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Liquid-Crystalline Polymers from Cationic Dendronized Polymer−Anionic Lipid Complexes

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During the past decade, ionic complexation of polyelectrolytes and oppositely charged low molecular mesogenic units has been gaining increasing attention as a viable route to design liquid-crystalline (LC) polymers with long-range order.[1,2] The main advantage of this strategy over other self-assembly methods is the simplicity with which complex architectures can be accessed by putting together simple constituents from a "toolbox". At the same time, the liquid-crystalline phases obtained for the ionic supramolecular complexes are comparable to those obtained in systems where mesogenic units are covalently attached to macromolecules.[3−5]

Various molecular architectures have been investigated for cationic and anionic polymers, including linear,[6] dendritic,[7] and hyperbranched polyelectrolytes.[8] Hydrocarbon-based cationic and anionic surfactants, which have been the most widely investigated class of mesogenic units, have also been shown to directly control the period and the structure of the complex mesophases.[9]

Here we report for the first time the use of cationic dendronized polymers[10] and anionic lipids as a model system in which the molecular architecture can be rationally controlled by two factors, the generation of the dendrons attached to the polymer backbone and the length of the lipid tail. Scheme 1 shows the molecular structures of the first (**PG1**) and second (**PG2**) generation dendronized polymers used in this study. They have two and four ammonium triflate end groups, respectively. The syntheses (see Supporting Information) follow closely the lines given for a similar **PG2** polymer.[11] The polymers were isolated on the multigram scale in their *tert*-butyloxycarbonyl (Boc)-protected form. The molar masses were determined by gel permeation chromatography (in DMF, 1% LiCl, 80 °C, referenced to PMMA standards using two-angle light scattering, refractive index, and viscometry detectors): **PG1** ($M_w = 1.5 \times 10^6$), **PG2** = ($M_w = 2.5 \times 10^6$).[12] The deprotection was achieved quantitatively by treatment with neat trifluoroacetic acid.

Complexation with the lipids was carried out by mixing polymers and lipids at a stoichiometric ratio in water at pH = 3, so that the dendrons' primary amines and the lipids' sulfonic groups are positively and negatively charged, respectively. Upon complexation, the comb-like supramolecule precipitates in water. After its re-precipitation into water from an ethanol/butanol mixture as solvent, drying, and annealing at 50 °C under ultrahigh vacuum (10^{-8} mBar), the complete complexation of NH_3^+/SO_4^- in the solid polymer/lipid complex was demonstrated by the appearance of the FTIR band at 1074 cm^{-1} corresponding to the bound sulfonic groups. All the comb-like complexes obtained as described above showed liquid-crystalline behavior as indicated by birefringency in cross-polarized optical microscopy.

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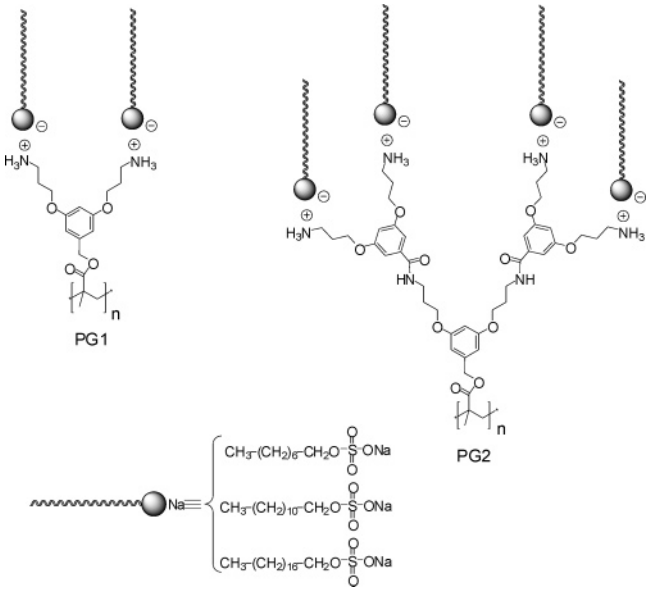
Scheme 1. Complexes of Dendronized Polymers and Surfactants Used



Small-angle X-ray scattering allowed us to determine the specific group space of the LC complexes as a function of the lipid tail length and dendron generation. The effect of the alkyl chains can be understood by comparing, in Figure 1, SAXS diffractograms of the same **PG1** complexed with C8, C12, and C18 sulfonated lipids (lowest three curves). The C8 lipid is too short to induce segregation of the backbone and alkyl chain, and the corresponding spectrum shows a single broad peak indicative of an amorphous structure. By increasing the alkyl chain length, however, segregation of the polymer backbone and lipid chains takes place. This is reflected in the SAXS spectrum of the **PG1**−C12 complex, where a first sharp peak centered at $q_1 = 1.9$ nm^{-1} appears together with a second reflection at $q_2 = 3.8$ nm^{-1}. The spacing ratio of 2 for q_2/q_1indicates a lamellar structure with periodicity $d = 2\pi/q_1 = 3.3$ nm. By further increasing the length of the alkyl chain to C18, increased segregation drives the system into a lamellar phase with very long range order, as revealed by the respective SAXS diffractogram showing as much as four consecutive reflections, q_1:q_2:q_3:q_4 spaced as 1:2:3:4. The first peak, centered at $q_1 = 1.52$ nm^{-1}, reveals a period of 4.13 nm for the C18-dendronized polymer complex lamellar phase, which is 0.8 nm larger compared to the lamellar phase obtained for the C12-dendronized polymer complex, consistent with the larger size of the alkyl chain.

The lamellar phases are made up of two segregated domains: the dendronized polymer and the lipid tails. Yet, the alkyl chains can form both a bilayer of facing lipid chains or a monolayer of intercalated lipid chains. Because the three lowest diffractograms

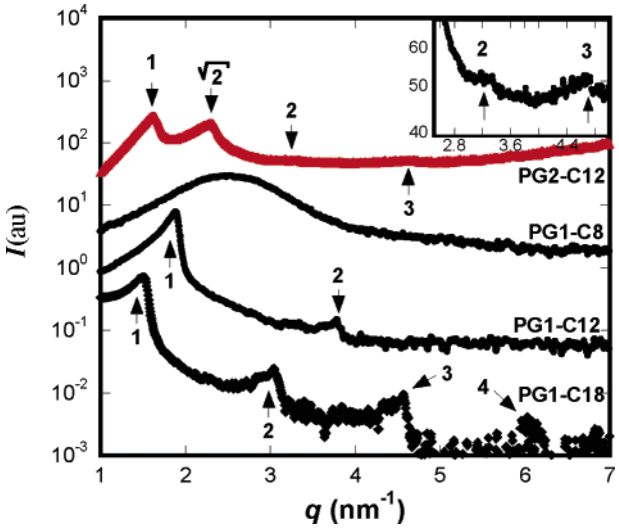


Figure 1. SAXS diffractograms for **PG1** (three lowest curves) and **PG2** (upper and inset curves) dendronized polymers complexed with C8, C12, and C18. Multiple reflections are indexed by arrows. The **PG2**−C12 spectrum (zoomed in the inset in the 2.5−5 nm^{-1} region) is given in $I \times q^2$.

in Figure 1 refer to complexes with the same **PG1** polymer but different alkyl tails, the difference in period of the lamellar phase can only arise from the difference in lengths of sulfonated C12 and C18 lipids. By considering fully stretched lipid chains, the difference in length between C18 and C12 chains is 0.65 nm. Because a bilayer model for lipids would then lead to an increase of 1.3 nm when going from C12 to C18, calculations are consistent with an intercalated alkyl tails model or a bilayer of tilted alkyl tails. Moreover, a fully stretched intercalated lipid chain model combined with SAXS period also yields the thickness of the dendron phase, calculated at 1.63 nm for **PG1**, indicating high space filling efficiency of dendronized polymers.[13]

Figure 1 also highlights the effect of generation of dendronized polymer when the surfactant is kept at fixed length, if one considers the **PG1**−C12 and **PG2**−C12 SAXS spectra. As discussed previously, when C12 is complexed to a **PG1**-dendronized polymer, the liquid-crystalline phase is lamellar with 3.3 nm period. When a **PG2** polymer is complexed with the same C12 alkyl chain, however, the diffractogram changes into four q_1:q_2:q_3:q_4 reflections spaced as 1:$\sqrt{2}$:2:3 (top curve and inset), which is the signature of a rarely observed and well-organized columnar tetragonal phase, with period 3.93 nm. The larger period of the tetragonal phase, whose existence has been reported in the literature for phthalocyanine derivatives[14−16] and dendrimer−lipid complexes,[9] is consistent with the increase of generation of the dendronized polymer. The change in structure is, however, more interesting. Presumably, in **PG1** polymers, the dendrons are still small enough to accept alkyl chains in a lamellar arrangement, similarly as linear polymer−lipid complexes.[1] With increasing generation, however, steric hindrance between dendrons starts to play an important role, further enhanced by the volume occupancy of alkyl chains. Thus, to optimize space-filling requirements and reduce lipid crowding, the dendron−lipid bulky moieties will have to twist each other with respect to the polymer backbone, leading to a columnar rather than a lamellar phase, thus undergoing a transition similar to that reported in dendrimer-based LC.[17]

On the basis of SAXS data and molecular calculations on the size of alkyl tails, we propose the molecular organization model sketched in Figure 2 for the LC polymers based on **PG1** and **PG2** complexed with sulfonated C8, C12, C18 lipids.

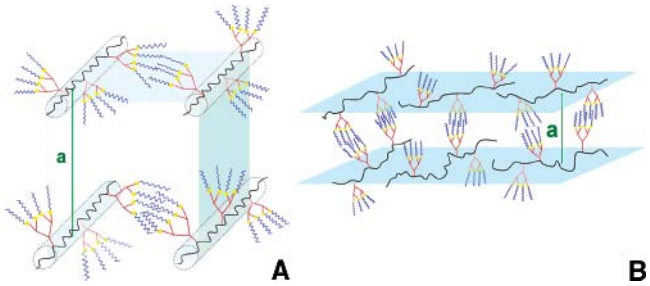


Figure 2. Schematic representation of (A) tetragonal columnar phase and (B) lamellar phase obtained for **PG2**−C12 and **PG1**−C12 dendronized polymer−surfactant complexes, respectively (see Supporting Information).

The present results demonstrate that self-assembly of dendronized polymers decorated by alkyl chains ionically attached onto the dendrons' "surfaces" is a viable route to design liquid-crystalline mesophases where both structure and period can be rationally tuned by either the dendron generation (and thus the cross-section of the polymers) or by the length of the alkyl chains. Owing to the reversible nature of the ionic complexation, this process proves high relevance for nanoporous channels, biomimetic, transport, and nanotemplating applications.

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Supporting Information for

Liquid-crystalline polymers from cationic dendronized polymer-anionic lipid complexes

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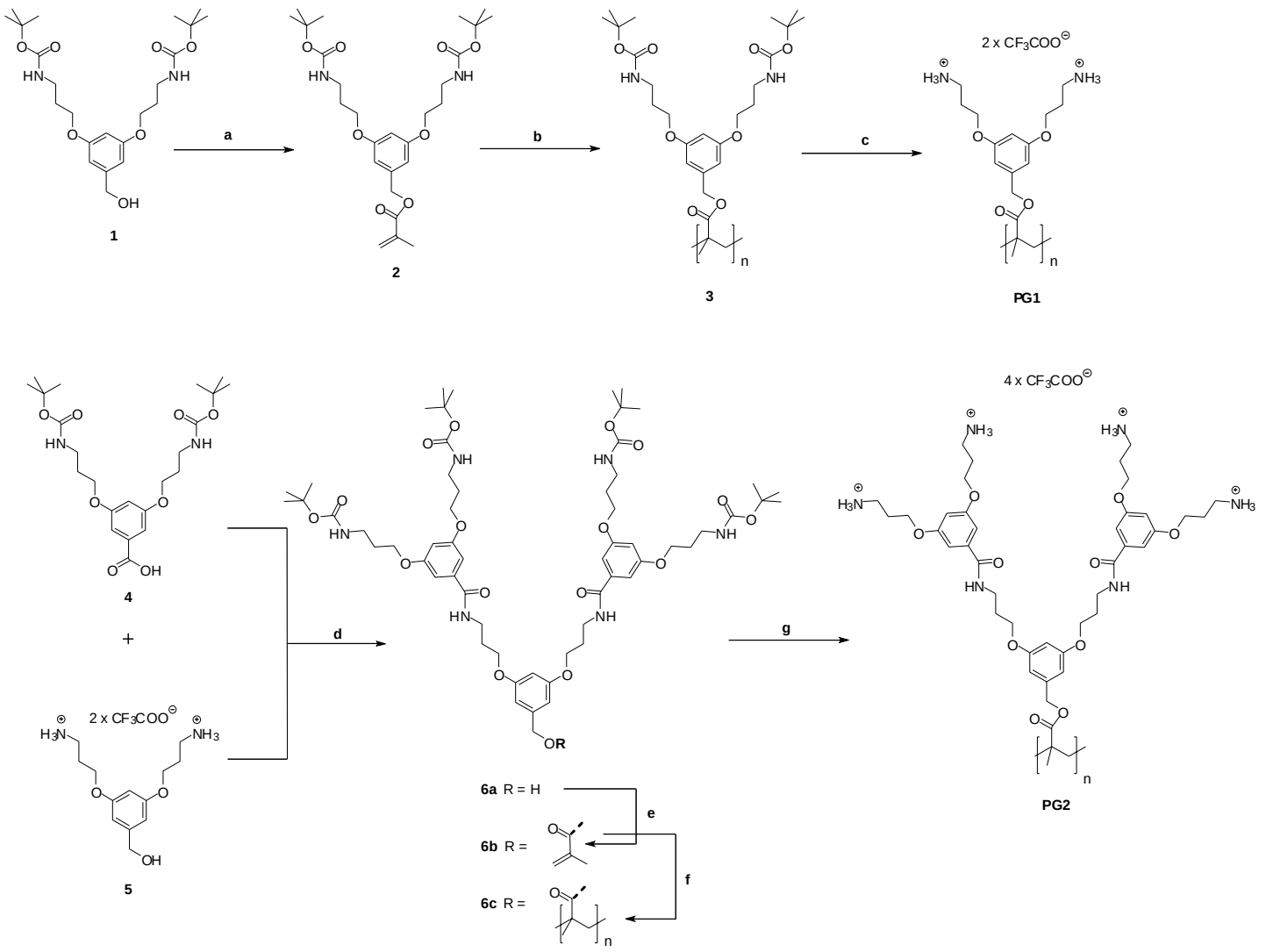


Scheme 1. Reagents and conditions: a) MAC, DMAP, THF, RT, 16h (91%) ; b) AIBN, DMF, 65°C , 16h (84%) ; c) TFA, RT, 48h (92%) ; d) HOBt, EDC, DCM, -20°C, 16h (73%) ; e) MAC, DMAP, DMF, RT, 16h (62%); f) AIBN, DMF, 65°C , 16h (86%) ; g) TFA, RT, 48h (90%)

Synthesis of the polymers:

General: Compounds **1**[11], **4**[11], and **5**[11] were synthesized according to literature methods. Other reagents were purchased from Aldrich, Across or Fluka. Methacryloyl chloride (MAC) was freshly distilled before use. Tetrahydrofuran (THF) and triethylamine (TEA) were refluxed over Na with benzophenone as indicator, dichloromethane (DCM) was dried by distilling over CaH_2. All other reagents and solvents were used as received. All reactions were performed under nitrogen atmosphere. Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm/ 230-400 mesh) was used as the stationary phase for column chromatography. Whenever possible, reactions were monitored by thin-layer chromatography (TLC) using TLC silica gel coated aluminum plates $60F_{254}$ (Merck). Compounds were detected by UV light (254 nm or 366 nm) and/or by treatment with a solution of ninhydrine in ethanol followed by heating. If not otherwise noted, ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and AV 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers at room temperature using chloroform-d as a solvent. High-resolution mass spectral (HRMS) and ESI-MS analyses were performed by the MS-service of the Laboratorium für Organische Chemie at ETH Zürich. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument. In the case of MALDI-MS, 2,5-dihydroxybenzoic acid (DHB), 2-[(2E)-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB) or 3-hydroxypyridine 2-carboxylic acid (3-HPA) served as the matrix. The FAB experiments were carried out with 3-nitrobenzyl alcohol (MNBA)/CH_2Cl_2. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. The samples were dried rigorously under vacuum prior to analysis to remove strongly adhering solvent molecules. Gel permeation chromatography (GPC) measurements were carried out using PL-GPC 220 instrument with 2x PL-Gel Mix-B LS column set equipped with RI (refractive index), viscosity and LS (Light Scattering with 15° and 90° angle) detectors [DMF + 1 gL^{-1} LiBr as eluent at 80°C]. Universal calibration was done using PMMA standards in a range of M_p = 2,680 to 3,900,000 (Polymer Labs. Ltd, UK).High-resolution thermogravimetric analysis (TGA) was performed on a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). All measurements were carried out in an air stream under the same conditions. The mass loss with increasing temperature as well as its first derivative (DTG) that represents the change in decomposition rate was plotted. The differential scanning calorimetry (DSC) was carried out under nitrogen at a heating or cooling rate of 10 °C/min on a DSC 7 (Perkin-Elmer, Norwalk, CT). Two heating and one cooling run were consecutively carried out in a cycle and the peak maxima were considered as the transition temperatures.

3,5-Bis(3-(tert-butoxycarbonylamino)propoxy)benzyl methacrylate (2)

A solution of MAC (3.77 g, 36.06 mmol) in THF (20 mL) was added dropwise to a mixture of **1** (7.31 g, 16.08 mmol), triethylamine (TEA; 3.94 g, 39.02 mmol), and DMAP (162 mg) in dry THF (100 mL) at 0°C over 30 min. The mixture was stirred for 16 h at room temperature, then washed with aqueous $NaHCO_3$ and brine, and dried with magnesium sulfate. After evaporation of the solvent under vacuum and two successive chromatographic separations (silica gel, DCM/methanol 30/1), **2** was obtained as colorless foam (7.63 g, 91%).;R_f = 0. 52 (30 :1 DCM/MeOH); m.p. = 69.8 – 71.3 °C; ^{1}H NMR : δ= 1.41 (s, 18 H; ^{t}Bu), 1.95 (m, 7 H; $OCH_2\underline{CH_2}CH_2N$+C=C$\underline{CH_3}$), 3.28 (m, 4 H; C$\underline{H_2}$NH), 3.97 (t, 4 H; $PhOCH_2$), 4.70 (br, 2 H; NH), 5.08 (s, 2 H; OCH_2Ph), 5.57 (m, 1 H; $C=CH_2$), 6.14 (m, 1 H; $C=CH_2$), 6.37 (t, 1 H; Ph), 6.47 (t, 2 H; Ph) ppm. ; ^{13}C NMR : δ= 18.34 (C=C$\underline{C}H_3$), 28.39 ($C(\underline{C}H_3)_3$), 29.52 ($OCH_2\underline{C}H_2CH_2N$), 38.05 ($OCH_2CH_2\underline{C}H_2N$), 65.73 ($O\underline{C}H_2CH_2CH_2N$), 66.18 ($CO_2\underline{C}H_2$), 79.22 ($\underline{C}(CH_3)_3$), 100.88, 106.44, 136.10, 160.06 (Ar), 125.94 ($\underline{C}H_2$=C), 138.37 (CH_2=$\underline{C}$), 156.04 (NHCOO), 167.11 (CO) ppm.; HR-ESI : *m/z* (%): 545.1 (100) $[M + Na]^+$; [$C_{27}H_{42}N_2O_8$ (522.64): C 62.05, H 8.10, N 5.36; found: C 61.89, H 8.38, N 5.32].

Poly [3,5-bis(3-(tert-butoxycarbonylamino)propoxy) benzyl methacrylate] (3)

To monomer **2** (8.46 g, 16.20 mmol) and AIBN (80 mg, 0.486mmol) in a Schlenk Tube was added DMF (9.44 g, 10 mL). The mixture was stirred for 30 min. until everything had dissolved. Then the Schlenk tube was weighed and vacuum of 2 mbar applied until 1.85 g of DMF had been removed. This was typically the case after 3 h at RT. The obtained highly concentrated solution was still homogenous. Then the Schlenk 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 reaction mixture was continued to be heated for another 12 h. After cooling, the polymer was dissolved in DCM and purified by column chromatography (silica gel, DCM eluent) which gave **3** as colorless foam (7.13 g, 84%) which was collected and dried under high vacuum.; Tg = 51.54 °C; ^{1}H NMR: δ= 0.68 (br, 2 H, CH_2), 0.94 (br, 3 H, CH_3), 1.37 (br, 18 H; ^{t}Bu), 1.84 (br, 4 H; $OCH_2\underline{CH_2}CH_2N_2$), 3.17 (br, 4 H; C$\underline{H_2}$NH), 3.82 (br, 4 H; $PhOCH_2$), 4.75 (br, 2 H; OCH_2), 6,26, 6.33 (br, 3 H; Ph) ppm.; ^{13}C NMR: δ= 25.13, 28.46, 29.53, 37.86, 44.91, 65.67, 66.76, 101.19, 106.79, 137.06, 156.12, 160.41, 162.52, 176.46, 177.11 ppm.;[$(C_{27}H_{42}N_2O_8)_n$ $(522.64)_n$: C 62.05, H 8.10, N 5.36; found: C 61.12, H 8.05, N 5.92].

Poly [3,5-bis(3-aminopropyl) benzyl methacrylate] · 2CF_3COOH (PG1)

To **3** (7.13 g, 13.65 mmol), TFA (21.48 mL, 31.12 g, 273 mmol) was added. After stirring for 24 h, 50 mL of methanol for 2 d. Evaporation of solvent gave **PG1** as brownish solid (6.89 g, 92 %);Tg = 59.39°C; ^{1}H NMR: δ= 0.75 (br, 2 H, CH_2), 0.99 (br, 3 H, CH_3), 2.07 (br, 4 H; $OCH_2\underline{CH_2}CH_2N_2$), 3.10 (br, 4 H; C$\underline{H_2}$NH), 3.94 (br, 4 H; $PhOCH_2$), 4.78 (br, 2 H; OCH_2), 6.44 (br, 3 H; Ph) ppm.; ^{13}C NMR: δ= 25.25, 28.31, 31.65, 38.46, 46.57, 66.41, 67.92, 102.57, 108.14, 138.84, 161.22, 178.25, 178.25 ppm.;

3,5-Bis{3-[3,5-bis(3-(*tert*-butoxycarbonylamino)propoxy)benzamido] propoxy} benzyl alcohol (6a)

N-Hydroxybenzotriazole (5.02 g, 37.2 mmol) was added to a solution of acid **4** (14.52 g, 31 mmol) in dry DCM (300 mL) at room temperature. After 10 min N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (7.84 g, 40.92 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (13 g, 127.7 mmol) and **5** (6.16 g, 12.27 mmol) in methanol/DCM (50 mL, 1/ 1) was added dropwise at -10°C. The resulting mixture was warmed to room temperature, stirred for 16 h, and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Chromatographic separation (silica gel, Hexane/Ethylacetate 1/10) yielded **6a** as a colorless foam (10.4 g, 73 %);R_f = 0.8 (10:1 EtOAc/MeOH); m.p.= 79 – 81 °C; ^{1}H NMR: δ= 1.41 (s, 36 H; ^{t}Bu), 1.93 (m, 8 H; CH_2), 2.07 (m, 4 H; CH_2), 3.27 (m, 8 H; C*H*$_2$NH), 3.63 (m, 4 H; C*H*$_2$NH), 3.97 (m, 8 H; PhOCH_2), 4.07 (m, 4 H; PhOCH_2), 4.59 (s, 2 H; OCH_2Ph), 4.82 (br, 4 H; NH), 6.34 (t, 1 H; Ph), 6.51 (t, 2 H; Ph), 6.53 (d, 2 H, Ph), 6.83 (d, 4 H; Ph), 6.81 (br, 2 H; NH)ppm;^{13}C NMR: 28.42 (C(*C*H$_3$)$_3$), 29.50 (OCH$_2$*C*H$_2$CH$_2$N), 37.90, 38.34 (OCH$_2$CH$_2$*C*H$_2$N), 64.79, 65.93 (O*C*H$_2$CH$_2$CH$_2$N), 67.03 (OCH$_2$), 79.43 (*C*(CH$_3$)$_3$), 104.56, 105.61, 105.68, 144.12, 159.91, 160.00 (Ar), 167.24, (CO) 174.58 (NHCOO) ppm; HRMS-MALDI: *m/z* (%): 1155.38 (100) $[M + Na]^+$; [$C_{59}H_{90}N_6O_{17}$ (1155.38): C 61.33, H 7.85, N 7.27; found: C 61.05, H 7.77, N 7.08].

3,5-Bis{3-[3,5-bis(3-(*tert*-butoxycarbonylamino)propoxy)benzamido] propoxy} benzyl methacrylate (6a)

A solution of MAC (1.87 g, 18 mmol) in dry DMF (10 mL) was added dropwise to a mixture of **6a** (10.4 g, 9 mmol), triethylamine (TEA; 2.22 g, 22 mmol), and DMAP (300 mg) in dry DMF (100 mL) at 0°C over 30 min. The mixture was stirred for 16 h at room temperature. Solvent was removed in vacuum and residue again dissolved in DCM and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuum. After evaporation of the solvent under vacuum and chromatographic separation (silica gel, DCM/methanol 30/1 and Hexane/Ethylacetate 1/10), compound **6b** was obtained as colourless foam (6.8 g, 62 %); R_f = 0.54 (Hexane/Ethylacetate 1/10); m.p. = 73 – 74 °C; ^{1}H NMR : δ= 1.40 (s, 36 H; ^{t}Bu), 1.93 (m, 11 H; OCH$_2$C*H*$_2$CH$_2$N+C=CC*H*$_3$), 2.08 (m, 4 H; OCH$_2$C*H*$_2$CH$_2$N), 3.27 (t, 8 H; C*H*$_2$NH), 3.61 (m, 4 H; C*H*$_2$NH), 3.98 (m, 8 H; PhOCH_2), 4.05 (m, 4 H; PhOCH_2), 6.51 (br, 4 H; NH), 5.07 (s, 2 H; OCH_2Ph), 5.56 (m, 1 H; C=CH_2), 6.12 (s, 1 H; C=CH_2), 6.38 (t, 1 H; Ph), 6.51 (br, d 2H; Ph), 6.77 (t, 2 H; Ph), 6.87 (d, 4 H; Ph), ppm.; ^{13}C NMR : δ= 18.33 (C=C*C*H$_3$), 28.40 (C(*C*H$_3$)$_3$), 28.90, 29.48 (OCH$_2$*C*H$_2$CH$_2$N), 37.81 (OCH$_2$CH$_2$*C*H$_2$N), 65.81, 66.18 (O*C*H$_2$CH$_2$CH$_2$N), 66.36 (OCH$_2$), 79.28 (*C*(CH$_3$)$_3$), 101.62, 104.33, 105.72, 106.46, 136.03, 138.43, 159.93, 159.95, (Ar), 126.07 (*C*H$_2$=C), 136.68 (CH$_2$=*C*), 167.16 (CO) , 167.40 (NHCOO) ppm.;HR-ESI: *m/z* (%): 1245.6 (100) $[M + Na]^+$;[$C_{63}H_{94}N_6O_{18}$ (1223.47): C 61.85, H 7.74, N 6.87; found: C 61.57, H 7.83, N 6.89].

Poly (3,5-Bis{3-[3,5-bis(3-(*tert*-butoxycarbonylamino)propoxy)benzamido] propoxy} benzyl) methacrylate (6c)

To monomer **6b** (5 g, 4.08 mmol) and AIBN (13.42 mg, 0.08 mmol) in a Schlenk Tube was added DMF (5.66 g, 6 mL). The mixture was stirred for 30 min. until everything had dissolved. Then the Schlenk tube was weighed and vacuum of 2 mbar applied until 1.91 g of DMF had been removed. This was typically the case after 3 h at RT. The obtained highly concentrated solution was still homogenous. Then the Schlenk 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 reaction mixture was continued to be heated for another 12 h. After cooling, the polymer was dissolved in DCM and purified by column chromatography (silica gel, DCM eluent) which gave **6c** as colorless foam (4.3 g, 86%) which was collected and dried under high vacuum.; Tg = 66.88 °C; ^{1}H NMR : δ= 0.63 (br, 2 H, CH_2), 0.87 (br, 3 H, CH_3), 1.33 (br, 36 H; ^{t}Bu), 1.79 (br, 12 H; $OCH_2\underline{CH_2}CH_2N$), 3.12 (br, 12 H; $\underline{CH_2}NH$), 3.79 (br, 12 H; $PhOCH_2$), 5.44 (br, 2 H; $PhCH_2$), 6.38 (br, 3 H; Ph), 6.88 (br, 6 H, Ph) 7.72 – 8.68 (br, 6 H; NH) ppm.; ^{13}C NMR: δ= 24.07, 28.43, 29.48, 34.43, 37.69, 65.72, 78.88, 105.89, 136.48, 156.24, 159.84, 167.63, 171.08 ppm.; $[(C_{63}H_{94}N_6O_{18})_n$ $(1223.47)_n$: C 61.85, H 7.74, N 6.87; found: C 61.07, H 7.37, N 6.60].

Poly (3,5-Bis{3-[3,5-bis(3-(*tert*-butoxycarbonylamino)propoxy)benzamido] propoxy} benzyl) methacrylate) · $4CF_3COOH$ (PG2)

To **6c** (3.73 g, 3.04 mmol), TFA (9.39 mL, 13.90 g, 121.95 mmol) was added. After stirring for 24 h, 50 mL of methanol was added and reaction mixture was left for another 2d. Evaporation of solvent gave **PG2** as brownish solid (3.55 g, 90 %); Tg = 58.21 °C; ^{1}H NMR : δ= 0.87 (br, 2 H, CH_2), 0.92 (br, 3 H, CH_3), 2.05 (br, 12 H; $OCH_2\underline{CH_2}CH_2N$), 3.08, 3.41 (br, 12 H; $\underline{CH_2}NH$), 3.97 (br, 12 H; $PhOCH_2$), 4.73 (br, 2 H; $PhCH_2$), 6.56 (br, 3 H; Ph), 6.90 (br, 6 H, Ph) 6.33 (br, 6 H; NH) ppm.; ^{13}C NMR: δ= 25.86, 28.24, 30.30, 38.42, 46.65 , 66.52, 105.77, 107.30, 137.67, 158.80, 161.09, 169.47 ppm. ;

Figure 1. 300 MHz ^{1}H NMR spectrum of macromonomer **2**, stars indicate solvent peaks.

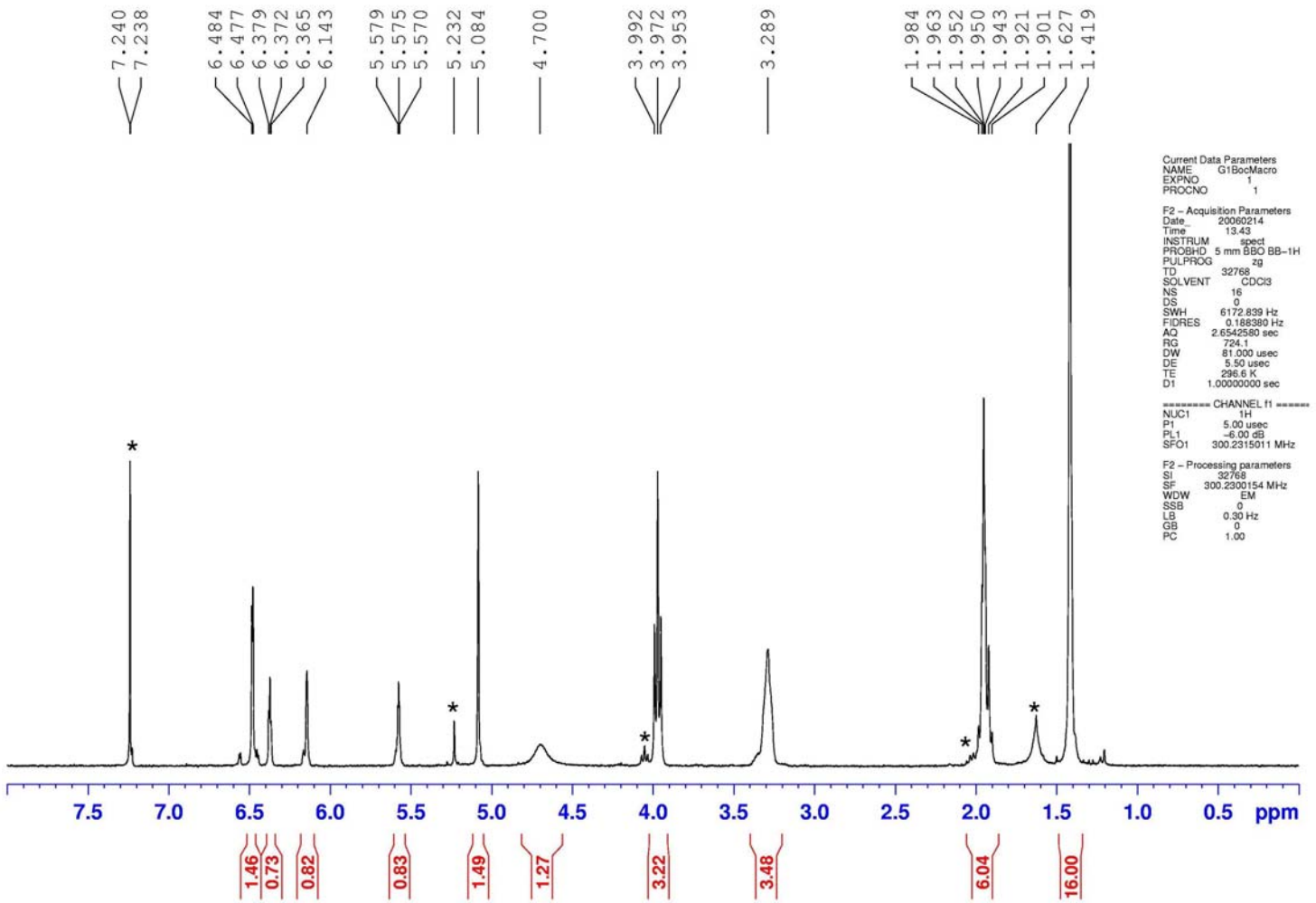


Figure 2. 75 MHz ^{13}C NMR spectrum of macromonomer **2.**

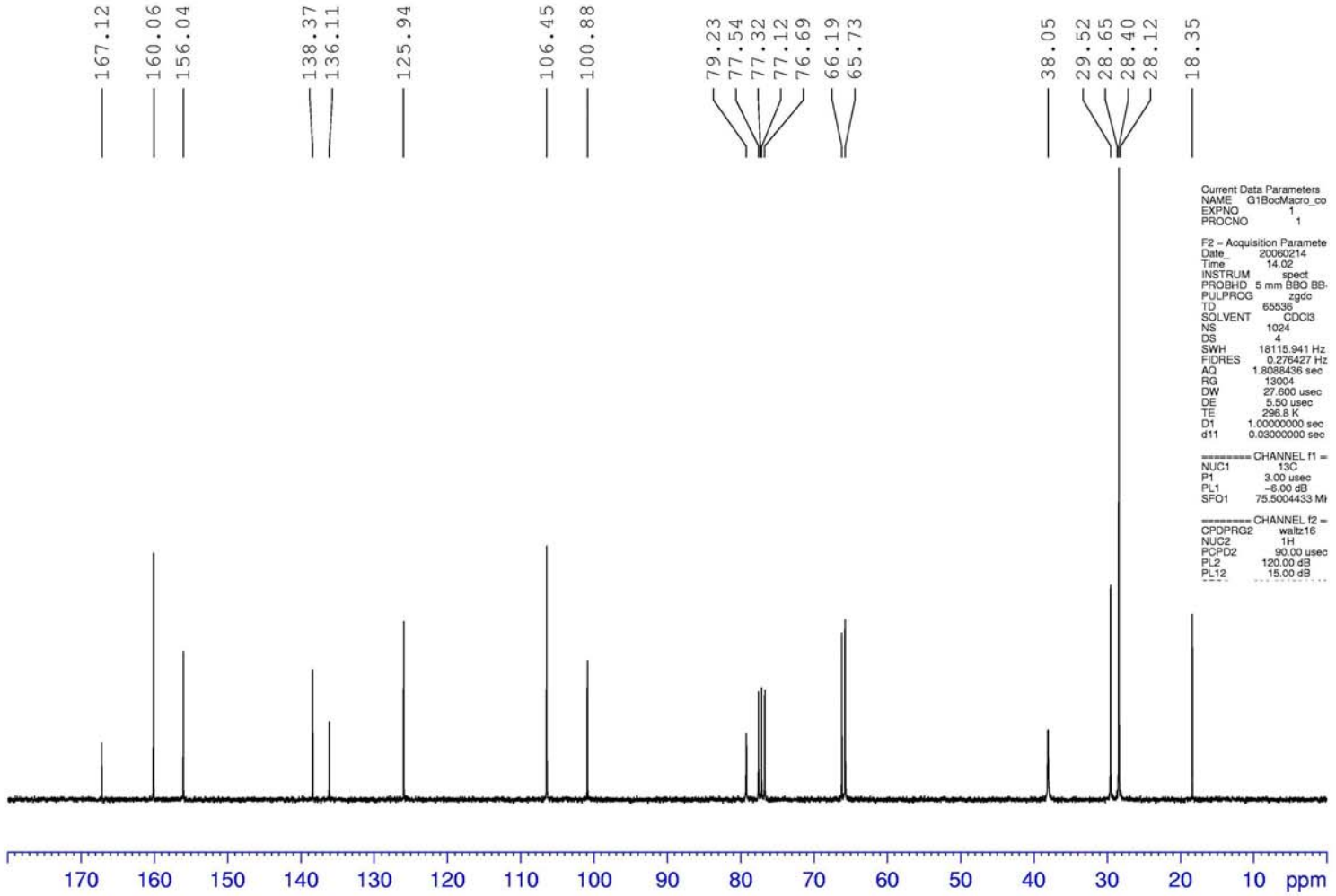


Figure 3. 300 MHz ^{1}H NMR spectrum of macromonomer **6b**, stars indicate solvent peaks.

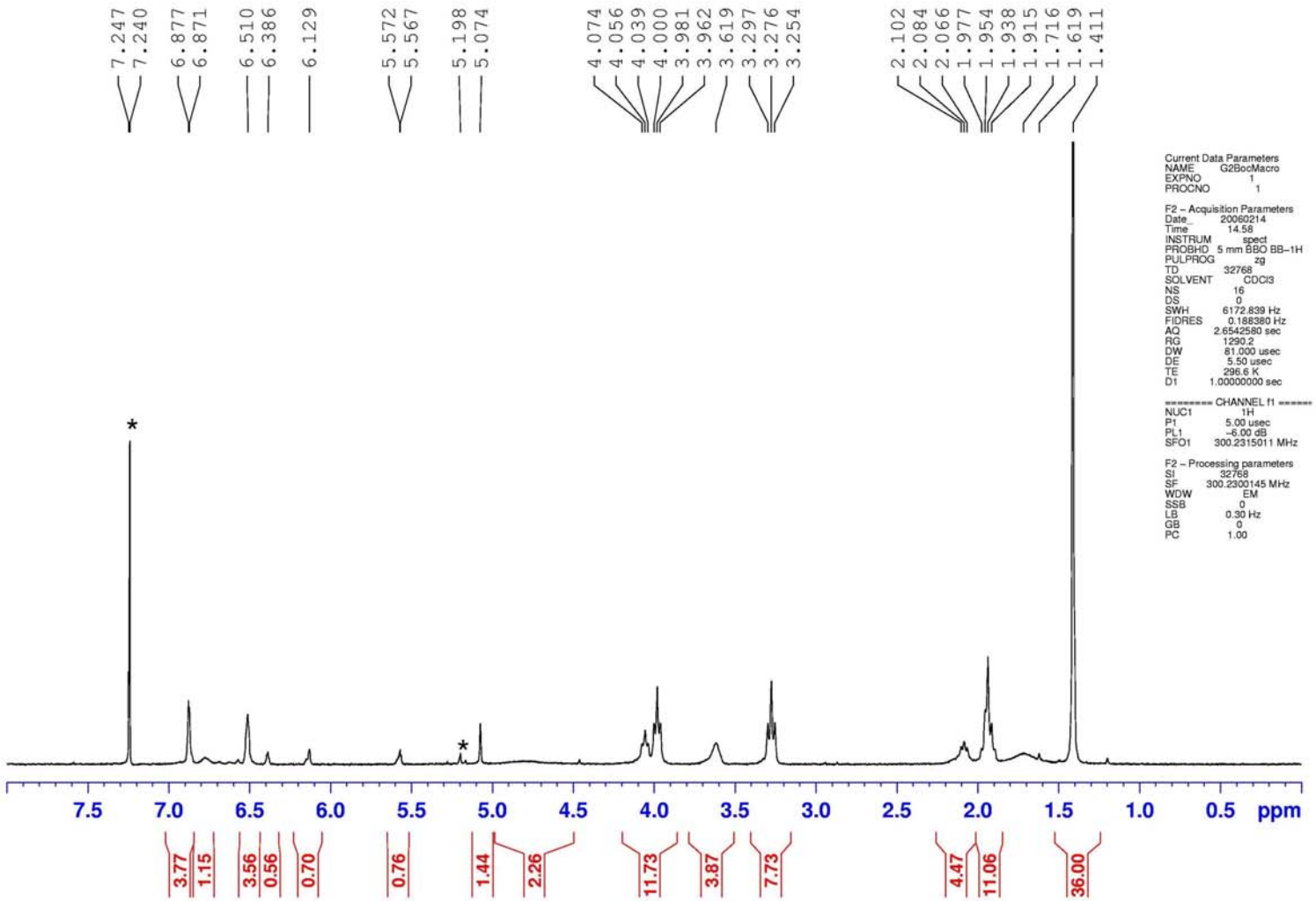


Figure 4. 75 MHz ^{13}C NMR spectrum of macromonomer **6b.**

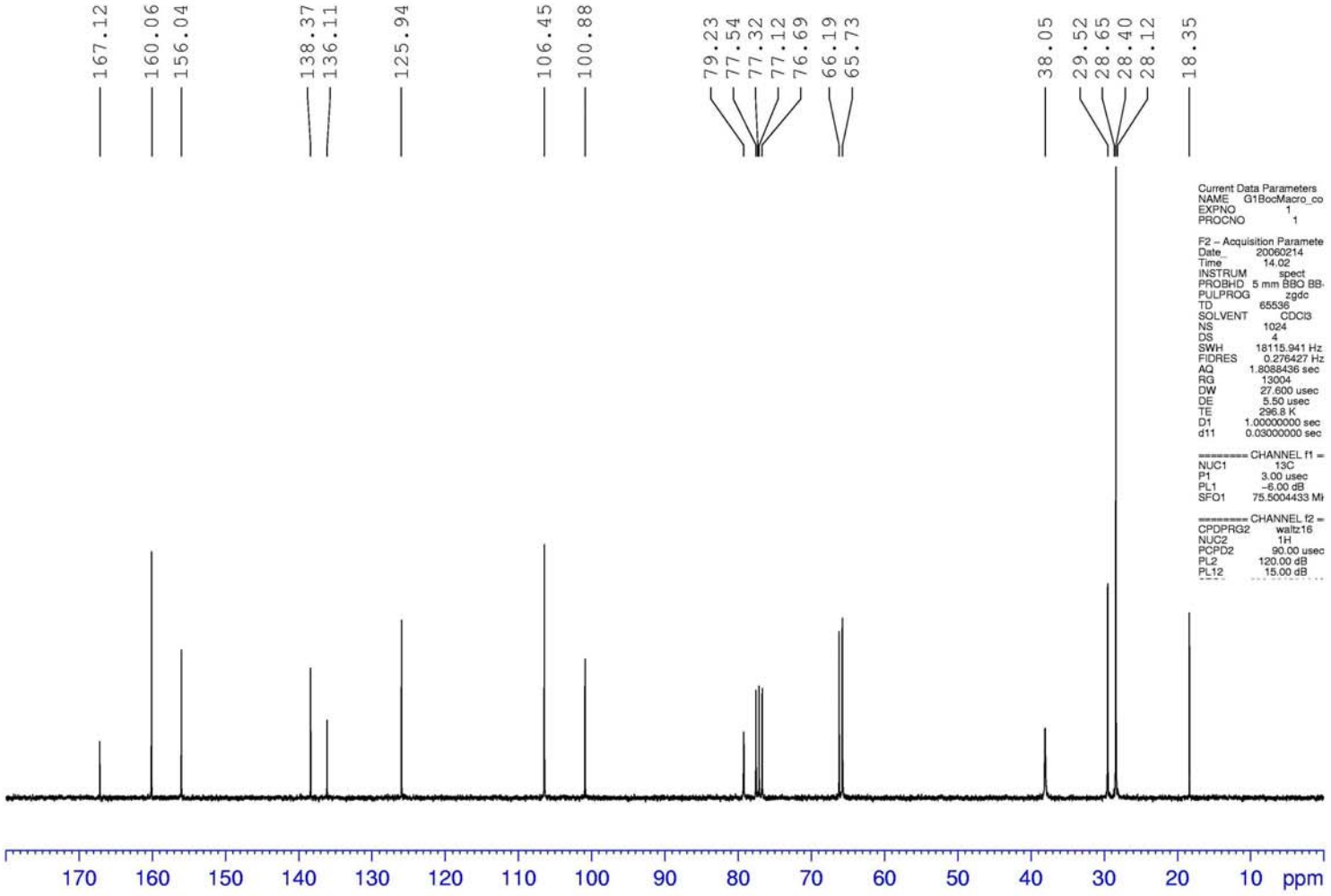


Figure 5. 500 MHz ^{1}H spectrum of the the deprotected denpol **PG1**. For comparison the spectrum of the starting material **3** is also shown.

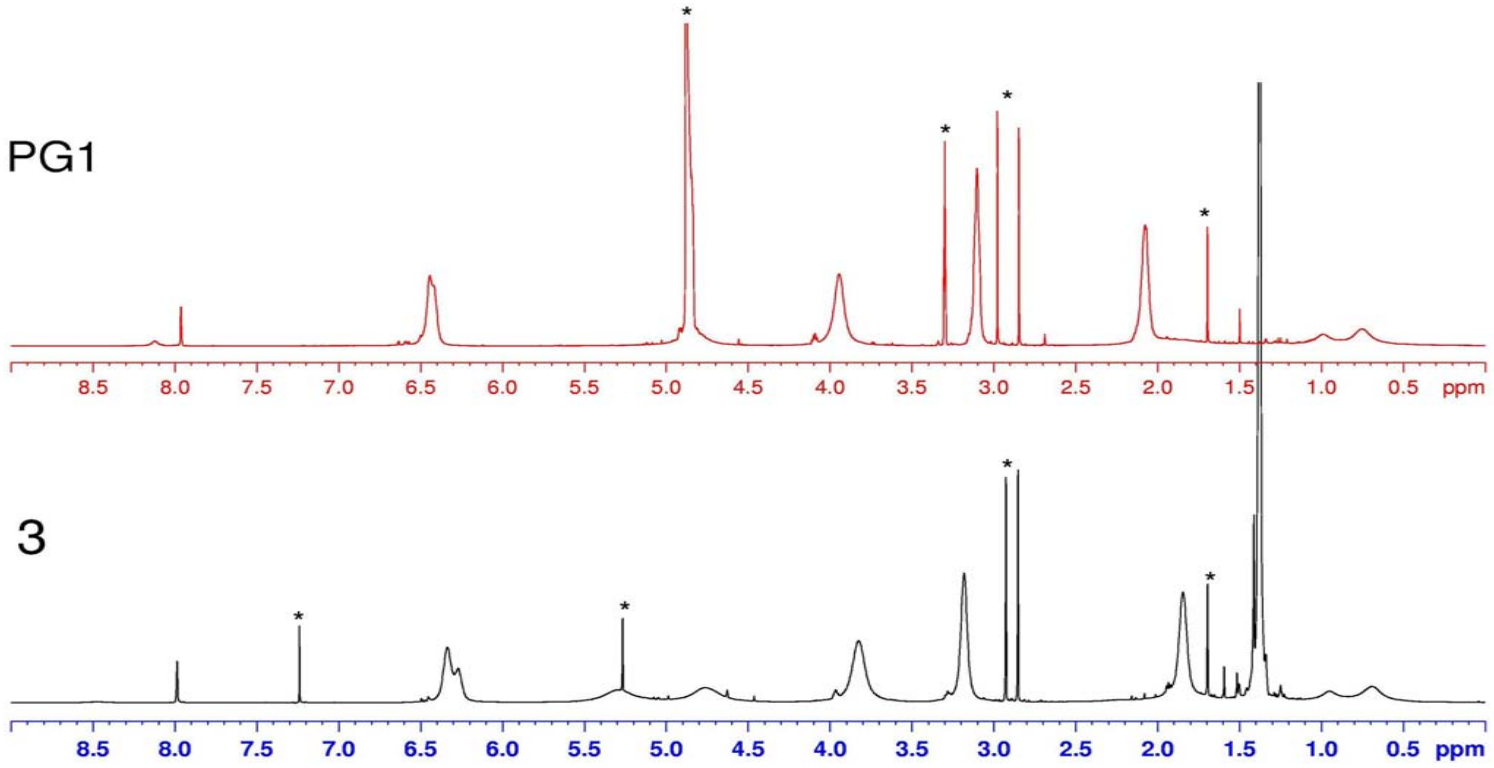


Figure 6. 500 MHz ^{1}H spectrum of the deprotected denpol **PG2.** For comparison the spectrum of the staring material **6c** is also shown.

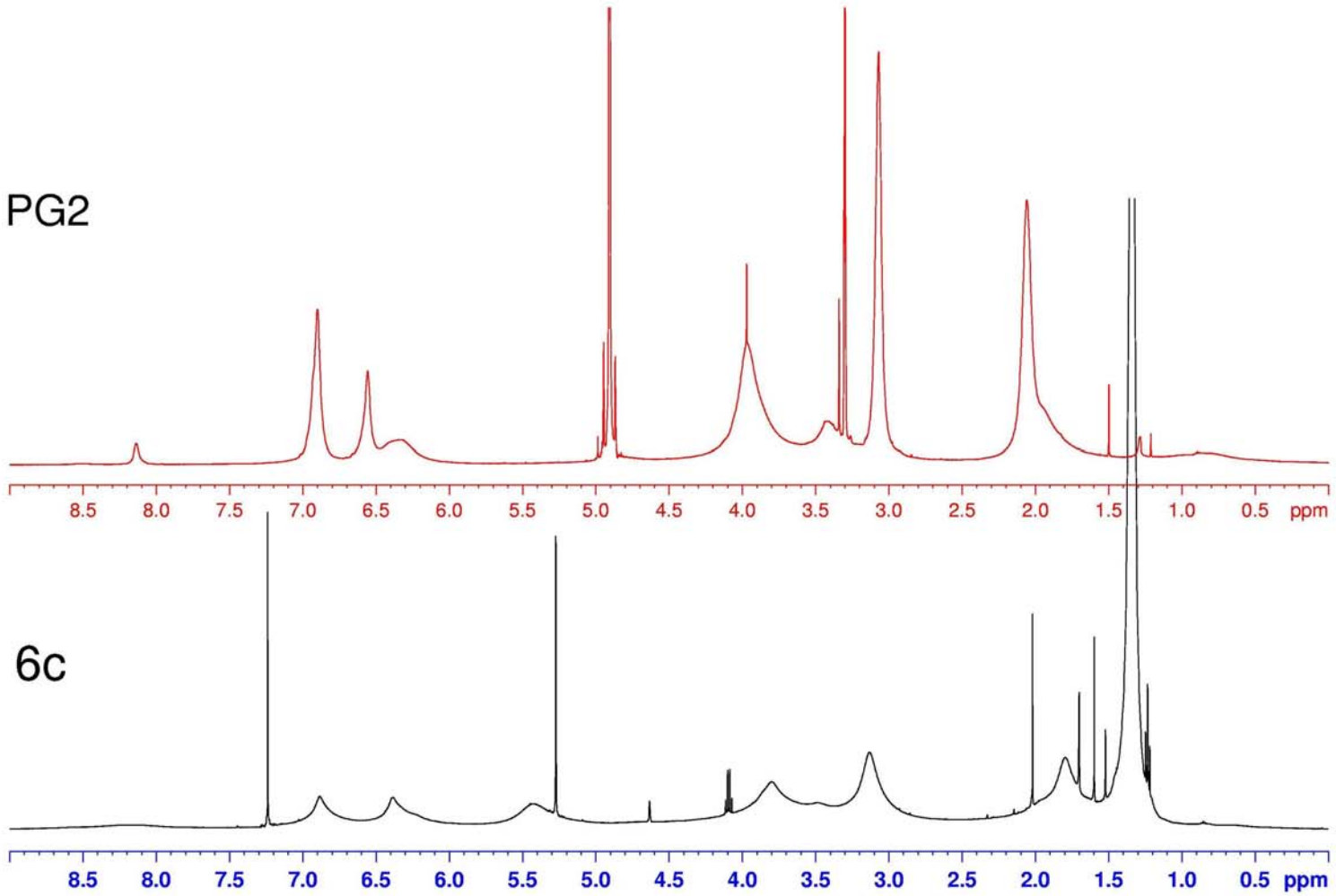


Figure 7. GPC elution curve of dendronized polymer **3** in DMF at 80°C.

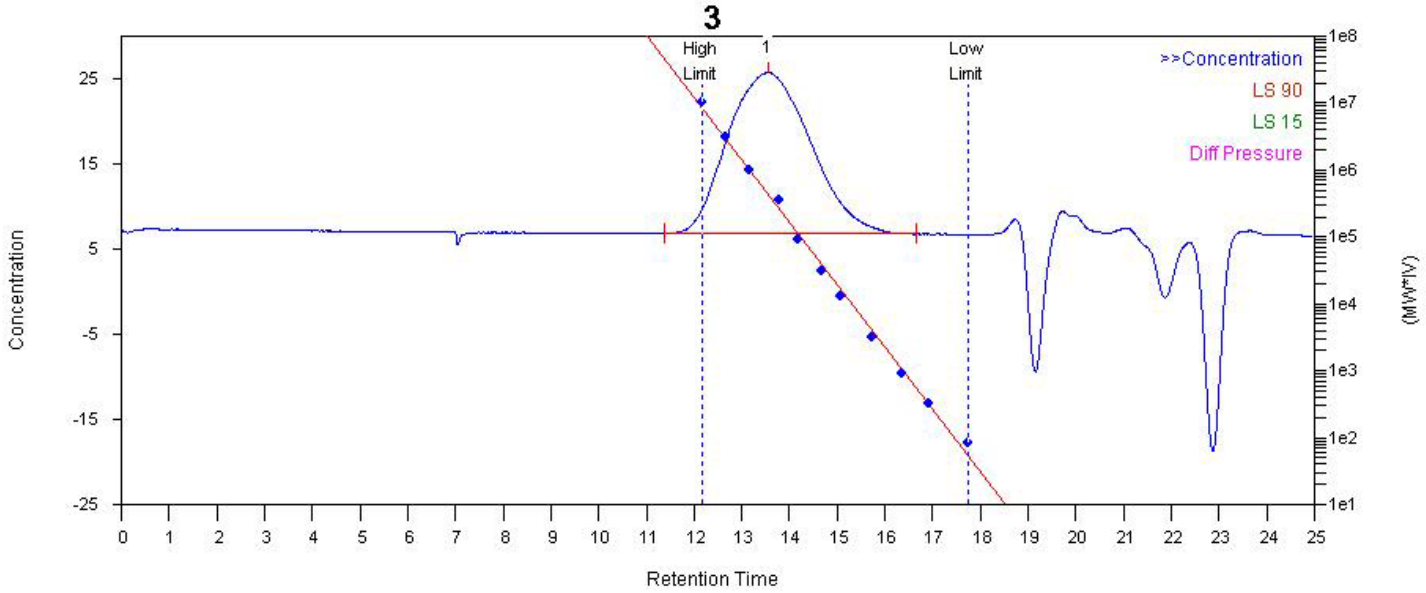
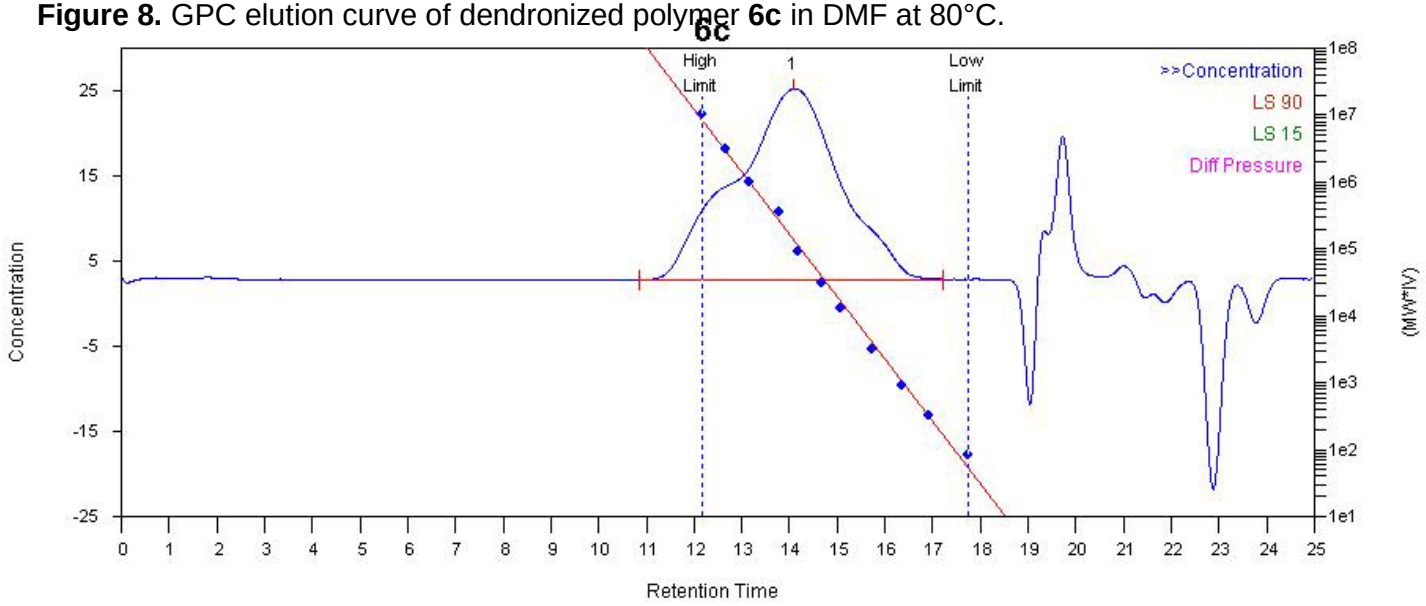


Figure 8. GPC elution curve of dendronized polymer **6c** in DMF at 80°C.



PHYSICAL PROPERTIES:

Attribution of G2-C12 to the tetragonal phase

The four reflections observed in the SAXS diffractogram of G2-C12 are attributed to (100) (110) (200) (300), giving a spacing ratio of $1, \sqrt{2}$, 2, 3. This spacing ratio is compatible with a columnar tetragonal phase. The tetragonal phase is a special case of the rectangular phase with a=b. In the general case for $a \neq b$, the spacing ratio of q is given by the general relationship $q = 2\pi\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2}$ which, for the G2-C12, gives the sequence $1, \sqrt{2}$, 2, 3 only for a=b. Then, the tetragonal phase can be either simple or centred tetragonal. The simple tetragonal is a special case of the P2m with a=b while the centred tetragonal is a special case of the C2/m rectangular phase with a=b. This latter phase follows the extinction rule typical of C2/m, $h+k \neq 2n+1$, which is incompatible with reflection at (300). Therefore we can attribute unambiguously the G2-C12 mesophase to simple tetragonal. Figure 9 illustrates the differences between P2m, C2/m, simple tetragonal, centred tetragonal

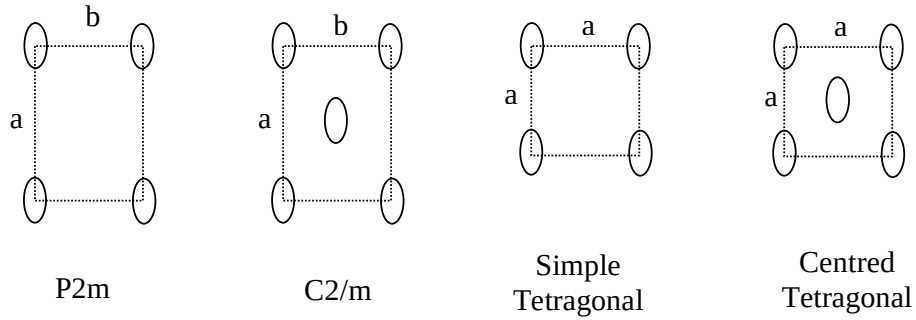


Figure 9. Different structures for rectangular, centred rectangular, tetragonal, centred tetragonal columnar phases

On Molecular Packing of the Alkyl Chains

The molecular model of the lamellar phase based on intercalated alkyl tails, has been derived in the hypothesis of untilted alkyl tails, e.g. lipid chains parallel to the normal of lamellar planes. This is motivated by the fact that the systematic increase in lattice period as measured by SAXS of the lamellar phase when going from G1-C12 to G1-C18 is less than twice the difference between C18 and C12 alkyl chains lengths, which would be expected for a lipid bilayer. Based on experimental data of columnar mesophases formed by low molecular weight compounds containing hydrocarbon tails [1,2], however, a tilt angle of the alkyl chains can be admitted. Under these conditions, both a monolayer and bilayer of lipids can lead to the observed increase in lattice parameters. Figure 10 shows possible packing structures of lipids in the lamellar phase of G1-C12 and G1-C18 when tilting of lipid chains is allowed of an angle θ with respect to the normal to lamellar planes.

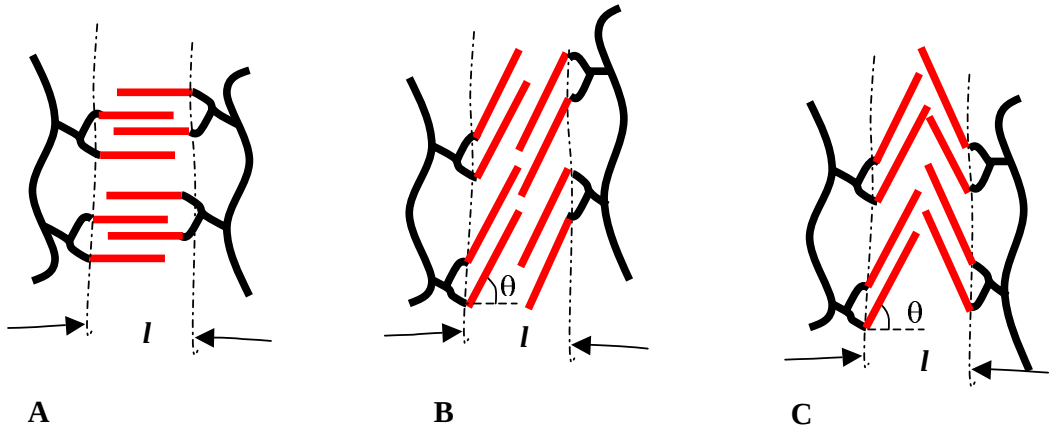


Figure 10. Possible packing structures of lipids in the lamellar phase leading to identical lattice constant.

Thus, since an effective increase in lattice parameter of 0.83 nm is observed in going from G1-C12 to G1-C18 corresponding to an increase of 0.65 in alkyl chain length, quick calculations show that bilayers such as those sketched in Figure 10 and with a tilt angle of 50° are compatible with observed mesophases. Exact determination of the alkyl tail tilt angle is possible by alignement of the anisotropic mesophases and collection of WAXS data on a 2D detector as reported by reference[1]. Work along these directions is in progress in order to provide more insight on alkyl tail molecular packing.

References

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2 Donnio, B.; Heinrich, B.; Allouchi, A.; Kein, J.; Diele, S.; Guillon. D.; Bruce, D.W. *J. Am. Chem. Soc.* **2004**, *126*, 12528.