

Electronic Supplementary Information

Unprecedented formation of reverse micellar vesicles from psuedopeptidic bottlebrush polymers

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1. Experimental section

1.1 Materials

Amino acids used were of L-configuration and were purchased from SRL India. Reagents were purchased from Sigma-Aldrich or Alfa Aesar. All commercial chemicals and reagents were used as received, without any further purification. The solvents employed in the reactions, were dried by standard protocols before use. All air sensitive reactions were carried out in oven dried glassware under an inert atmosphere of argon. All reactions were monitored by silica gel thin layer chromatography (TLC). Compounds were purified by silica gel (100-200 mesh) column chromatography. Characterization of synthesized compounds was done by ^1H NMR, ^{13}C NMR, IR and High Resolution Mass Spectrometry (HRMS). Melting points were recorded on a Fisher-Scientific melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker-DPX-300 MHz spectrometer and the chemical shifts are reported downfield relative to tetramethylsilane (TMS). ^1H NMR data are reported as s (singlet), d (doublet), br (broad), q (quartet), t (triplet) and m (multiplet). ^1H NMR coupling constants are reported in Hz. High resolution mass spectra (HRMS) were recorded in Bruker MicrO-TOF-QII model using Electrospray Ionization (ESI) technique. Attenuated Total Reflectance Infrared (ATR-IR) spectra were recorded on an Agilent-Cary 660 Series FTIR spectrometer. For ATR-IR, the samples were placed on the diamond sample holder and 32 scans were performed on each sample.

1.2 Methods

1.2.1 Scanning Electron Microscopy (SEM)

Samples were prepared by dissolving 2 mg of polymer per mL of the solvent system. A fresh glass coverslip was attached to a stub using carbon tape. About 10 μL of the sample solution was

drop-casted onto the coverslip. The sample was dried at room temperature. The sample was coated with ~10 nm of gold and viewed using ZEISS EVO 50 Scanning Electron Microscope. Images were captured at room temperature and processed using ImageJ software.

1.2.2 Atomic Force Microscopy (AFM)

About 10 μL of the sample solution was drop-casted onto a freshly cleaned quartz substrate. The sample was allowed to dry at room temperature and imaged using AFM. Bruker Dimension Icon atomic force microscope was used for imaging the samples in tapping mode. Images were recorded at room temperature and data analysis was performed using nanoscope 5.31r software.

1.2.3 High Resolution Transmission Electron Microscopy (HR-TEM)

5 μL of polymer solution in respective solvent system was allowed to adsorb onto Formavar-coated 300-mesh copper grids (Electron Microscopy Sciences) for 2 min. Excess solution was then removed by blotting using a Whatman filter paper, followed by air-drying. Grids were viewed using a Tecnai G² F20 FEG Transmission Electron Microscope (FEI), operating at 200 kV. Images were recorded using TIA software on a 4K \times 4K CCD camera.

1.2.4 Cryo-TEM Imaging

For cryo-freezing, 3 μL of **P1** at a concentration of 2 mg/ml in methanol-chloroform solvent was drop-casted on a quantifoil R2/2 holey carbon grid at room temperature. After blotting for 2 s using a 2 μm Whatman filter paper, the grid was immediately plunge frozen in liquid nitrogen. The grid was then loaded into a FEI Tecnai F20 G² FEG Transmission Electron Microscope operating at 200 kV using a precooled cryo-TEM specimen holder (Gatan model 626). Images were recorded on 4K \times 4K CCD camera (FEI Eagle) using TIA software.

1.2.5 Confocal Microscopy

Polymer solutions were prepared in 1:1 chloroform:methanol solvent systems and were mixed with 0.1 equiv. of 2 mM Rhodamine B (RB) dye solution (prepared in the same solvent system). 10 μ L of the sample solution was placed onto a freshly cleaned glass slide and allowed to air dry. The unbound/excess RB was removed by washing with distilled water. The slides were further dried by flushing with nitrogen gas. Individual slides were mounted and images were captured on a confocal laser scanning biological microscope (Olympus FV1000, Japan) at 60 \times magnification. All samples were excited using a 540 nm laser.

1.2.6 Dynamic Light Scattering (DLS) Studies

Polymers were dissolved in respective solvent systems. NanoPlus-3 zeta/nano particle analyzer was used for measuring the particle size. The scattered intensities from the sample solution were recorded at an angle of 165.5°. Measurements were carried out in a quartz cell at 25 °C.

1.2.7 Gel Permeation Chromatography (GPC)

Molecular weight distribution and polydispersity index of the polymers were analyzed by Waters gel permeation chromatography (GPC) equipped with L-2414 refractive index detector and Waters styragel HR3 and HR4 columns in series using THF as eluent (flow rate 1 mL/min; polystyrene standards).

1.2.8 Water Contact Angle (WCA) Measurement

The water contact angles were measured using KRÜSS goniometer drop shape analysis system (Application version KRÜSS ADVANCE 1.6.2.0) at room temperature.

1.2.9 Fluorescence Spectroscopic Studies

The stock solutions of 0.1 mM Rhodamine B (RB), 1.28 mM Pyrene (Py) and 0.94 mM Nile Red (NR) were prepared in 1:1 chloroform:methanol solvent system. The required amount of dyes to prepare stock solution was weighed using a Denver Instrument balance having a precision of \pm 0.1 mg. An appropriate amount of dye from the stock was transferred to 1 cm quartz cuvette and diluted with 1:1 chloroform:methanol to make up the desired concentration for analysis. The concentrated polymer solution (4 mg in 25 μ L chloroform) was added to the same cuvette for further analysis. Fluorescence spectra were acquired on model FL 3-11, Fluorolog-3 modular/FLS-1000 spectrofluorometer with single Czerny–Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector with single cell TEC holder. The fluorimeter was purchased from Horiba–Jobin Yvon, Inc./Edinburgh Instruments Ltd. All data were acquired using 1 cm path length quartz cuvettes. Spectral response from appropriate blanks was subtracted before data analysis and corrected for dilution. Data analysis was performed by OriginPro 8.5 software.

1.3 Synthesis and Characterization

1.3.1 Synthesis of A1

To an ice-cooled and well-stirred solution of *tert*-butyloxycarbonyl (Boc) protected L-Leucine **1** (0.400 g, 1.74 mmol) in 50 mL of dry CH₂Cl₂ was added *N*-hydroxysuccinimide (NHS) (0.240 g, 2.08 mmol), dicyclohexylcarbodiimide (DCC) (0.430 g, 2.08 mmol) and stirred for 10 min. To the reaction mixture was added 1-hexylamine (0.27 mL, 2.08 mmol) followed by NEt₃ (1.45 mL, 10.44 mmol) and stirred for 24 h at RT. The reaction mixture was filtered and washed sequentially with aq. 0.2 N H₂SO₄, saturated NaHCO₃ solution and water. The organic layer was

dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was chromatographed over silica gel (100-200 mesh) using EtOAc:Hexane (3:7) as eluent to afford 0.485 g of **A1**.

Yield: 89 %; Appearance: Transparent solid; M.P: 42-44 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.83-0.98 (br m, 6H+3H), 1.29 (br s, 6H), 1.44 (br s, 9H+2H), 1.60-1.90 (m, 3H), 3.23 (m, 2H), 4.05 (br s, 1H), 4.93 (br s, 1H), 6.21 (br s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 13.94, 22.06, 22.49, 22.86, 24.75, 26.48, 28.29, 31.43, 39.44, 41.37, 53.11, 79.82, 155.78, 172.51; IR (ATR): 3776, 3474, 3025, 1765, 1652, 1184, 1032 cm⁻¹; HRMS calcd. for C₁₇H₃₄N₂O₃Na, m/z = 337.2462, obtained m/z = 337.2445.

1.3.2 Synthesis of M1

To an ice-cooled solution of **A1** (0.229 g, 0.73 mmol) in DCM (10 mL) was added trifluoroacetic acid (TFA) (1.2 mL, 14.62 mmol), and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was concentrated under high vacuum. To the resulting deprotected amine was added NEt₃ (3 mL) and dissolved in 50 mL of dry toluene, added *exo*-norbornene dicarboxylic anhydride (0.100 g, 0.61 mmol) and was refluxed overnight at 120 °C. The reaction mixture was evaporated and the residue was chromatographed over silica-gel (100-200 mesh) and eluted using EtOAc:Hexane (2:8) to yield 0.180 g of **M1**.

Yield: 82 %; Appearance: White solid; M.P: 99-101 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.81-1.05 (m, 9H), 1.17-1.81 (m, 8H+4H), 2.23 (m, 1H), 2.70 (m, 2H), 3.15-3.42 (m, 4H), 4.70 (m, 1H), 6.11 (br s, 1H), 6.30 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.93, 21.27, 22.46, 23.01, 25.40, 26.45, 29.32, 31.37, 36.96, 39.80, 42.91, 45.48, 47.56, 53.71, 137.86, 168.63, 177.94 ; IR (ATR): 3347, 3290, 2928, 2857, 1696, 1642, 1546, 1460, 1365, 1283, 1194, 1138 cm⁻¹; HRMS calcd. for C₂₁H₃₂N₂NaO₃ m/z 383.2305, found m/z 383.2304.

1.3.3 Synthesis of P1

To a well-stirred solution of **M1** (0.050 g, 0.14 mmol) in dry THF (0.5 ml) was added Grubbs IInd generation catalyst (0.0012 g, 0.0014 mmol) and left stirred for 12 h at room temperature under argon atmosphere. After completion of reaction as monitored by TLC, the resultant mixture was quenched by adding 3 mL of ethyl vinyl ether. The polymer was precipitated using methanol and the precipitate was dried under vacuum to yield **P1**.

Yield: Quantitative; Appearance: Light brown film.

¹H NMR (300 MHz, CDCl₃): δ 0.71-1.01 (m, 9H), 1.08-1.85 (m, 8H+4H), 2.15 (br m, 1H), 2.60-3.90 (m, 6H), 4.65 (br s, 1H), 5.46 (br m, 1H), 5.74 (br s, 1H), 6.00-6.81 (br m, 1H); IR (ATR): 3332, 2928, 2864, 1701, 1656, 1535, 1373, 1185 cm⁻¹.

1.3.4 Synthesis of A2

To an ice-cooled and well-stirred solution of **1** (1.000 g, 4.34 mmol) in 100 mL of dry DCM was added NHS (0.600 g, 5.21 mmol), DCC (1.075 g, 5.21 mmol) and stirred for 10 min. To the reaction mixture was added 1-dodecylamine (0.966 g, 5.21 mmol) followed by NEt₃ (3.6 mL, 26.04 mmol) and stirred for 24 h at RT. The reaction mixture was filtered and washed sequentially with 0.2 N H₂SO₄, saturated NaHCO₃ solution and water. The organic layer was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was chromatographed over silica gel (100-200 mesh) using EtOAc:Hexane (1.5:8.5) as eluent to afford 1.489 g of pure **A2**.

Yield: 86 %; Appearance: White semi-solid; Mp: 43-45 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.92 (br m, 6H+3H), 1.25 (br m, 20H), 1.43-1.80 (s+m, 9H+3H), 3.17 (br m, 2H), 4.14 (br s, 1H), 5.33 (br s, 1H), 6.84 (br s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 14.06, 22.06, 22.63, 22.85, 24.70, 26.86, 28.28, 29.29, 29.30, 29.52, 29.57, 29.59, 29.62, 31.87,

39.41, 41.50, 53.04, 79.63, 155.84, 172.71; IR (ATR): 3288, 2919, 2853, 1657, 1537, 1364, 1243, 1168 cm^{-1} ; HRMS calcd. for $\text{C}_{23}\text{H}_{46}\text{N}_2\text{O}_3\text{Na}$, $m/z = 421.3401$, obtained $m/z = 421.3400$.

1.3.5 Synthesis of **M2**

To an ice-cooled solution of **A2** (0.350 g, 0.88 mmol) in DCM (5 mL) was added TFA (1.35 mL, 17.56 mmol), and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was evaporated under high vacuum. The resulting amine was added to NEt_3 (3 mL) and dissolved in 50 mL of dry toluene, added *exo*-norbornene dicarboxylic anhydride (0.120 g, 0.73 mmol) and was refluxed overnight at 120 °C. The reaction mixture was evaporated and the residue was chromatographed over silica-gel (100-200 mesh) and eluted using EtOAc:Hexane (2:8) to yield 0.250 g of **M2**.

Yield: 77 %; Appearance: White solid; MP: 78-80 °C.

^1H NMR (300 MHz, CDCl_3): δ 0.93 (m, 9H), 1.17-1.78 (m, 18H+6H), 2.23 (m, 1H), 2.70 (m, 2H), 3.17-3.55 (m, 4H), 4.70 (m, 1H), 6.11 (br s, 1H), 6.29 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.08, 21.33, 22.64, 23.04, 25.42, 26.83, 29.22, 29.30, 29.39, 29.49, 29.53, 29.60, 31.87, 36.99, 39.83, 42.94, 45.52, 47.63, 53.77, 137.96, 168.62, 178.06 ; IR (ATR): 3286, 2920, 2852, 1766, 1698, 1640, 1549, 1373, 1284, 1195 cm^{-1} ; HRMS calcd. for $\text{C}_{27}\text{H}_{44}\text{N}_2\text{NaO}_3$ m/z 467.3244, found m/z 467.3243.

1.3.6 Synthesis of **P2**

To a well-stirred solution of **M2** (0.065 g, 0.146 mmol) in dry THF (0.5 mL) was added Grubbs II^{nd} generation catalyst (1.243 mg, 0.0015 mmol) and stirred overnight at room temperature under argon atmosphere. After completion of reaction as monitored by TLC, the resultant

mixture was quenched by adding 3 mL of ethyl vinyl ether. The polymer was precipitated using methanol and the precipitate obtained was dried under vacuum to yield pure polymer **P2**.

Yield: Quantitative; Appearance: Brown solid.

^1H NMR (300 MHz, CDCl_3): δ 0.87 (m, 9H), 1.11-1.95 (m, 18H+5H), 2.16 (br m, 2H), 2.65-3.95 (m, 2H+4H), 4.65 (br m, 1H), 5.47 (br s, 1H), 5.75 (br s, 1H), 6.01-6.99 (br m, 1H); IR (ATR): 3337, 2923, 2855, 1773, 1701, 1535, 1373, 1184 cm^{-1} .

1.3.7 Synthesis of A3

To an ice-cooled and well-stirred solution of Boc-L-glutamic acid **2** (1.500 g, 6.07 mmol) in dry DCM (100 ml) was added sequentially NHS (1.536 g, 13.35 mmol), DCC (2.755 g, 13.35 mmol) and stirred for 10 min. To the reaction mixture was added 1-hexylamine (1.70 mL, 13.35 mmol) and NEt_3 (5.1 mL, 36.42 mmol). The resultant mixture was stirred for 24 h at room temperature. The reaction mixture was filtered and washed sequentially with 0.2 N H_2SO_4 , saturated NaHCO_3 solution and water. The organic layer was dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The crude product was chromatographed over silica gel (100-200 mesh) using EtOAc:Hexane (4:6) as eluent to afford 2.30 g of pure **A3**.

Yield: 92 %; Appearance: White solid; M.P: 84-86 $^\circ\text{C}$.

^1H NMR (300 MHz, CDCl_3): δ 0.88 (m, 6H), 1.19-1.61 (s+m, 9H+16H), 1.84-2.16 (m, 2H), 2.31 (m, 2H), 3.21 (m, 4H), 4.09 (m, 1H), 5.70 (br d, 1H), 6.02 (br s, 1H), 6.63 (br s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.96, 22.49, 26.54, 28.30, 29.43, 31.44, 32.80, 39.52, 39.69, 53.90, 79.69, 155.96, 171.64, 172.67; IR (ATR): 3317, 2927, 2859, 1681, 1644, 1523, 1452, 1243, 1164 cm^{-1} . HRMS calcd. for $\text{C}_{22}\text{H}_{43}\text{N}_3\text{O}_4\text{Na}$, $m/z = 436.3146$, obtained $m/z = 436.3150$.

1.3.8 Synthesis of M3

To an ice-cooled solution of **A3** (0.830 g, 2.01 mmol) in DCM (5 mL) was added TFA (3.081 mL, 40.14 mmol), and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was concentrated under reduced pressure. To the resulting amine was added NEt₃ (3 mL) and dissolved in 50 mL of dry toluene, added *exo*-norbornene dicarboxylic anhydride (0.150 g, 0.91 mmol) and was refluxed overnight at 120 °C. The reaction mixture was evaporated and the residue was chromatographed over silica-gel (100-200 mesh) and eluted using EtOAc:Hexane (6:4) to yield 0.335 g of pure **M3**.

Yield: 80 %; Appearance: White solid; M.P: 73-75 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.88 (m, 6H), 1.19-1.58 (m, 17H), 1.65 (d, *J* = 9.9 Hz, 1H), 2.10-2.58 (m, 4H), 2.70 (m, 2H), 3.12-3.40 (m, 4H+2H), 4.59 (m, 1H), 5.83 (br t, 1H), 6.29 (s, 2H), 6.87 (br t, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 13.98, 22.51, 24.82, 26.53, 29.47, 31.42, 33.40, 39.75, 43.01, 45.52, 47.65, 54.62, 137.96, 167.90, 171.64, 177.98 ; IR (ATR): 3329, 2926, 2860, 1698, 1651, 1539, 1372, 1200, 1169 cm⁻¹ ; HRMS calcd. for C₂₆H₄₁N₃O₄Na m/z 482.2989, found m/z 482.2998.

1.3.9 Synthesis of **P3**

To a well-stirred solution of **M3** (0.090 g, 0.196 mmol) in dry THF (0.5 mL) was added Grubbs IInd generation catalyst (1.66 mg, 0.0020 mmol) and stirred overnight at room temperature under argon atmosphere. After completion of reaction as monitored by TLC, the resultant mixture was quenched by adding 3 mL of ethyl vinyl ether. The polymer was precipitated using methanol and the precipitate obtained was dried under vacuum to yield pure polymer **P3**.

Yield: Quantitative; Appearance: Light brown film.

^1H NMR (300 MHz, CDCl_3): δ 0.87 (m, 6H), 1.04-1.90 (m, 18H), 2.25 (br m, 4H), 3.19 (m, 8H), 4.53 (br s, 1H), 5.30-5.96 (m, 1H+1H) 6.28-7.10 (br m, 1H), 7.31-8.29 (br m, 1H); IR (ATR): 3305, 2926, 2859, 1773, 1701, 1645, 1539, 1376, 1162 cm^{-1} .

1.3.10 Synthesis of **M4**

To L-leucine methyl ester hydrochloride **3** (0.199 g, 1.10 mmol), added NEt_3 (3 mL) and dissolved in dry toluene (50 mL), followed by *exo*-norbornene dicarboxylic anhydride (0.150 g, 0.91 mmol) and refluxed for 4-5 h at 60-80 $^\circ\text{C}$. The reaction mixture was evaporated and the residue was purified by silica-gel chromatography (100-200 mesh) using EtOAc:Hexane (2:8) as eluent to obtain 0.210 g of pure product **M4**.

Yield: 79 %; Appearance: Yellow syrup.

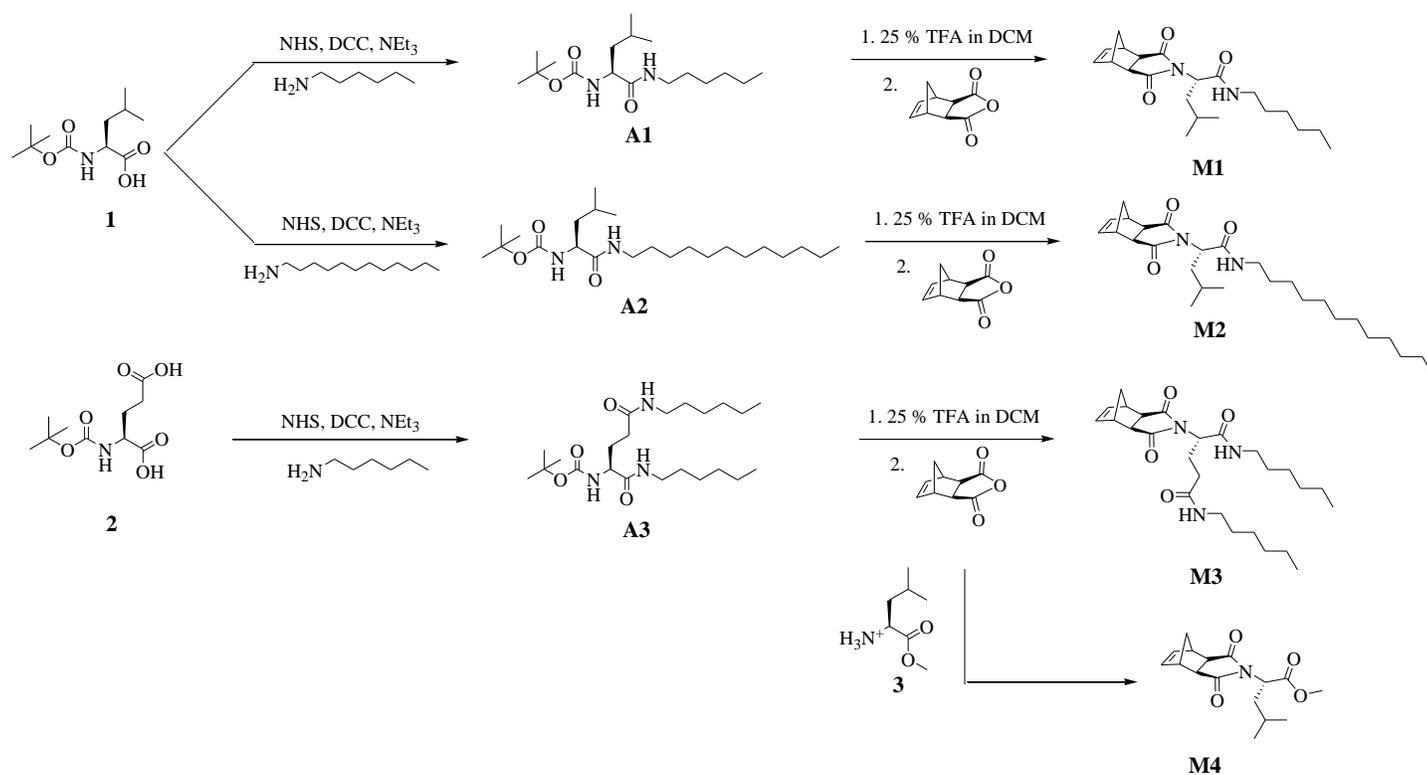
^1H NMR (300 MHz, CDCl_3): δ 0.92 (d, $J = 6.6$ Hz, 6H), 1.42 (m, 1H), 1.56 (m, 2H), 1.89 (m, 1H), 2.15 (m, 1H), 2.73 (m, 2H), 3.32 (br s, 2H), 3.72 (s, 3H), 4.75 (m, 1H), 6.31 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.09, 23.09, 25.09, 36.51, 42.76, 45.38, 47.60, 50.95, 52.61, 137.98, 169.77, 177.35 ; IR (ATR): 2955, 2929, 1745, 1700, 1379, 1262, 1188 cm^{-1} ; HRMS calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_4\text{Na}$ m/z 314.1363, found m/z 314.1353.

1.3.11 Synthesis of **P4**

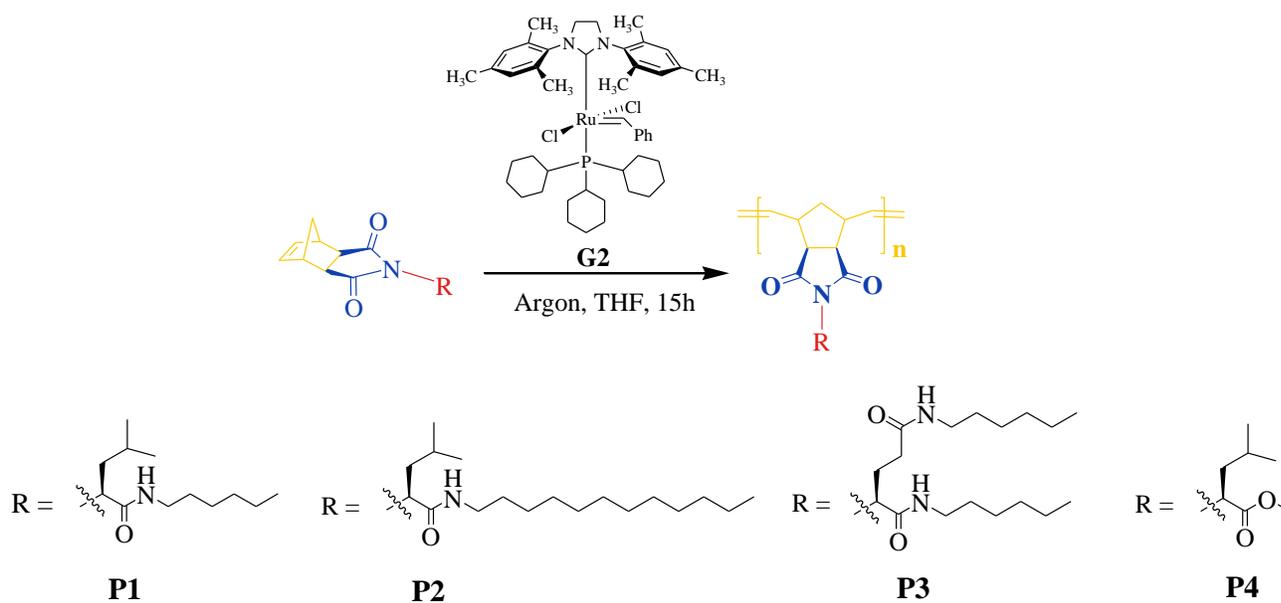
To a solution of **M4** (0.058 g, 0.199 mmol) in dry THF (0.5 mL) was added Grubbs IInd generation catalyst (1.69 mg, 0.002 mmol) and stirred overnight at room temperature under argon atmosphere. Monitored the reaction by TLC and after the completion, reaction was quenched by the addition of ethyl vinyl ether (3 ml). The polymer was precipitated using methanol and the precipitate obtained was dried under vacuum to yield pure polymer **P4**.

Yield: Quantitative; Appearance: White solid with brownish tinge.

^1H NMR (300 MHz, CDCl_3): δ 0.90 (br s, 6H), 1.05-1.49 (m, 3H), 1.86 (m, 1H), 2.16 (m, 1H), 2.65-3.44 (m, 4H), 3.71 (s, 3H), 4.71 (br s, 1H), 5.49 (br s, 1H), 5.75 (br s, 1H); IR (ATR): 2954, 2869, 1743, 1703, 1379, 1262, 1185 cm^{-1} .



Scheme S1: Synthesis of lipidated leucine and glutamic acid appended *exo*-norbornene-cored monomers **M1-M4**.



Scheme S2: ROMP of monomers in the presence of Grubbs IInd generation catalyst to give corresponding polymers **P1-P4**.

Table S1: Molecular weight distribution of polymers **P1-P4**.

Polymer	Mw (Dalton)	Mn (Dalton)	PDI
P1	46373	35099	1.32
P2	75357	66722	1.13
P3	36519	26197	1.39
P4	42707	31198	1.37

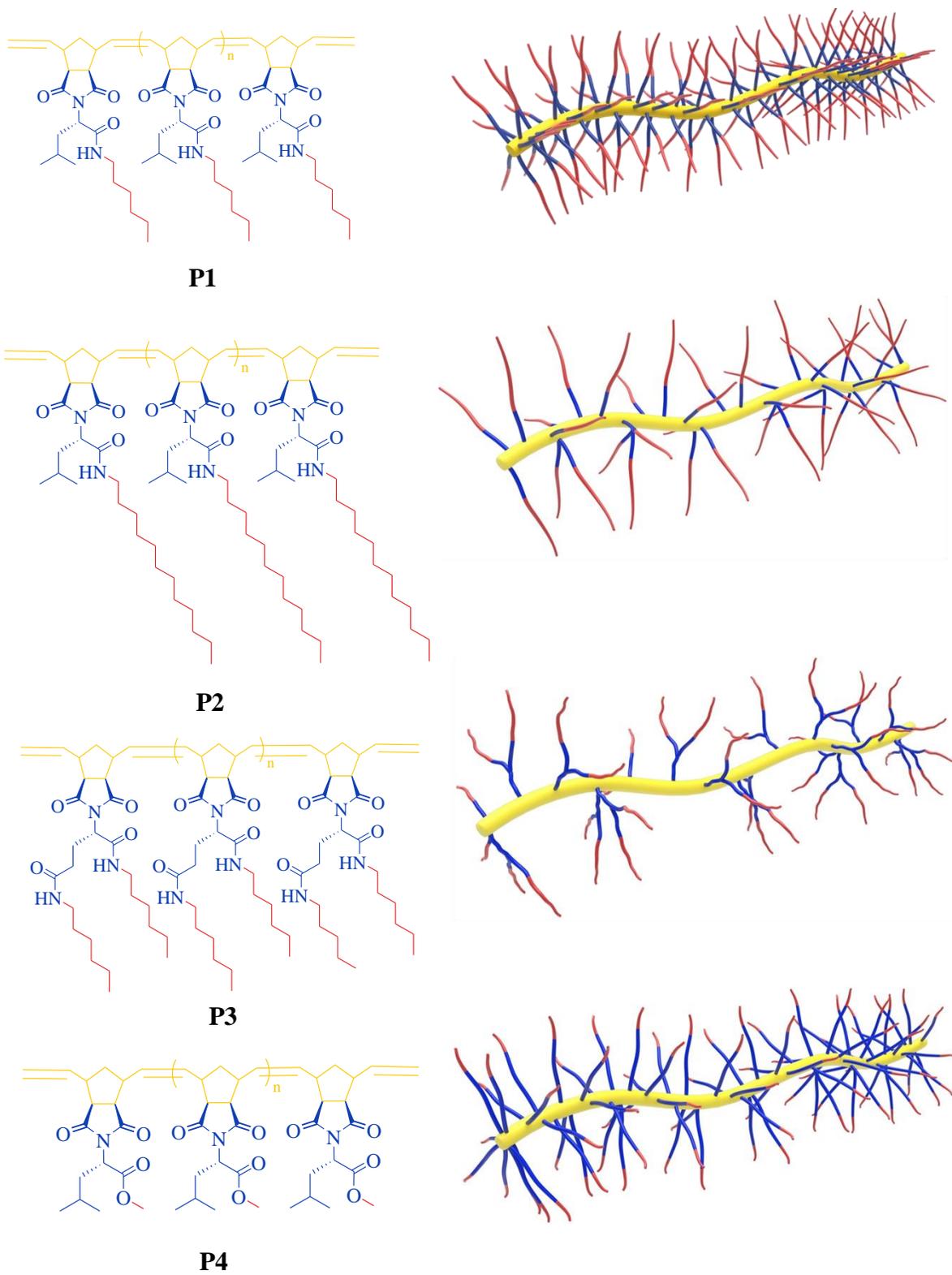


Figure S1: Chemical structures of polymers **P1-P4** along with the graphical representation of corresponding bottlebrush polymeric architecture.

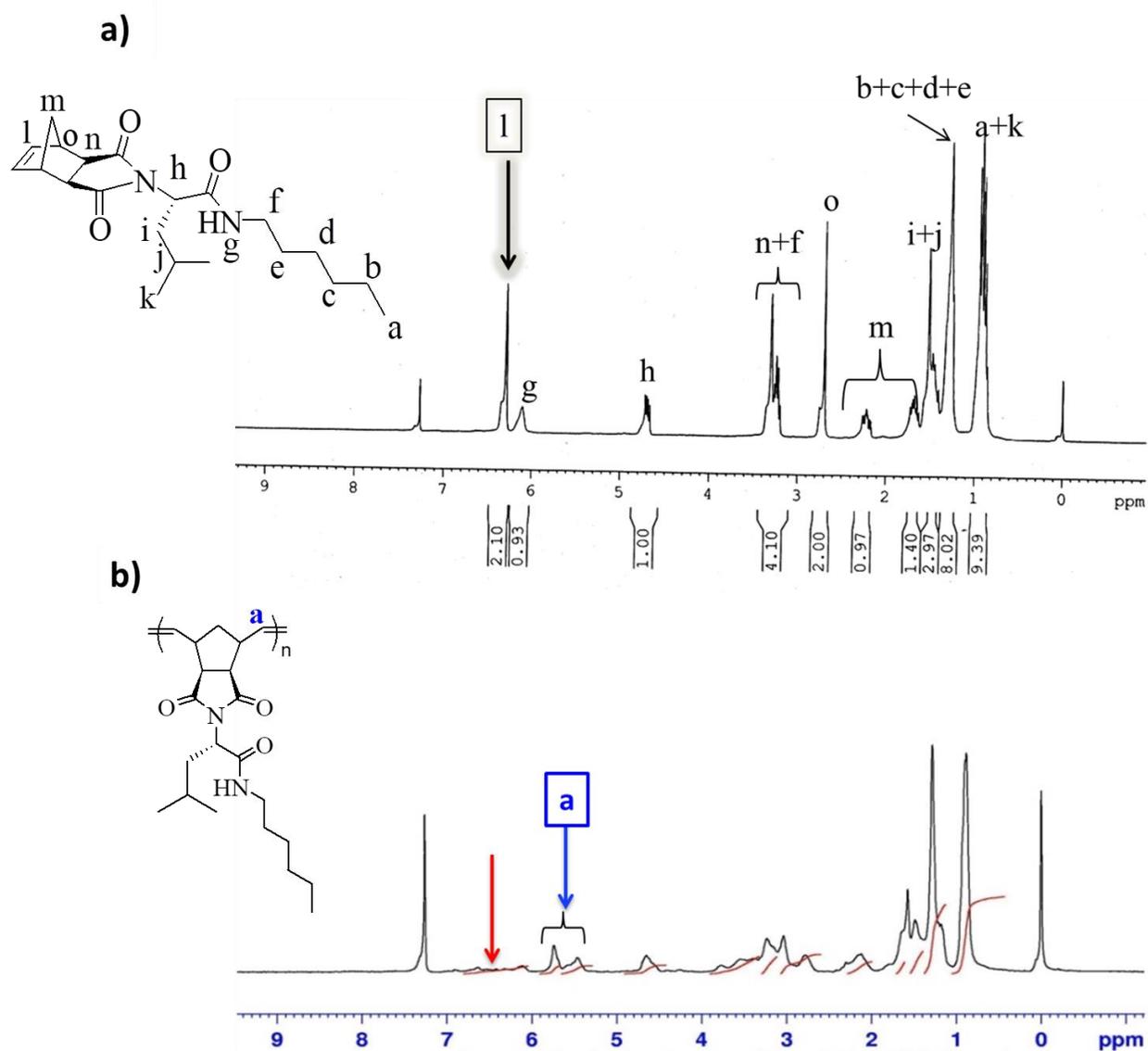


Figure S2: ^1H NMR (300 MHz, CDCl_3) spectral comparison of (a) monomer **M1** and (b) polymer **P1**.

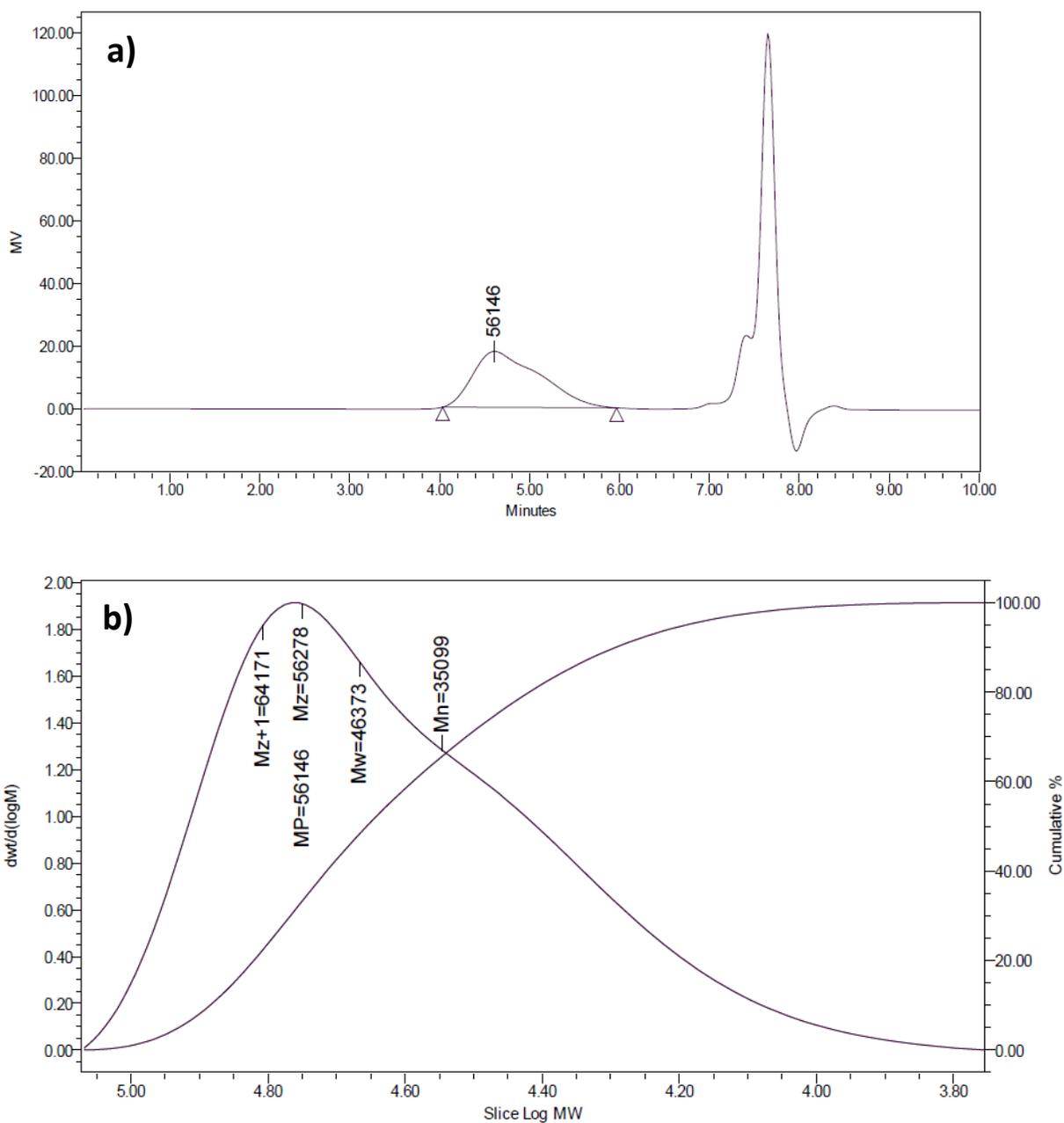


Figure S3: GPC profiles of **P1** (a) The complete chromatogram (b) Expanded region of polymer peak.

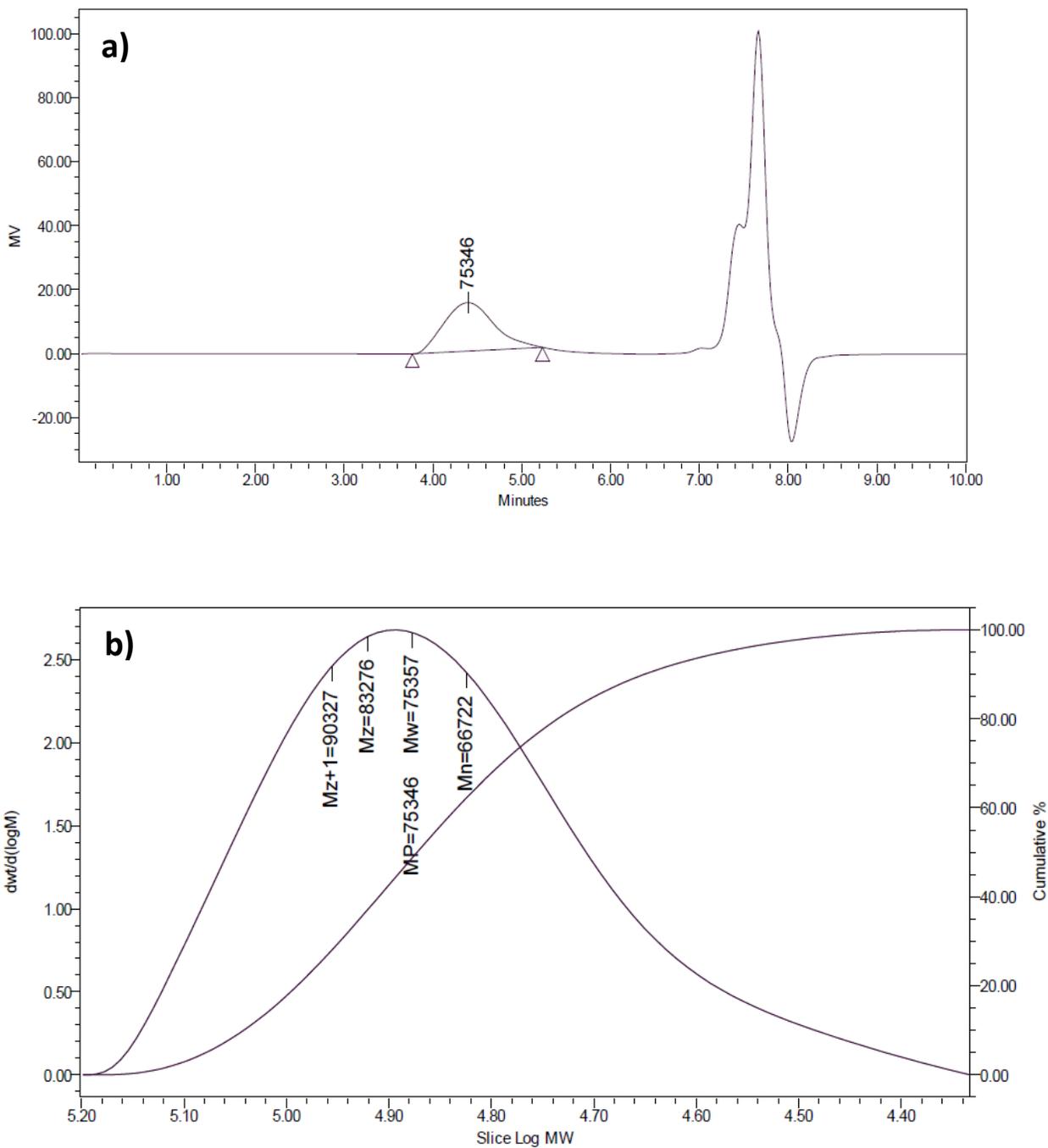


Figure S4: GPC profiles of **P2** (a) The complete chromatogram (b) Expanded region of polymer peak.

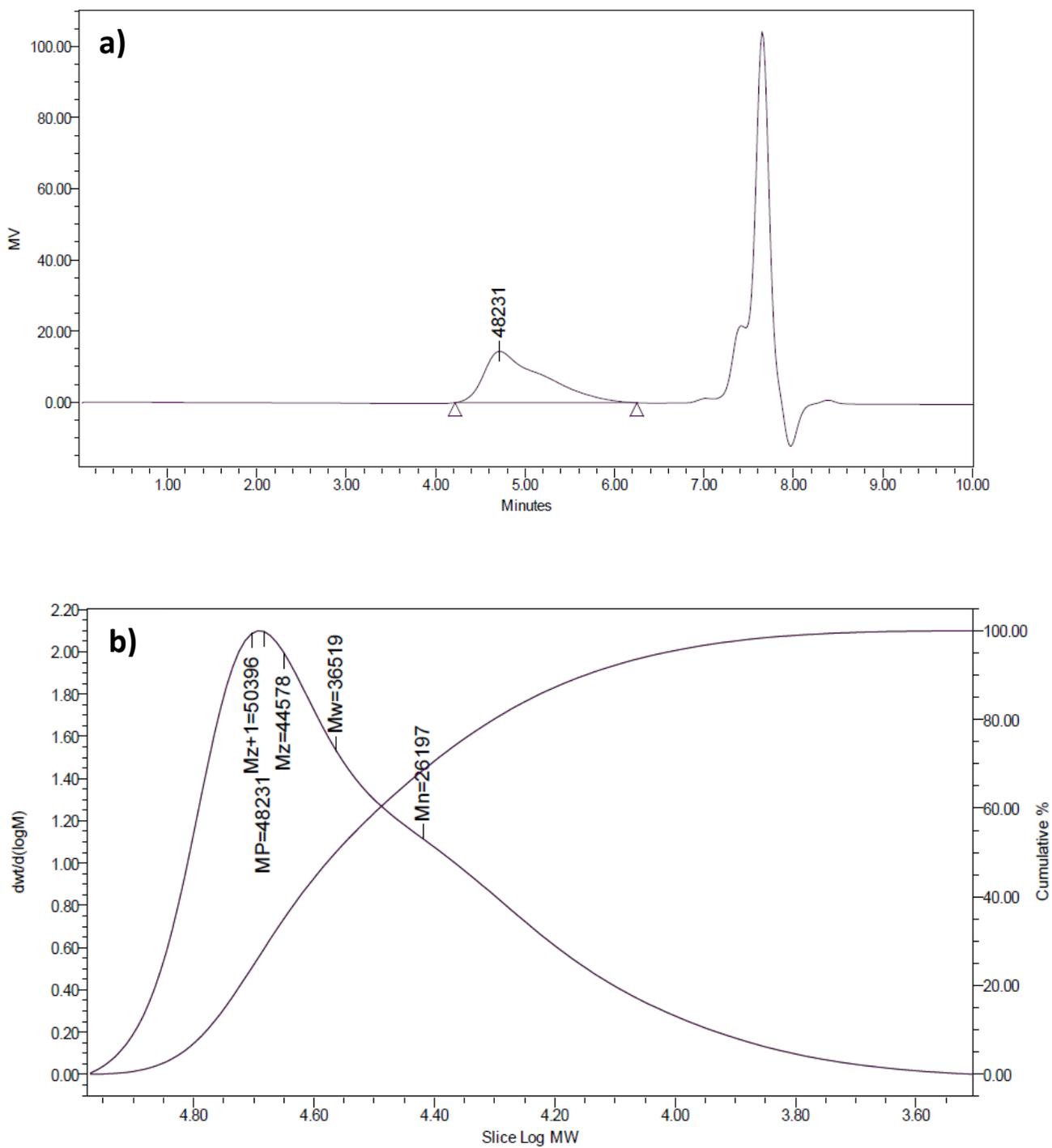


Figure S5: GPC profiles of **P3** (a) The complete chromatogram (b) Expanded region of polymer peak.

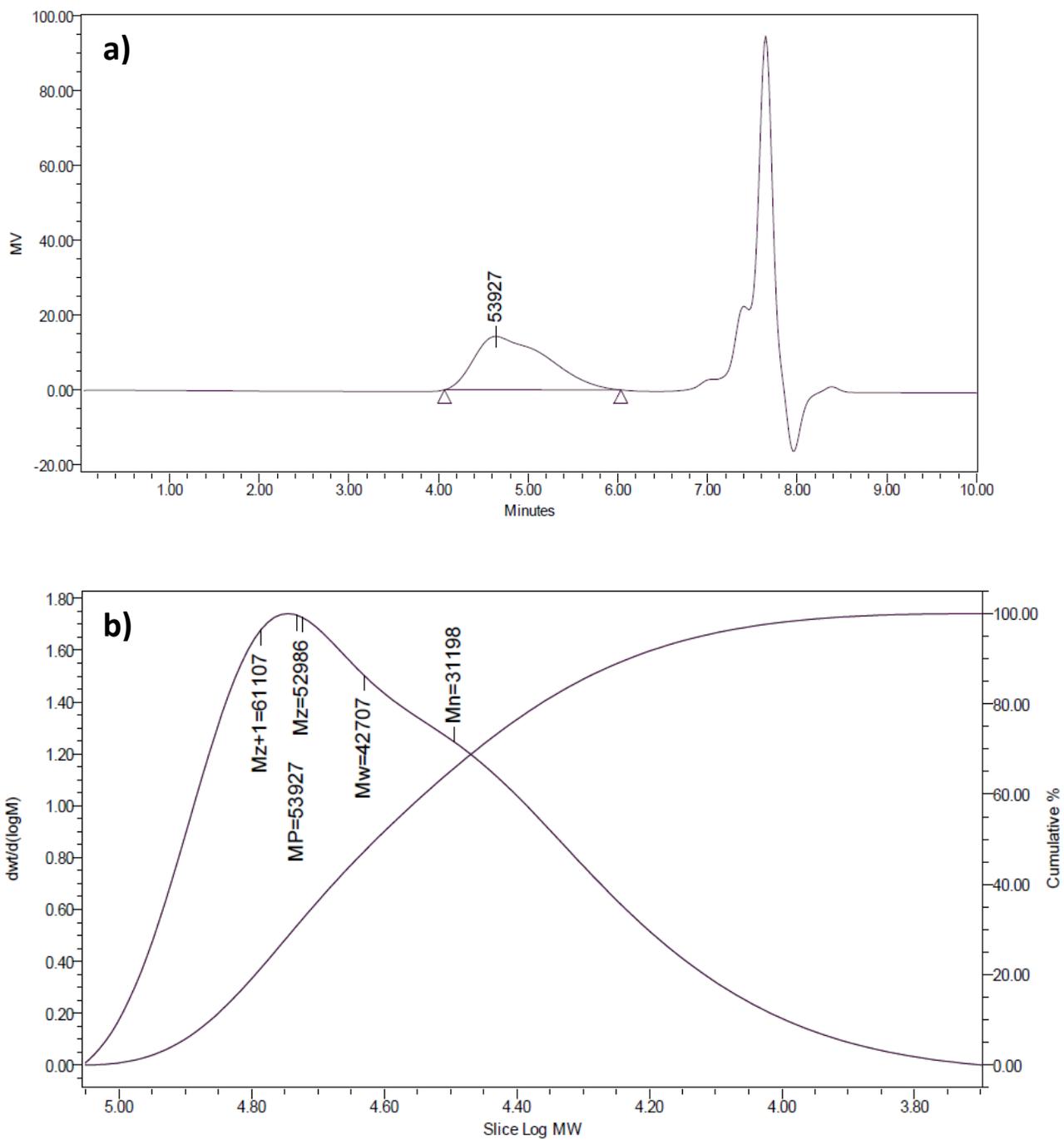


Figure S6: GPC profiles of **P4** (a) The complete chromatogram (b) Expanded region of polymer peak.

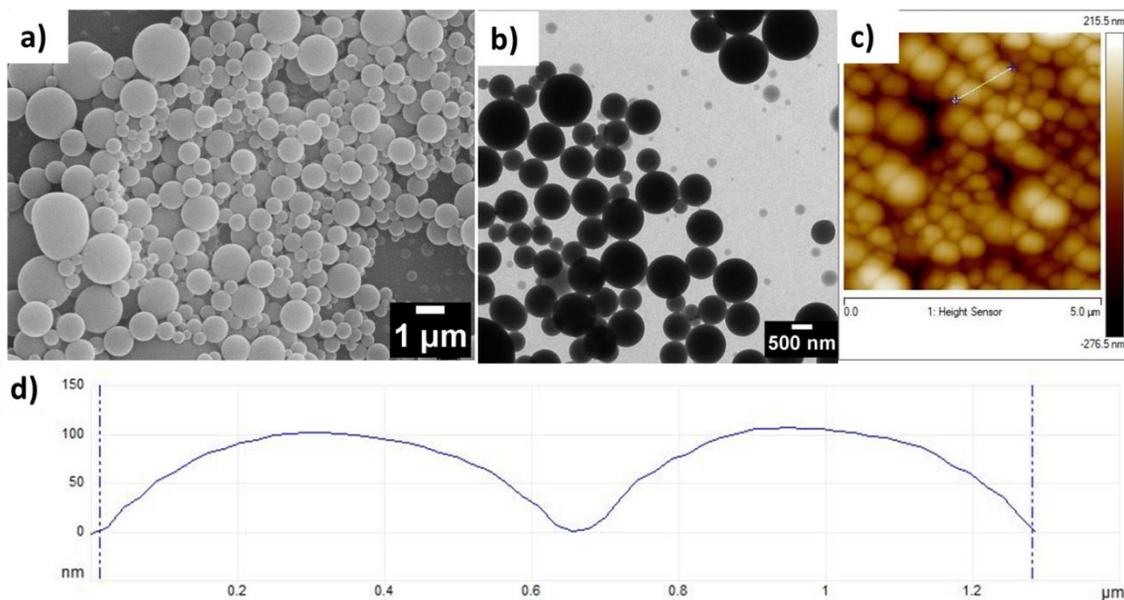


Figure S7: Microscopic analysis of polymer **P2** (2 mg/ml) in 1:1 chloroform:methanol (a) SEM, (b) TEM, (c) AFM, (d) Height profile analysis of AFM along the line.

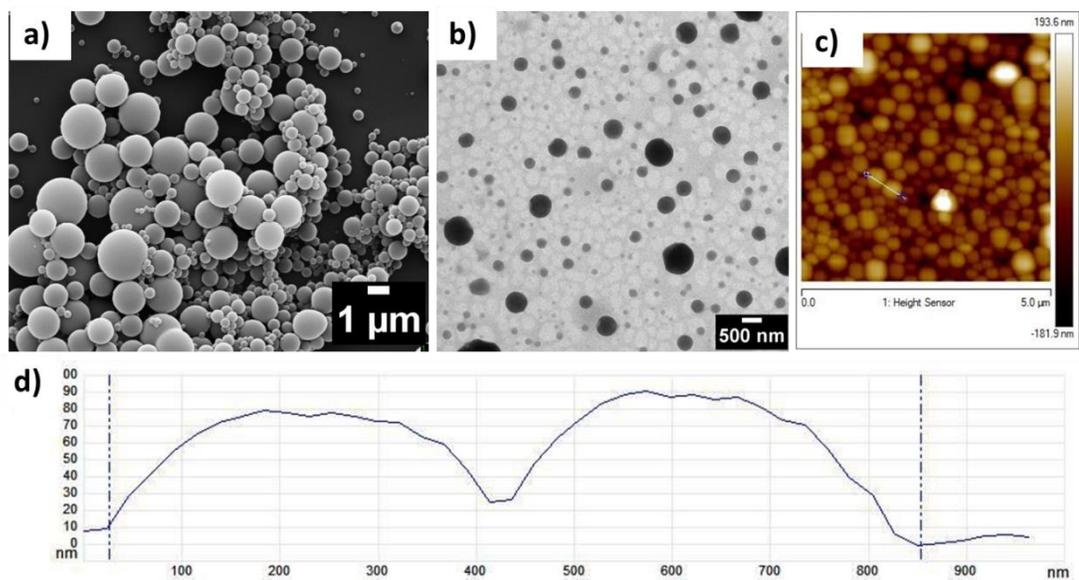


Figure S8: Microscopic analysis of polymer **P3** (2 mg/ml) in 2:1 chloroform:methanol (a) SEM, (b) TEM, (c) AFM, (d) Height profile analysis of AFM along the line.

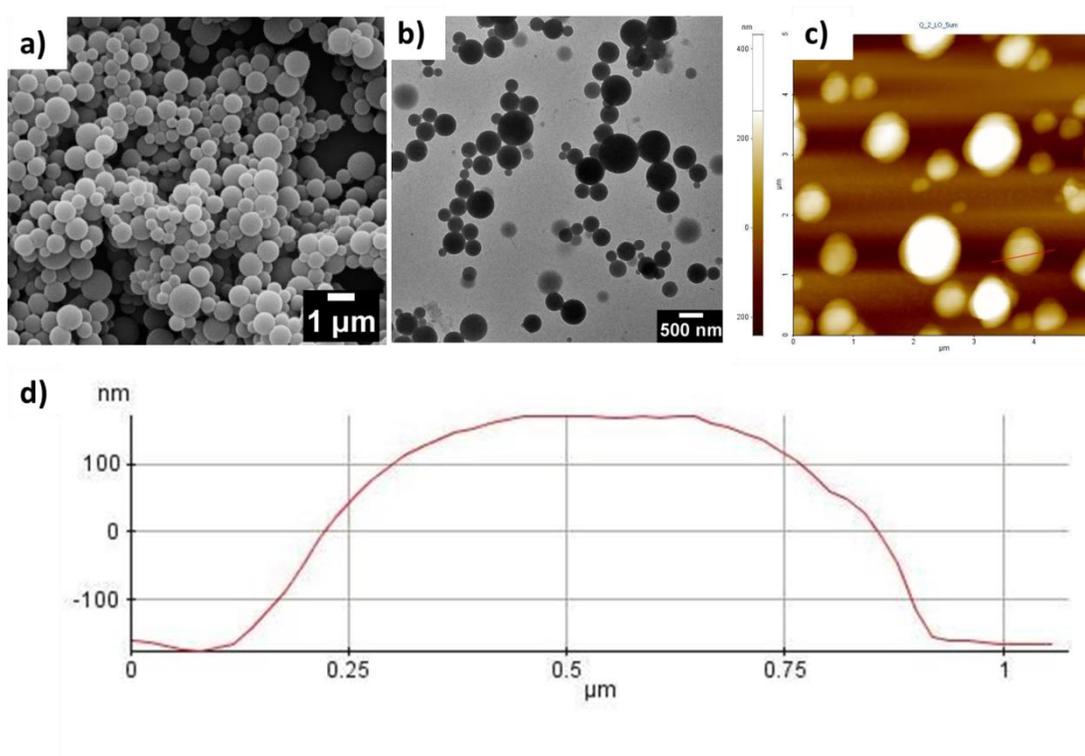


Figure S9: Microscopic analysis of polymer **P4** (2 mg/ml) in 1:1 chloroform:methanol (a) SEM, (b) TEM, (c) AFM, (d) Height profile analysis of AFM along the line.

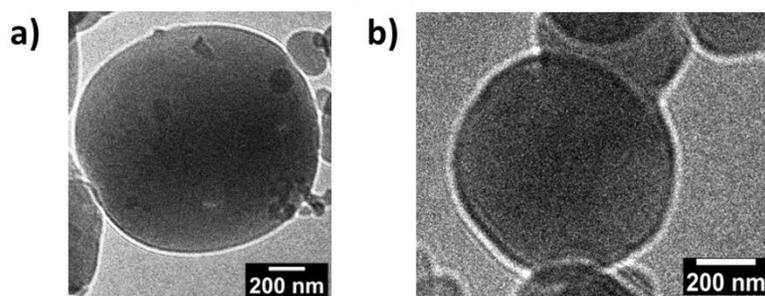


Figure S10: Cryo-TEM images of **P1** (2 mg/ml) in 1:1 chloroform:methanol solvent system.

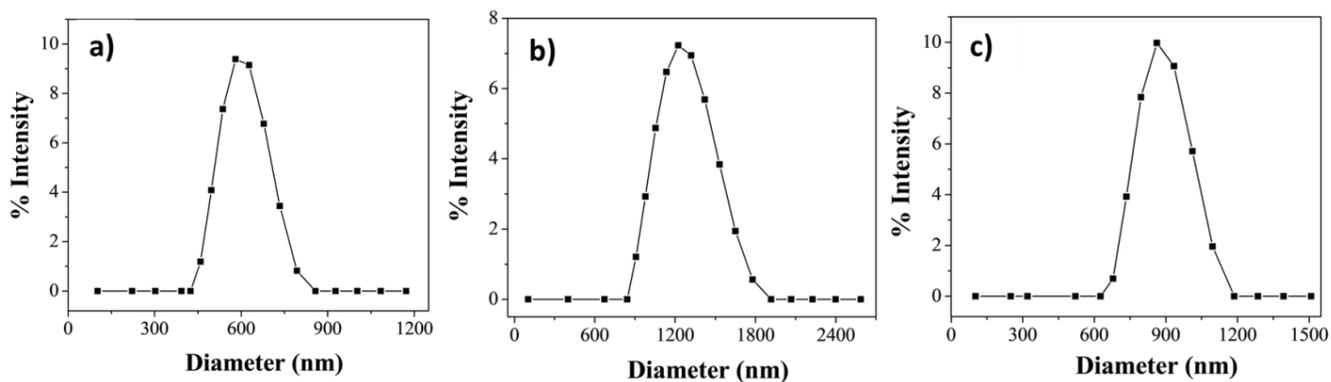


Figure S11: Dynamic light scattering (DLS) profiles of polymers showing the average size distribution (a) **P2** (2 mg/ml) in 1:1 chloroform:methanol, (b) **P3** (2 mg/ml) in 2:1 chloroform:methanol, (c) **P4** (2 mg/ml) in 1:1 chloroform:methanol.

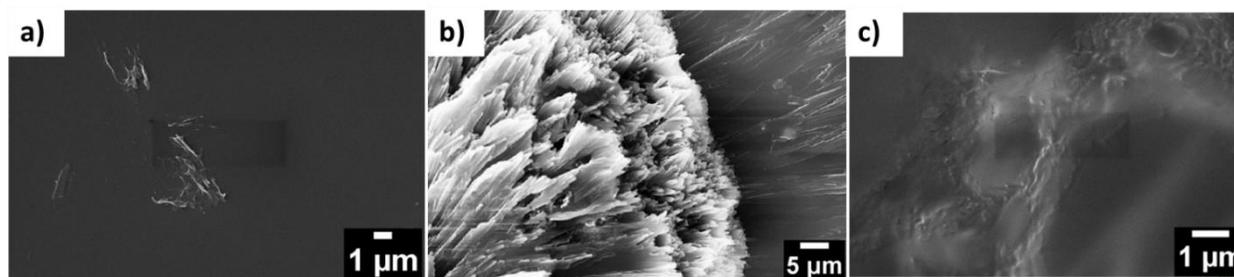


Figure S12: SEM images of monomers (a) **M1** (2 mg/ml) in 1:1 chloroform:methanol, (b) **M2** (2 mg/ml) in 1:1 chloroform:methanol, (c) **M3** (2 mg/ml) in 2:1 chloroform:methanol. The SEM of **M4** was not recorded due to its sticky nature.

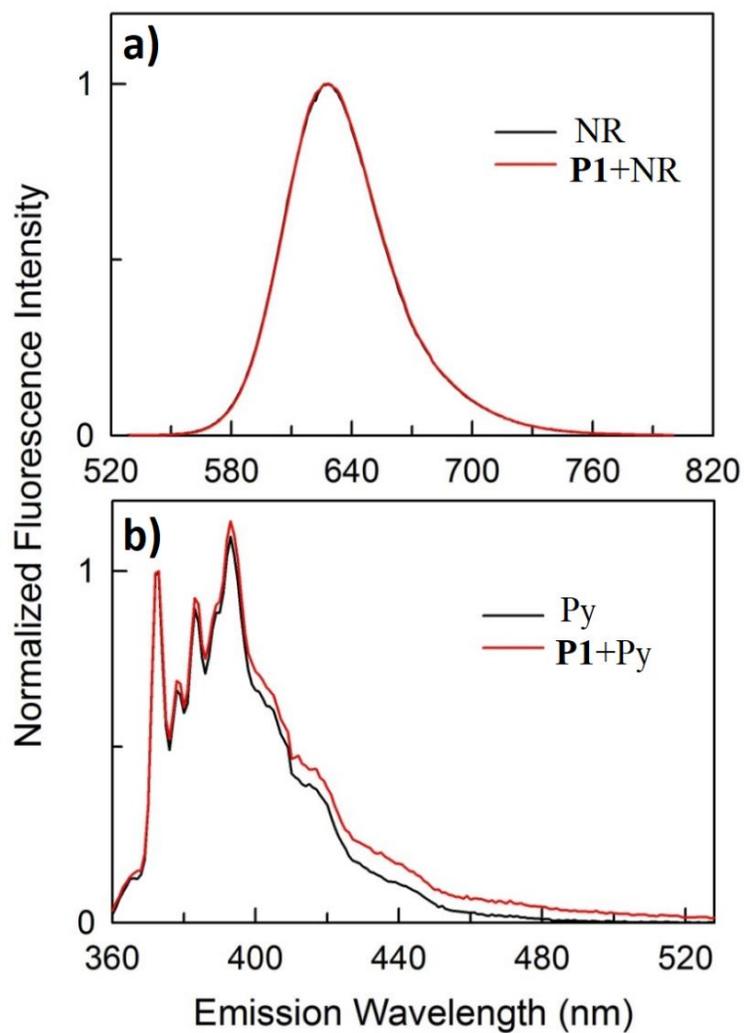


Figure S13: Normalized fluorescence emission spectra of (a) Nile red [NR concentration = 5 μM , slit width = 1 nm, λ_{ex} = 500 nm, λ_{em} = 628 ± 1 nm and (b) pyrene [Py concentration = 5 μM , slit width = 1 nm, λ_{ex} = 337 nm, ratio of the intensity band 1-to-band 3 (I_1/I_3) = 1.12 ± 0.05 and 1.08 ± 0.05 for Py and **P1**+Py, respectively] dissolved in 1:1 methanol:chloroform under ambient conditions.

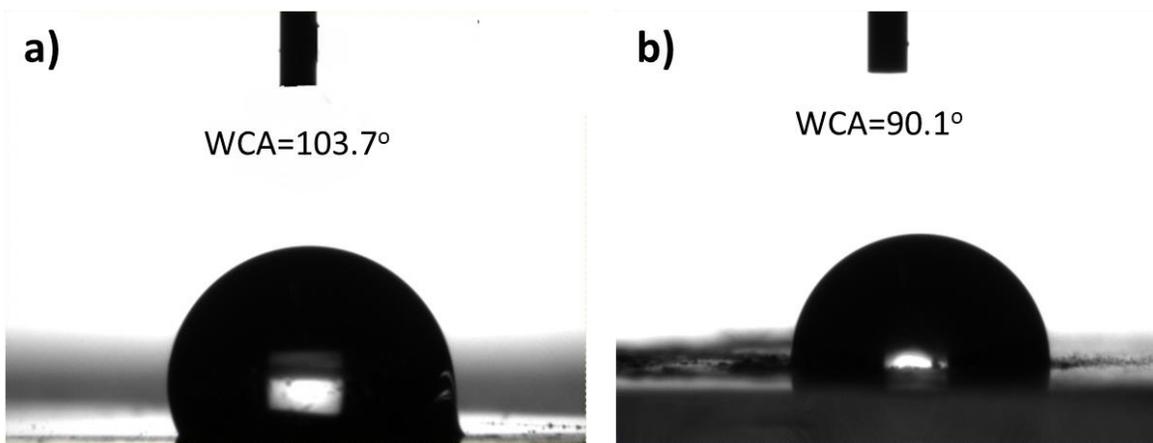


Figure S14: WCA measurement on the glass surface coated with (a) **P2** and (b) **P4**.

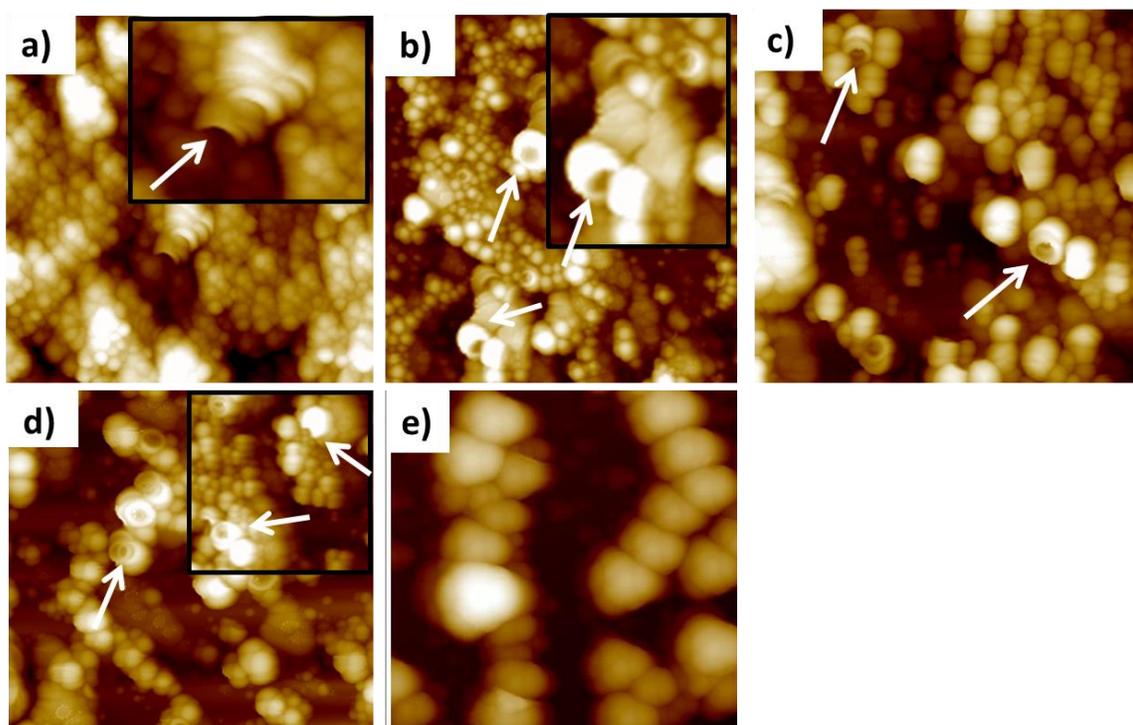


Figure S15: Concentration-dependent AFM analysis of **P1** (a) 0.0625 mg/ml, (b) 0.125 mg/ml, (c) 0.25 mg/ml, (d) 0.5 mg/ml, (e) 2 mg/ml (insets show the zoomed images; Relevant parts are marked by arrows).

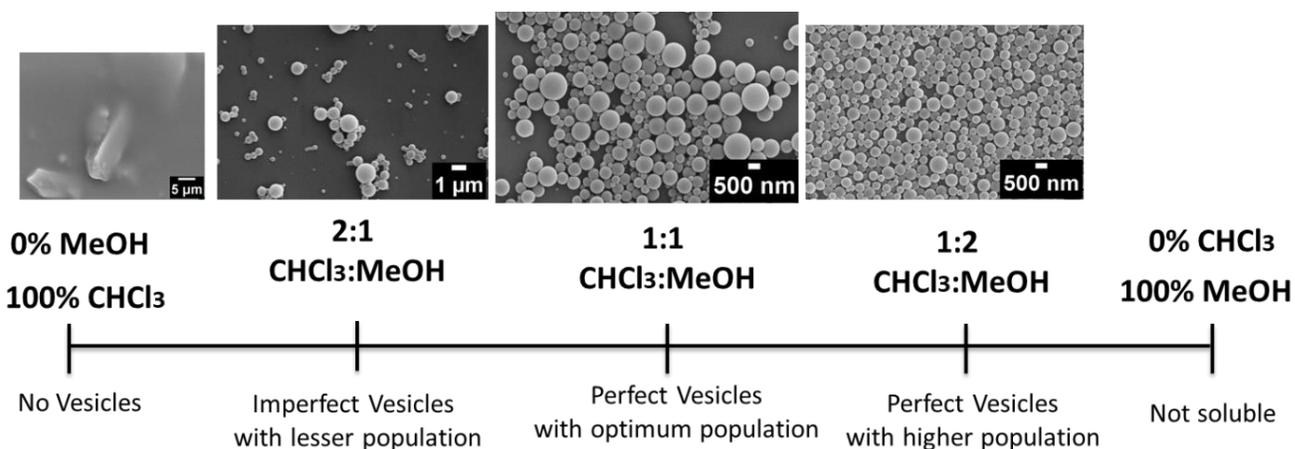


Figure S16: SEM images of **P1** (2 mg/ml) in varying composition of methanol and chloroform.

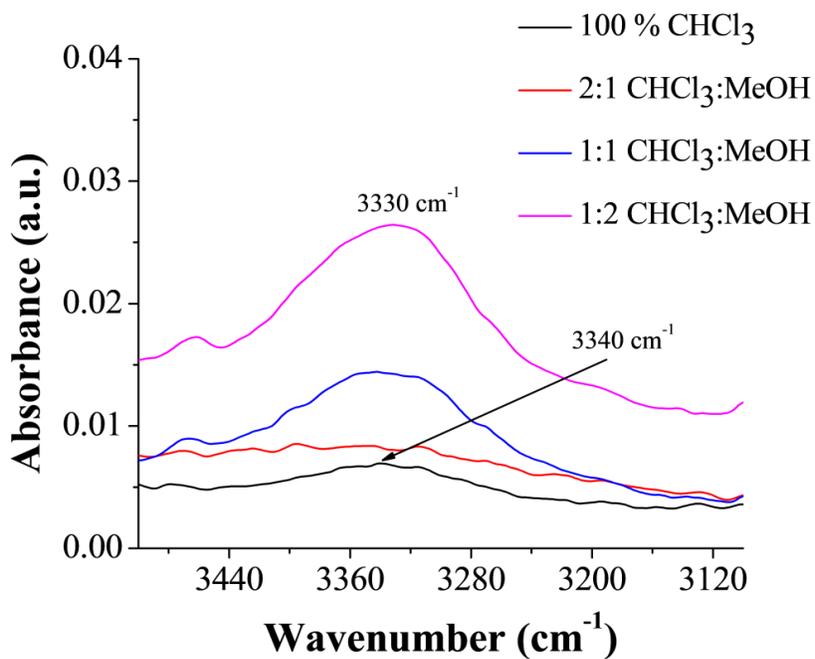


Figure S17: Partial ATR FT-IR spectra of **P1** in different solvent compositions showing amide A region.

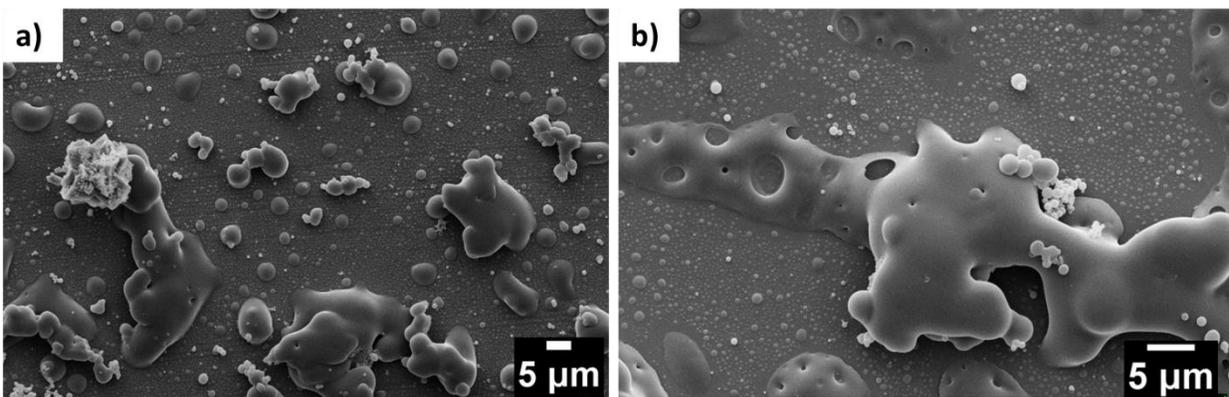


Figure S18: SEM images of **P3** (2 mg/ml) in 1:1 chloroform:methanol.

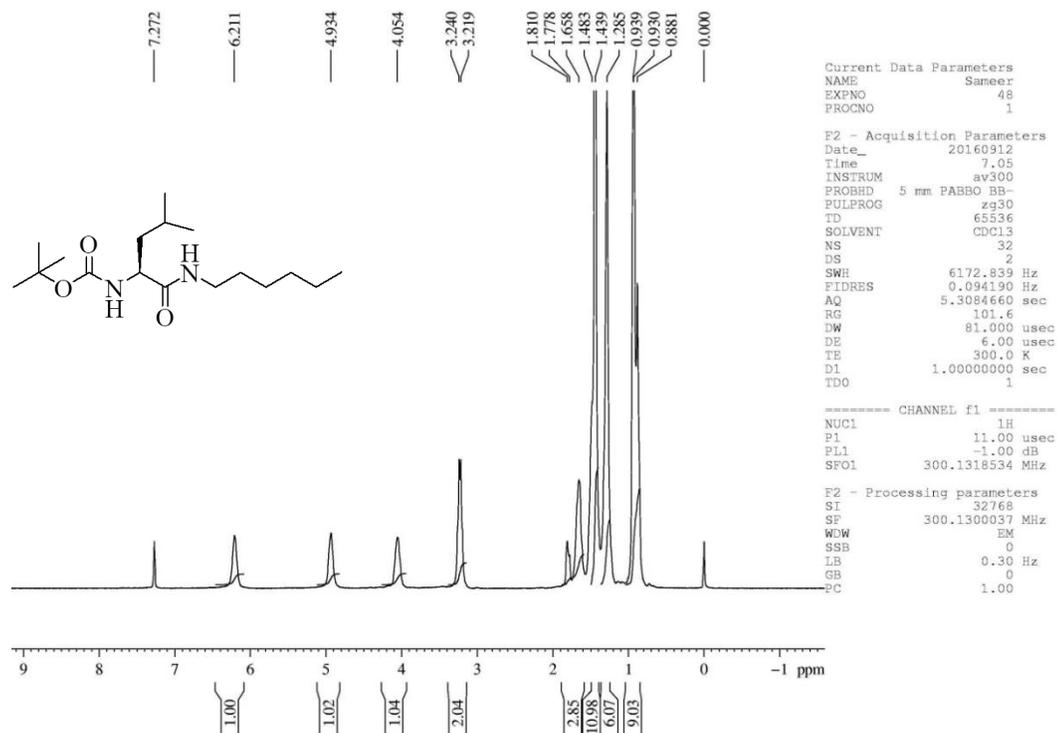


Figure S19: ^1H NMR (300 MHz, CDCl_3) spectrum of A1

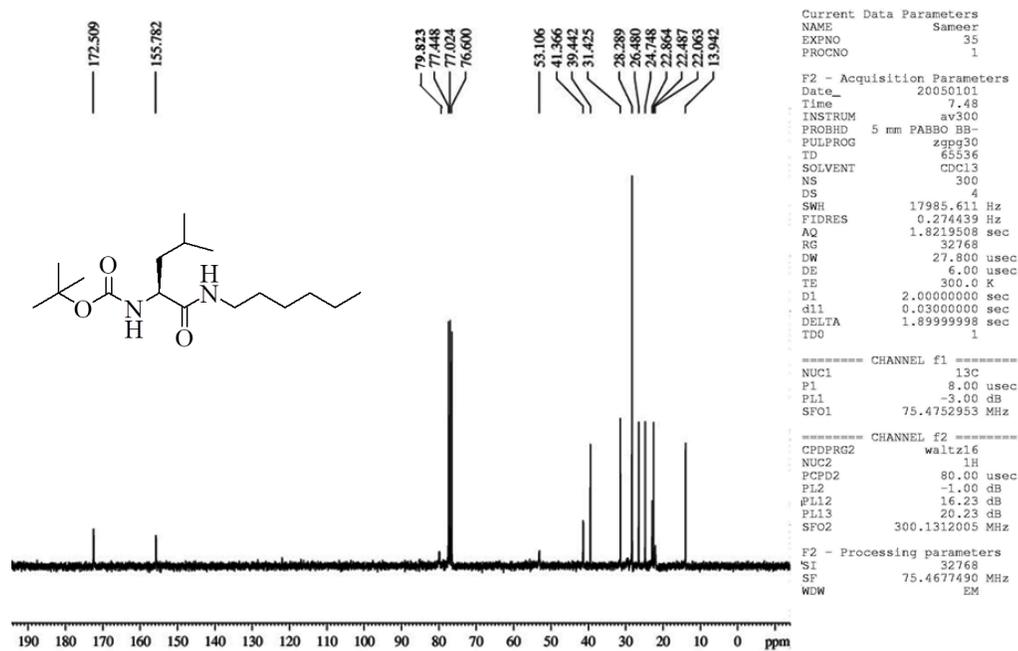


Figure S20: ^{13}C NMR (75 MHz, CDCl_3) spectrum of A1

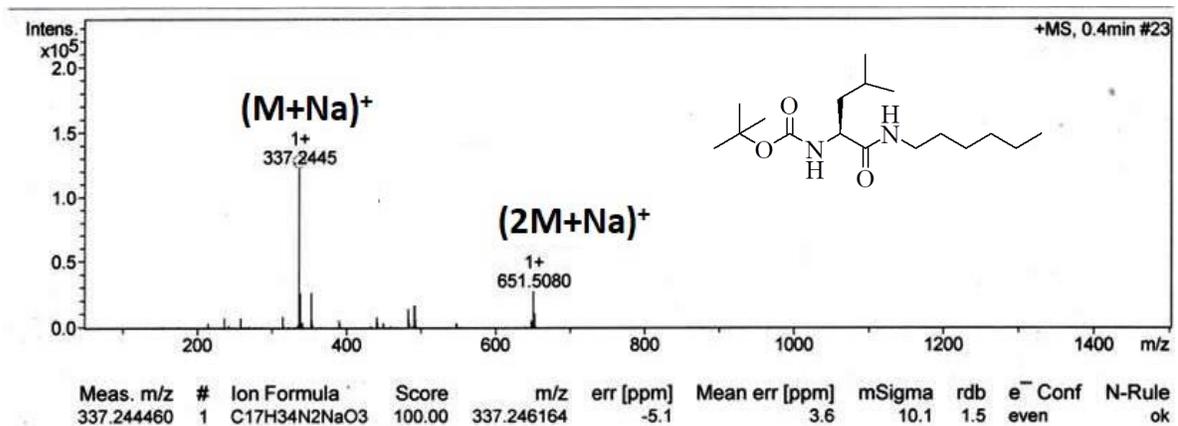


Figure S21: High Resolution Mass spectrum of A1

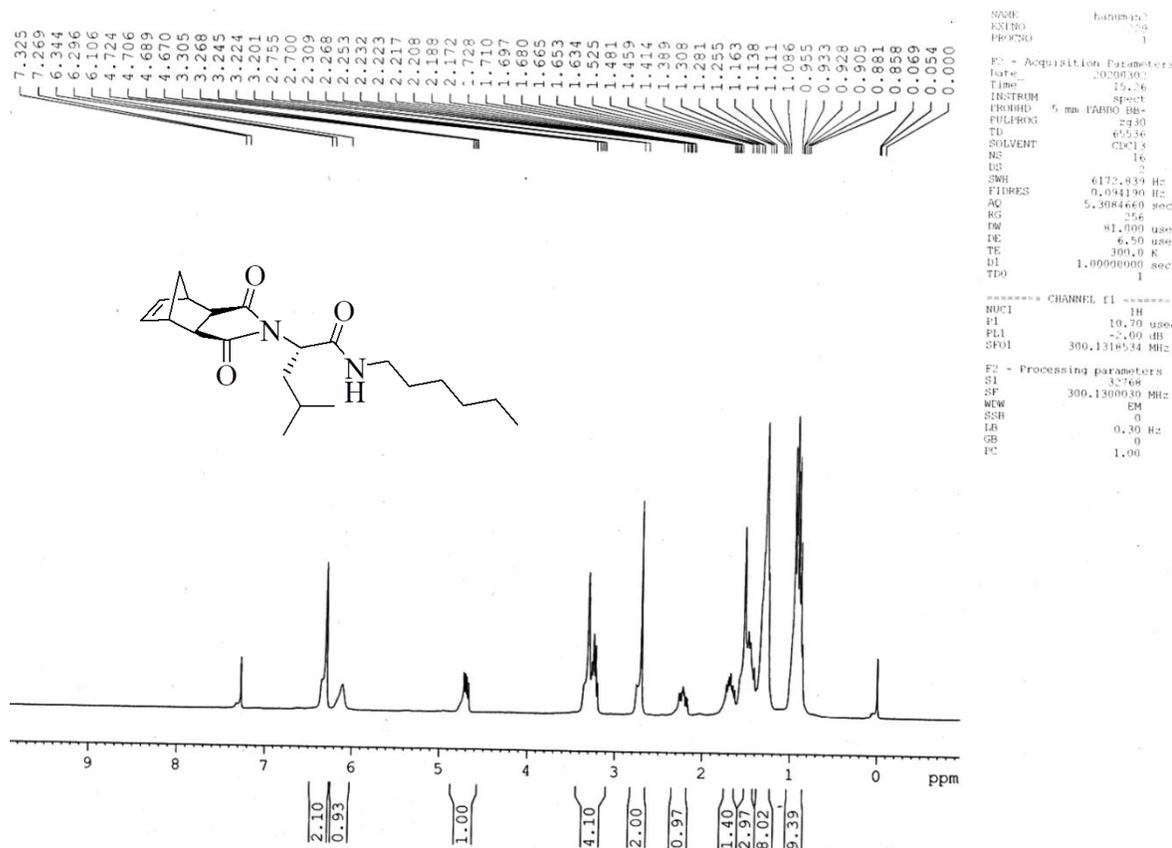


Figure S22: ¹H NMR (300 MHz, CDCl₃) spectrum of M1

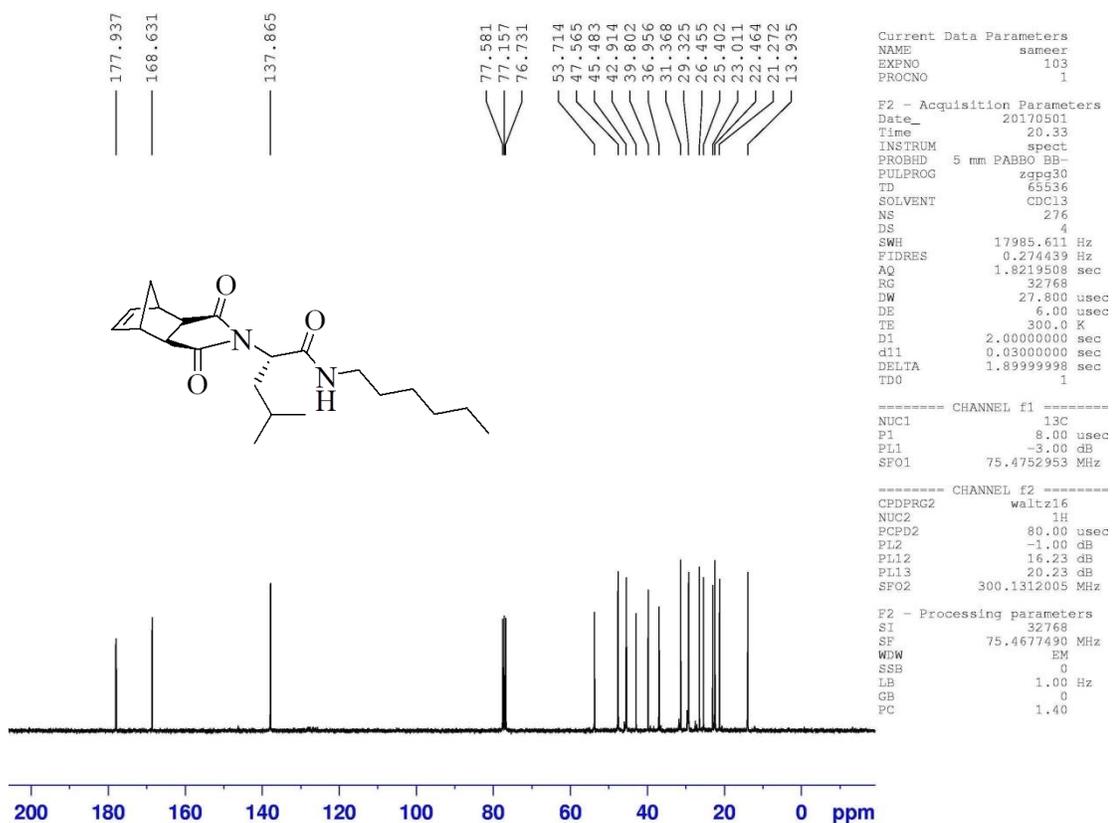


Figure S23: ^{13}C NMR (75 MHz, CDCl_3) spectrum of M1

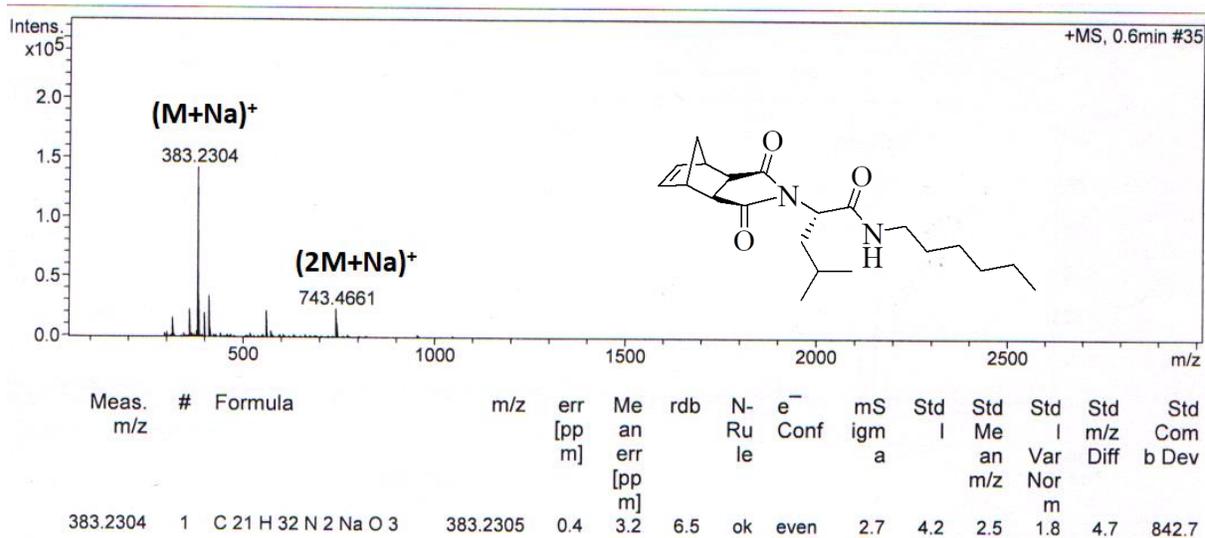


Figure S24: High Resolution Mass spectrum of M1

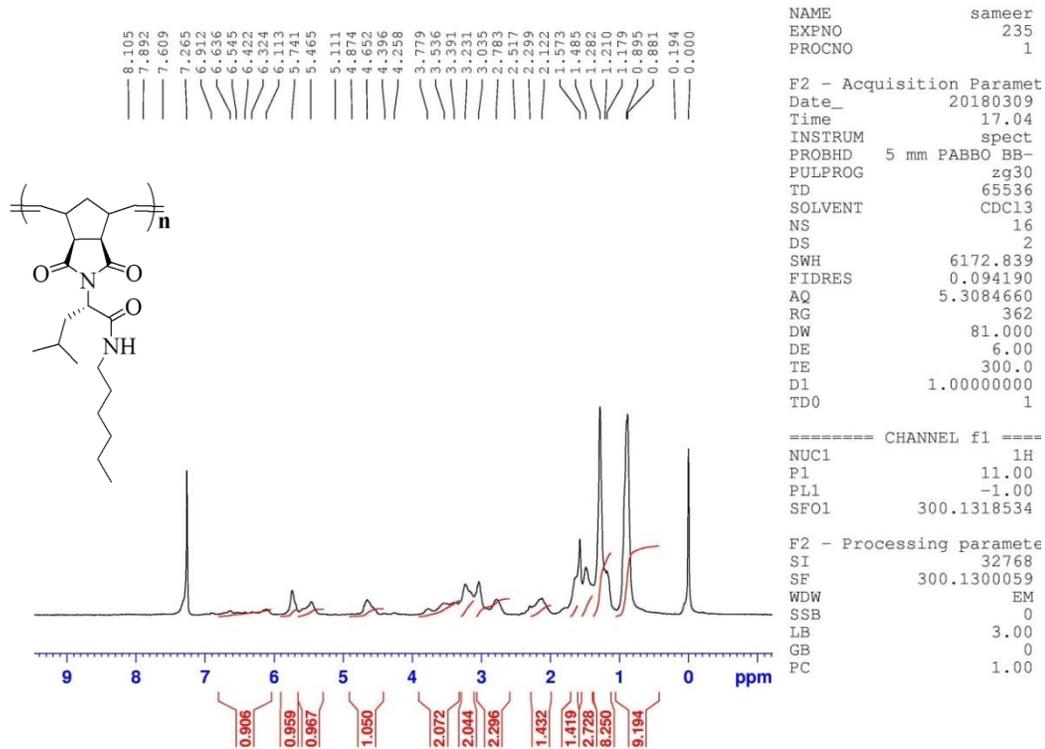


Figure S25: ^1H NMR (300 MHz, CDCl_3) spectrum of **P1**

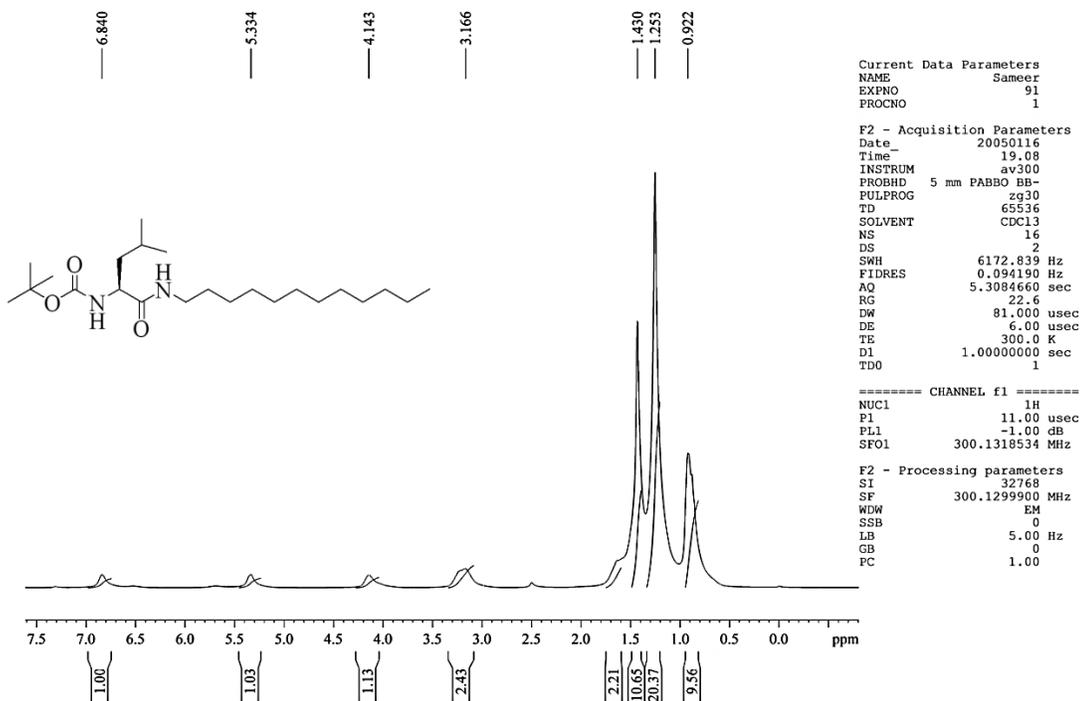


Figure S26: ^1H NMR (300 MHz, CDCl_3) spectrum of **A2**

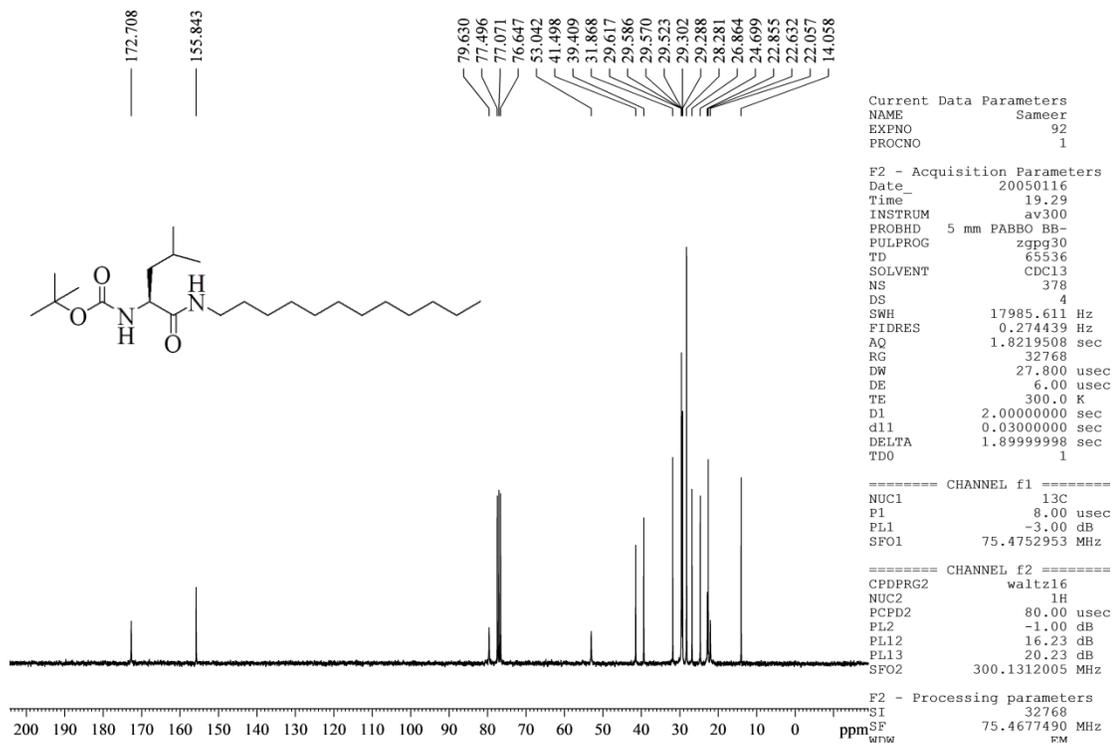


Figure S27: ^{13}C NMR (75 MHz, CDCl_3) spectrum of A2

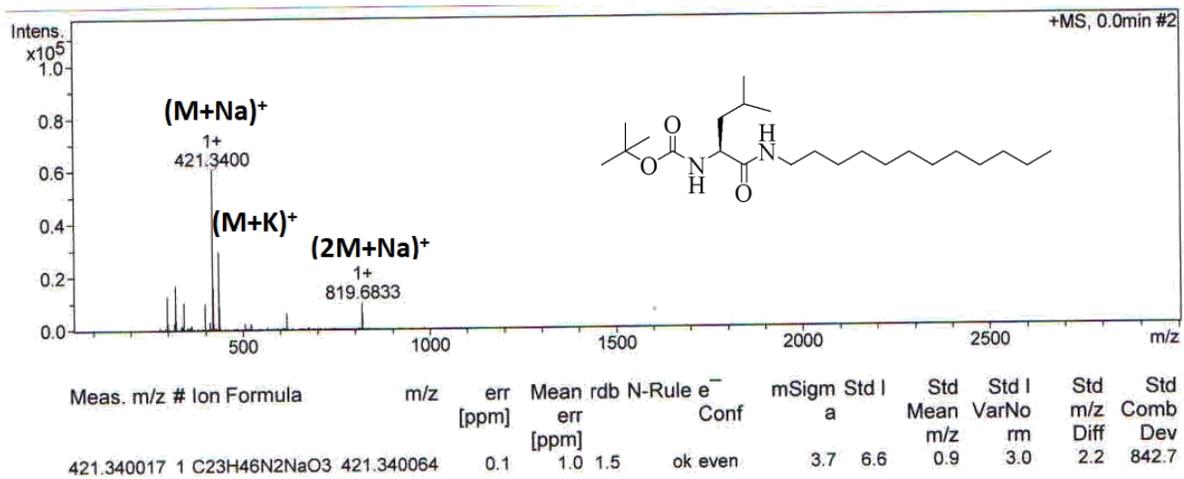


Figure S28: High Resolution Mass spectrum of A2

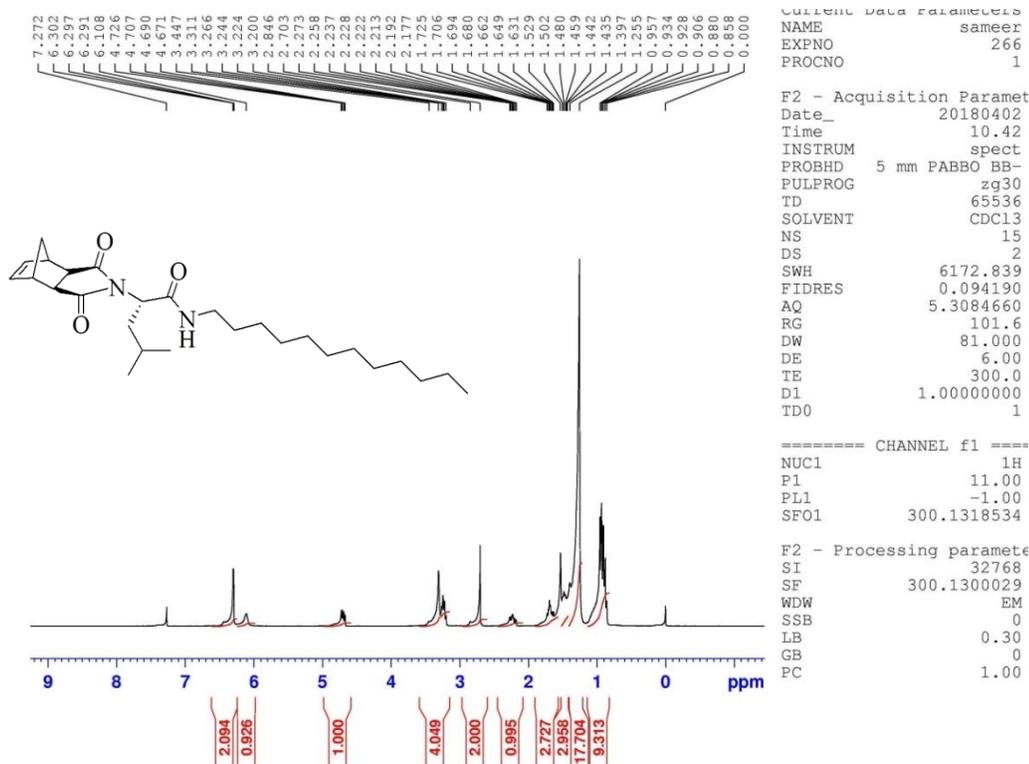


Figure S29: ^1H NMR (300 MHz, CDCl_3) spectrum of M2.

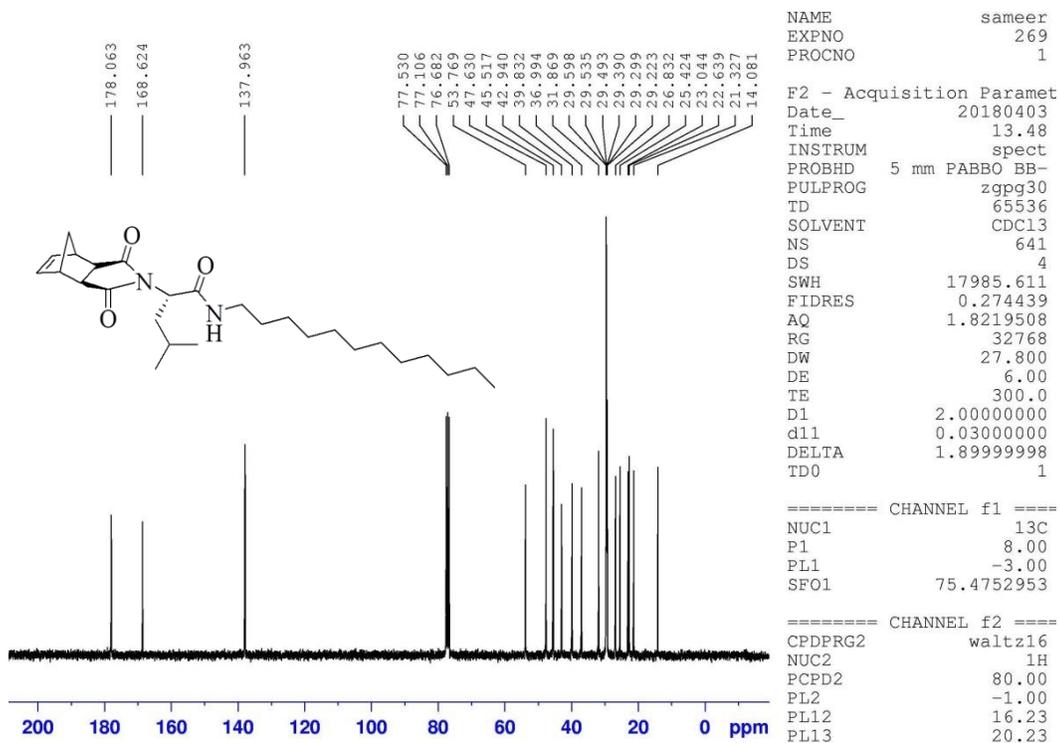


Figure S30: ^{13}C NMR (75 MHz, CDCl_3) spectrum of M2

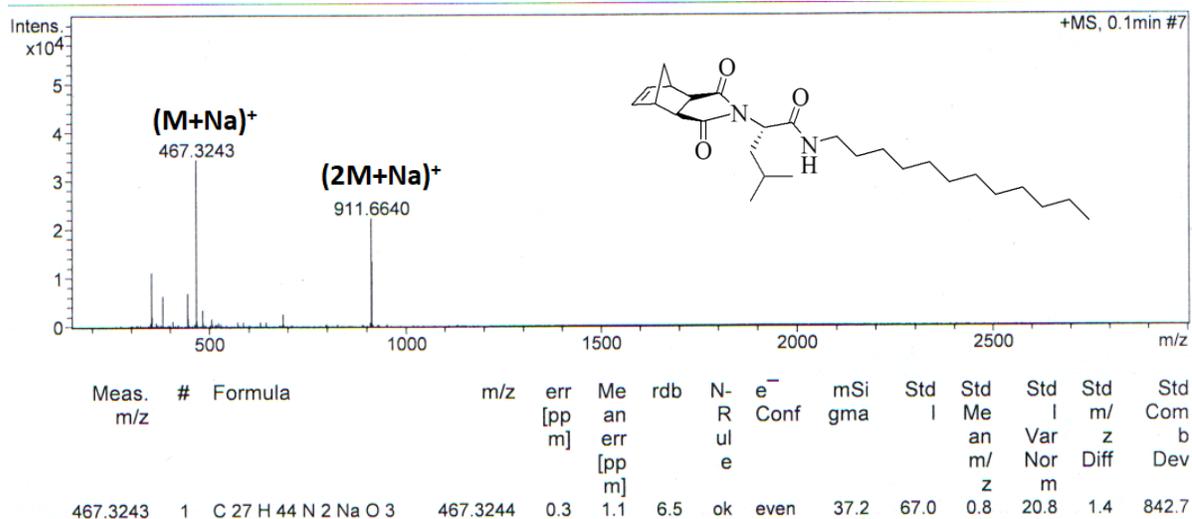


Figure S31: High Resolution Mass spectrum of M2

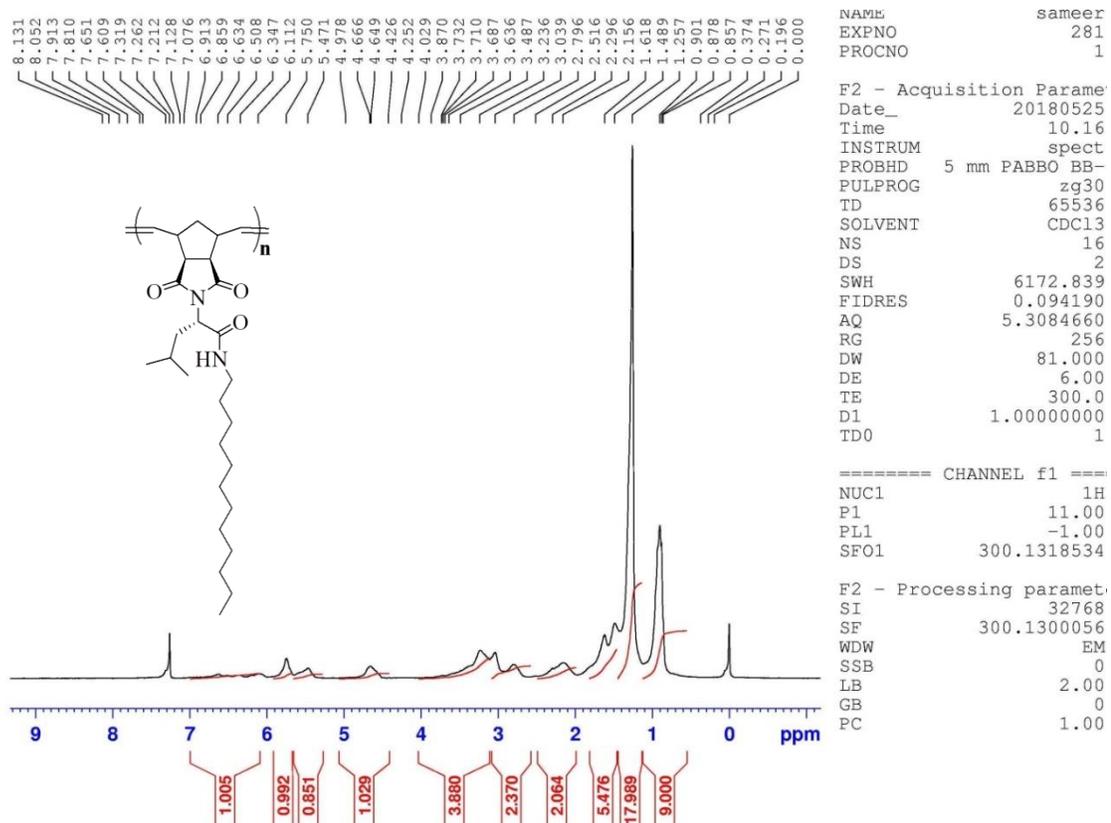


Figure S32: ¹H NMR (300 MHz, CDCl₃) spectrum of P2

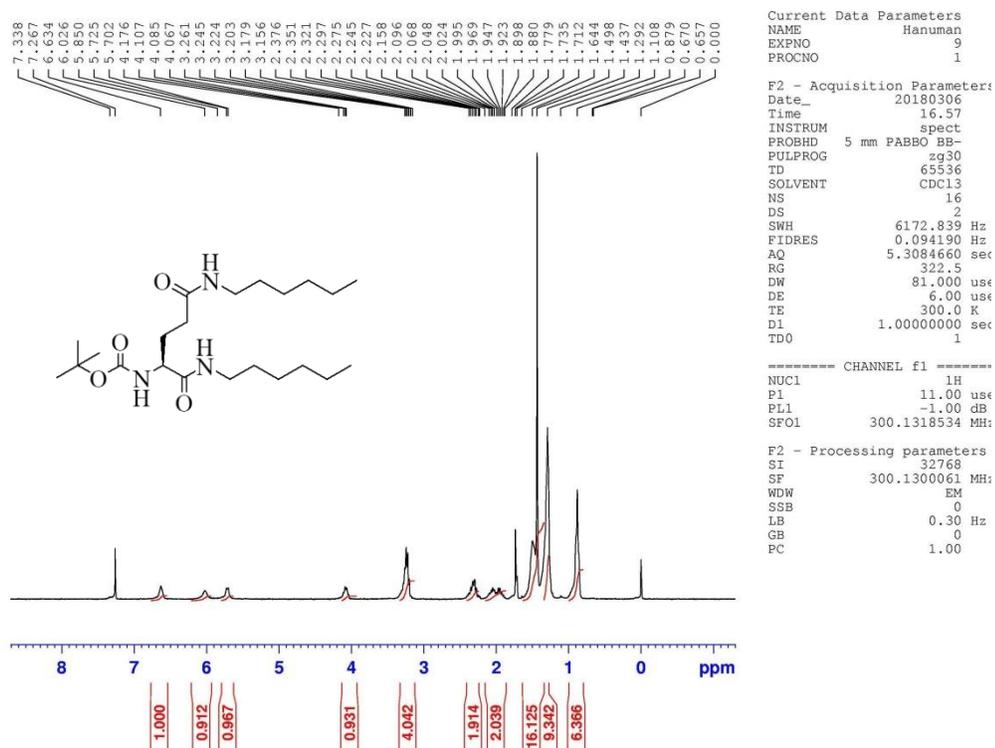


Figure S33: ^1H NMR (300 MHz, CDCl_3) spectrum of **A3**

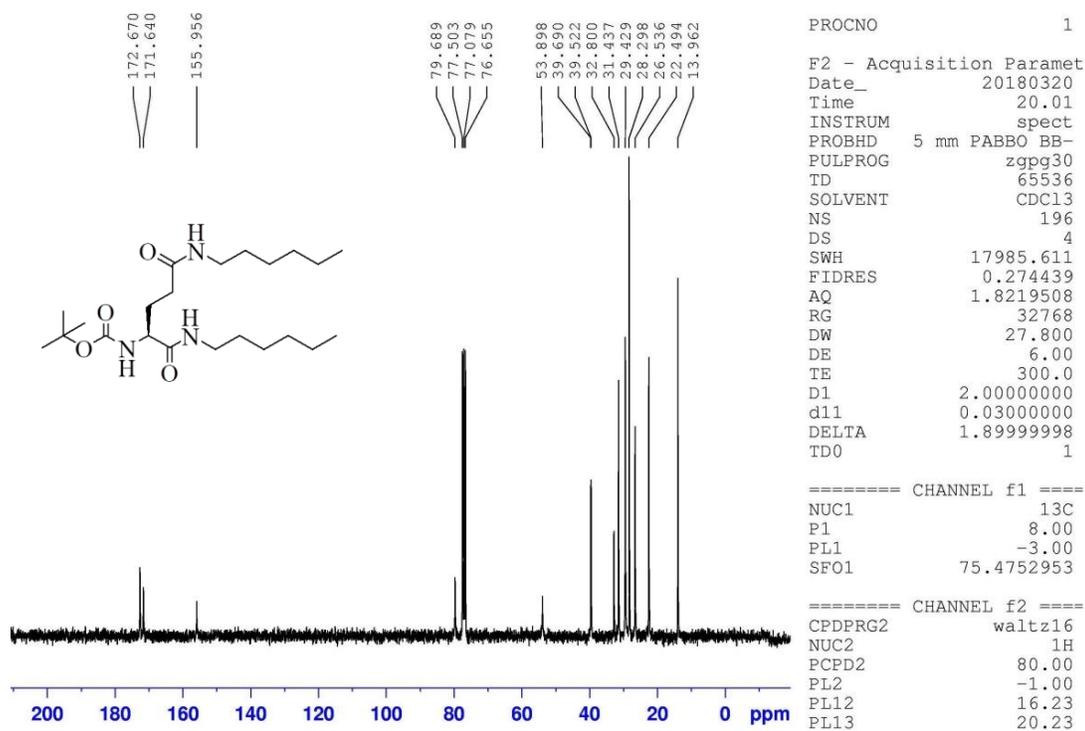


Figure S34: ^{13}C NMR (75 MHz, CDCl_3) spectrum of **A3**

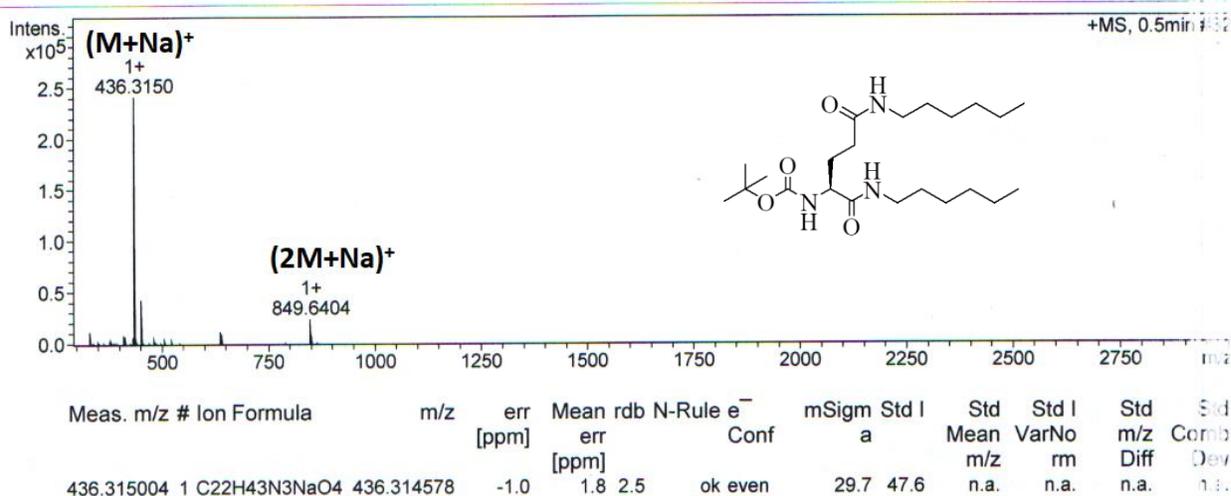


Figure S35: High Resolution Mass spectrum of A3

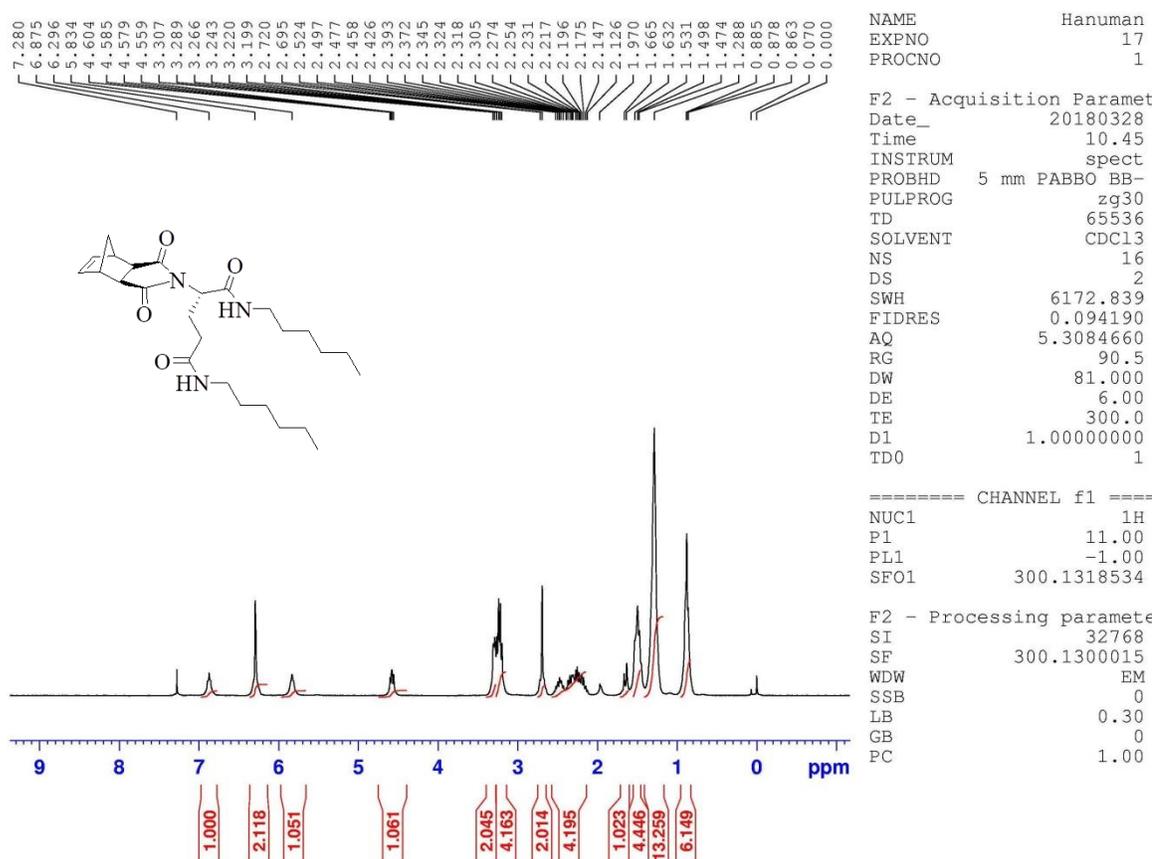


Figure S36: ¹H NMR (300 MHz, CDCl₃) spectrum of M3

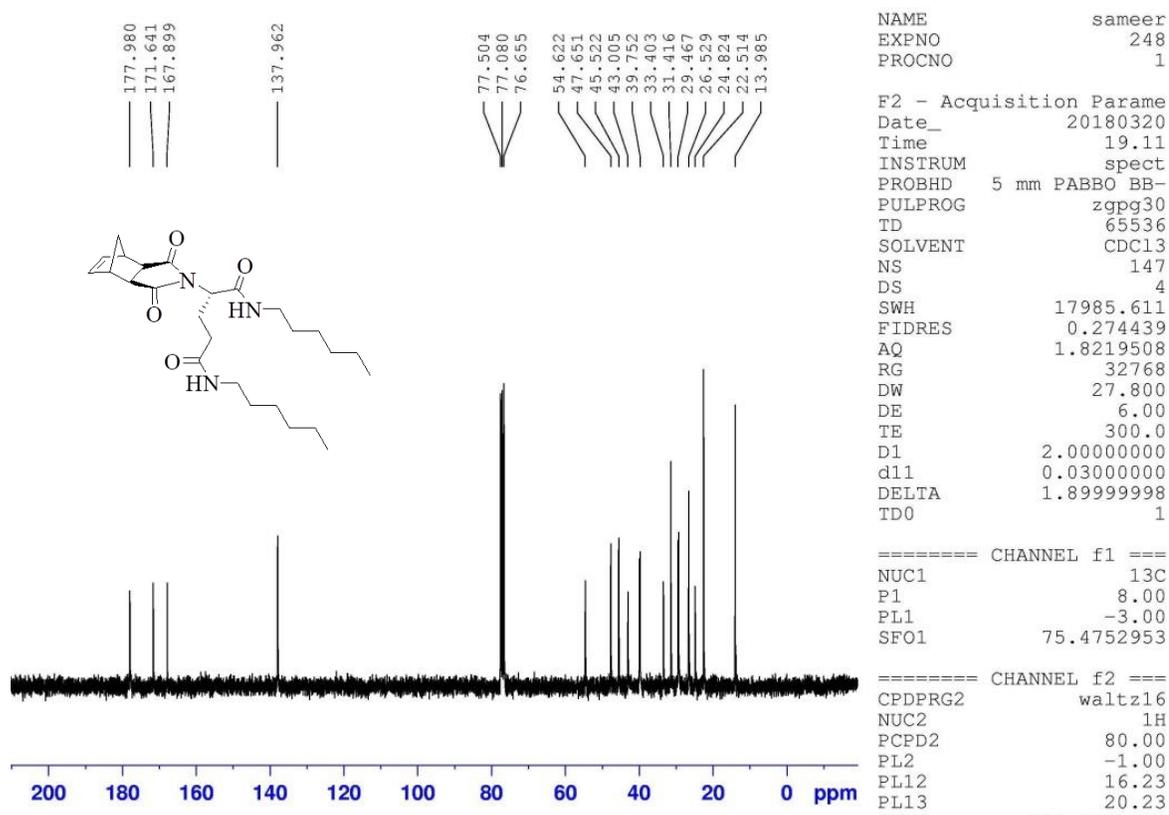


Figure S37: ¹³C NMR (75 MHz, CDCl₃) spectrum of **M3**

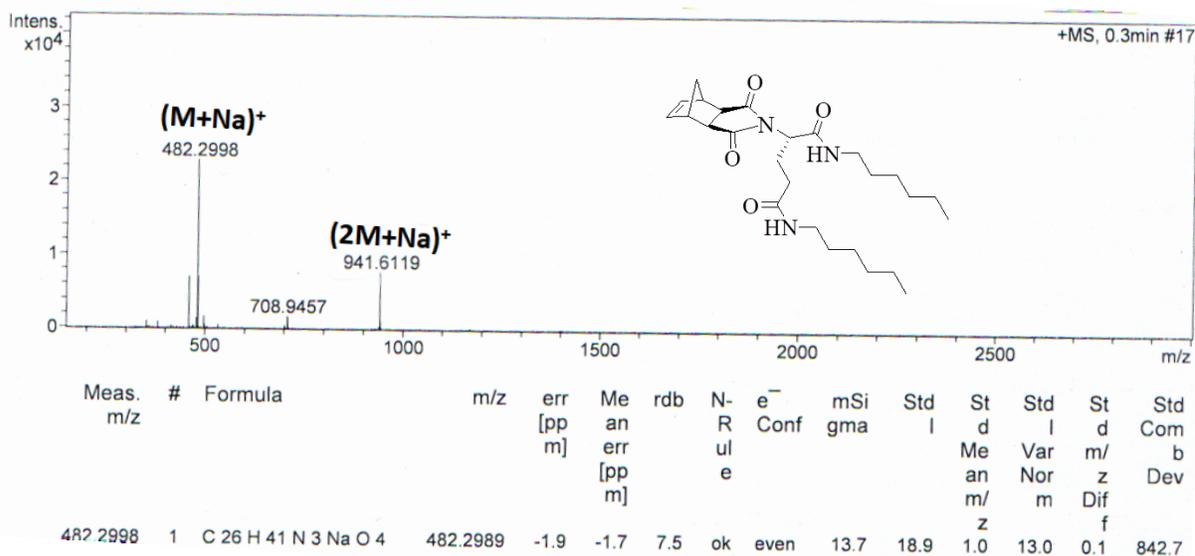


Figure S38: High Resolution Mass spectrum of **M3**

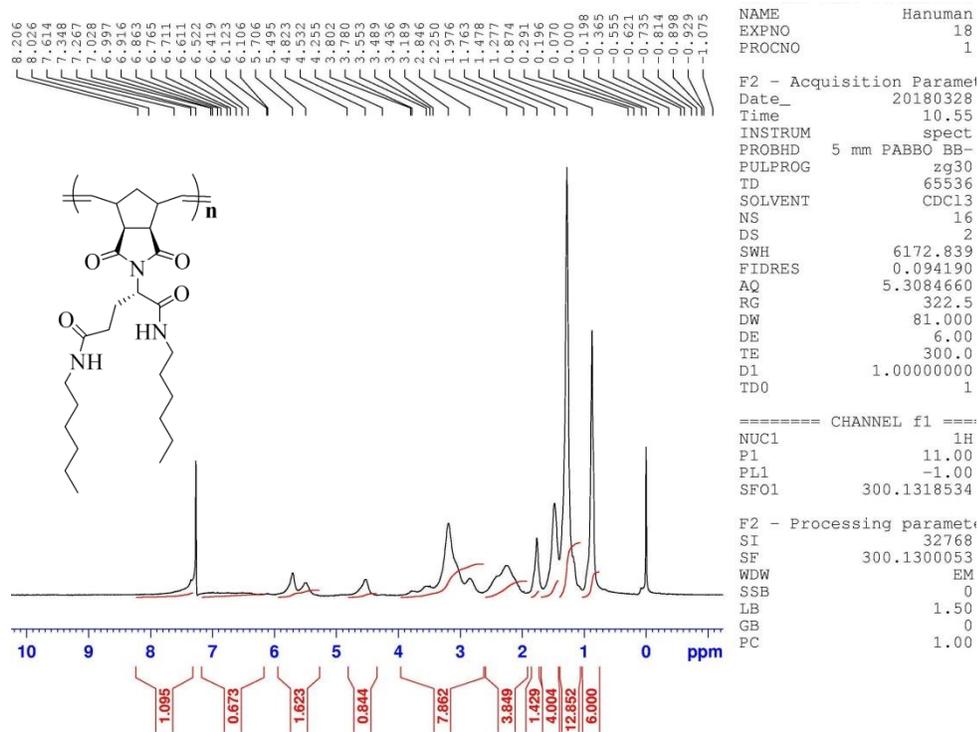


Figure S39: ¹H NMR (300 MHz, CDCl₃) spectrum of P3

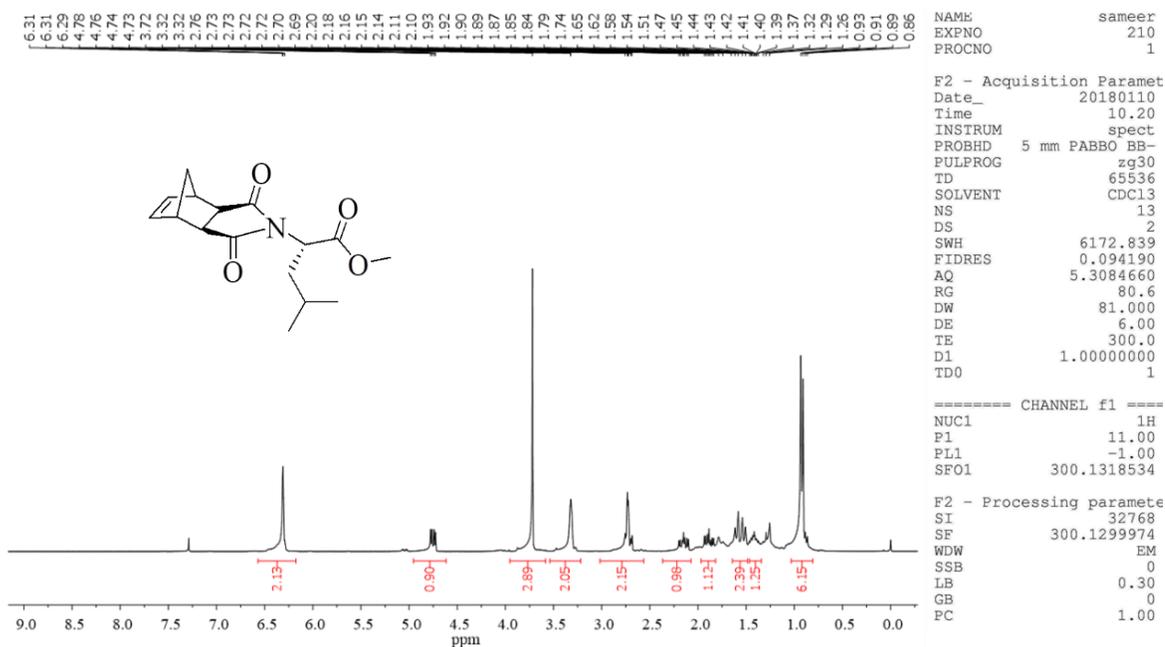


Figure S40: ¹H NMR (300 MHz, CDCl₃) spectrum of M4

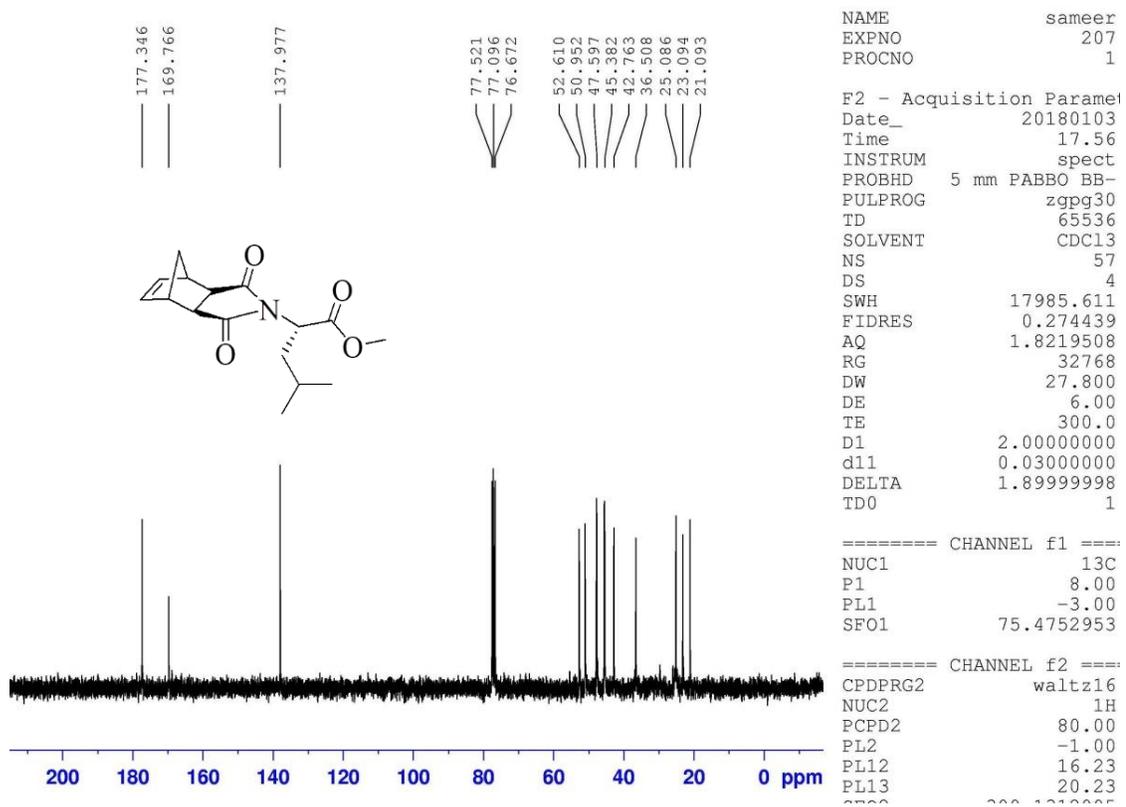


Figure S41: ¹³C NMR (75 MHz, CDCl₃) spectrum of M4

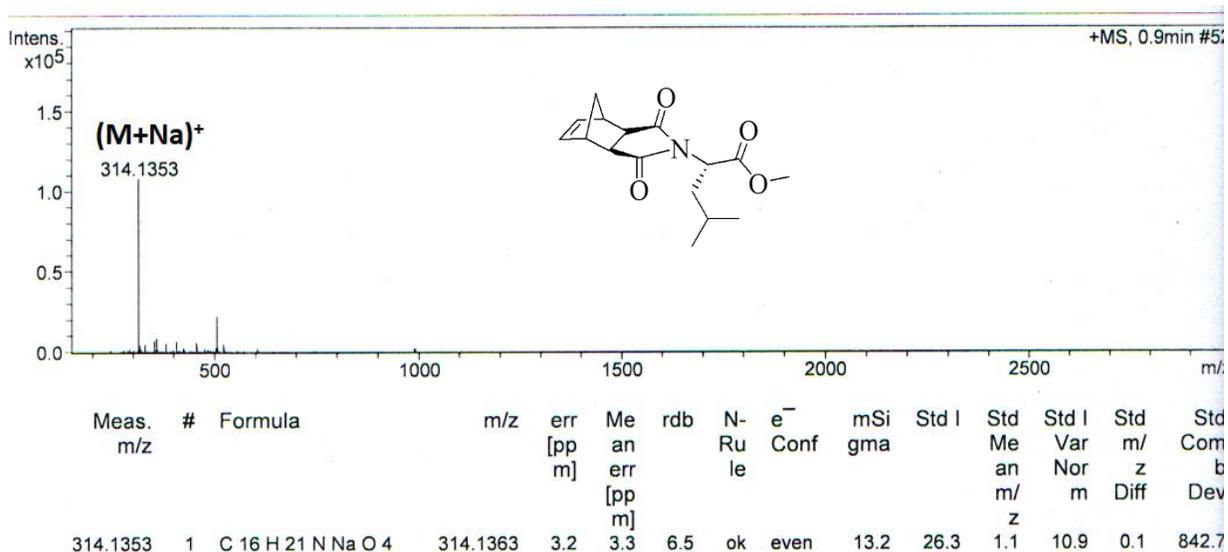


Figure S42: High Resolution Mass spectrum of M4

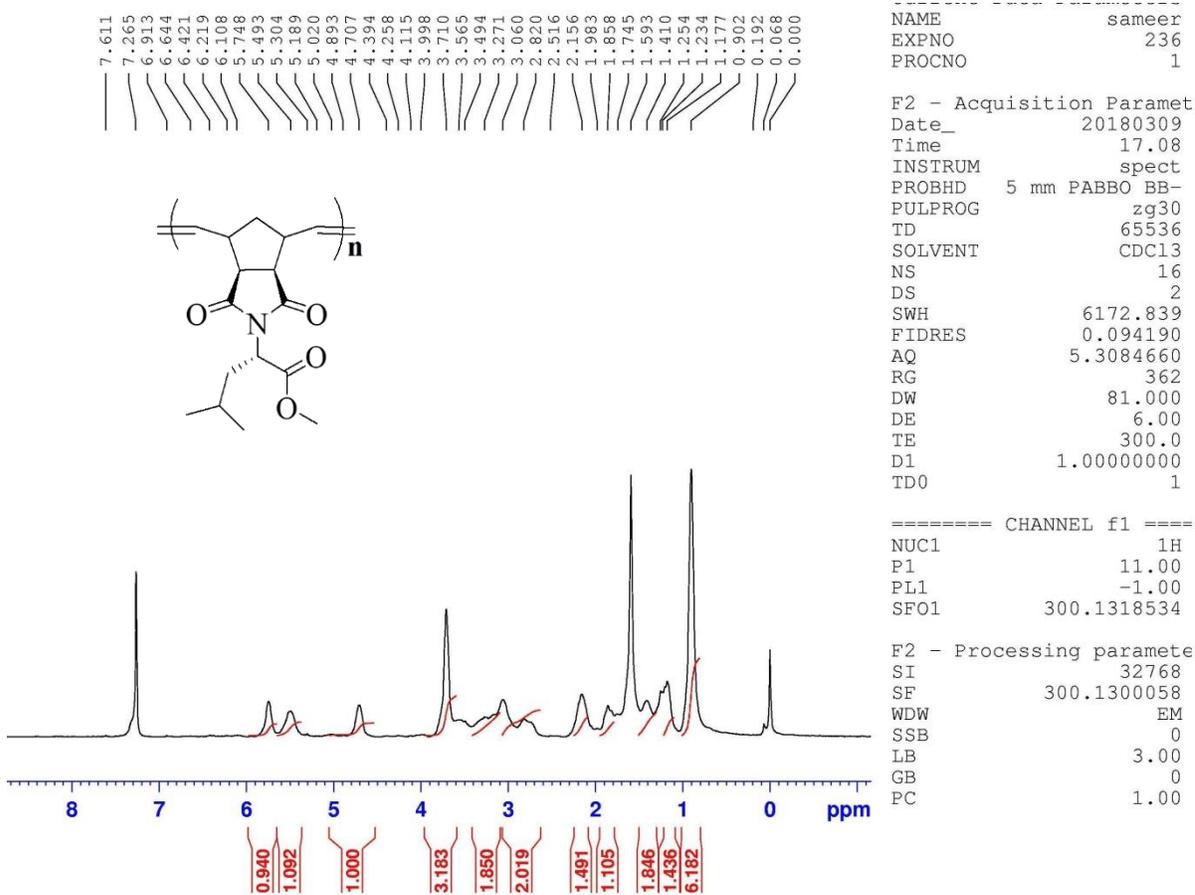


Figure S43: ¹H NMR (300 MHz, CDCl₃) spectrum of **P4**

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1. K.-D. Zhang, T.-Y. Zhou, X. Zhao, X.-K. Jiang and Z.-T. Li, *Langmuir*, 2012, **28**, 14839–14844.
2. S. Dhawan, M. B. Bijesh and V. Haridas, *Polymer*, 2018, **138**, 218–228.
3. S. Dhawan, S. Ghosh, R. Ravinder, S. S. Bais, S. Basak, N. M. A. Krishnan, M. Agarwal, M. Banerjee and V. Haridas, *Bioconjug. Chem.*, 2019, **30**, 2458–2468.