Supporting Information

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Supporting Information to:

A covalent chemistry approach to giant macromolecules and their wetting behavior on solid substrates

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1. General Procedures
Dendron 1 was synthesised according to literature method.[⁹] Other reagents were purchased from Aldrich or Fluka. Hydroxylethyl methacrylate (HEMA) was freshly distilled before use. THF and dichloromethane (DCM) were distilled from LAH and CaH₂, respectively. All other reagents and solvents were used as received. All reactions were run under nitrogen atmosphere. Silica gel 60M (Macherey-Nagel, 0.04-0.063 mm/230 – 400 mesh) was used as the stationary phase for column chromatography. ¹H and ¹³C NMR spectra were recorded on Bruker AM270 and AC500 spectrometers at room temperature. Mass spectrometry was carried out on a Varian MAT 112 S spectrometer, MNBA/CH₂Cl₂ as matrix. Elemental analysis was performed on a Perkin-Elmer EA 240. The samples were dried rigorously under vacuum prior to the analysis in order to remove strongly adhering solvent molecules. Gel permeation chromatography (GPC) measurements were carried out at room temperature on Waters ultra styrigel columns (10⁴ + 10³ + 10² nm), r.i. and u.v. (268 nm) detectors either using polystyrene or a recently developed denpol standard.[⁹] Eluent: DMF + 1 g/L LiBr.
Scanning force microscopy (SFM) images were recorded using a MultiMode microscope (Digital Instruments, Inc., Santa Babara, CA) in tapping mode. Olympus etched silicon cantilevers were
used with a typical resonance frequency in the range of 200-400 kHz and a spring constant of 42 N/m. All samples were spinning coated (50 rps) from CHCl₃ solution on freshly cleaved substrates and measured at room temperature in air environment. SFM height measurements were based on the cross-sectional profiles.

2. Syntheses

2,5-Dioxo-pyrrolidin-1-yl 2-bromo-isobutyrate. To a solution of 2-bromoisobutyric acid (15.0 g, 90.0 mmol) in dry DCM (40 mL) was added hydroxysuccinimide (HOSu) (12.4 g, 107.7 mmol) at r.t. After 15 min, 1,3-dicyclohexylcarbodiimide (DCC) (23.2 g, 112.5 mmol) was added at −30 °C. The resulting mixture was warmed to r.t. and kept stirring for another 15 h. After the solid was filtered off, chromatographic separation (silica gel, hexane / ethyl acetate 3:1 / v:v) yielded the target substance (21.2 g, 89%) as colorless oil. ¹H NMR (CDCl₃): δ = 2.04 (s, 6H, CH₃), 2.82 (s, 4H, CH₂). ¹³C NMR (CDCl₃): δ = 25.51, 30.55, 51.16, 167.39, 168.66. FAB-MS (3 kV), m/z (%): 264 (90.38) [M+H]^+. Elemental analysis calcd for C₈H₁₀BrNO₄ (264.07): C, 36.39; H, 3.82; N, 5.30. Found: C, 36.26; H, 3.68; N, 5.40.

3,5-Bis-(3-{3,5-bis-[3-(2-bromo-2-methyl-propionylamino)-propyl]-benzoylamino}-propyl)-benzoic acid (2a). A solution of 2,5-dioxo-pyrrolidin-1-yl-2-bromo-isobutyrate (7.38 g, 28.0 mmol) in DCM (200 mL) was added dropwise to a mixture of 1 (3.74 g, 4.57 mmol) and TEA (9.43 g, 93.2 mmol) in methanol (50 mL) over 30 min at −30 °C. The resulting mixture was stirred for 15 h. The solid was filtered off and the residue washed with NaCO₃ and brine. The organic phase was then dried over magnesium sulfate. Chromatographic separation (silica gel, DCM / methanol 20:1 / v:v) yielded 2a (5.00 g, 86 %) as colorless foam. ¹H NMR (CDCl₃): δ = 1.82 (m, 12H, CH₂), 1.90 (s, 24H, CH₃), 2.59 (m, 8H, CH₂Ph), 2.70 (m, 4H, CH₂Ph), 3.21 (m, 8H, CH₂NH), 3.41 (m, 4H, CH₂NH), 4.60 (b, 1H, COOH), 6.90 (b, 4H, NH), 7.06 (s, 2H, Ph), 7.16 (b, 2H, NH), 7.20 (s, 1H, Ph), 7.36 (s, 4H, Ph), 7.71 (s, 2H, Ph). ¹³C NMR (CDCl₃): δ = 30.31, 30.69, 30.76, 32.23, 32.43, 39.47, 39.61, 62.28, 124.90, 127.50, 131.56, 134.60, 141.48, 142.00, 168.15, 172.18. FAB-MS (3 kV), m/z (%): 1269 (14.36) [M+H]^+. Elemental analysis calcd for C₅₅H₇₆Br₄N₆O₈ (1268.84): C, 52.06; H, 6.04; N, 6.62. Found: C, 51.96; H, 5.96; N, 6.53.

3,5-Bis-(3-{3,5-bis-[3-(2-bromo-2-methyl-propionylamino)-propyl]-benzoyleoxyethyl methacrylate (2b). A solution of DCC (1.06 g, 5.14 mmol) in DCM (50 mL) was dropped to a mixture of 2a (5.40 g, 4.26 mmol), HEMA (0.61 g, 4.69 mmol), and DMAP (0.2 g) in DCM (300 mL) at r.t. and the resulting mixture was stirred for 15 h. The solid was filtered off and the residue washed with NaCO₃ and brine. The organic phase was then dried over magnesium. After evaporation of the solvents, chromatographic separation (silica gel, DCM/methanol = 20:1 / v:v) gave 2b (4.00 g, 68%) as colorless foam. ¹H NMR (CDCl₃): δ = 1.85 (m, 8H, CH₃), 1.90 (s, 27H, CH₃), 1.98 (m, 4H, CH₂), 2.60 (m, 8H, CH₂Ph), 2.70 (m, 4H, CH₂Ph), 3.20 (m, 8H, CH₂NH), 3.41 (m, 4H, CH₂NH), 4.46 (m, 2H, CH₂O), 4.51 (m, 2H, CH₂O), 5.55 (m, 1H, CH₂=), 6.10 (m, 1H, CH₂=), 6.80 (b, 4H, NH), 7.06 (s, 3H, Ph), 7.40 (m, 4H, Ph), 7.67 (m, 2H,
Poly (3,5-bis-(3-{3,5-bis-[3-(2-bromo-2-methyl-propionylamino)-propyl]-benzoylamino}-propyl)-benzoyloxyethyl–methacrylate) (2c). Monomer 2b (0.6 g) was dissolved in benzene (0.4 mL). The mixture was immediately degassed by freeze-pump-thaw cycles and then kept at 55°C for 36 h. The polymer was dissolved in DCM (3 mL) and purified by precipitating it into hexane/ethyl acetate (1:1/v:v). Lyophilization with dioxane gave 2c (0.51 g, 85 %) as colorless foam. $^1$H NMR (CDCl$_3$): $\delta$ = 0.66 (br, 3 H, CH$_3$), 0.82 (br, 2 H, CH$_2$), 1.59-1.95 (br, 36 H, CH$_3$+CH$_2$), 2.60 (br, 12 H, CH$_2$Ph), 3.20 (br, 8 H, CH$_2$NH), 3.41 (br, 4 H, CH$_2$NH), 4.08-4.35 (br, 4 H, CH$_2$O), 5.26 (br, 4 H, NH), 6.92-7.06 (br, 3 H, Ph), 7.39-7.56 (br, 6 H, Ph), 7.88 (br, 2 H, NH). $^{13}$C NMR (CDCl$_3$): $\delta$ = 30.41, 30.76, 32.46, 32.90, 34.61, 62.74, 124.91, 127.34, 131.50, 134.84, 141.54, 142.03, 167.94, 172.04. Elemental analysis calcd for (C$_{61}$H$_{84}$Br$_4$N$_6$O$_{10}$)$_n$ (1376.30) n: C, 53.05; H, 6.13; N, 6.09. Found: C, 53.13; H, 6.08; N, 6.11.

Procedure for ATRP with MMA and initiators 4 or 4 (A): To a Schlenk tube were added MMA, DMF, CuBr and PMDETA. The resulting mixture was stirred until it turned homogeneously green. It was then immediately degassed by freeze-pump-thaw cycles. The initiator was added whereupon the mixture turned homogeneously blue, indicating the start of the polymerization. It was kept at 55°C and samples were taken in predetermined times. The catalyst was removed by filtering the mixture through a silica column. The resulting polymer was purified by silica gel column chromatography using DCM as eluent.

Synthesis of hairy denpol 3, poly [3,5-Bis-(3-[3,5-bis-[3-{2-{polymethyl methacrylate}-2-methyl-propionylamino]-propyl]-benzoylamino)-propyl]-benzoyloxyethyl–methacrylate], and estimation of its ratio to non-bound PMMA. According to procedure A. 5.11 g of MMA, 12 mg of CuBr, 44 mg of PMDETA, 58 mg of 2c, and 20 ml of DMF were used. The raw product was dried in high vacuum until all remained MMA was removed. In independent experiments between 2.2 (polymerization time 0.5 h) and 2.9 g (polymerization time 2 h) of raw product were obtained. GPC analysis showed that the product contained both 3 and parent PMMA. The proportion between these two components was determined by integration of the GPC elution curves assuming that the extinction coefficients for both polymers are comparable or do, at least, not lead to an overestimation of the denpol's concentration. For three independent runs the ratios were determined as 3 : PMMA = 94 : 6, 92 : 8, and 96 : 4. This results in an average ratio 3 : PMMA = 94 : 6. Thus the raw material contained between 2.2 g x 0.94 = 2.1 g and 2.9 g x 0.94 = 2.7 g of denpol 3. The raw material was then passed through a silica gel column (mesh 100) in order to remove the last traces of Cu salts. This afforded for these extreme cases between 1.0 and 1.2 g, respectively, of a completely colorless, film-forming material (after removal of PMMA). Obviously considerable and different parts of the organic material got lost during that operation. Since under the conditions applied PMMA eluted easily and completely, it must have been part of
the denpol 3, most likely its high molar mass fraction, which got lost on the column. The loss was higher (75%) if finer silica gel was used instead (mesh 400).

**Synthesis of a G1 model polymer 5 from initiator 4:** According to procedure A, the same ratios were applied as for 3. Product 5 (4.02 g, 46 %).

Initiator 4 was synthesized analogously to 2a from 2,5-dioxo-pyrrolidin-1-yl 2-bromo-isobutyrate and the corresponding G1 dendron.

3. Experimental determination of hair lengths

**Procedure for hydrolysis of denpol 3 and model polymer 5 (B):** To a solution of either the hairy denpol 3 or model polymer 5 in THF and n-butanol (20:1) was added 20% KOH (1.5 equivalent to all ester groups) and the resulting mixture refluxed for 48 h under N₂. Then 1% aqueous HCl were added until a pH = 6~7 was reached. The mixture was then evaporated to dryness and the residue extracted with DMF. After filtration, the solution was evaporated to dryness which afforded a colorless foam. Figure s1 compares the GPCs of starting material and hydrolysate.

**Scheme s1.** Synthesis of a G1 model polymer 5 with two PMMA hairs

**Experimental determination of hair length by hydrolyzing denpol 3 and G1 model polymer 5.** Basic hydrolysis according to procedure B of denpol 3 with an apparent \( M_n = 3,400,000 \) g/mol and PDI = 1.37 afforded a product whose GPC elugram showed two peaks at \( M_n = 280,000 \) g/mol (PDI = 1.85) and \( M_n = 20,600 \) g/mol (PDI = 1.26) (Figure s1). The first was assigned to not completely hydrolyzed 3 and the latter to cleaved off hairs. One should note that the hairs are not only cleaved off by this process but their ester functions are also converted into carboxylic acids. Thus instead of PMMA polymethacrylic acid is formed. This was confirmed by NMR
spectroscopy. In the (low) molar mass regime of $M_n = 20,000$ g/mol the hydrodynamic radius of the hairs will not depend much on whether the esters are hydrolyzed or not and it is assumed for the present estimation that the molar mass of the PMMA hairs in 3 equals that of the cleaved polymethacrylic acid. Thus, the hairs have a molar mass of approximately $M_n = 20,000$ g/mol (corresponding to 200 r.u.’s). The molar mass of the hydrolyzed hairs does not depend much on the GPC standard used. If instead of polystyrene PMMA standards were used the values $M_n = 20,600$ (PDI = 1.26) changed to $M_n = 21,500$ (PDI = 1.23).

![Figure s1. GPC elution curves of starting polymers and hydrolysis products of (a) model polymer 5 (a) and hairy denpol 3 (b). The molar mass values given refer to polystyrene standards.](image)

**Hydrolysis of model polymer 5.** Basic hydrolysis of 5 according to procedure B gave polymethacrylic acid with with $M_n = 24,700$ g/mol (PDI = 1.23) corresponding to 250 r.u.s.
4. Calculation of hair lengths

Hairy denpol 3. Of the 2.1 g of denpol 3 2.04 g (= 2.1 g – 58 mg) are associated with PMMA hairs. 58 mg of macroinitiator 2c equals 58/1,100 = 0.053 mmols r.u. and thus 4 x 0.053 = 0.21 mmols initiator sites. Assuming that each initiator site actually initiates, this amounts to a molar mass per chain of 2.04 g : 0.21 mmol = 9.700 g/mol which corresponds to approximately 97 r.u.’s. If one assumes instead of all four only 3, 2, and 1 initiator the corresponding values are given in Table s1.

Table s1a. The dependence of hair molar mass (b), hair r.u.’s (c), and hair length (d) in the all-trans zigzag conformation on the number of actually active initiator sites per r.u. (a) of 2c calculated for the experiment in which 2.1 g of denpol 3 were obtained.

<table>
<thead>
<tr>
<th>a</th>
<th>b  [g/mol]</th>
<th>c</th>
<th>d  [nm]</th>
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<td>4</td>
<td>9,700</td>
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</tr>
<tr>
<td>3</td>
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<td>32</td>
</tr>
<tr>
<td>2</td>
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<td>49</td>
</tr>
<tr>
<td>1</td>
<td>38,800</td>
<td>388</td>
<td>97</td>
</tr>
</tbody>
</table>

Table s1b. The dependence of hair molar mass (b), hair r.u.’s (c), and hair length (d) in the all-trans zigzag conformation on the number of actually active initiator sites per r.u. (a) of 2c calculated for the experiment in which 2.7 g of denpol 3 were obtained.

<table>
<thead>
<tr>
<th>a</th>
<th>b  [g/mol]</th>
<th>c</th>
<th>d  [nm]</th>
</tr>
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<tbody>
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<tr>
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</tr>
<tr>
<td>1</td>
<td>50,400</td>
<td>504</td>
<td>126</td>
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</table>

5. Estimation of initiation efficiency

Denpol macroinitiator 2c: Comparing the calculated hair length dependency on initiation efficiency (Tables s1a and s1b) with the experimentally determined hair lengths of roughly 20,000-25,000 g/mol (which are also in agreement with the SFM images on mica) suggests an initiation efficiency of 50% (2 of the 4 initiator sites per r.u.)

Error bars give the interval containing 96% of the values. $\Theta$ is the change in orientation between two points along the contour. $\langle \cos \Theta \rangle$ is therefore the mean scalar product of two tangent vectors which are separated by a chain segment of length $\ell$. For worm-like chains (WLC) in 2D the correlation function would be an exponential $\exp(-\ell/(2l_P))$, so that the persistence length $l_P$ could be determined by fitting [See e.g. Unser PIC-Paper, Rivetti, ...].

The straight lines are fits for the interval $\ell = 10...50$ nm and clearly show deviations to the WLC-behaviour for larger $\ell$-values. The decay rate corresponds to $l_P = 65$ nm and 164 nm for the mica- and MoS$_2$-curves respectively. The larger value of the latter agrees with the visual impression that chains on MoS$_2$ are smoother. A possible explanation is that chains on MoS$_2$ are more mobile and can therefore rearrange locally after adsorption. One should be cautious in interpreting the value as persistence length since the interaction of side-chains to the substrate can drastically influence the main-chain conformation.