found: 308.173 48 $[M - 2HCl]^+$. $C_{16}H_{24}N_2O_4$ requires *M*, 308.173 61).

3-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosylthio)propionic acid 8

A solution of $BF_3{\cdot}Et_2O$ (7.50 ml, 60.0 mmol) was added dropwise to a solution of 1,2,3,4,6-penta-*O*-acetyl-D-glucose **6** (20.0 g, 50.0 mmol) and 3-mercaptopropionic acid **7** (5.30 g, 50.0 mmol) in 300 ml of dichloromethane. The reaction mixture was stirred for 2 h at ambient temperature, washed with 1 M hydrochloric acid, and dried with magnesium sulfate. After removal of the solvent *in vacuo* chromatographic separation [silica gel; hexane–ethyl acetate (2 : 1 v/v)] gave title compound **8** (18.8 g, 86%) as a wax-like solid, ^{1}H-NMR δ($CDCl_3$) 1.97, 2.04, 2.05 and 2.10 (4 s, 12H, CH_3), 2.70 (m, 2H, SCH_2CH_2), 2.91 (m, 2H, SCH_2CH_2), 3.63 (m, 1H, H-5), 4.20 (m, 2H, H_2-6), 4.50 (d, 1H, H-1), 5.03 (m, 2H, H-2, -4), 5.20 (m, 1H, H-3) and 10.24 (br s, 1H, CO_2H); ^{13}C-NMR δ($CDCl_3$) 20.5, 20.6 and 20.7 (CH_3), 25.0 (SCH_2), 35.1 (CH_2CO_2H), 62.1 (C-6), 68.2 and 69.6 (C-2 and -4), 73.6 (C-3), 75.7 (C-5), 83.8 (C-1), 169.4, 170.1 and 170.7 ($COCH_3$) and 176.5 (CO_2H); (−)FAB 435 (22) $[M - H]^-$; [$C_{17}H_{24}O_{11}S$ (436.43): Found: C, 46.55; H, 5.4. Calc. C, 46.79; H, 5.54%].

Allyl 3,5-bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)propionamide]propoxy}benzoate 9

A solution of acid **8** (14.0 g, 37.1 mmol) and HOBT (5.36 g, 35.0 mmol) in dry dichloromethane (500 ml) was stirred for 10 min. G-1 Amino dendron **5** (5.34 g, 14.0 mmol) and DIPEA (10.9 g, 14.6 ml, 84.0 mmol) were added and the reaction mixture was stirred until the reactants completely dissolved. Then EDC (6.71 g, 35.0 mmol) was added. The solution was stirred for 18 h, diluted with 300 ml of dichloromethane, and washed successively with saturated aq. sodium hydrogen carbonate, aq. (20%) citric acid and brine. The organic layer was dried with magnesium sulfate and evaporated. Column chromatography of the oily residue (silica gel; dichloromethane–2–4% methanol) afforded title compound **9** (14.7 g, 91%) as a solidified foam, ^{1}H-NMR δ($CDCl_3$) 1.97–2.10 (m, 28H, 8 × CH_3, CH_2CH_2-CH_2), 2.48 (m, 4H, $COCH_2CH_2S$), 2.90 (m, 4H, $COCH_2CH_2S$), 3.46 (q, 4H, NHCH_2), 3.70 (m, 2H, H-5), 4.09 (t, 4H, $ArOCH_2$), 4.12 (m, 4H, H_2-6), 4.51 (d, 2H, H-1), 4.75 (d, 2H, CO_2CH_2), 4.94 (m, 4H, H-2 and -4), 5.10 (m, 2H, H-3), 5.25 (dd, 2H, CH=CH_2), 5.96 (ddd, 1H, CH=CH_2), 6.25 (br t, 2H, NH), 6.64 (t, 1H, ArH) and 7.20 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 20.5, 20.6 and 20.7 (CH_3), 26.8 ($COCH_2CH_2S$), 28.8 (CH_2CH_2-CH_2), 36.8 ($NHCH_2$), 37.3 ($COCH_2CH_2S$), 61.8 (C-6), 65.8 (CO_2CH_2), 65.9 (OCH_2), 68.1 and 69.5 (C-2 and -4), 73.7 (C-3), 76.0 (C-5), 84.4 (C-1), 106.5 (ArC-H), 107.9 (ArC-H), 118.4 (CH=CH_2), 132.0 and 132.1 (*C*H=CH_2, Ar*C*-CO_2R), 159.8 (ArC-O), 165.8 ($ArCO_2R$), 169.3, 170.0 and 170.6 ($COCH_3$) and 171.1 (CONH); EI-MS (280 °C) *m*/*z* (%) 1144 (0.33) $[M]^+$, 813 (22) $[M - Glu\ (C_{14}H_{19}O_9)]^+$ and 331 (22) [Glu ($C_{14}H_{19}O_9$)]$^+$; HRMS (Found: 813.253 41 $[M - Glu\ (C_{14}H_{19}O_9)]^+$. $C_{36}H_{49}N_2O_{15}S_2$ requires *m*/*z*, 813.257 44).

3,5-Bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)-propionamido]propoxy}benzoic acid 10

To a solution of G-1 allylic ester **9** (14.6 g, 12.7 mmol) and $PdCl_2(PPh_3)_2$ (210 mg, 0.30 mmol) in 100 ml of dry dichloromethane was added TBTH (5.82 g, 20.0 mmol) at 0 °C. The reaction mixture was stirred for 2 h, and was then evaporated *in vacuo*. Chromatographic separation of the residue (silica gel; dichloromethane–2–10% methanol) yielded acid **10** (13.2 g, 94%) as a solidified foam, containing slight amounts of tin impurities.

Alternative method. Ester **9** (1.15 g, 1.00 mmol), $Pd(PPh_3)_4$ (156 mg, 0.10 mmol) and morpholine (871 mg, 10.0 mmol) in 20 ml of dry dichloromethane were stirred for 24 h. Chromatographic separation yielded acid **10** (327 mg, 30%) as analytically pure material; ^{1}H-NMR δ($CDCl_3$) 1.95–2.10 (m, 28H, 8 × CH_3, $CH_2CH_2CH_2$), 2.50 (m, 4H, $COCH_2CH_2S$), 2.95 (m, 4H, $COCH_2CH_2S$), 3.42 (q, 4H, NHCH_2), 3.64 (m, 2H, H-5), 4.15 (t, 4H, $ArOCH_2$), 4.18 (m, 4H, H_2-6), 4.55 (d, 2H, H-1), 4.90 (m, 4H, H-2 and -4), 5.10 (m, 2H, H-3), 6.40 (br t, 2H, NH), 6.62 (br t, 1H, ArH) and 7.18 (br d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 20.5, 20.6 and 20.7 (CH_3), 26.9 ($COCH_2CH_2S$), 28.9 ($CH_2CH_2CH_2$), 36.7 (CH_2NH), 37.4 ($COCH_2CH_2S$), 61.9 (C-6), 65.9 ($ArOCH_2$), 68.2 and 69.6 (C-2 and -4), 73.8 (C-3), 76.1 (C-5), 84.4 (C-1), 107.2 and 108.2 (ArC-H), 131.6 (Ar*C*-CO_2H), 159.8 (ArC-O), 169.4 ($COCH_3$), 169.5 ($ArCO_2H$), 170.1 and 170.7 ($COCH_3$) and 171.4 (CONH); (−)FAB-MS *m*/*z* (%) 1103 (7) $[M - H]^-$; [$C_{47}H_{64}N_2O_{24}S_2$ (1105.1): Found: C, 50.7; H, 6.1; N, 2.6. Calc. C, 51.08; H, 5.84; N, 2.53%].

Allyl 3,5-bis-[3-(3,5-bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)propionamide]propoxy}benzamido)propoxy]-benzoate 11

A solution of G-1 carboxylic acid **10** (1.68 g, 1.52 mmol) and HOBT (0.26 g, 1.70 mmol) in dry dichloromethane (100 ml) was stirred for 10 min. Amino dendron **5** (0.29 g, 0.75 mmol) and DBU (0.60 g, 0.59 ml, 3.95 mmol) were added and the reaction mixture was stirred until the reactants completely dissolved. Then EDC (0.33 g, 1.70 mmol) was added. The solution was stirred for 18 h, then was diluted with 100 ml of dichloromethane and washed successively with water and brine. The organic layer was dried with magnesium sulfate and evaporated. Column chromatography of the oily residue (silica gel; dichloromethane–3–10% methanol) afforded title ester **11** (1.27 g, 68%) as a solidified foam; ^{1}H-NMR δ($CDCl_3$) 1.85–2.12 (m, 60H, 16 × CH_3, $CH_2CH_2CH_2$), 2.47 (m, 8H, $COCH_2CH_2S$), 2.92 (m, 8H, $COCH_2CH_2S$), 3.39 (q, 8H, NHCH_2), 3.56–3.72 (m, 8H, H-5, NHCH_2), 3.90–4.22 (m, 20H, $ArOCH_2$, H_2-6), 4.54 (d, 4H, H-1), 4.79 (d, 2H, CO_2CH_2), 4.96 (m, 8H, H-2 and -4), 5.18 (m, 4H, H-3), 5.30 (dd, 2H, CH=CH_2), 6.00 (ddd, 1H, CH=CH_2), 6.42–6.55 (m, 6H, NHCOCH$_2$, ArH), 6.65 (t, 1H, ArH), 6.82 (d, 4H, ArH), 7.08 (br t, 2H, NHCOAr) and 7.13 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 20.5, 20.6 and 20.7 (CH_3), 26.9 ($COCH_2CH_2S$), 28.8 ($CH_2CH_2CH_2$), 36.7 ($CH_2NHCOCH_2$), 37.2 ($COCH_2CH_2S$), 37.8 ($CH_2NHCOAr$), 61.9 (C-6), 65.8 ($ArOCH_2$), 66.7 (CO_2CH_2), 68.3 and 69.6 (C-2 and -4), 73.7 (C-3), 76.0 (C-5), 84.4 (C-1), 104.5, 105.7, 106.9 and 108.1 (ArC-H), 118.4 (CH=CH_2), 132.1 (*C*H=CH_2, Ar*C*-CO_2R), 136.8 (Ar*C*-CONH), 159.8 (ArC-O), 160.0 (ArC-O), 165.8 ($ArCO_2R$), 167.4 (ArCONH), 169.4, 170.0 and 170.7 ($COCH_3$) and 171.3 (CH_2CONH); (+)FAB-MS *m*/*z* (%) 2482.8 (7) $[M + H]^+$; [$C_{110}H_{148}N_6O_{50}S_4$ (2482.6): Found: C, 52.8; H, 5.85; N, 3.3. Calc. C, 53.22; H, 6.01; N, 3.39%].

3,5-Bis-[3-(3,5-bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-gluco-pyranosylthio)propionamido]propoxy}benzamido)propoxy]-benzoic acid 12

To a solution of G-2 allylic ester **11** (880 mg, 0.35 mmol) and $PdCl_2(PPh_3)_2$ (5.64 mg, 8.05 μmol) in 20 ml of dry dichloromethane was added TBTH (160 mg, 0.55 mmol) at 0 °C. The reaction mixture was stirred for 2 h, and was then evaporated *in vacuo*. Chromatographic separation of the residue (silica gel; dichloromethane–2–10% methanol) yielded title acid **12** (502 mg, 60%) as a solidified foam, containing small amounts of tin impurities; ^{1}H-NMR δ($CDCl_3$) 1.80–2.15 (m, 60H, 16 × CH_3, $CH_2CH_2CH_2$), 2.49 (m, 8H, $COCH_2CH_2S$), 2.90 (m, 8H, $COCH_2CH_2S$), 3.38 (m, 8H, $NHCH_2$), 3.53–3.75 (m, 8H, H-5, $NHCH_2$), 3.85–4.20 (m, 20H, $ArOCH_2$, H_2-6), 4.58 (d, 4H, H-1), 4.90–5.05 (m, 8H, H-2 and -4), 5.20–5.30 (m, 4H, H-3), 6.42–6.60 (m, 6H, $NHCOCH_2$, ArH), 6.65 (t, 1H, ArH), 6.85 (d, 4H, ArH), 7.00 (br t, 2H, NHCOAr) and 7.21 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 20.6, 20.7 and 20.8 (CH_3), 26.9 ($COCH_2CH_2S$), 28.9 ($CH_2CH_2CH_2$), 29.9 ($CH_2CH_2CH_2$), 36.9 ($CH_2NHCOCH_2$), 37.3 ($COCH_2CH_2S$), 38.3 (CH_2NH-COAr), 61.9 (C-6), 65.8 ($ArOCH_2$), 67.3 ($ArOCH_2$), 68.2 and 69.6 (C-2 and -4), 73.7 (C-3), 76.0 (C-5), 84.4 (C-1), 104.7, 105.5, 108.6 and 111.3 (ArC-H), 132.6 (Ar*C*-CO_2R), 136.9 (Ar*C*-CONH), 159.7 (ArC-O), 160.0 (ArC-O), 167.4 (ArCONH), 169.4 ($COCH_3$), 169.5 (CO_2H), 170.1 and 170.8 ($COCH_3$) and 171.5 (CH_2CONH); (+)FAB-MS *m*/*z* (%) 2443 (0.3) $[M + H]^+$.

4-(*tert*-Butoxycarbonylaminomethyl)benzoic acid 13b

To a solution of 4-(aminomethyl)benzoic acid **13a** (30.0 g, 149 mmol) and potassium hydroxide (8.3 g, 149 mmol) in a mixture of 600 ml of THF and 100 ml of water, was added di-*tert*-butyldicarbonate (39.0 g, 179 mmol) and the mixture was stirred at RT for 1 h. The layers were separated and the organic layer was washed with brine, dried with magnesium sulfate, and evaporated *in vacuo*. The raw material was dried *in vacuo* to give title acid **13b** (35.1 g, 94%) as an oil, ^{1}H-NMR δ($CDCl_3$–CD_3OD) 1.30 (s, 9H, CH_3), 4.10 (br s, 1H, OH), 4.17 (br s, 1H, NH), 4.60 (s, 2H, CH_2), 7.17 (d, 2H, ArH) and 7.82 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$–CD_3OD) 27.9 (CH_3), 43.7 (CH_2NH), 80.4 [$C(CH_3)_3$], 126.6 (ArC-H), 129.4 (ArC-H), 129.9 (Ar*C*-CO_2H), 143.9 (Ar*C*-CH_2), 156.4 ($NHCO_2$) and 169.2 (CO_2H); MS (80 eV) *m*/*z* (%) 251 (3.8) $[M]^+$; $[C_{13}H_{17}NO_4$ (251.3): Found: C, 61.9; H, 6.8; N, 5.4. Calc. C, 62.12; H, 6.82; N, 5.57%].

4-(*tert*-Butoxycarbonylaminomethyl)benzyl alcohol 13c

Lithium aluminium hydride (3.0 g, 78 mmol) was suspended in 250 ml of dry THF. The protected benzoic acid **13b** (20.92 g, 78 mmol) was slowly added and the reaction mixture was heated to 40 °C for 14 h. The reaction was stopped by addition of water, and acetic acid was added to give a pH of 5. The layers were separated and the organic layer was washed with brine. Extraction of the aqueous layer with diethyl ether was carried out carefully. The combined organic layers were dried with magnesium sulfate and evaporated *in vacuo*. The raw material was dried *in vacuo* to give title alcohol **13c** (11.6 g, 63%) as a solid, ^{1}H-NMR δ($CDCl_3$) 1.41 (s, 9H, CH_3), 2.63 (br s, 1H, OH), 4.29 (d, 2H, CH_2NH), 4.63 (s, 2H, CH_2OH), 4.80 (br s, 1H, NH), 7.22 (d, 2H, ArH) and 7.33 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 28.4 (CH_3), 44.4 (CH_2NH), 64.8 (CH_2OH), 79.5 [$C(CH_3)_3$], 127.2 (ArC-H), 127.5 (ArC-H), 138.2 (Ar*C*-CH_2OH), 140.1 (Ar*C*-CH_2NH) and 155.9 ($NHCO_2$); MS (80 eV) *m*/*z* (%) 237 (0.24) $[M]^+$.

4-(*tert*-Butoxycarbonylaminomethyl)benzyl acrylate 13d

To a mixture of the alcohol **13c** (2.87 g, 12 mmol), triethylamine (4.85 g, 6.7 ml, 48 mmol) and DMAP (10 mg) in 100 ml of dry THF was added acryloyl chloride (1.53 g, 1.38 ml, 17 mmol) dropwise. The reaction mixture was stirred at RT for 16 h, then was extracted successively with saturated aq. sodium hydrogen carbonate and brine. The organic layer was dried with magnesium sulfate and evaporated *in vacuo*. Chromatographic separation (silica gel; dichloromethane) gave title acrylate **13d** (2.68 g, 76%) as an oil; ^{1}H-NMR δ($CDCl_3$) 1.42 (s, 9H, CH_3), 4.27 (d, 2H, CH_2NH), 4.95 (br s, 1H, NH), 5.14 (s, 2H, CH_2OR), 5.80 (dd, 1H, CH=CH_2), 6.11 (dd, 1H, C*H*=CH_2), 6.40 (dd, 1H, CH=CH_2), 7.25 (d, 2H, ArH) and 7.31 (d, 2H, ArH); ^{13}C-NMR δ($CDCl_3$) 28.3 (CH_3), 44.3 (CH_2NH), 66.0 (CH_2OR), 79.4 [$C(CH_3)_3$], 121.6 (CH=CH_2), 128.2 (ArC-H), 128.5 (ArC-H), 131.0 (*C*H=CH_2), 134.8 (Ar*C*-CH_2OH), 139.1 (Ar*C*-CH_2NH), 155.8 ($NHCO_2$) and 165.9 (CO_2R); MS (80 eV); *m*/*z* (%) 237 (0.24) $[M]^+$.

4-(Aminomethyl)benzyl acrylate hydrochloride 13e

Hydrochloric acid (25%; 6.48 ml, 45 mmol) was added to a solution of the protected acrylate **13d** (6.6 g, 23 mmol) in 150 ml of THF. The reaction mixture was stirred at RT for 36 h. The solvent was evaporated off and the crude product was dissolved in ethanol. Precipitation with diethyl ether gave **13e** (5.43 g, 83%) as a solid, ^{1}H-NMR δ(CD_3OD) 4.12 (s, 2H, CH_2NH), 5.22 (s, 2H, CH_2OR), 5.90 (dd, 1H, CH=CH_2), 6.19 (dd, 1H, C*H*=CH_2), 6.40 (dd, 1H, CH=CH_2) and 7.47 (s, 4H, ArH); ^{13}C-NMR δ(CD_3OD) 43.9 (CH_2NH), 66.9 (CH_2OR), 129.0 (CH=CH_2), 129.8 (ArC-H), 130.3 (ArC-H), 132.7 (*C*H=CH_2), 134.4 (Ar*C*-CH_2OH), 138.3 (Ar*C*-CH_2NH) and 168.0 (CO_2R); MS (80 eV) *m*/*z* (%) 191 (16.9) $[M]^+$; $[C_{11}H_{14}ClNO_2$ (227.69): Found: C, 57.5; H, 6.2; N, 5.9. Calc. C, 58.03; H, 6.20; N, 6.15%].

4-[(3,5-Bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-thio)propionamido]propoxy}benzamido)methyl]benzyl acrylate 14

A solution of G-1 carboxylic acid **10** (3.47 g, 3.14 mmol) and HOBT (0.51 g, 3.30 mmol) in dry dichloromethane (50 ml) was stirred for 10 min. 4-(Aminomethyl)benzyl acrylate **13e** (0.68 g, 3.0 mmol) and DIPEA (0.83 g, 1.11 ml, 6.40 mmol) were added and the reaction mixture was stirred until the reactants completely dissolved. Then EDC (0.63 g, 3.30 mmol) was added. The solution was stirred for 24 h, diluted with 100 ml of dichloromethane and washed successively with water and brine. The organic layer was dried with magnesium sulfate and was then evaporated. Column chromatography of the oily residue (silica gel, dichloromethane–2–5% methanol) afforded title compound **14** (3.53 g, 88%) as a solidified foam, which could be lyophilized from dioxane; ^{1}H-NMR δ($CDCl_3$) 1.85–2.10 (m, 28H, CH_3, $CH_2CH_2CH_2$), 2.47 (m, 4H, $COCH_2CH_2S$), 2.89 (m, 4H, $COCH_2CH_2S$), 3.35 (q, 4H, $NHCH_2$), 3.64 (m, 2H, H-5), 3.90–4.22 (m, 8H, $ArOCH_2$, H_2-6), 4.50 (d, 2H, H-1), 4.59 (d, 2H, $ArCH_2NH$), 4.92 (t, 4H, H-2 and -4), 5.10–5.25 (m, 4H, H-3, $ArCH_2O$), 5.82 (dd, 1H, CH=CH_2), 6.10 (dd, 1H, C*H*=CH_2), 6.34–6.46 (m, 3H, CH=CH_2, $CONHCH_2CH_2$), 6.48 (t, 1H, ArH), 6.86 (d, 2H, ArH), 7.08 (br t, 1H, $CONHCH_2Ar$) and 7.35 (s, 4H, ArH); ^{13}C-NMR δ($CDCl_3$) 20.5, 20.6 and 20.7 (CH_3), 26.9 ($COCH_2CH_2S$), 28.7 ($CH_2CH_2CH_2$), 36.6 (CH_2-$NHCOCH_2$), 37.2 ($COCH_2CH_2S$), 43.7 ($CONHCH_2Ar$), 61.8 (C-6), 65.7 ($ArCH_2OCO$), 65.9 ($ArOCH_2$), 68.1 and 69.5 (C-2 and -4), 73.6 (C-3), 75.8 (C-5), 84.4 (C-1), 104.4, 105.8 and 128.0 (ArC-H), 128.2 (*C*H=CH_2), 128.5 (ArC-H), 131.1 (CH=*C*H_2), 134.8 (Ar*C*-CONH), 136.6 (Ar*C*-CH_2NH), 138.5 (Ar*C*-CH_2O), 159.9 (ArC-O), 165.9 (CH_2=$CHCO_2R$), 167.1 (ArCONH), 169.4, 170.0 and 170.6 ($COCH_3$) and 171.0 (CH_2CONH); (+)FAB-MS *m*/*z* (%) 1316 (0.3) $[M + K]^+$, 1300 (0.6) $[M + Na]^+$, 1278 (3) $[M + H]^+$, 946 (1) $[M - Glu(C_{14}H_{19}O_9)]^+$, 476 (16) $[GluSC_2H_4CONHC_3H_6]^+$ and 331 (10) $[Glu(C_{14}H_{19}O_9)]^+$; $[C_{58}H_{75}N_3O_{25}S_2$ (1278.3): Found: C, 54.4; H, 5.7; N, 3.0. Calc. C, 54.50; H, 5.91; N, 3.29%].

4-({3,5-Bis-[3-(3,5-bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)propionamido]propoxy}benzamido)propoxy]benzamido}methyl)benzyl acrylate 16

A solution of G-2 carboxylic acid **12** (472 mg, 0.19 mmol) and HOBT (46.0 mg, 0.3 mmol) in dry dichloromethane (50 ml) was stirred for 10 min. 4-(Aminomethyl)benzyl acrylate **13e** (68.0 g, 0.3 mmol) and DBU (91.0 mg, 0.60 mmol) were added and the reaction mixture was stirred until the reactants completely dissolved. Then EDC (56.0 mg, 0.3 mmol) was added. The solution was stirred for 24 h, diluted with 100 ml dichloromethane, and washed successively with water and brine. The organic layer was dried with magnesium sulfate and evaporated. Column chromatography of the oily residue (silica gel; dichloromethane–2–10% methanol) afforded title compound **16** (380 mg, 76%) as a solidified foam, which could be lyophilized from 1,4-dioxane, ^{1}H-NMR δ(D_7-DMF) 1.91 (m, 8H, $CH_2CH_2CH_2$), 1.95–2.10 (m, 52H, 16 × CH_3, $CH_2CH_2CH_2$), 2.51 (m, 8H, $COCH_2CH_2S$), 2.93 (m, 8H, $COCH_2CH_2S$), 3.32 (m, 8H, $NHCH_2CH_2$), 3.50–3.60 (m, 8H, H-5, $NHCH_2CH_2$), 4.00–4.28 (m, 20H, $ArOCH_2$, H_2-6), 4.58 (d, 4H, H-1), 4.85–5.07 (m, 10H, H-2 and -4, $ArCH_2NH$), 5.20 (s, 2H, $ArCH_2O$), 5.32 (m, 4H, H-3), 5.94 (dd, 1H, CH=CH_2), 6.32 (dd, 1H, CH=CH_2), 6.63 (d, 1H, CH=CH_2), 6.68 (br t, 2H, ArH), 7.11 (br d, 4H, ArH), 7.20 (br d, 2H, ArH), 7.32 (br t, 1H, ArH), 7.40 (br s, 4H, ArH), 7.99 (br t, 4H, NH), 8.61 (br t, 2H, NH) and 9.03 (br t, 1H, NH); ^{13}C-NMR δ(D_7-DMF) 20.4, 20.5 and 20.6 (CH_3), 26.7 ($COCH_2CH_2S$), 36.5 ($CH_2CH_2CH_2$), 37.2 ($COCH_2CH_2S$), 43.6 (CH_2CH_2NH), 62.8 (C-6), 64.0 ($ArCH_2NH$), 66.3 ($ArOCH_2$), 66.5 ($ArOCH_2$), 67.4 (CO_2CH_2), 69.2 and 70.7 (C-2 and -4), 74.1 (C-3), 75.7 (C-5), 83.6 (C-1), 104.4, 104.8, 106.4 and 106.5 (ArC-H), 128.1 ($COCH$=CH_2) 128.4 and 129.1 (ArC-H), 131.9 (COCH=CH_2), 135.6 (Ar*C*-CONH), 137.4 (Ar*C*-CH_2), 137.6 (Ar*C*-CONH), 140.7 (Ar*C*-CH_2), 160.7 (ArC-O), 160.8 (ArC-O), 166.2 (ArCONH), 166.6 (CO_2R), 166.8 (ArCONH), 170.0, 170.2, 170.4, 170.9 and 171.1 ($COCH_3$, CH_2CONH); (+)FAB-MS *m/z* (%) 2616 (0.3) $[M + H]^+$.

Poly-{4-[(3,5-bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)propionamido]propoxy}benzamido)methyl]benzyl acrylate} 15

To a solution of G-1 monomer **14** (0.13 g, 0.10 mmol) in 100 µl of freshly distilled and degassed benzene was added a freshly prepared solution of AIBN (100 µl, 0.2 µmol). The reaction mixture was vigorously stirred in a sealed flask at 55 °C for 16 h; GPC of raw material: **15** (92%): **14** (8% recovery); polymer **15** was isolated by successive precipitation from hexane and water–methanol (1 : 1), ^{1}H-NMR δ(3 CD_3OD–1 $CDCl_3$) 1.84–2.10 (br m, 30H), 2.48 (br s, 4H), 2.89 (br m, 4H), 3.25 (br s, 4H), 3.72–4.00 (br m, 6H), 4.10–4.40 (br m, 6H), 4.50–4.80 (br m, 12H), 4.90–5.02 (br m, 4H), 5.20 (br m, 2H), 6.51 (br s, 1H), 6.90 (br s, 1H) and 7.12 (br s, 1H); ^{13}C-NMR δ(3 CD_3OD–1 $CDCl_3$) 20.9, 21.0, 21.1, 27.3, 29.8, 30.3, 37.2, 37.6, 63.0, 66.4, 68.6, 69.3, 70.9, 74.7, 76.4, 82.4, 84.6, 106.7, 128.0, 128.4, 128.6, 137.1, 137.2, 139.7, 160.9, 168.7, 170.7, 171.2, 171.9 and 173.0; $[(C_{58}H_{75}N_3O_{25}S_2)_n$ $(1278.3)_n$: Found: C, 53.7; H, 5.8; N, 3.1. Calc. C, 54.50; H, 5.91; N, 3.29%].

Poly-4-({3,5-bis-[3-(3,5-bis-{3-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)propionamido]propoxy}benzamido)propoxy]-benzamido}methyl)benzyl acrylate 17

To G-2 monomer **16** (0.05 g, 0.02 mmol) was added a freshly prepared solution of ′BPB (38 µl, 0.04 µmol) in degassed toluene. The reaction mixture was vigorously stirred in a sealed flask at 90 °C for 16 h; GPC of raw material: **17** (46%): **16** (54% recovery); ^{1}H-NMR δ(D_7-DMF) 1.90–2.15 (m, 60H), 2.58 (m, 8H), 2.90 (m, 8H), 3.35 (m, 8H), 3.48–3.62 (m, 8H), 4.00–4.35 (m, 20H), 4.60 (m, 4H), 4.95–5.12 (m, 10H), 5.20 (br s, 2H), 5.38 (m, 4H), 6.60 (br s, 2H), 7.10 (br s, 4H), 7.32 (br s, 2H), 7.40 (br s, 1H), 7.48 (br s), 8.00 (br t, 4H), 8.62 (br t, 2H) and 9.05 (br t, 1H).

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