

Supporting Information for

On the synthesis of an anionically chargeable, high molar mass, second generation dendronized polymer and the observation of branching by scanning force microscopy

Edis Kasëmi,[§] Wei Zhuang,^{\$} Jürgen P. Rabe,^{*,§} Karl Fischer,[%] Manfred Schmidt,[%] Helmut Keul,[&] Ding Yi,^x Helmut Cölfen,^x A. Dieter Schlüter^{*,§}

[§] Department of Materials, Institute of Polymers, Swiss Federal Institute of Technology, ETH-Hönggerberg, HCI J 541, 8093 Zürich (Switzerland)

^{\$} Department of Physics, Humboldt University Berlin, Newtonstrasse 15, D-12489 Berlin (Germany)

[%] Institute for Physical Chemistry, University of Mainz, Jakob-Welder-Weg 11, D-55099 Mainz (Germany)

[&] Institute for Technical and Macromolecular Chemistry, RWTH Aachen, Paulwelsstrasse 8, D-52056 Aachen (Germany)

^x Max Planck Institute of Colloids and Interfaces, Am Mühlenberg, D-14476 Golm-Potsdam (Germany)

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Synthetic procedures and analytical data for all new compounds

3,5-Bis(3-(*tert*-butoxycarbonyl)propoxy)benzyl alcohol (1b**)**

A solution of **1a** (19.2 g, 39.7 mmol) in THF (200 mL) was added dropwise to a slurry of LiAlH₄ (3.1 g, 79.6 mmol) in THF (600 mL) over 30 min. at 0°C. The reaction mixture was warmed to room temperature, stirred for another 16 h before it was quenched by the dropwise addition of water (30 mL), followed by 20% NaOH (50 mL) and again water (30 mL) until a white precipitate had formed. This precipitate was filtered and the solvent evaporated off. Chromatographic separation (DCM/methanol 20/1) gave **1b** as a white solid (15.6 g, 86%). R_f = 0.57 (10:1 DCM/MeOH). M.p. = 87 – 88 °C. ¹H NMR: δ = 1.36 (s, 18 H; ^tBu), 1.85 (m, 4 H; CH₂), 3.19 (t, 4 H; CH₂NHBoc), 3.88 (t, 4 H; PhOCH₂), 4.51 (s, 2 H; OCH₂Ph), 4.96 (br, 2 H; NH) 6.26 (t, 1 H; Ph), 6.42 (d, 2 H, Ph). ¹³C NMR: 28.39 (C(CH₃)₃), 29.47 (OCH₂CH₂CH₂N), 37.87 (OCH₂CH₂CH₂N), 64.75 (OCH₂CH₂CH₂N), 65.68 (OCH₂), 79.20 (C(CH₃)₃), 100.40, 105.68, 143.86, 160.00, (Ar), 156.15 (CO). HRMS-MALDI: *m/z* (%): 477 (100) [M+Na]⁺; elemental analysis (%) calcd. for C₂₃H₃₈N₂O₇ (454.27): C 60.77, H 8.43, N 6.16; found: C 60.97, H 8.24, N 6.14.

3,5-Bis(3-aminopropoxy)benzyl alcohol · 2 HCl (2a)

30% HCl (12.50 g, 343 mmol) was added to a solution of **1b** (15.6 g, 34.3 mmol) in THF (200 mL) over 30 min. at 0°C. The reaction mixture was stirred for 6 h until deprotection was completed (TLC). Remaining solvent was evaporated in high vacuum without further purification giving **2a** as a colorless solid (15.6 g, 95%).

m.p.= 227 – 230 °C. ¹H NMR (CD₃OD): 2.18 (m, 4 H; CH₂), 3.18 (t, 4 H; CH₂NH), 4.12 (t, 4 H; PhOCH₂), 4.57 (s, 2 H; OCH₂Ph), 6.49 (t, 1 H; Ph), 6.61 (d, 2 H, Ph). 8.04 (br, 4 H; NH). ¹³C NMR (CD₃OD): 26.97 (OCH₂CH₂CH₂N), 37.87 (OCH₂CH₂CH₂N), 63.63 (OCH₂CH₂CH₂N), 65.04 (OCH₂), 100.10 105.33, 144.07, 159.81 (Ar). ESI-MS: *m/z* (%): 291 (3) [M – Cl]⁺, 255.3 (25) [M – 2 x Cl]⁺; Elemental analysis (%) calcd. for C₁₃H₂₄N₂O₃Cl₂ (327.25): C 74.74, H 7.39, N 8.56; found: C 74.97, H 7.40, N 8.49.

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

N-Hydroxybenzotriazole (8.65 g, 64.1 mmol) was added to a solution of 4-*tert*-butoxy-4-oxobutanoic acid **3** (9.30 g, 53.4 mmol) in dry DCM (200 mL) at room temperature. After 10 min N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (13.51 g, 70.0 mmol) was added to the cooled solution at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h) at this temperature. Then the mixture was warmed to -10 °C and a solution of TEA (13.4 g, 132 mmol) and **2b** (11.5 g, 22.1 mmol) in DCM/methanol (80 mL, 1/1) was added dropwise at -10°C. The resulting mixture was warmed to room

temperature, stirred for 16 h, and then washed with aqueous NaHCO_3 and brine. The organic layer was dried with magnesium sulfate and the solvent removed in vacuo. Chromatographic separation (silica gel, ethyl acetate/methanol 50/1) yielded **4a** as a colorless liquid (10.5 g, 76%). $R_f = 0.5$ (DCM/MeOH 20/1). ^1H NMR: $\delta = 1.39$ (s, 18 H; $t\text{Bu}$), 1.96 (m, 4 H; CH_2), 2.38 (t, 4 H; $\text{CH}_2\text{CO}_2t\text{Bu}$), 2.54 (t, 4 H; NHCOCH_2), 3.41 (m, 4 H; CH_2NH), 4.00 (t, 4 H; PhOCH_2), 4.77 (d, 2 H; CO_2CH_2), 5.30 (dd, 2 H; $\text{CH}=\text{CH}_2$), 5.98 (ddd, 1 H; $\text{H}=\text{CH}_2$), 6.05 (t, 2 H, NH), 6.61 (t, 1 H, Ph), 7.15 (d, 2 H, Ph). ^{13}C NMR: $\delta = 27.91$ ($\text{C}(\text{CH}_3)_3$), 28.92 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{N}$), 30.74 ($\text{CH}_2\text{COC}t\text{Bu}$), 31.13 ($\text{CH}_2\text{CH}_2\text{COC}t\text{Bu}$), 36.75 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{N}$), 65.57 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{N}$), 66.02 (CO_2CH_2), 80.53 ($\text{C}(\text{CH}_3)_3$), 106.47, 107.84, 131.90, 159.67 (Ar), 118.21 ($\text{CH}_2=\text{C}$), 132.60 ($\text{CH}_2=\text{C}$), 165.73 (CO), 171.75, 172.14 (NHCOO). FAB MS (3 kV): m/z (%): 619.9 (4.30) $[\text{M}]^+$, 546.9 (26.10) $[\text{M} - \text{C}_4\text{H}_9\text{O}]^+$, 490.8 (40) $[\text{M} - \text{C}_7\text{H}_{13}\text{O}_2]^+$. Elemental analysis (%) calcd. for $\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_{10}$ (620.73): C 61.92, H 7.79, N 4.51; found: C 61.97, H 7.80, N 4.22.

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

A solution of *p*-toluene sulfinic acid hydrate (3.61 g, 20.31 mmol) in methanol (15 mL) was added dropwise at RT to a mixture of **4a** (10.5 g, 16.93 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (1.00 g, 0.86 mmol) in DCM (100 mL). The reaction was monitored with TLC and stopped after 4 h. The solvent was removed under vacuum at RT and chromatographic separation (silica gel, DCM/methanol 20/1) and ethyl acetate/methanol 15/1 yielded **4b** as colorless liquid (8.2 g, 80%). $R_f = 0.38$ (15:1 EtOAc/MeOH). ^1H NMR: $\delta = 1.40$ (s, 18 H; $t\text{Bu}$),

1.96 (m, 4 H; CH₂), 2.43 (t, 4 H; CH₂CO₂^tBu), 2.57 (t, 4 H; NHCOCH₂), 3.43 (m, 4 H; CH₂NH), 3.99 (t, 4 H; PhOCH₂), 6.33 (t, 2 H, NH), 6.61 (t, 1 H, Ph), 7.12 (d, 2 H, Ph). ¹³C NMR: δ = 27.94 (C(CH₃)₃), 28.90 (OCH₂CH₂CH₂N), 30.82 (CH₂COC^tBu), 31.15 (CH₂CH₂COC^tBu), 36.85 (OCH₂CH₂CH₂N), 65.95 (OCH₂CH₂CH₂N), 80.76 (C(CH₃)₃), 106.77, 108.13, 131.88, 159.62 (Ar), 169.07 (CO), 172.31 (NHCOO). FAB MS (3 kV): *m/z* (%): 624.9 (7) [C₂₉H₄₃N₂O₁₀Na + Na]⁺, 603.2 (60) [M + Na]⁺, 581 (15) [M + H]⁺. Elemental analysis (%) calcd. for C₂₉H₄₄N₂O₁₀ (580.67): C 59.98, H 7.64, N 4.82; found: C 59.84, H 7.73, N 4.57.

3,5-Bis{3-[3,5-bis(3-(4-tert-butoxy-4-oxobutanamido)propoxy)benzamido]propoxy} benzyl alcohol (5)

N-Hydroxybenzotriazole (2.56 g, 19 mmol) was added to a solution of acid **4b** (8.54 g, 14.72 mmol) in dry DCM (100 mL) at room temperature. After 10 min N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (4.00 g, 20.1 mmol) was added to the cooled solution (-20°C), and the reaction mixture was stirred until the hydrochloride had dissolved completely (ca. 4 h). Then a solution of TEA (7.45 g, 73.6 mmol) and **2a** (5.92 g, 12.27 mmol) in methanol/DCM (70 mL, 1/ 1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature, stirred for 16 h, and then washed with aqueous NaHCO₃ and brine. The organic layer was dried with magnesium sulfate and the solvent removed in vacuo. Chromatographic separation (silica gel, DCM/methanol 10/1) and ethyl acetate/methanol 10/1) yielded **5** as a colorless foam (10.2 g, 60%).

R_f = 0.62 (10:1 EtOAc/MeOH). M.p. = 89 – 94 °C. ¹H NMR: δ = 1.39 (s, 36 H; ^tBu), 1.91 (m, 8 H; CH₂), 2.05 (m, 4 H; CH₂), 2.38 (t, 8

H; CH₂CO₂^tBu), 2.52 (t, 8 H; NHCOCH₂), 3.36 (m, 8 H; CH₂NH), 3.58 (m, 4 H; CH₂NH), 3.92 (m, 8 H; PhOCH₂), 4.03 (m, 4 H; PhOCH₂), 4.55 (s, 2 H; OCH₂Ph), 6.30 (t, 1 H; Ph), 6.42 (br, 4 H; NH), 6.46 (t, 2 H; Ph), 6.49 (d, 2 H, Ph), 6.84 (d, 4 H; Ph), 7.19 (br, 2 H; NH). ¹³C NMR: 28.04 (C(CH₃)₃), 28.83, 29.01 (OCH₂CH₂CH₂N), 30.80 (CH₂COC(CH₃)₃), 31.00 (CH₂CH₂COC^tBu), 36.67, 37.69 (OCH₂CH₂CH₂N), 64.55, 65.74 (OCH₂CH₂CH₂N), 66.21 (OCH₂), 80.66 (C(CH₃)₃), 100.2, 104.31, 105.26, 105.66, 136.53, 144.17, 159.81, 159.88, (Ar), 167.49, (CO), 172.17, 172.35 (NHCOO). HRMS-MALDI: *m/z* (%): 777 (100) [M – 4 x (C₈H₁₃O₃) + Na]⁺. Elemental analysis (%) calcd. for C₇₁H₁₀₆N₆O₂₁ (1379.63): C 61.81, H 7.74, N 6.09; found: C 61.86, H 7.77, N 5.98.

3,5-Bis{3-[3,5-bis(3-(4-*tert*-butoxy-4-oxobutanamido)propoxy)benzamido]propoxy} benzyl methacrylate (6)

A solution of MAC (0.98 g, 9.34 mmol) in THF (10 mL) was added dropwise to a mixture of **5** (6.45 g, 4.67 mmol), triethylamine (TEA; 1.41 g, 14.2 mmol), and DMAP (60 mg) in dry THF (100 mL) at 0°C over 30 min. The mixture was stirred for 16 h at room temperature, then washed with aqueous NaHCO₃ and brine, and dried with magnesium sulfate. After evaporation of the solvent under vacuum, repeated chromatographic separation (silica gel, ethyl acetate/methanol 10/1) yielded pure **6** as colorless foam (5.99 g, 85%). *R*_f = 0.47 (10:1 EtOAc/MeOH). M.p. = 68 – 74 °C ¹H NMR: δ = 1.40 (s, 36 H; ^tBu), 1.92 (m, 11 H; PhOCH₂+C=CCH₃), 2.07 (m, 4 H; PhOCH₂), 2.39 (t, 8 H; CH₂CO₂^tBu), 2.52 (t, 8 H; NHCOCH₂), 3.38 (m, 8 H; CH₂NH), 3.60 (m, 4

H; CH₂NH), 3.94 (m, 8 H; PhOCH₂), 4.04 (m, 4 H; PhOCH₂), 5.06 (s, 2 H; OCH₂Ph), 5.56 (m, 1 H; C=CH₂), 6.12 (s, 1 H; C=CH₂), 6.34 - 6.36 (br, 4 H; NH), 6.38 (t, 1 H; Ph), 6.46 (t, 2 H; Ph), 6.49 (d, 2 H, Ph), 6.86 (d, 4 H; Ph), 7.15 (br, 2 H; NH) ppm. ¹³C NMR: δ = 18.33 (C=CCH₃), 28.04 (C(CH₃)₃), 28.99, 29.04 (OCH₂CH₂CH₂N), 30.81 (CH₂COC^tBu), 31.08 (CH₂CH₂COC^tBu), 36.72, 37.69 (OCH₂CH₂CH₂N), 65.80, 66.18 (OCH₂CH₂CH₂N), 66.29 (OCH₂), 80.67 (C(CH₃)₃), 101.10, 104.25, 105.68, 106.41, 136.01, 138.41, 159.82, 160.00, (Ar), 126.11 (CH₂=C), 136.60 (CH₂=C), 167.20, 173.1 (CO) , 167.41, 172.34 (NHCOO) ppm. HRMS-MALDI: *m/z* (%): 845 (100) [M – 4 x (C₈H₁₃O₃) + Na]⁺. Elemental analysis (%) calcd. for C₇₅H₁₁₀N₆O₂₂ (1447.72): C 62.22, H 7.66, N 5.81; found: C 61.81, H 7.65, N 5.63.

Poly[3,5-bis(3-{3,5-bis[3-(4-*tert*-butoxy-4-oxobutanamido)propoxy]benzamido}propoxy) benzyl methacrylate] (7a)

To monomer **6** (2.22 g, 1.53 mmol) and AIBN (1.75 mg, 0.011 mmol) in a Schlenk tube was added DMF (1.32 g, 1.4 mL) and the mixture stirred under nitrogen for 30 min. until everything had dissolved. Then the tube was weighed and vacuum of 2 mbar applied until 320 mg of DMF had been removed. This was typically the case after 1 h at RT. The obtained highly concentrated solution was still homogenous. Then the tube was put into a 65°C preheated oil bath. After 4-5 h the viscosity had increased to the point that

magnetic stirring was not possible anymore, but heating was continued for another 12 h. After cooling, DCM (3 mL) was added and the resulting solution precipitated into CH₃OH/H₂O (3/1). This procedure was repeated four times to give **7a** as colorless precipitate (2.06 g, 90%) which was collected and dried under high vacuum. ¹H NMR: δ = 0.65 (br, 2 H, CH₂), 0.80 (br, 3 H, CH₃), 1.30 (br, 36 H; ^tBu), 1.76 (br, 12 H; PhOCH₂), 2.34 (br, 8 H; CH₂CO₂^tBu), 2.40 (br, 8 H; NHCOCH₂), 3.19 (br, 12 H; CH₂NH), 3.75 (br, 12 H; OCH₂CH₂CH₂N), 4.65 (br, 2 H; OCH₂Ph), 6.34 (br, 3 H; Ph), 6.80 (br, 6 H, Ph) 7.46 – 8.21 (br, 6 H; NH) ppm. ¹³C NMR: δ = 28.01, 29.04, 30.83, 36.46, 65.37, 65.65, 105.77, 159.78, 172.30, 172.45 ppm. Elemental analysis (%) calcd. for (C₇₅H₁₁₀N₆O₂₂)_n (1447.72)_n: C 62.22, H 7.66, N 5.81; found: C 61.95, H 7.69, N 5.82.

Poly[3,5-bis(3-{3,5-bis[3-(4-amino-4-oxobutanoic acid)propoxy]benzamido}propoxy) benzyl methacrylate] (7b)

To **7a** (0.50 g, 0.35 mmol), TFA (5 mL, 7.4 g, 65 mmol) was added. After stirring for 12 h at r.t., methanol (1 mL) and TFA (2 mL) were added to the mixture and stirring was continued for 7 d. Precipitation in DCM gave **7b** as colorless solid (0.4 g, 95 %). ¹H NMR (CD₃OD/CDCl₃ 4/1): δ = 0.65 (br, 2 H, CH₂), 0.80 (br, 3 H, CH₃), 1.84 (br, 12 H; PhOCH₂), 2.43 (br, 8 H; CH₂CO₂H), 2.53 (br, 8 H; NHCOCH₂), 3.26 (br, 12 H; CH₂NH), 3.86 (br, 12 H; OCH₂CH₂CH₂N), 4.68 (br, 2 H; OCH₂Ph), 6.50 (br, 3 H; Ph), 6.90 (br, 6 H, Ph). ¹³C NMR (CD₃OD/CDCl₃ 4/1): δ = 30.02, 31.25, 37.22, 66.54, 67.01 105.77, 173.66, 174.48. Elemental analysis (%) calcd. for (C₅₉H₇₈N₆O₂₂)_n (1223.29)_n: C 57.93, H 6.43, N 6.87; found: C 56.47, H 6.47, N 6.27.

Experiments to provoke chain transfer

Experiment A: To the G3 dendron acid **8** (150 mg, 0.050 mmol) and AIBN (2 mg, 0.012 mmol) in a Schlenk tube were added freshly distilled methacrylic acid methyl ester (300 mg, 3 mmol) and DMF (0.150 mL). The mixture was stirred for 30 min until everything had dissolved. After two freeze-pump-thaw degassing cycles the Schlenk tube was placed into a 65°C preheated oil bath and left there overnight. The polymer formed was dissolved in DCM and purified by column chromatography using DCM as eluent to give 212 mg of PMMA. The column then was washed again with DCM/MeOH 10/1 to give 98 mg of unchanged **8**.

Experiment B: To the G3 dendron acid **8** (100 mg, 0.033 mmol) and AIBN (2.5 mg, 0.015 mmol) in a Schlenk tube were added freshly distilled methacrylic acid methyl ester (150 mg, 1.5 mmol) and DMF (0.050 mL). The mixture was stirred for 30 min until everything had dissolved and two freeze-pump-thaw cycles were applied. Then the tube was put into a 65°C preheated oil bath and left overnight. The polymer formed was dissolved in DCM and purified by column chromatography using DCM as eluent to give 102 mg of PMMA. The column was then washed with the solvent mixture DCM/MeOH = 10/1 to give 62 mg of unchanged **8**.

Synthesis of PMMA for comparison purposes: To a freshly distilled methacrylic acid methyl ester (150 mg, 1.5 mmol) and AIBN (2.5 mg, 0.015 mmol) in a Schlenk tube was added and DMF (0.050 mL). The mixture was stirred for 30 min. until everything had dissolved. Then two times freeze-pump-thaw degas cycles were done and Schlenk tube was put into a 65°C preheated oil bath and left overnight. The polymer formed was dissolved in DCM and purified by column chromatography using DCM as eluent to give 122 mg of PMMA.

Figure 1. Differential scanning calorimetry (DSC) curves for compounds **7a-c** after a completed heating and cooling cycle (heating rate: 10 °/min, under nitrogen).

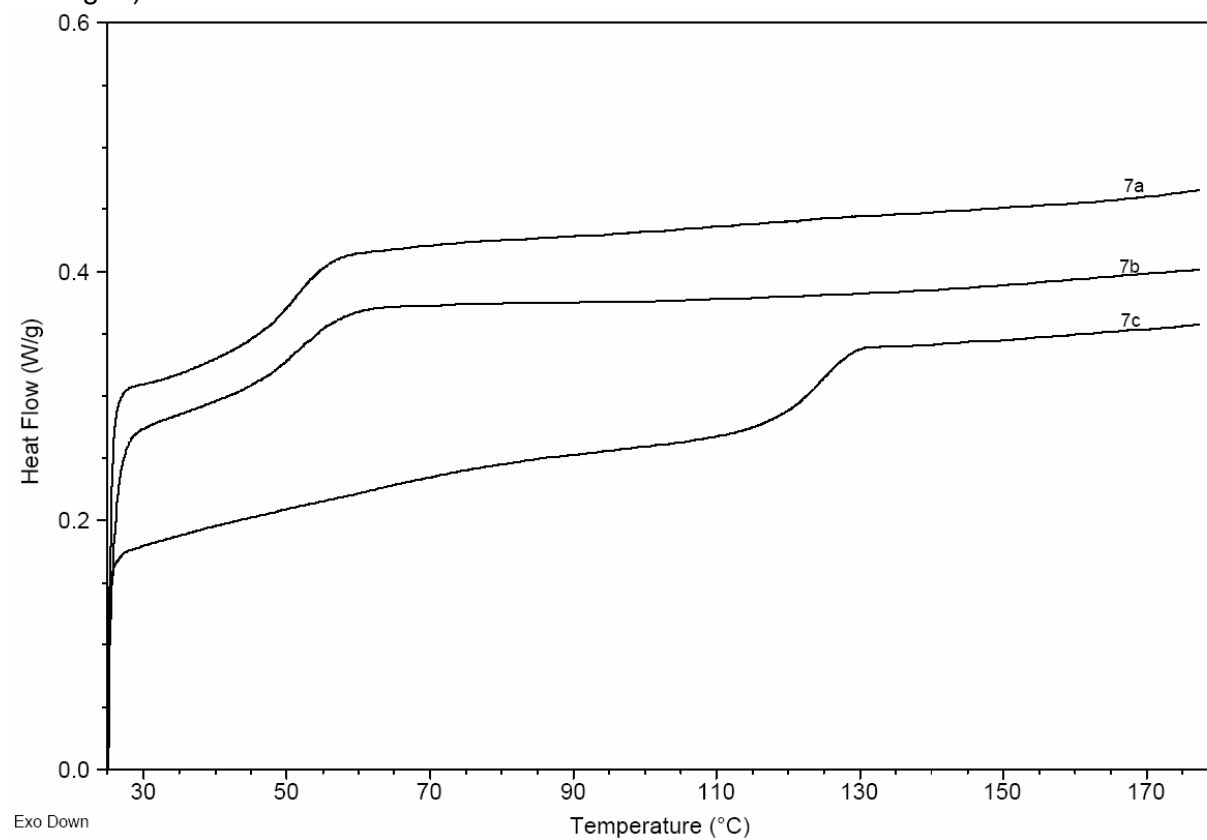
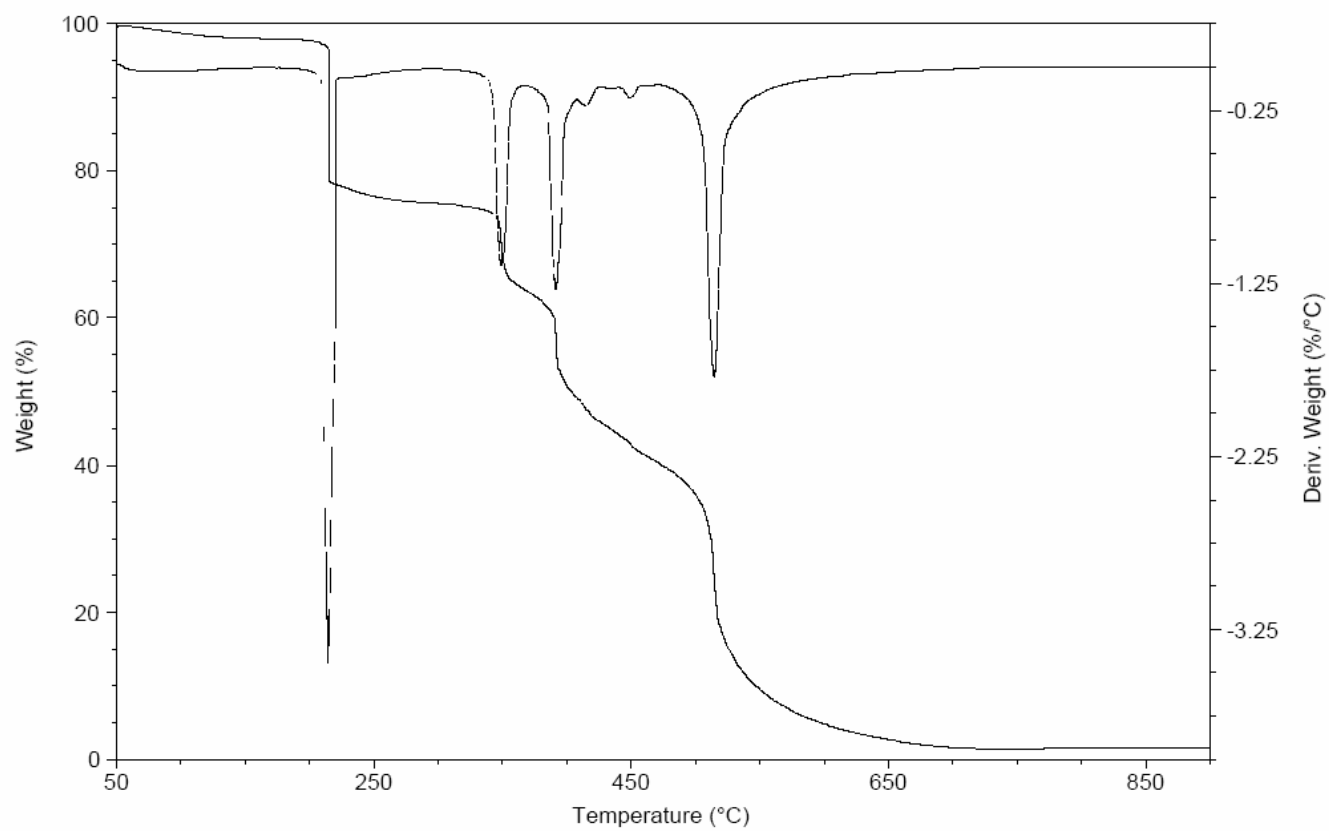


Figure 2a. High-resolution thermogravimetric analysis (TGA) of compound **7a** (Heating rate: 10 °/min, open to air).



S13

Figure 2b: High-resolution thermogravimetric analysis (TGA) of compound **7b** (Heating rate: 10 °/min, open to air).

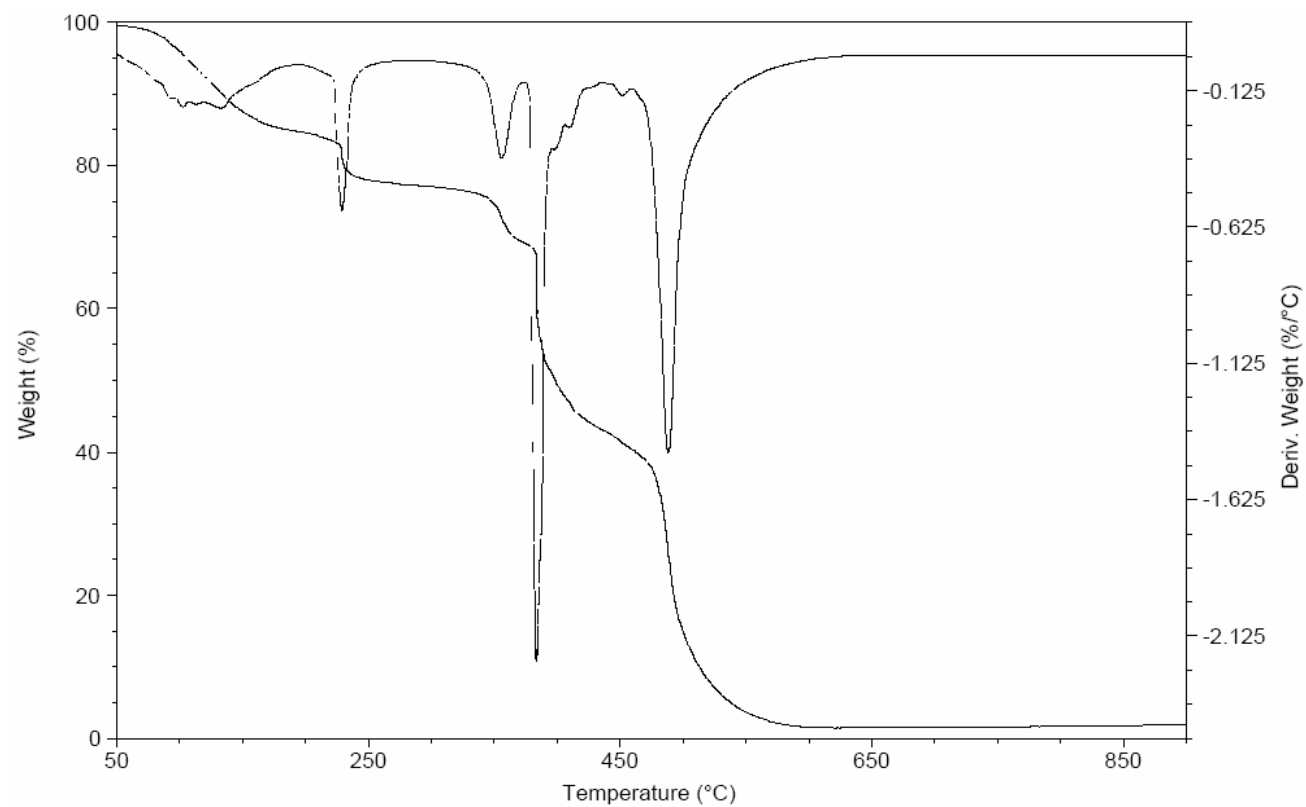


Figure 2c: High-resolution thermogravimetric analysis (TGA) of compound **7c** (Heating rate: 10 °/min, open to air).

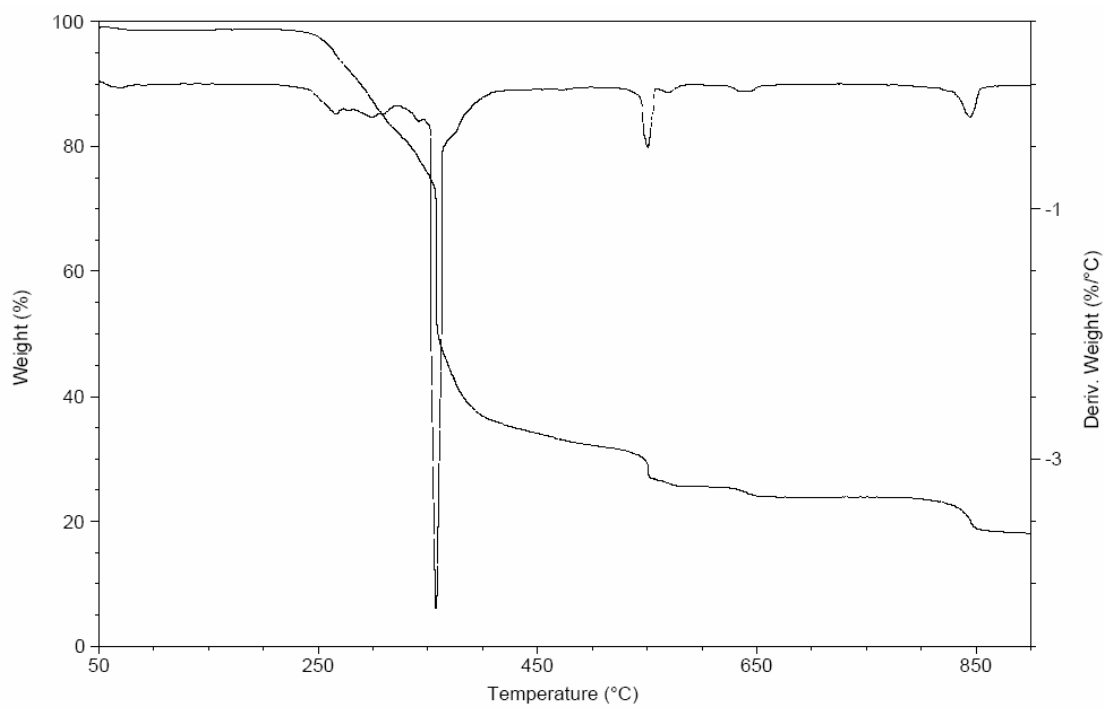
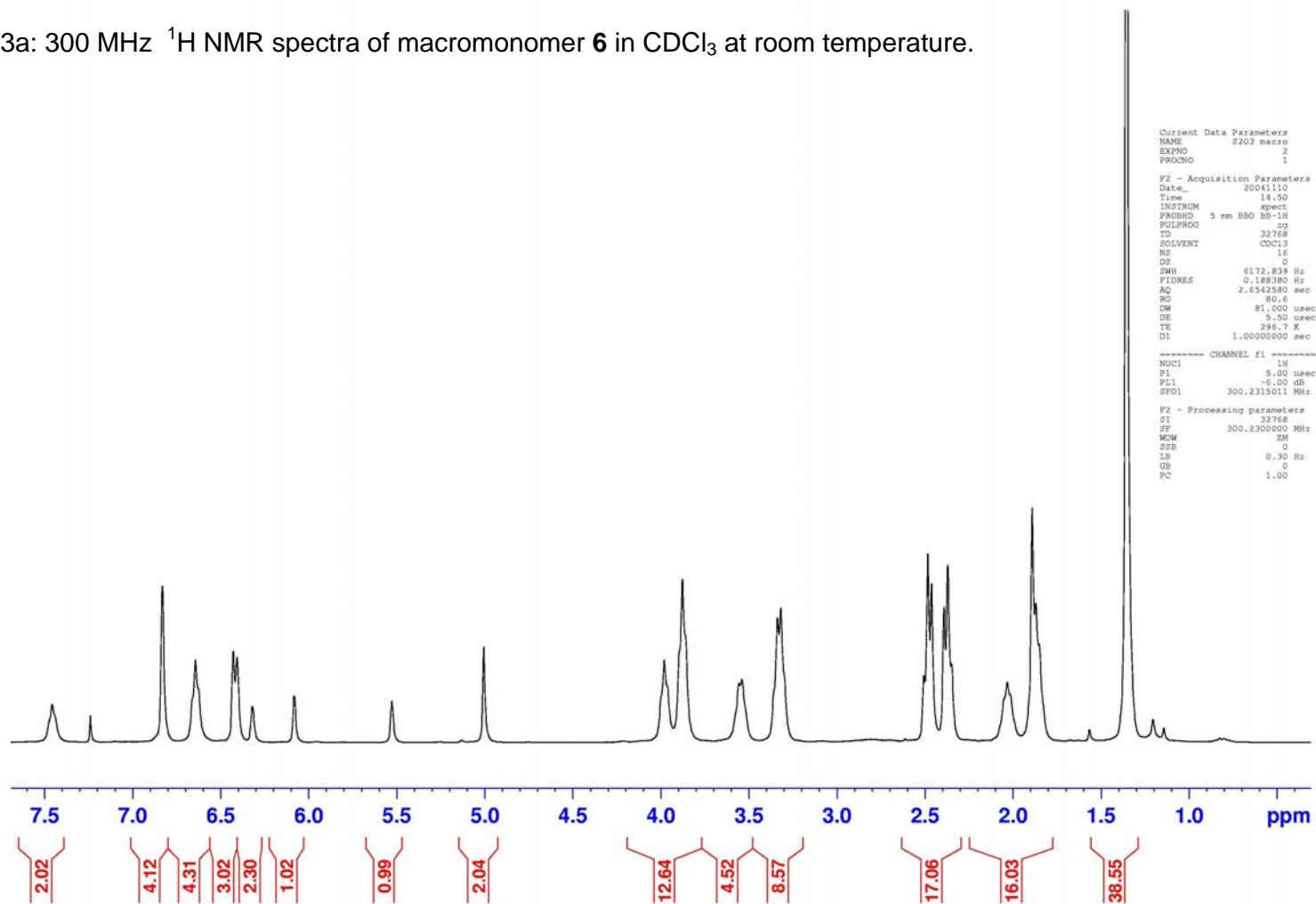


Figure 3a: 300 MHz ^1H NMR spectra of macromonomer **6** in CDCl_3 at room temperature.



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Figure 3b: 75 MHz ^{13}C NMR spectra of macromonomer **6** in CDCl_3 at room temperature.

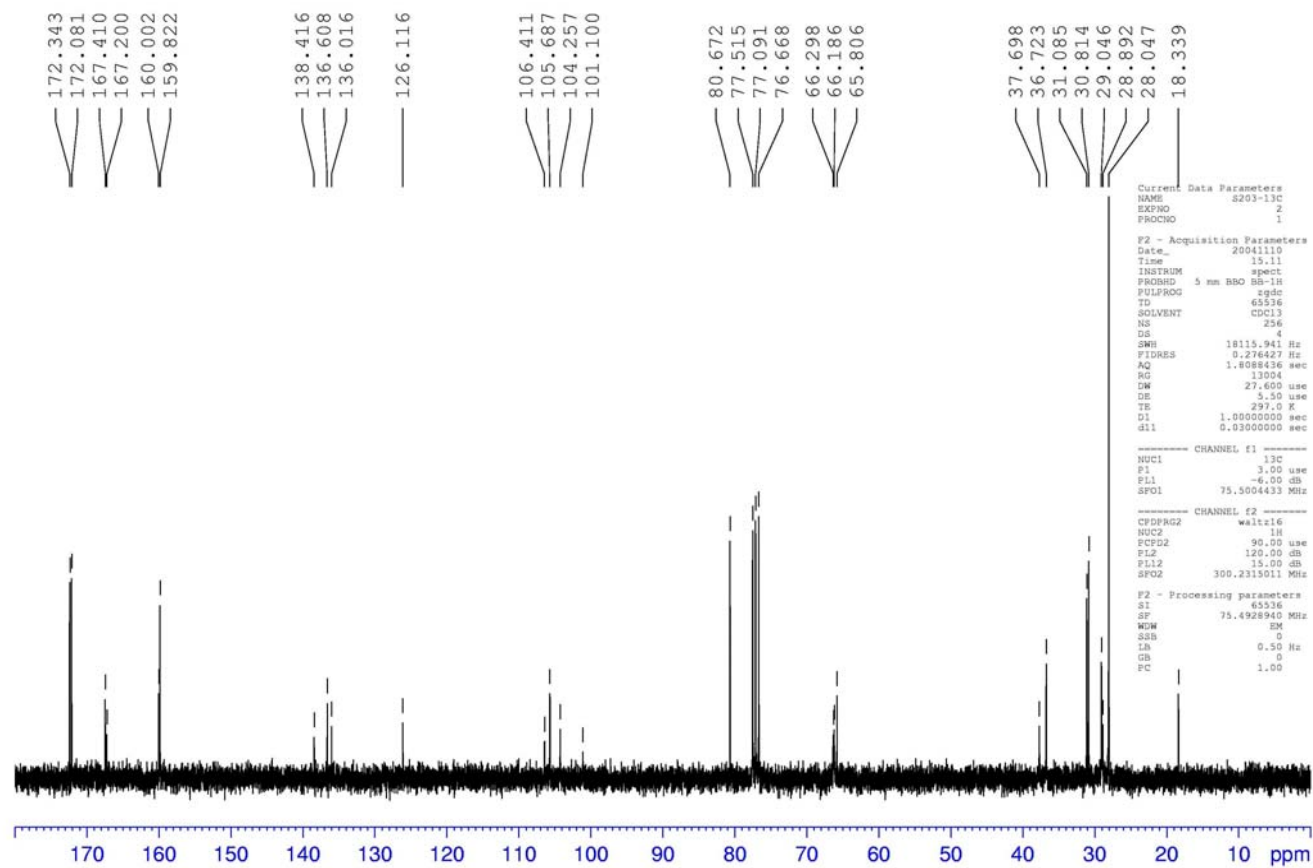


Figure 4a: Deprotection of denpol **7a** (entry 5, Table 1) to give **7b** in DCM with a large excess of trifluoro acetic acid. A low intensity *ter.*-butyl signal can still be observed.

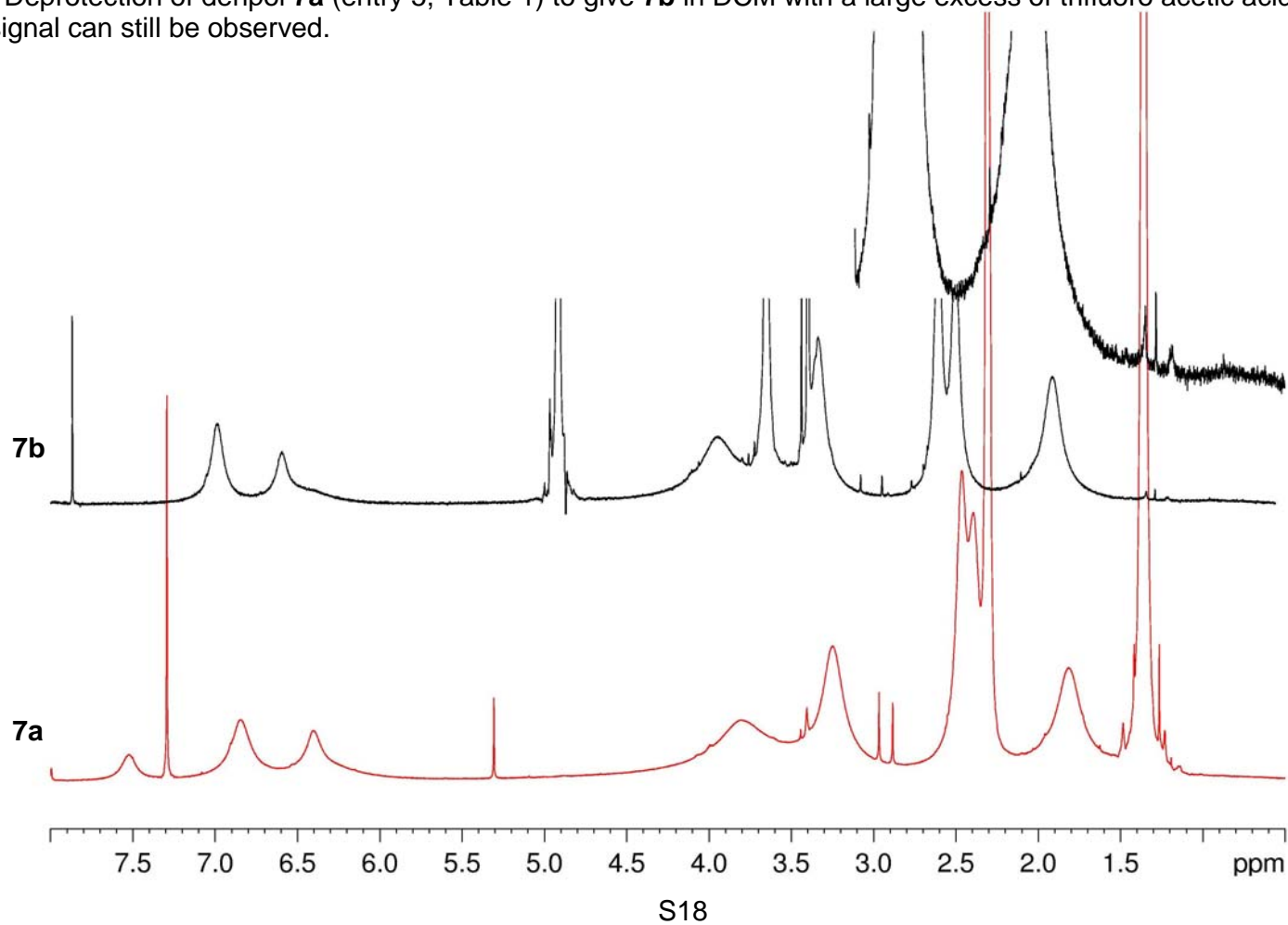


Figure 4b: Deprotection of denpol **7a** (entry 5, Table 1) to give **7b** with trifluoro acetic acid in bulk followed by a second treatment in DCM solution. No remaining *tert.*-butyl signal is observed.

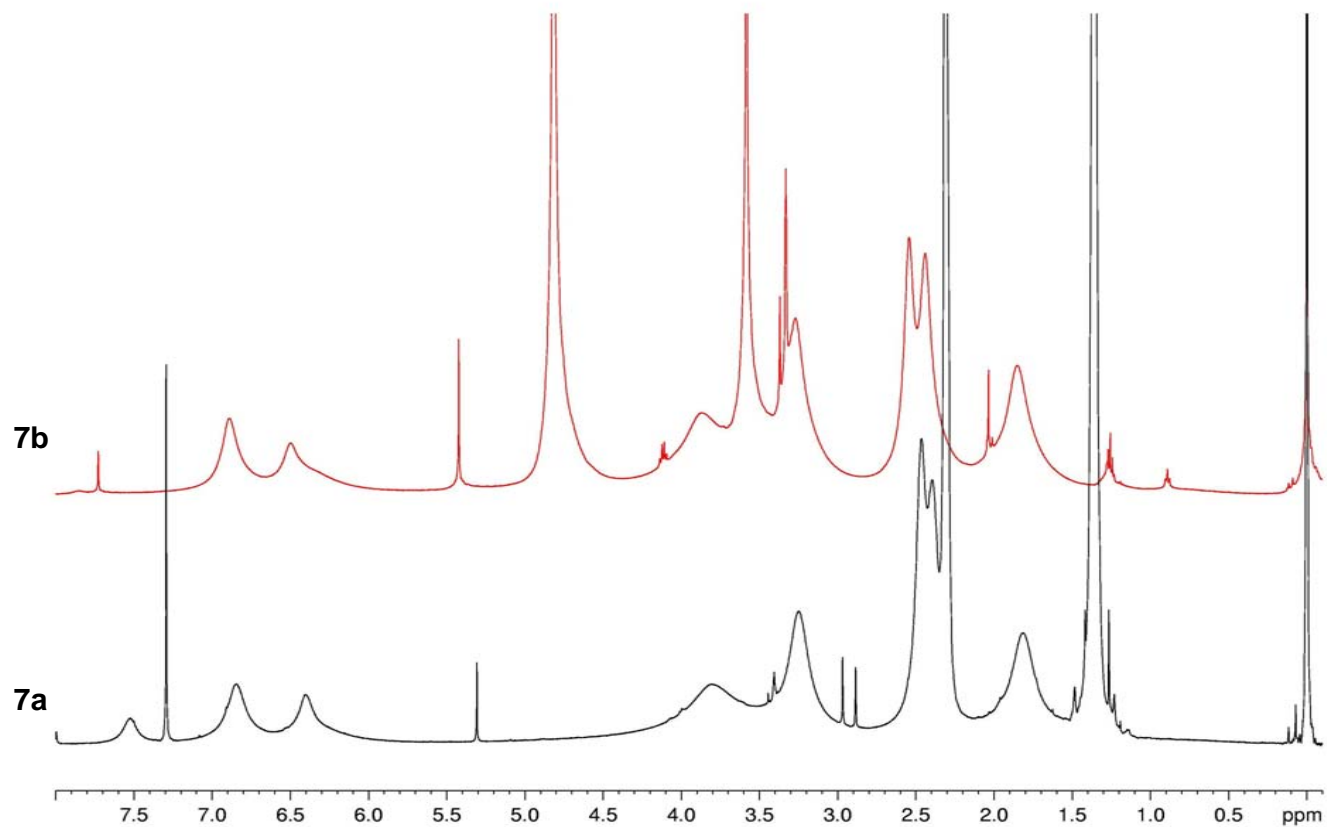
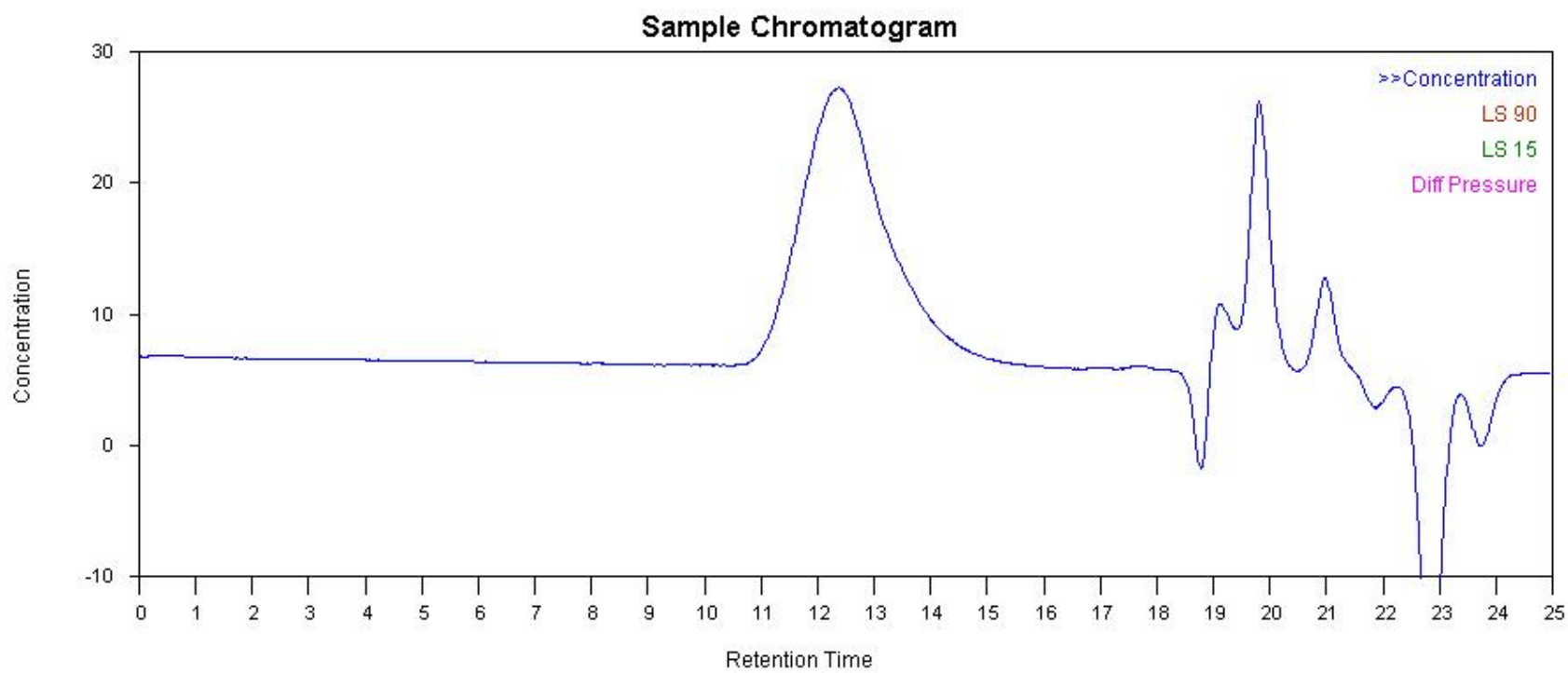


Figure 5: Representative monomodal GPC curve of denpol **7a** (entry 5, Table 1) obtained in DMF with 1 g/L LiBr at 80°C



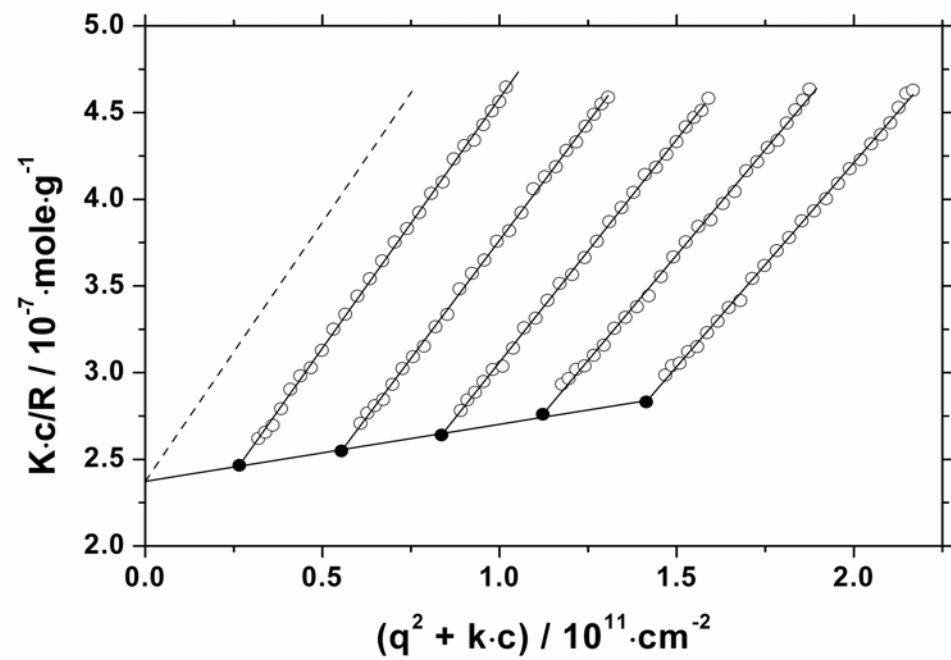


Figure 6: Zimm-plot of entry 3, Tab. 1, yielding $M_w = 4.2 \times 10^6$, $R_g = 61 \text{ nm}$, $A_2 = 1.3 \cdot 10^{-4} \text{ cm}^3 \text{ mole/g}^2$

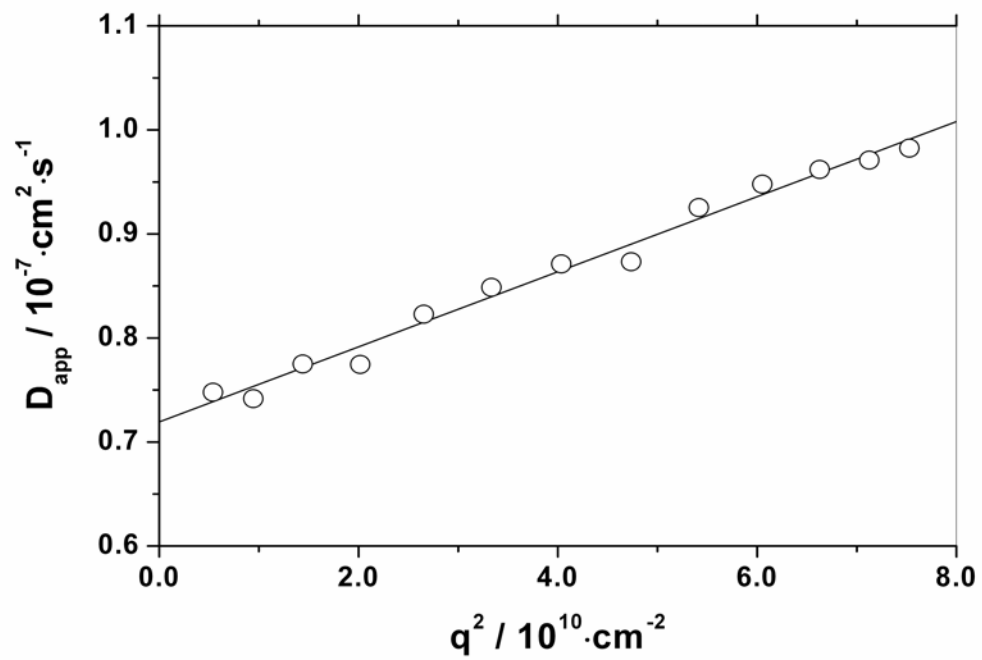


Figure 7: Angular dependence of the apparent diffusion coefficient D_{app} for entry 3, Tab 1, for $c = 0.038$ g/L.

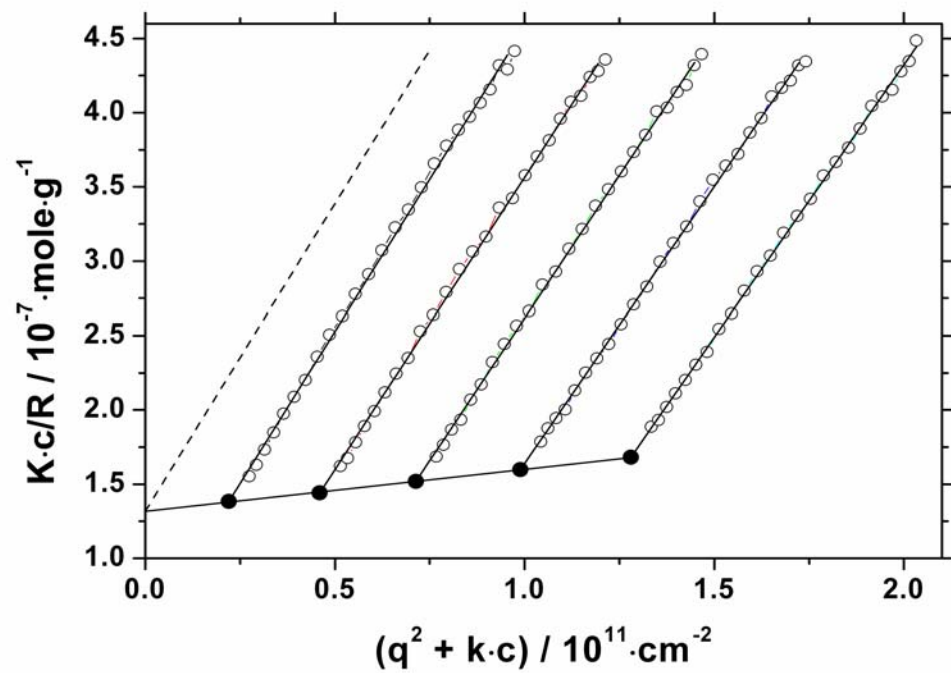


Figure 8: Zimm-plot of entry 5, Tab. 1, yielding $M_w = 7.6 \times 10^6$, $R_g = 97 \text{ nm}$, $A_2 = 5.7 \cdot 10^{-5} \text{ cm}^3 \text{ mole/g}^2$

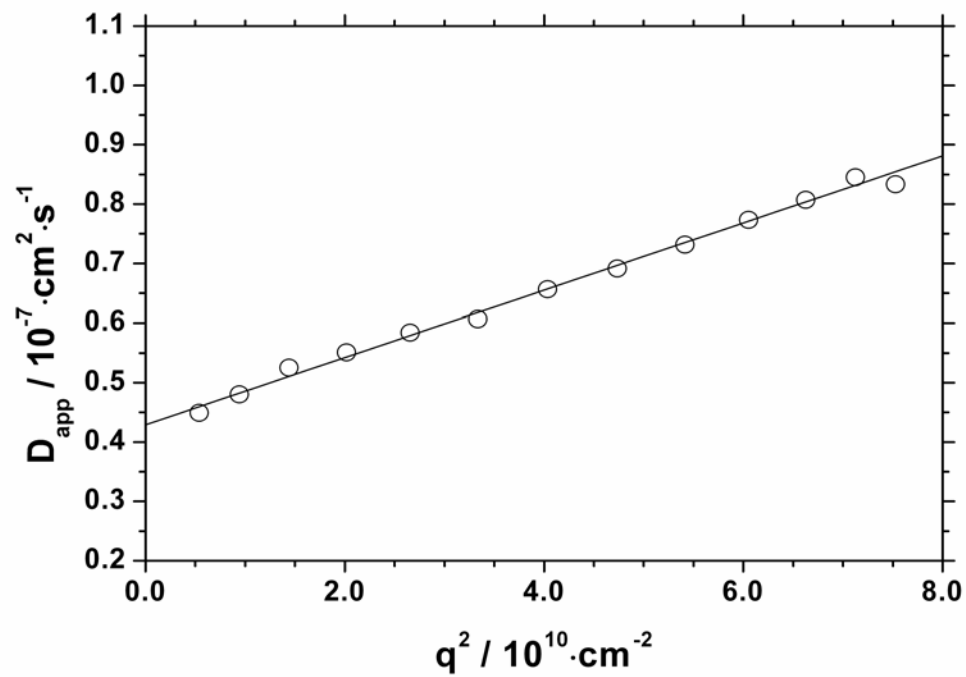


Figure 9: Angular dependence of the apparent diffusion coefficient D_{app} for entry 5, Tab 1, $c = 0.055 \text{ g/L}$.

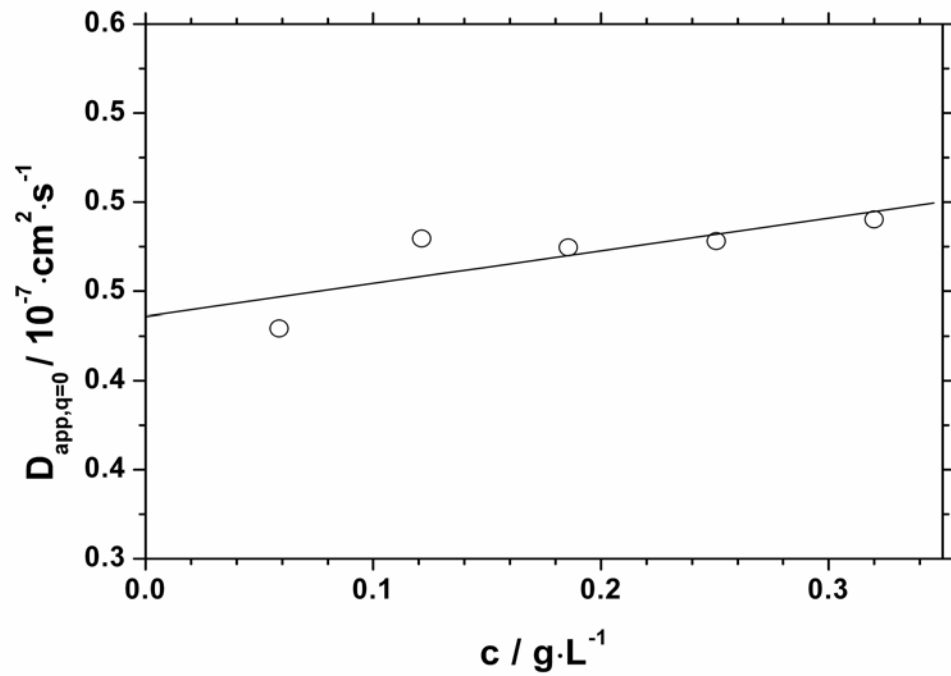


Fig. 10: Concentration dependence of the z-average diffusion coefficient D_z for entry 5, Tab. 1, yielding $D_z = 4.36 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $R_h = 56 \text{ nm}$.

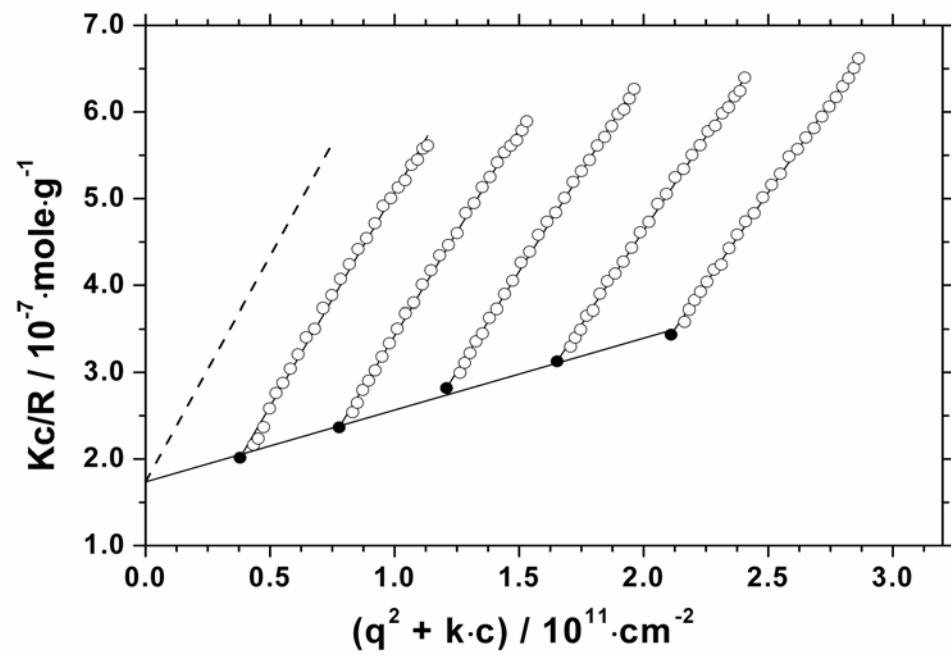


Figure 11: Zimm-plot of entry 4, Tab. 1, yielding $M_w = 5.8 \times 10^6$, $R_g = 94 \text{ nm}$, $A_2 = 2.1 \cdot 10^{-4} \text{ cm}^3 \text{ mole/g}^2$

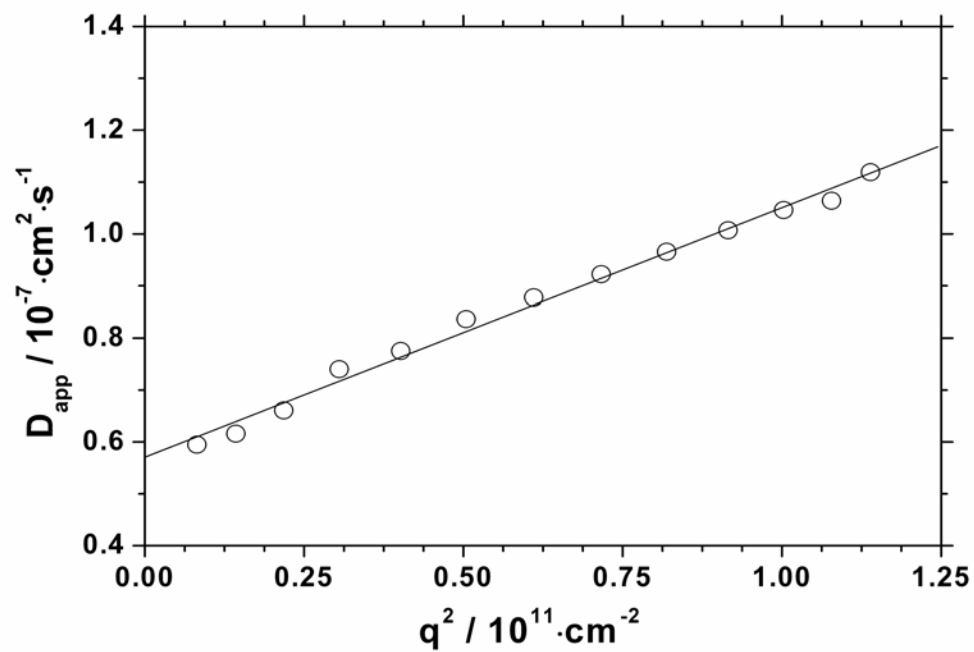


Figure 12: Angular dependence of the apparent diffusion coefficient D_{app} for entry 4, Tab 1, $c = 0.073 \text{ g/L}$.

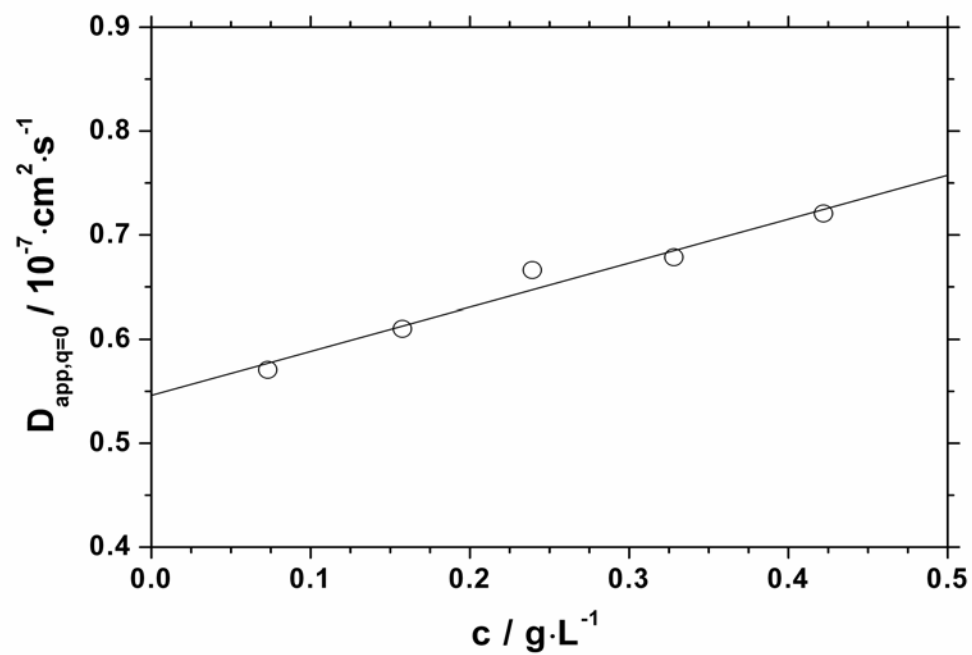


Figure 13: Concentration dependence of the z-average diffusion coefficient D_z for entry 4, Tab. 1, yielding $D_z = 5.71 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $R_h = 45 \text{ nm}$.