

Supporting Information for:
**Consequences of dispersity on the self-assembly of ABA-type amphiphilic
block co-oligomers**

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1. Materials and Methods

All chemicals were purchased from commercial sources and used without further purification. Water was demineralized prior to use. Dry solvents were obtained with an MBRAUN Solvent Purification System (MB-SPS). Toluene was dried over 4Å molecular sieves before use. Oven-dried glassware (120 °C) was used for all reactions carried out under argon atmosphere. Monodisperse MeOoEG₁₁-OH was purchased from Polypure. L-lactide was dried overnight at 50°C under vacuum prior to polymerization reactions. Reactions were followed by thin-layer chromatography (TLC) using 60-F254 silica gel plates from Merck and visualized by UV light at 254 nm and/or cerium molybdate (CeMo) staining. In all notations, LLA₁₆ denotes the 16-mer with exactly 16 lactic acid repeat units and a discrete molecular weight, whereas LLA_{~16} denotes the 16-mer with an average number of 16 repeat units and a molar mass dispersity of 1.20.

Automated column chromatography was conducted on a Grace Reveleris X2 Flash Chromatography System using Reveleris Silica Flash Cartridges.

NMR spectra were recorded on Bruker 400 MHz Ultrashield spectrometers (400 MHz for ¹H-NMR/ ¹³C NMR). Deuterated CDCl₃ was used as reference solvent and assigned with “ * ” in the spectrum. Chemical shifts (δ) are expressed in ppm, and are referred to the residual peak of the solvent. Peak multiplicity is abbreviated as s: singlet; d: doublet; t: triplet; dt: doublet of triplets; td: triplet of doublets; q: quartet; ABq: AB quartet; m: multiplet; bs: broad singlet.

Matrix assisted laser absorption/ionization-time of flight (MALDI-ToF) mass spectra were obtained on a Bruker Autoflex Speed spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as matrix.

Size exclusion chromatography (SEC) measurements were conducted on a Shimadzu Prominence-i LC-2030C 3D with a Shimadzu RID-20A Refractive Index detector, using an eluent flow of 1 mL min⁻¹ (THF or CHCl₃). The molecular weight was determined based on narrow dispersity polystyrene standards purchased from Polymer Source Inc.

Differential scanning calorimetry (DSC) data were collected on a DSC Q2000 from TA instruments, calibrated with an indium standard. The samples (4–8 mg), after drying for 3 hours under vacuum, were weighed directly into aluminum pans and hermetically sealed. The samples were initially heated to 180 °C and then subjected to two cooling/heating cycles from -60 °C to 180 °C with a rate of 10 °C min⁻¹. The data presented, represents the second heating/cooling cycle.

Bulk small angle X-ray scattering (SAXS) was performed on an instrument from Ganesha Lab. The flight tube and sample holder were all under vacuum in a single housing, with a GeniX-Cu ultra-low divergence X-ray generator. The source produced X-rays with a wavelength (λ) of 0.154 nm and a flux of 1×10^8 ph s⁻¹. All samples were annealed by heating at 130 °C in the vacuum oven and slowly cooled back to room temperature, smeared onto glass or kapton tape, and positioned directly in the beamline. Measurements were performed at room temperature. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 × 619 pixel resolution. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.431 m (MAXS mode). The instrument was calibrated with diffraction patterns from silver behenate.

General method for sample preparation for solution self-assembly studies: Polymers were weighed in 1.5 mL LCMS vial. To this measured volume of THF from the commercial source was added to make a stock solution of 20 mg/mL. The solution was sonicated for 10 sec to make sure there is no preformed aggregate.

From the stock, 80 μ L of the solution was taken in a separate vial. To this 720 μ L mineralized water (filtered with 0.2 μ m filter) was added dropwise to make a final concentration of 2 mg / mL in 1:9 THF:water. The solution was sonicated for 10 sec and again filtered with 0.45 μ m filter. Same protocol was followed for all the experiments unless otherwise stated.

Multi angle light scattering (MALS) experiments were performed on an ALVCGS-3 Compact Goniometer, in the angular range of 30 to 150 degrees. The incident beam was produced by a HeNe laser operating at 532 nm. The intensity signal was sent to an ALV5000 digital correlator, using a typical acquisition time of 100 s for each angle.

Micro-DSC: The measurements were taken in TA multi-cell micro differential scanning calorimeter (micro-DSC). 1.0 mL polymer solutions ($c = 2.5 - 5.0$ mg /mL in 1:9 THF : water) were prepared following the above procedure and transferred to the designed DSC pan for the machine, with a sealed cap. Unlike DLS, the final solutions were not filtered. For the reference pan, 1 mL 1:9 THF:water was used. The samples were initially cooled to 5 °C and then subjected to one heating / cooling cycle from 5 °C to 70 °C and back with a rate of 0.1 °C min⁻¹. The data presented, represents the first heating and second cooling runs.

Solution SAXS: Synchrotron radiation x-ray scattering data was collected at the BM29 BioSAXS beamline of the European Synchrotron Radiation Facility (Grenoble, France) operating at 12.5 keV. The scattering intensity was measured as a function of the momentum transfer vector $q = 4\pi(\sin\theta)/\lambda$, where $\lambda = 0.992$ Å is the radiation wavelength, and 2θ is the scattering angle. The beam size was set at about 700 µm × 700 µm, and two-dimensional scattering profiles were collected using a Pilatus 1M detector. Samples were measured at a fixed sample-to-detector distance of 2.867 m to cover an angular range of 0.025 to 5 nm⁻¹. Samples were loaded via an automated sample changer and flowed through a quartz capillary of 1.8 mm in diameter, while collecting 10 frames of 0.1 s with a reduced flux of 1012 photons s⁻¹. The averaged value of buffer scattering measured before and after the sample measurements was subtracted from the averaged sample scattering curve before fitting the data using SasView.

Cryogenic transmission electron microscopy (cryoTEM) was performed using samples with a concentration of 2 or 5 mg/mL. Vitrified films were prepared using a computer controlled vitrification robot (FEI VitrobotTM Mark III, FEI Company) at 22°C, and at a relative humidity of 100%. In the preparation chamber of the ‘Vitrobot’, 3 µl sample was applied on either a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH), or a Lacey film (LC200-CU, Electron Microscopy Sciences). These films were surface plasma treated just prior to use, with a Cressington 208 carbon coater operating at 5 mA for 40 s. Excess sample was removed by blotting using filter paper for 3 s at -3 mm, and the thin film thus formed was plunged (acceleration about 3 g) into liquid ethane just above its freezing point. Vitrified films were transferred into the vacuum of a Tecnai Sphera microscope with a Gatan 626 cryoholder and observed at temperatures below -170 °C. The microscope is equipped with an LaB₆ filament that was operated at 200 kV, and a bottom mounted 1024x1024 Gatan charged-coupled device (CCD)

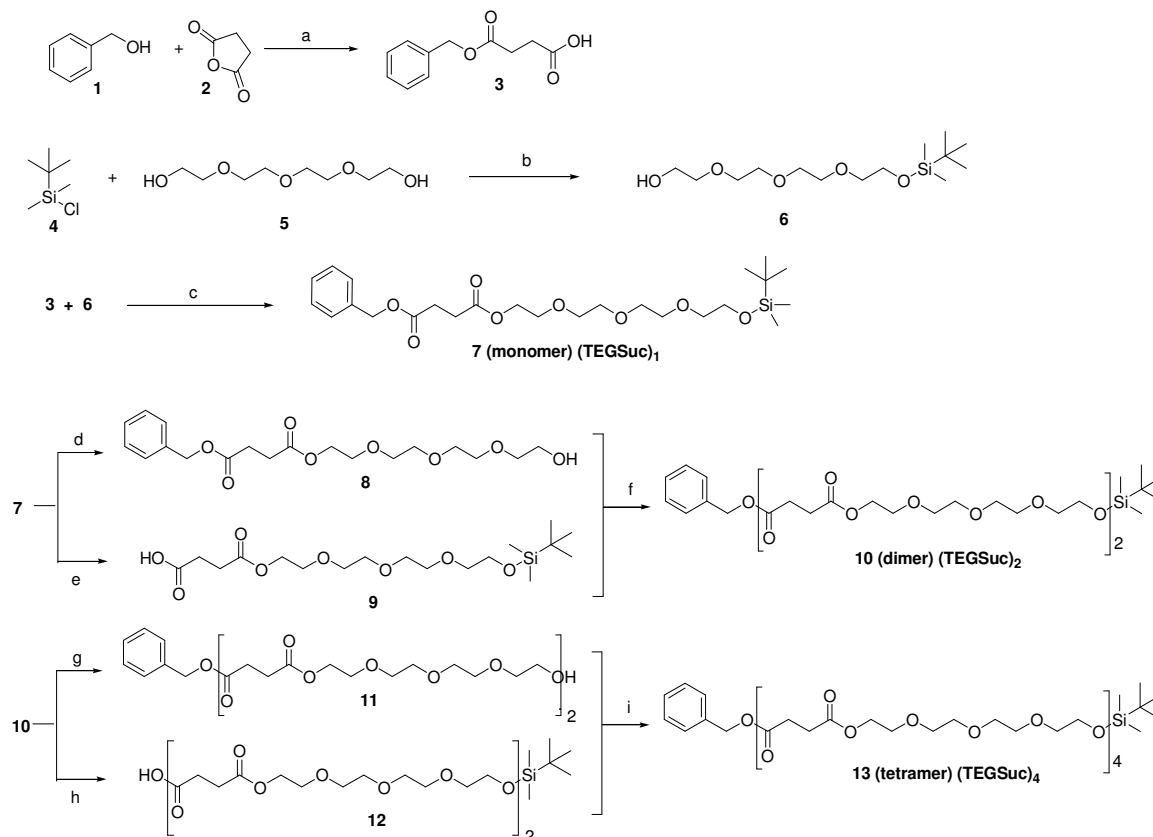
camera. Micrographs were taken at low dose conditions, starting at a magnification of 6500 with a defocus setting of 40 μm , and at a magnification of 25000 with defocus settings of 5, 10 and 12 μm .

TIRF microscopy: TIRF microscopy was performed on samples prepared by adding 2.0 mg of the polymer **P2** into a vial, followed by the addition of 0.1 mL THF affording a clear solution. Then 0.9 mL of deionized water was added while sonicating the solution. To visualize the aggregates, the dye Nile Red was added to the solution. The samples were not filtered before measuring. TIRF images were acquired with a Nikon N-STORM system. Nile Red was excited using a 561 nm laser. Fluorescence was collected by means of a Nikon $\times 100$, 1.4NA oil immersion objective and passed through a quad-band pass dichroic filter (97335 Nikon). Images were recorded with an EMCCD camera (ixon3, Andor, pixel size 0.17 μm).

Gelation Experiment: 5.0 mg of the polymer **P1**^{discrete} was taken in a vial. To this 0.1 mL THF was added to make a clear solution, followed by 0.9 mL of deionized water. The solution was gently heated with a heat gun and cooled back to room temperature. While heating, the solution showed lower critical solution temperature (LCST). On cooling it formed a transparent gel. The T_{gel} was observed between 42 – 48 $^{\circ}\text{C}$. Under identical conditions, no gelation was observed for disperse **P1**^{disperse} or for **P2**^{discrete}/**P2**^{disperse}.

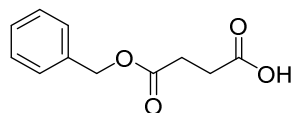
2. Synthesis Procedures

Scheme S1: Synthesis of the tetraethylene glycol succinate (TEGSuc) $_x$ oligomers by iterative deprotecting and coupling technique.



Conditions: a) DMAP, NEt₃, DCM, r.t., overnight, yield = 85%; b) Imidazole, DCM, 0 °C- r.t., overnight, yield = 91%; c) DPTS, EDC.HCl, DCM, 0 °C- r.t., overnight, yield = 70%; d) BF₃OEt₂, DCM, overnight, yield = 91%; e) H₂, Pd-C ethylene diamine complex, ethylacetate, 3 h, yield = 97%; f) DPTS, EDC.HCl, DCM, 0 °C- r.t., overnight, yield = 71%; g) BF₃OEt₂, DCM, overnight, yield = 83%; h) H₂, Pd-C ethylene diamine complex, ethylacetate, 3 h, yield = 99%; i) DPTS, EDC.HCl, DCM, 0 °C- r.t., overnight, yield = 70%

Synthesis of (3):

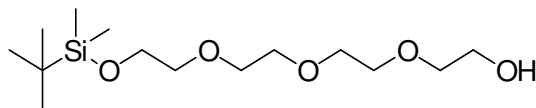


Compound **3** was prepared followed a slightly modified reported procedure.¹ Benzyl alcohol **1** (15.1 g, 140 mmol) and 5 mL of dry DCM were added to a 250 mL flask. After addition of DMAP (12.2 g, 99 mmol) and Et₃N (4.2 mL, 29 mmol) succinic anhydride **2** (10 g, 99 mmol) was added and the reaction mixture was stirred overnight under Argon flow at room temperature. The DCM layer was extracted twice 25 mL of 5% Na₂CO₃. The aqueous layer was acidified with 1.0 N HCl and the acidic layer was extracted twice with 100 mL of EtOAc, dried over MgSO₄ and evaporated to yield 17.5 g (85%) of **3** as a waxy off white solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 5H), 5.15 (s, 2H), 2.70 (td, *J* = 4.2, 1.1 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 177.95, 171.94, 135.69, 128.58, 128.30, 128.21, 77.22, 66.67, 28.90.

HRMS (MALDI-TOF): *m/z* calcd for C₁₁H₁₂O₄+Na⁺: 231.06 [M+Na]⁺; found 231.22

Synthesis of (6):

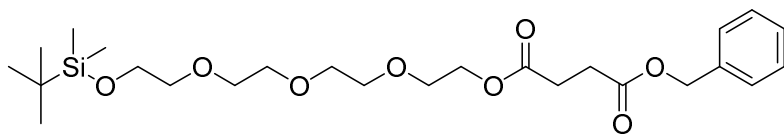


Tetraethylene glycol **5** (20 g, 103 mmol) and imidazole (1.67 g, 25 mmol) were dissolved in 10 mL dry DCM. The mixture was cooled down with an ice bath and TBDMS-Cl **4** (3.1 g, 20.5 mmol) dissolved in 32 mL of dry DCM was added dropwise over 2 hours. The reaction mixture was stirred at rt overnight. 30 mL of water were added and the organic layer was washed thrice with 30 mL of water to remove the excess **5**. Organic layer was dried over MgSO₄ and the solvent was evaporated yielding 5.45 g (91%) of **6** as a viscous colourless liquid.

¹H NMR (400 MHz, Chloroform-*d*) δ 3.93 – 3.46 (m, 16H), 2.55 (t, *J* = 5.7 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 77.25, 72.91, 72.65, 72.64, 72.55, 70.72, 70.67, 70.64, 70.62, 70.60, 70.53, 70.33, 70.00, 62.70, 61.69, 61.55, 25.91, 25.65, 18.35, 17.97, -3.59, -5.28, -5.29.

HRMS (MALDI-TOF): *m/z* calcd for C₁₄H₃₂O₅Si+Na⁺: 331.19 [M+Na]⁺; found 331.28

Synthesis of monomer (7) (TEGSuc)₁:

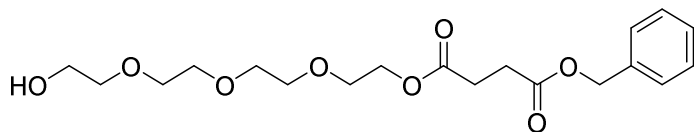


3 (11 g, 0.053 mol) and *N,N*-dimethylamino-pyridinium *p*-toluene sulfonate (DPTS) (6.91 g, 0.023 mol) were transferred into a Schlenk flask, degassed and cooled in an ice-bath. Dry DCM (40 mL) was added. When both solids were fully dissolved, EDC-HCl (13.5 g, 0.07 mol) was added as a solid. After 10 minutes, when the solution became clear, **6** (14.4 g, 0.047 mol) dissolved in 25 mL of dry DCM, was added. The reaction was stirred overnight at room temperature. The reaction mixture was diluted with 50 mL of DCM and extracted with water (3x 50 mL) and brine (1x 50 mL). The crude product was purified using automated column chromatography with a gradient of EtOAc (30-70%) in heptane in 10 column volume (CV) yielding **7** (16.4 g, 70%) as a colourless liquid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 5H), 5.13 (s, 2H), 4.24 – 4.22 (m, 2H), 3.76 (t, *J* = 5.4 Hz, 2H), 3.68 – 3.64 (m, 10H), 3.54 (t, *J* = 5.5 Hz, 2H), 2.68 (s, 4H), 0.88 (s, 9H), 0.06 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 172.20, 172.04, 135.79, 128.60, 128.55, 128.30, 128.25, 128.20, 128.17, 77.24, 72.67, 70.75, 70.73, 70.69, 70.67, 70.60, 69.04, 66.53, 63.87, 62.71, 29.15, 29.06, 28.62, 28.57, 25.94, 18.37, -5.26.

HRMS (MALDI-TOF): *m/z* calcd for C₂₅H₄₂O₈Si+Na⁺: 521.26 [M+Na]⁺; found 521.28

Synthesis of (8):



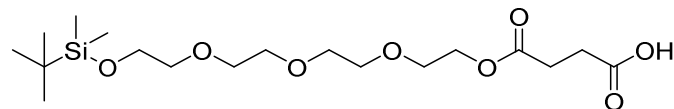
7 (3.0 g, 6.016 mmol) was dissolved in 12 mL dry DCM under argon atmosphere and cooled in an ice bath. To this BF₃ etherate (3.0 mL, 24.06 mmol) was added dropwise and the reaction was stirred overnight. The reaction mixture was washed with 10 mL sat NaHCO₃:brine (3:1) followed by 20 mL brine. After drying over MgSO₄, the crude product was purified using automated column chromatography with a gradient of EtOAc (50-100%) in heptane in 20 CV yielding the product (2.3 g, 99%) as a viscous colorless liquid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.34 (m, 5H), 5.13 (s, 2H), 4.26 – 4.23 (m, 2H), 3.72 – 3.60 (m, 14H), 2.69 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 172.24, 172.10, 135.80, 128.57,

128.27, 128.22, 77.21, 72.51, 70.67, 70.58, 70.56, 70.37, 69.08, 66.55, 63.84, 61.79, 29.16, 29.06.

HRMS (MALDI-TOF): m/z calcd for $C_{19}H_{28}O_8+Na^+$: 407.18 $[M+Na]^+$; found 407.21

Synthesis of (9):

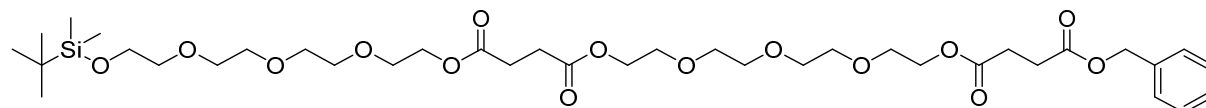


8 (900 mg, 1.8 mmol) was dissolved in 3 mL EtOAc and purged with N_2 . Pd/C – ethylene diamine complex (96 mg, 0.09 mmol of Pd) was added and the reaction was stirred at rt with H_2 flow. After completion the reaction mixture was filtered through celite yielding **9** (712 mg, 97%). 1H NMR (400 MHz, Chloroform-*d*) δ 4.31 – 4.22 (m, 2H), 3.77 (t, $J = 5.3$ Hz, 2H), 3.73 – 3.61 (m, 10H), 3.58 (t, $J = 5.3$ Hz, 2H), 2.86 – 2.40 (m, 4H), 0.89 (s, 9H), 0.09 – 0.03 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 77.20, 72.58, 70.77, 70.63, 70.50, 70.41, 69.04, 63.86, 62.64, 61.57, 29.22, 29.09, 25.92, 25.64, -3.58, -5.30.

HRMS (MALDI-TOF): m/z calcd for $C_{18}H_{36}O_8Si+Na^+$: 431.22 $[M+Na]^+$; found 431.23

Note: For selective deprotection of benzyl ester in presence of TBDMS-ether, 10% Pd/C-ethylene diamine complex was used instead of commercial 10% Pd/C which would otherwise cleave the TBDMS-ether.² 10% Pd/C-ethylene diamine complex was prepared according to reported procedure.³ Commercially available 10% Pd/C (2.1 g, 1.98 mmol of Pd) and ethylene diamine (11 mL, 164 mmol) were taken with 7 mL MeOH and stirred for 48 h under argon flow. Excess ethylene diamine was filtered off. The solid was purified by repeated washing with MeOH followed by diethyl ether. The complex was dried under vacuum for 24 h. It was used as obtained without further characterization.

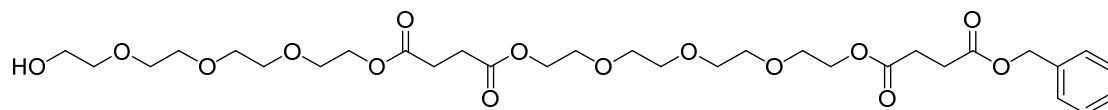
Synthesis of the dimer (10) (TEGSuc)₂:



9 (2.51 g, 6.14 mmol) and DPTS (770 mg, 2.61 mmol) were transferred into a schlenk flask, degassed and cooled in an ice-bath. Dry DCM (12 mL) was added. When both solids were fully

dissolved, EDC-HCl (1.47 g, 7.67 mmol) was added as a solid. After 10 minutes, when the solution became clear, **8** (1.968 g, 5.12 mmol) dissolved in 5 mL of dry DCM, was added. The reaction was stirred overnight at room temperature. The reaction mixture was diluted with 10 mL of DCM and extracted with sat. NaHCO₃ (5 mL) and brine (5 mL). After drying over Na₂SO₄, the crude product was purified using automated column chromatography with a gradient of EtOAc (45-100%) in heptane in 10 CV yielding the dimer **10** (2.8 g, 71%) as a viscous colourless liquid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 (m, 5H), 5.13 (s, 2H), 4.24 (m, 6H), 3.82 – 3.50 (m, 26H), 2.67 (d, *J* = 10.5 Hz, 8H), 0.89 (s, 9H), 0.06 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 172.25, 172.21, 172.06, 135.78, 128.56, 128.26, 128.21, 77.22, 72.68, 70.74, 70.70, 70.61, 70.59, 69.07, 69.05, 66.54, 63.87, 63.86, 63.84, 62.71, 29.14, 29.05, 28.98, 25.94, 18.38, -5.25. HRMS (MALDI-TOF): *m/z* calcd for C₃₇H₆₂O₁₅Si+Na⁺: 796.41 [M+Na]⁺; found 797.41

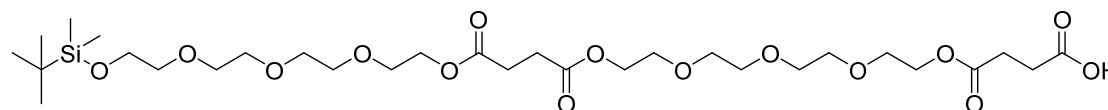
Synthesis of (11):



10 (723 mg, 0.93 mmol) was dissolved in 0.5 mL dry DCM under argon atmosphere and cooled with an ice bath. To this BF₃ etherate (0.47 mL, 3.73 mmol) was added dropwise and the reaction was stirred for 5 h at rt. The reaction mixture was diluted with 2 mL of DCM and washed with 75:25 NaHCO₃:brine and dried over MgSO₄. After evaporation of DCM, the crude product was purified using automated column chromatography with 20% MeOH in EtOAc yielding **11** (511 mg, 83%) as a viscous faint yellow liquid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 5H), 5.13 (s, 2H), 4.34 – 4.15 (m, 6H), 3.80 – 3.55 (m, 26H), 2.67 (d, *J* = 8.9 Hz, 8H), 2.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 172.29, 172.27, 172.22, 172.07, 135.78, 128.56, 128.26, 128.20, 77.24, 72.55, 70.65, 70.60, 70.58, 70.56, 70.53, 70.33, 69.08, 69.06, 69.04, 66.54, 63.85, 63.82, 61.75, 53.43, 29.14, 29.05, 28.99. HRMS (MALDI-TOF): *m/z* calcd for C₃₁H₄₈O₁₅+Na⁺: 683.30 [M+Na]⁺; found 683.29

Synthesis of (12):

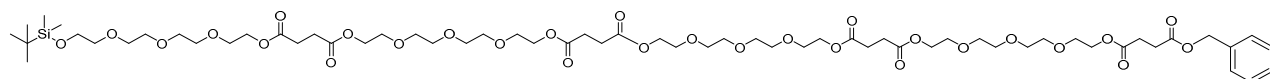


10 (290 mg, 0.37 mmol) was dissolved in 5 mL EtOAc and purged with N₂. Pd/C – ethylene diamine complex (21 mg, 0.015 mmol of Pd) was added and the reaction was stirred at rt with H₂ flow. After completion, the reaction mixture was filtered through celite yielding **12** (253 mg, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.30-4.21 (m, 6H), 3.76 (t, *J* = 5.4 Hz, 2H), 3.74 – 3.61 (m, 22H), 3.56 (t, *J* = 5.5 Hz, 2H), 2.65 (m, 8H), 0.89 (s, 9H), 0.06 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 174.33, 172.49, 172.44, 172.13, 77.36, 72.80, 70.95, 70.86, 70.80, 70.71, 70.62, 70.56, 69.21, 69.17, 69.12, 64.02, 63.95, 63.90, 62.85, 29.72, 29.14, 26.08, 18.52, -5.11.

HRMS (MALDI-TOF): *m/z* calcd for C₃₀H₅₆O₁₅Si+Na⁺: 707.34 [M+Na]⁺; found 707.41

Synthesis of the tetramer (**13**) (TEGSuc)₄:

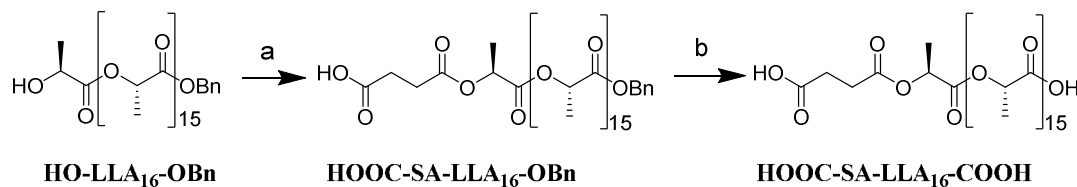


12 (123 mg, 0.18 mmol), **11** (99.2 mg, 0.15 mmol) and DPTS (31 mg, 0.11 mmol) were transferred into a schlenk flask, degassed and cooled in an ice-bath. Dry DCM (1.5 mL) was added. When all solids were fully dissolved, EDC-HCl (67 mg, 0.35 mmol) was added as a solid. The reaction was stirred overnight at room temperature. The reactions mixture was diluted with 2 mL of DCM and extracted with brine (1x 3 mL). The crude product was purified using automated column chromatography with a gradient of EtOAc (80 – 100 %) in heptane in 10 CV yielding **13** (140 mg, 70%) as a faint yellow colourless liquid.

¹H NMR (399 MHz, Chloroform-*d*) δ 7.34 (m, 5H), 5.13 (d, *J* = 1.4 Hz, 2H), 4.24 (t, *J* = 4.9 Hz, 14H), 3.80 – 3.51 (m, 52H), 2.66 (d, *J* = 9.3 Hz, 16H), 0.89 (d, *J* = 1.5 Hz, 9H), 0.06 (d, *J* = 1.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 172.24, 172.20, 172.04, 135.79, 128.56, 128.26, 128.20, 77.23, 72.68, 70.74, 70.70, 70.61, 70.58, 69.07, 69.05, 66.53, 63.87, 63.84, 62.71, 29.14, 29.05, 28.98, 25.94, 18.38, -5.25.

HRMS (MALDI-TOF): *m/z* calcd for C₆₁H₁₀₂O₂₉Si+Na⁺: 1349.63 [M+Na]⁺; found 1349.98

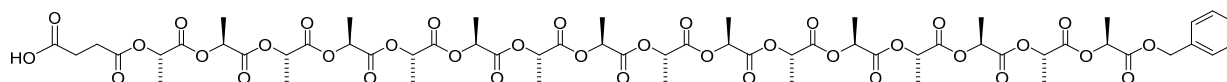
Scheme S2: Synthesis of monodisperse telechelic L-lactic acid 16-mer (LLA₁₆) based diacid linker.



Conditions: a) DMAP, Et₃N, succinic anhydride, DCM, 0 °C- r.t., overnight, yield = 71%; b) H₂, Pd-C, EtOAc, 3 h-on, yield = 91%.

HO-LLA₁₆-Bn was synthesized according to a reported procedure.⁴

Synthesis of HOOC-SA-LLA₁₆-OBn:

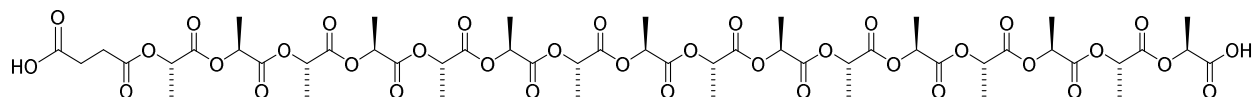


HO-LLA₁₆-OBn (1.551 g, 1.229 mmol) was dissolved in dry DCM under Argon atmosphere and cooled to 0°C. Then triethylamine (0.18 mL, 1.229 mmol) and 4-dimethylaminopyridine (DMAP) (343 mg, 2.808 mmol) were added. When everything was dissolved, the succinic anhydride (280 mg, 2.798 mmol) was added. The reaction mixture was stirred overnight. The reaction mixture was washed with 10 mL 0.1M HCl and thrice with the 50 mL saturated brine. The organic layer was dried over MgSO₄ and the solvent was evaporated. The crude was purified using automated column chromatography using DCM/methanol (100/0 to 10/10) resulting in **HOOC-SA-LLA₁₆-OBn** (1.204 g, 71%) as a white powder.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.28 (m, 5H), 5.26 – 5.02 (m, 18H), 2.86 – 2.53 (m, 4H), 1.64 – 1.42 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.76, 155.20, 128.78, 128.69, 128.40, 77.36, 69.17, 28.37, 16.80.

HRMS (MALDI-TOF): *m/z* calcd for C₅₉H₇₆O₃₆+Na⁺: 1383.41 [M+Na]⁺; found 1383.42

Synthesis of HOOC-SA-LLA₁₆-COOH:

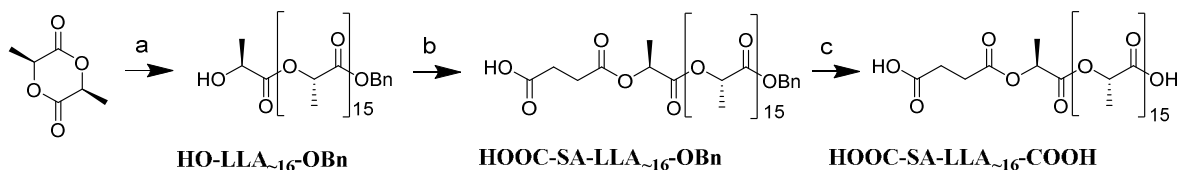


HOOC-SA-LLA₁₆-OBn (1.204g, 0.88mmol) was dissolved in 5 mL EtOAc and flushed with N₂. Pd/C (6.43mg, 0.05mmol) was added and the reaction was stirred overnight under H₂ atmosphere. Filtration over celite yielded **HOOC-SA-LLA₁₆-COOH** (1.025 g, 91 %) as a fine white powder.

¹H NMR (400 MHz, Chloroform-*d*) δ 5.25 – 5.05 (m, 16H), 2.80 – 2.62 (m, 4H), 1.76-1.38 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.69, 77.36, 69.19, 16.80.

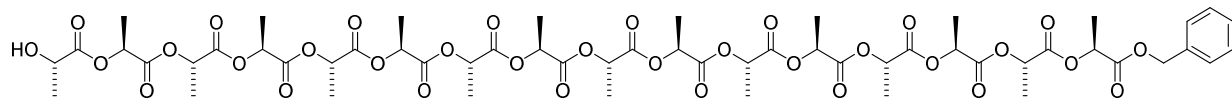
HRMS (MALDI-TOF): *m/z* calcd for C₅₂H₇₀O₃₆+Na⁺: 1293 [M+Na]⁺; found 1293.35

Scheme S3: Synthesis of disperse telechelic L-lactic acid 16-mer (LLA_{~16}) based diacid linker.



Conditions: a) BnOH, DBU, benzoic acid, DCM, rt, 2h, 94% ; b) DMAP, Et₃N, succinic anhydride, DCM, 0 °C- r.t., overnight, yield = 71%; c) H₂, Pd-C, EtOAc, 3 h-on, yield = 91%.

Synthesis of HO-LLA_{~16}-OBn:



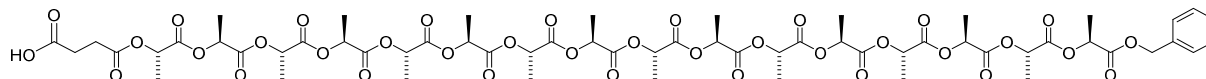
L-lactide (6.293 g, 0.044 mol), DBU (5 μL, 0.046 mmol) were dissolved in dry DCM (6 mL) and benzyl alcohol (502 μL, 0.0048 mol) was added. After 2 hours all benzyl alcohol has been

consumed and the reaction was quenched with benzoic acid (160 mg, 0.0013 mol). The crude was purified by automated column chromatography using a gradient of MeOH (0-15%) in DCM yielding **HO-LLA₁₆-OBn** (5.9 g, 94%) as an off-white pasty solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39-7.30 (m, 5H), 5.22 – 5.10 (m, 17H), 4.29-4.21 (m, 1H), 2.70 (s, 1H), 1.63 – 1.45 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.75, 169.69, 128.77, 128.42, 128.40, 69.17, 16.80.

From end-group analysis, by comparing integration of benzyl protons with lactic acid, the degree of polymerization (DP) was estimated to be 16.5.

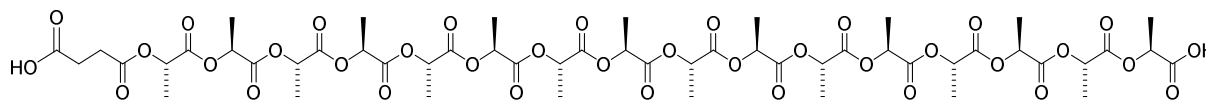
Synthesis of HOOC-SA-LLA₁₆-OBn:



HO-LLA₁₆-Bn (5.83 g, 4.62 mol) and 4-dimethylaminopyridine (1.13 g, 9.24 mol) were dissolved in 25 mL dry DCM under argon atmosphere. Then triethylamine (150 μL, 1.13 mmol) was added. When everything was dissolved, the succinic anhydride (613 μL, 4.62 mmol) was added followed by the addition of 5 mL dry DCM. The reaction mixture was stirred overnight. The reaction mixture was washed twice with 10 mL 0.1 M HCl and collected with 25 mL DCM. The organic layer was washed with brine (15 mL) and dried over MgSO₄ and evaporated in vacuo. Then the product was purified by automated column chromatography using a gradient of MeOH (0-30%) in DCM yielding **HOOC-SA-LLA₁₆-OBn** (4.43 g, 70.4%) as an off-white pasty solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39-7.30 (m, 5H), 5.25 – 4.99 (m, 16H), 2.86 – 2.62 (m, 4H), 1.66 – 1.45 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.76, 128.77, 128.68, 128.40, 77.37, 69.17, 16.90, 16.80, 16.73.

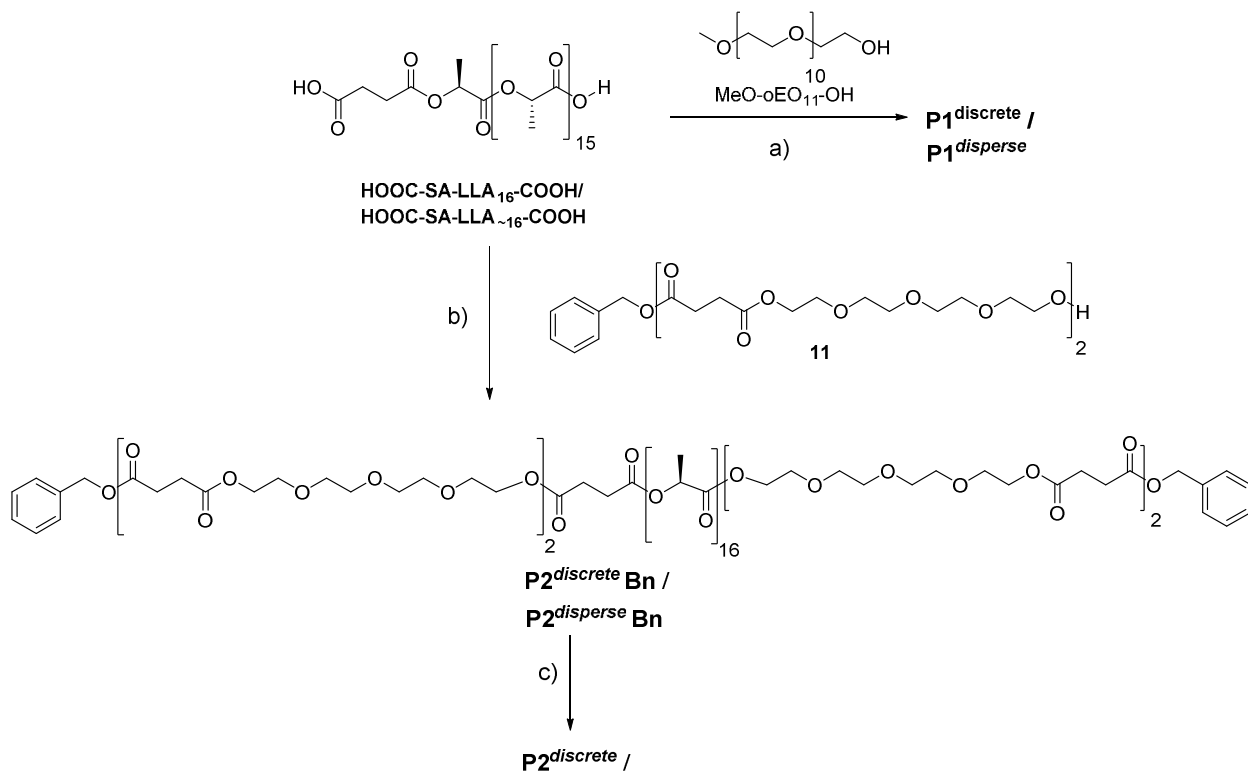
Synthesis of HOOC-SA-LLA₁₆-COOH:



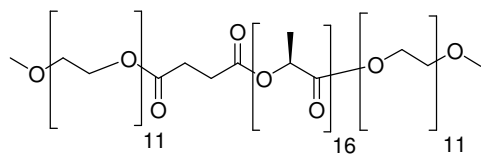
HOOC-SA-LLA-₁₆-OBn (4.2 g, 3.09 mmol) was dissolved in 120 mL EtOAc and purged with N₂. Pd/C (99 mg, 0.092 mmol of Pd) was added and the reaction stirred at RT with H₂ flow. After completion the reaction mixture was filtered through Celite yielding **HOOC-SA-LLA-₁₆-COOH** (3.15 g, 80.2 %) as an off-white pasty solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 5.21-5.09 (m, 16H), 2.79-2.62 (m, 4H), 1.66-1.50 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.74, 77.36, 69.18, 68.86, 60.57, 21.21, 16.80, 14.35.

Scheme S4: Synthesis of discrete (**P1^{discrete}/P2^{discrete}**) and disperse (**P1^{disperse}/P2^{disperse}**) amphiphiles.



Synthesis of P1^{discrete}:

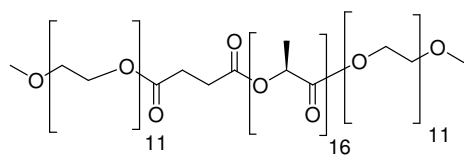


HOOC-SA-LLA₁₆-COOH (103 mg, 0.081 mmol) was dissolved in 2 mL dry DCM under Argon atmosphere and cooled to 0°C. Then DPTS (23.6 mg, 0.080 mmol) and EDC-HCl (60.5mg, 0.316mmol) were added. When everything was dissolve, **MeO-oEG₁₁-OH** (92 mg, 0.18 mmol) was added with 2 mL of dry DCM. The reaction mixture was stirred overnight. Full conversion was confirmed by TLC (hept/EtAc 50:50; CeMo stain).The reaction mixture was washed with 10 mL 0.1 M HCl and three times with the 50 mL saturated brine. Organic layer was dried with MgSO₄ and evaporated. The crude was purified using automated column chromatography using DCM/methanol (100/0 to 90/10) yielding **P1^{discrete}** (105 mg, 57%) as white solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 5.16 (m, 16H), 4.40 – 4.14 (m, 4H), 3.74 – 3.60 (m, 84H), 3.58 – 3.50 (m, 4H), 3.38 (s, 6H), 2.82 – 2.53 (m, 4H), 1.66 – 1.45 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.76, 77.36, 72.10, 70.73, 69.16, 59.20, 16.81.

HRMS (MALDI-TOF): *m/z* calcd for C₉₈H₁₆₂O₅₈+Na⁺: 2289.97 [M+Na]⁺; found 2291.02

Synthesis of **P1^{disperse}**:

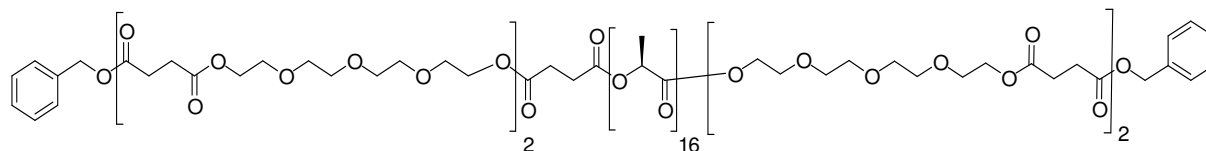


HOOC-SA-LLA₁₆-COOH (235 mg, 0.185 mmol) was dissolved in 2 mL dry DCM under Argon atmosphere and cooled to 0°C. Then DMAP (54 mg, 0.185 mmol) and EDC-HCl (141.5 mg, 0.74 mmol) were added. When everything was dissolve, **MeO-PEG₁₁-OH** (210 mg, 0.407 mmol) was added with 2 mL of dry DCM. The reaction mixture was stirred overnight. Full conversion was confirmed by TLC (hept/EtAc 50:50; CeMo stain).The reaction mixture was washed with 10mL 0.1M HCl and thrice with the 50 mL saturated brine. Organic layer was dried

with MgSO₄ and evaporated. The crude was purified using automated column chromatography using DCM/methanol (100/0 to 90/10) yielding **P1^{disperse}** (304 mg, 72%) as off-white pasty solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 5.36 – 4.90 (m, 16H), 4.38 – 4.12 (m, 4H), 3.96 – 3.42 (m, 88H), 3.38 (s, 6H), 2.89 – 2.53 (m, 4H), 1.84 – 1.29 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 172.05, 171.70, 170.14, 170.03, 169.71, 169.58, 169.52, 77.36, 71.92, 70.60, 70.59, 70.56, 70.49, 69.24, 69.03, 69.00, 68.94, 68.87, 68.79, 68.54, 64.44, 63.88, 59.02, 28.86, 28.77, 16.79, 16.75, 16.65.

GPC (THF, RI, calibrated using PS) $M_n = 3114$ g/ mol; $M_w = 3717$ g/ mol; $\bar{D} = 1.19$

Synthesis of **P2^{discrete} Bn**:

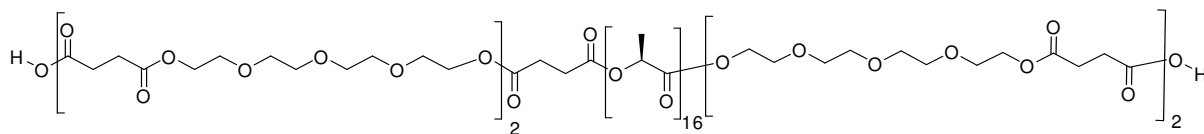


HOOC-SA-LLA₁₆-COOH (159 mg, 0.125 mmol) and DMAP (35 mg, 0.118 mmol) were transferred into a schlenk flask, degassed and cooled in an ice-bath. Dry DCM (2 mL) was added. When both solids were fully dissolved, EDC-HCl (68 mg, 0.35 mmol) was added as a solid. After 10 minutes, when the solution became clear, **11** (190 mg, 0.29 mmol) dissolved in 0.5 mL of dry DCM, was added. The reaction was stirred overnight at room temperature. The reactions mixture was diluted with 3 mL of DCM and washed with brine (5 mL). After drying over Na₂SO₄, the crude product was purified using automated column chromatography with a gradient of MeOH (0-10%) in EtOAc in 10 CV yielding **P2^{discrete} Bn** (151 mg, 47%) as a sticky viscous off-white solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 10H), 5.23 – 5.06 (m, 20H), 4.34 – 4.19 (m, 16H), 3.88 – 3.47 (m, 48H), 2.79 – 2.58 (m, 20H), 1.68 – 1.42 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.60, 128.57, 128.27, 128.21, 77.21, 70.62, 70.59, 69.06, 69.01, 66.54, 63.85, 29.15, 29.05, 28.98, 16.65.

HRMS (MALDI-TOF): m/z calcd for C₁₁₄H₁₆₂O₆₄+Na⁺: 2577.94 [M+Na]⁺; found 2578.96

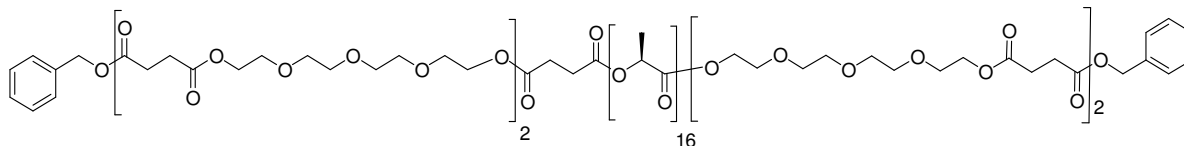
Synthesis of **P2^{discrete}**:



P2^{discrete} Bn (70 mg, 0.03 mmol) was dissolved in 2 mL EtOAc and purged with N₂. Pd/C (1.3 mg, 0.001 mmol of Pd) was added and the reaction was stirred at rt with H₂ flow. After completion the reaction mixture was filtered through celite yielding **P2^{discrete}** (74 mg, 99%) as an off-white colored paste.

¹H NMR (400 MHz, Chloroform-*d*) δ 5.17 (q, *J* = 7.1 Hz, 16H), 4.38 – 4.12 (m, 16H), 3.86 – 3.45 (m, 48H), 2.83 – 2.51 (m, 20H), 1.67 – 1.45 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 172.44, 169.88, 169.76, 77.36, 70.75, 70.73, 70.71, 70.61, 70.53, 69.21, 69.16, 69.10, 64.03, 64.00, 63.95, 63.89, 29.85, 29.13, 16.80. HRMS (MALDI-TOF): *m/z* calcd for C₁₀₀H₁₅₀O₆₄+Na⁺: 2397.85 [M+Na]⁺; found 2398.87

Synthesis of **P2^{disperse} Bn**:



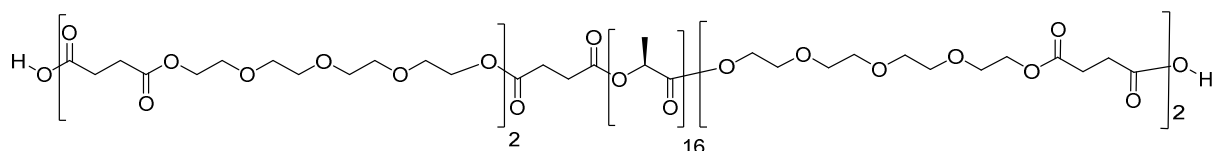
HOOC-SA-LLA₋₁₆-COOH (200 mg, 0.16 mmol) and DMAP (47 mg, 0.16 mmol) were transferred into a schlenk flask, degassed and cooled in an ice-bath. Dry DCM (2.5 mL) was added. When both solids were fully dissolved, EDC-HCl (90 mg, 0.47 mmol) was added as a solid. After 10 minutes, when the solution became clear, **11** (239 mg, 0.36 mmol) dissolved in 0.5 mL of dry DCM, was added. The reaction was stirred overnight at room temperature. The reactions mixture was diluted with 3 mL of DCM and washed with brine (5 mL). After drying over Na₂SO₄, the crude product was purified using automated column chromatography with a gradient of MeOH (0-10%) in EtOAc in 10 CV yielding **P2^{disperse} Bn** (166 mg, 41%) as an off-white paste.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 10H), 5.30 – 4.95 (m, 20H), 4.38 – 4.13 (m, 16H), 3.83 – 3.52 (m, 48H), 2.83 – 2.56 (m, 20H), 1.73 – 1.43 (m, 48H). ¹³C NMR (100

MHz, CDCl₃) δ 172.36, 169.75, 128.71, 128.41, 128.36, 77.48, 77.36, 77.16, 76.84, 70.76, 69.20, 69.16, 66.69, 64.00, 29.29, 29.19, 29.12, 16.80, 0.15.

GPC (THF, RI detector, calibrated using PS): $M_n = 4505$ g/ mol; $M_w = 4673$ g/ mol; $D = 1.04$

Synthesis of **P2^{disperse}**:

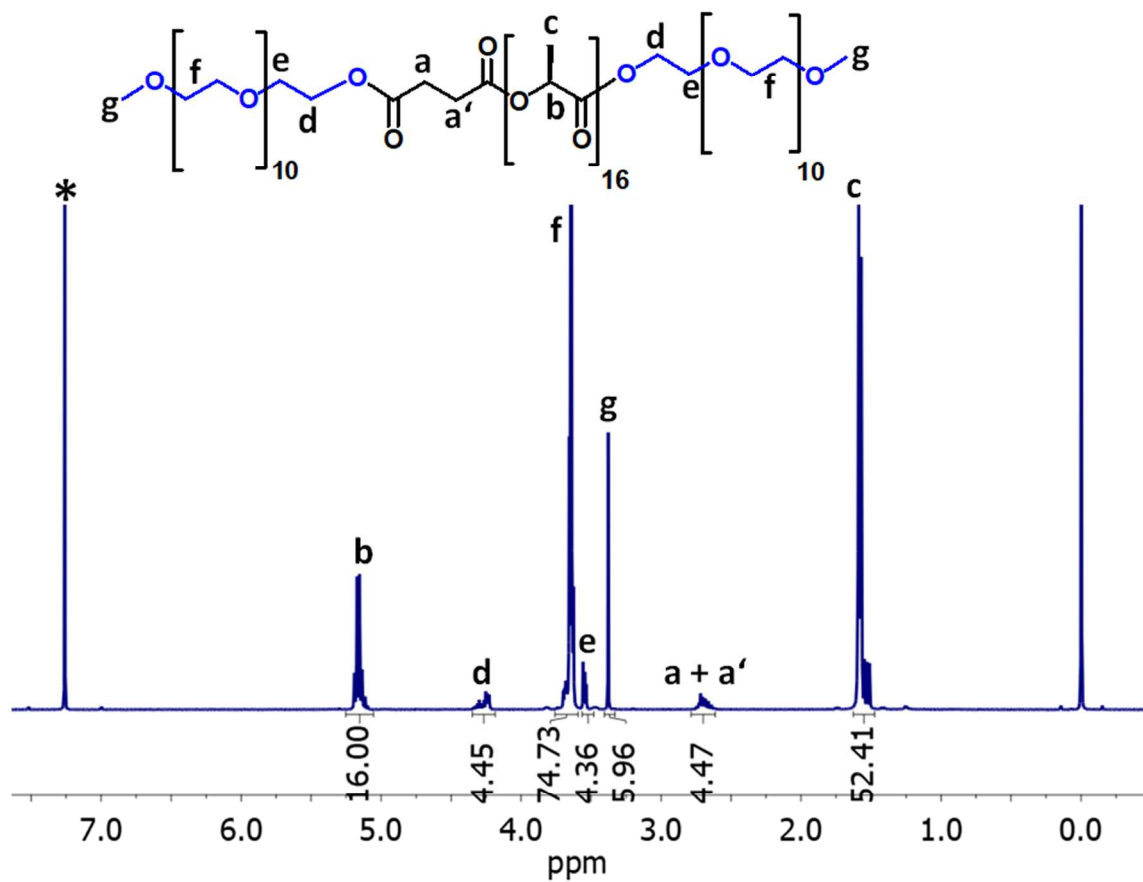


P2^{disperse}Bn (80 mg, 0.031 mmol) was dissolved in 1.5 mL EtOAc and purged with N₂. Pd/C (1.5 mg, 0.001 mmol of Pd) was added and the reaction stirred at rt with H₂ flow. After completion the reaction mixture was filtered through celite yielding **P2^{disperse}** (57 mg, 77%) as a white solid.

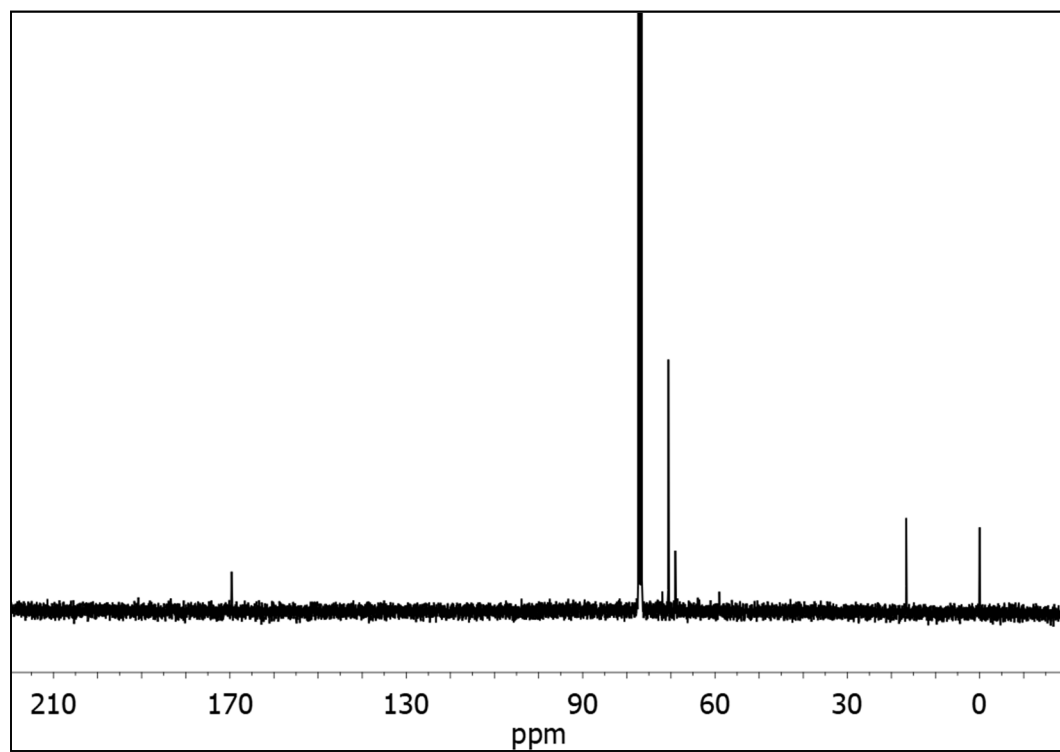
¹H NMR (400 MHz, Chloroform-*d*) δ 5.17 (q, $J = 7.1$ Hz, 16H), 4.44 – 4.15 (m, 16H), 3.90 – 3.30 (m, 48H), 2.86 – 2.41 (m, 20H), 1.69 – 1.43 (m, 48H). ¹³C NMR (100 MHz, CDCl₃) δ 169.75, 77.36, 70.72, 70.61, 70.54, 69.21, 69.16, 69.10, 64.57, 64.02, 63.98, 63.95, 29.85, 29.13, 29.12, 16.80.

3. Additional Figures

a) ^1H NMR spectrum of $\text{P1}^{\text{discrete}}$



b) ^{13}C NMR spectrum of $\text{P1}^{\text{discrete}}$



c) MALDI-TOF MS spectrum of $\text{P1}^{\text{discrete}}$

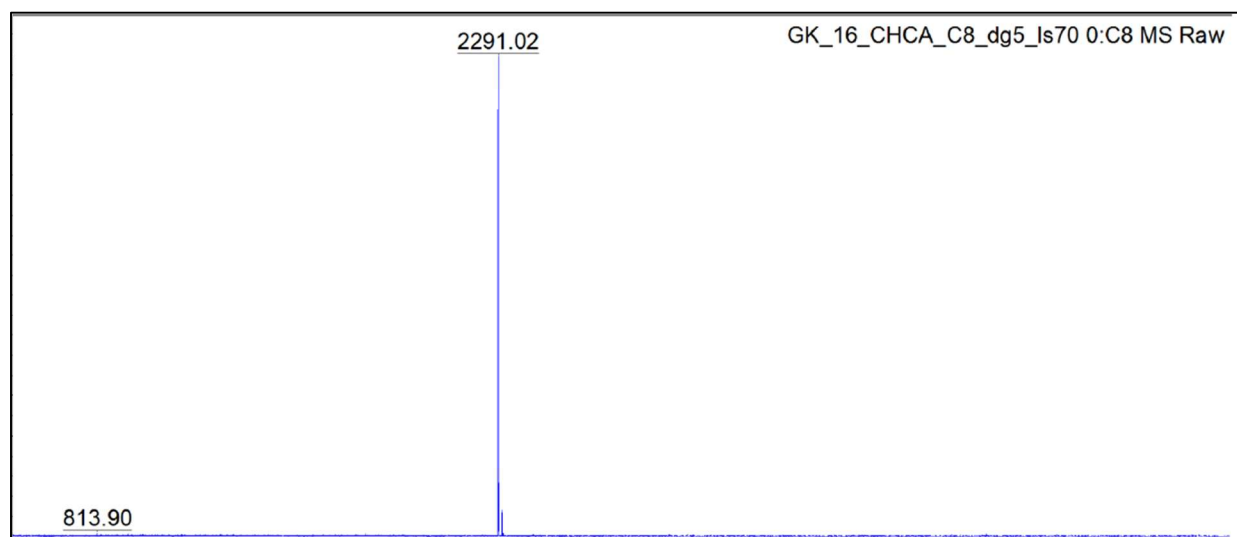
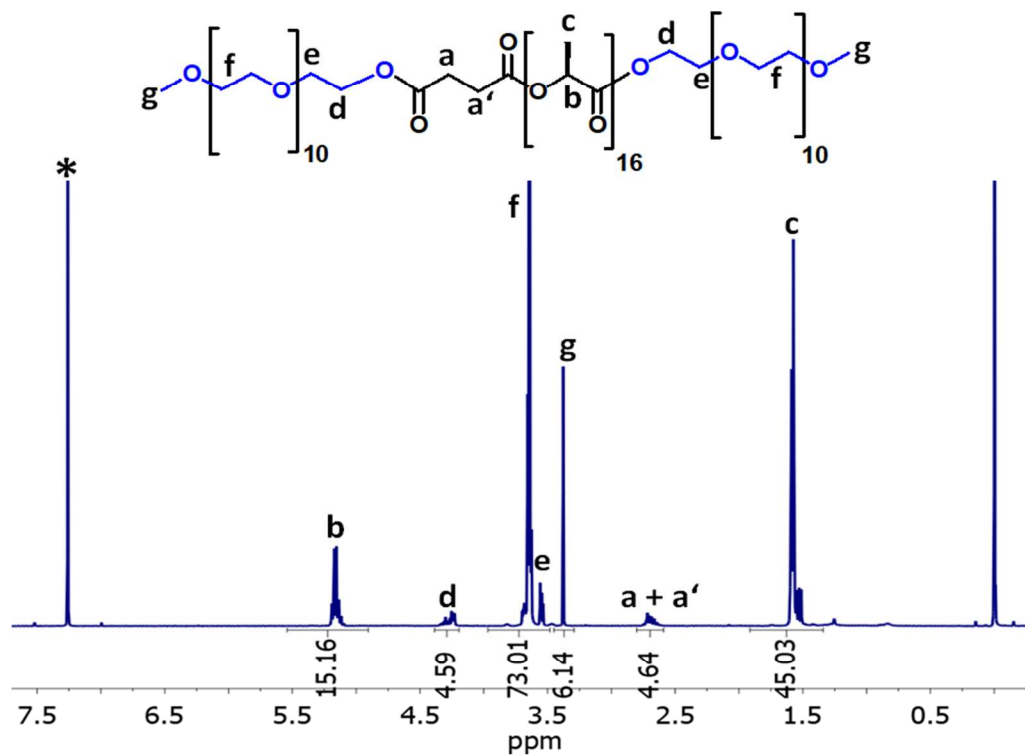
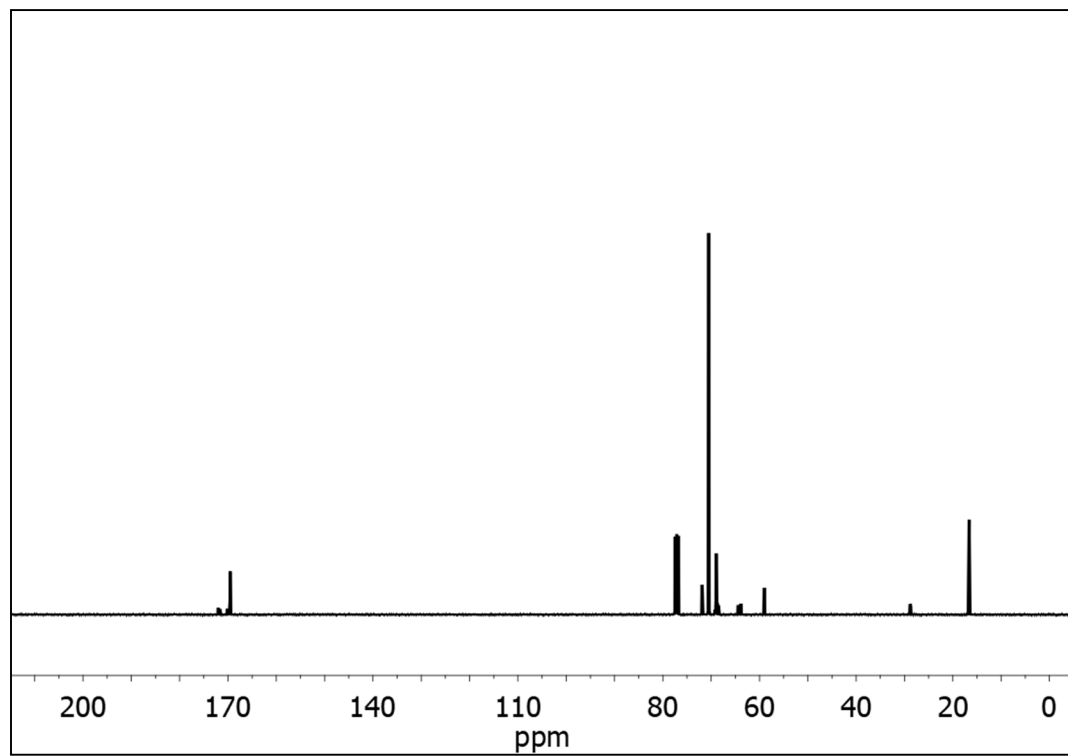


Figure S1: Molecular characterization of $\text{P1}^{\text{discrete}}$: a) ^1H -NMR and b) ^{13}C -NMR and c) MALDI-TOF MS spectrum.

a) ^1H NMR spectrum of $\text{P1}^{\text{disperse}}$



b) ^{13}C NMR spectrum of $\text{P1}^{\text{disperse}}$



c) MALDI-TOF MS spectrum of $P1^{disperse}$

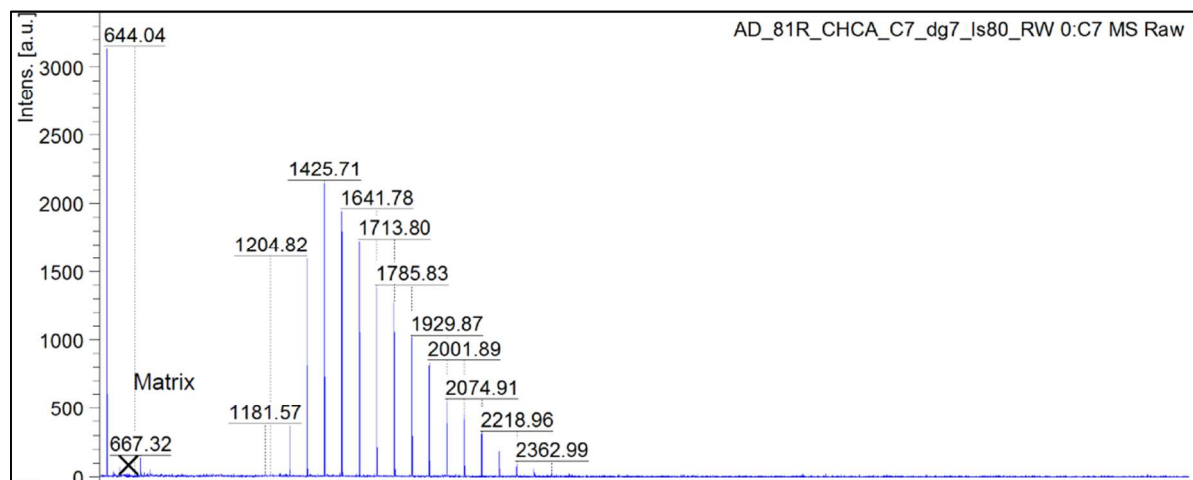
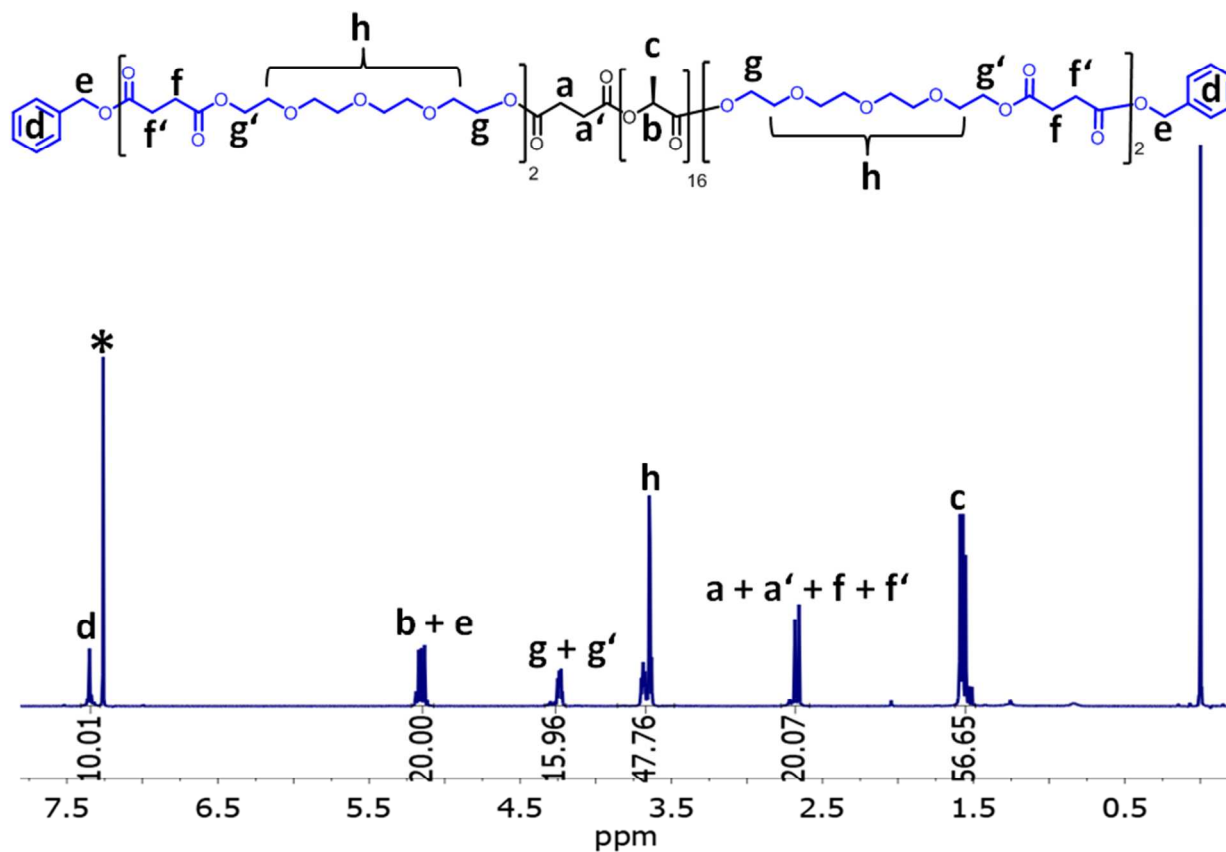
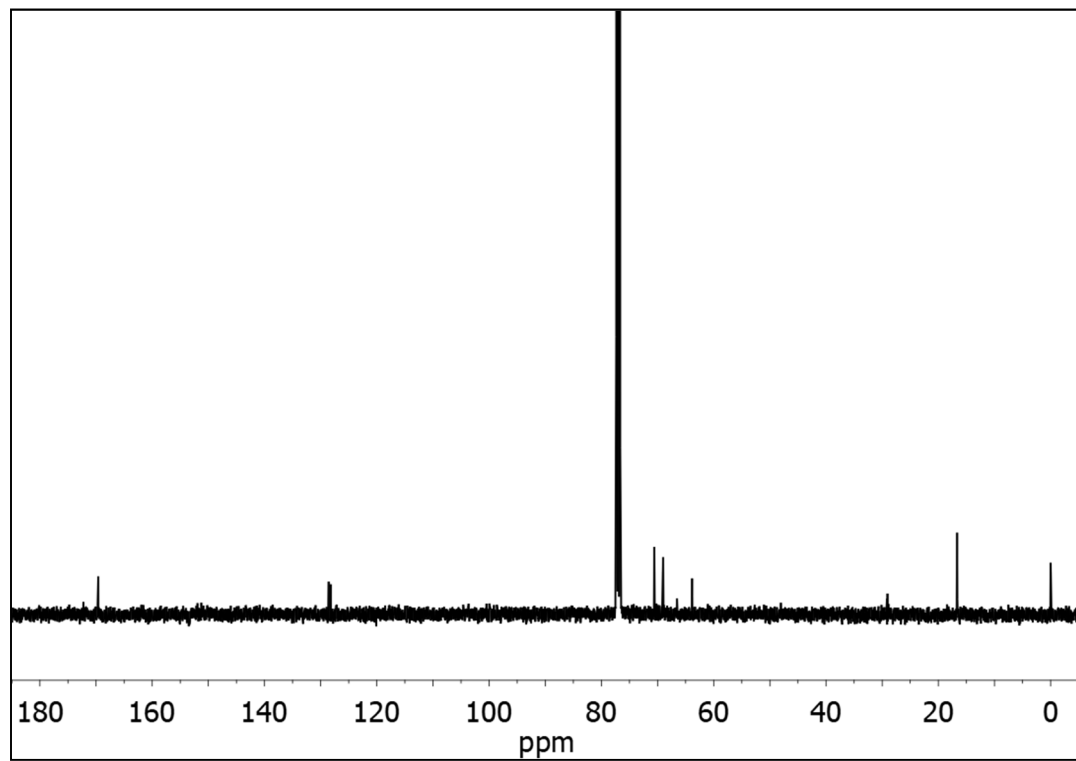


Figure S2: Molecular characterization of $P1^{disperse}$: a) 1H -NMR and b) ^{13}C -NMR and c) MALDI-TOF MS spectrum.

a) 1H NMR spectrum of $P2^{discrete}Bn$



b) ^{13}C NMR spectrum of $\text{P2}^{\text{discrete}}\text{Bn}$



c) MALDI-TOF MS spectrum of $\text{P2}^{\text{discrete}}\text{Bn}$

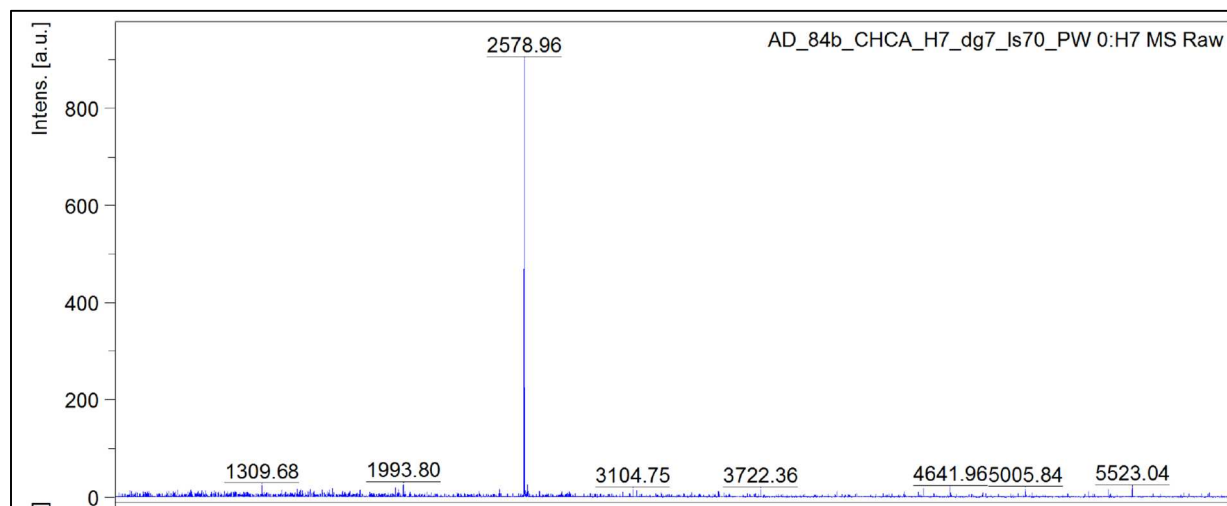
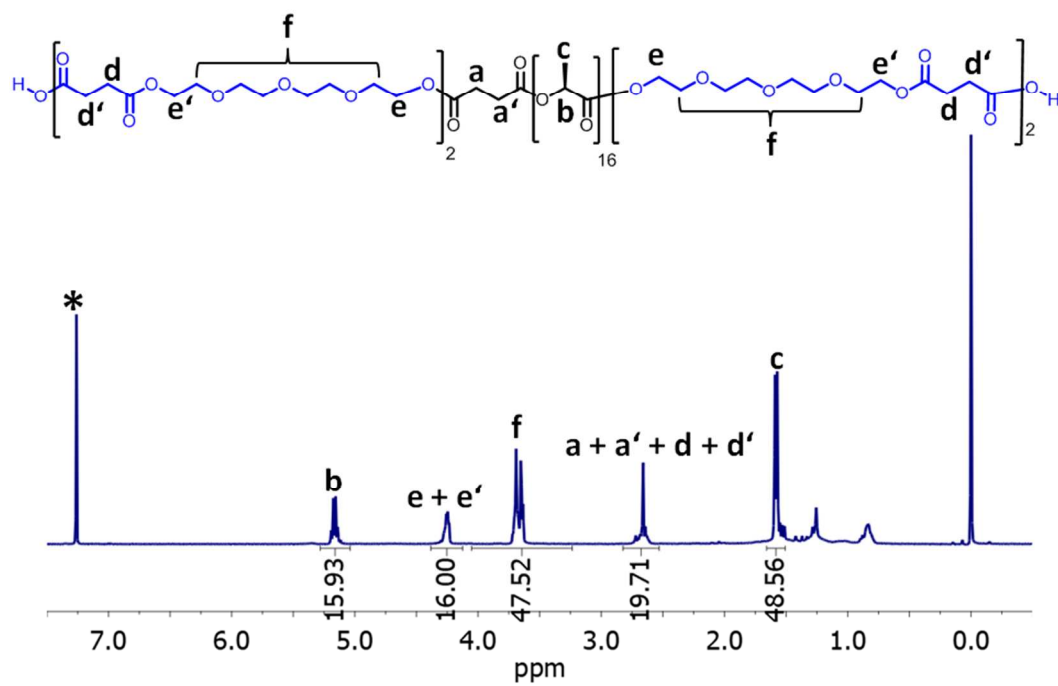
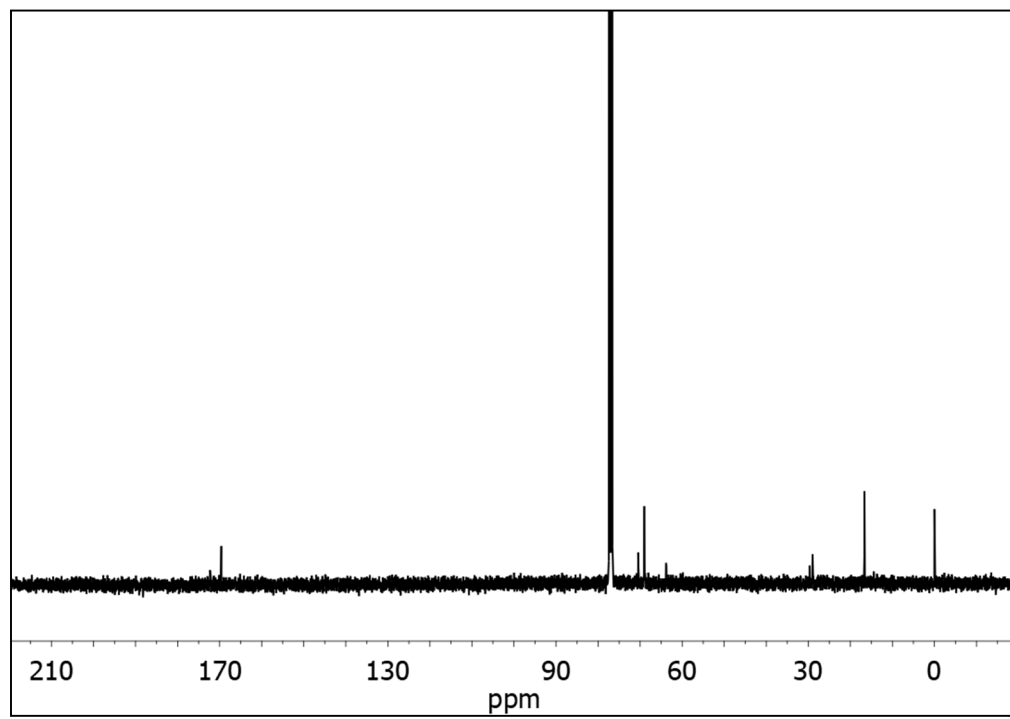


Figure S3: Molecular characterization of $\text{P2}^{\text{discrete}}\text{Bn}$: a) ^1H -NMR and b) ^{13}C -NMR and c) MALDI-TOF-MS spectrum.

a) ^1H NMR spectrum of $\text{P2}^{\text{discrete}}$



b) ^{13}C NMR spectrum of $\text{P2}^{\text{discrete}}$



c) MALDI-TOF MS spectrum of $P2^{discrete}$

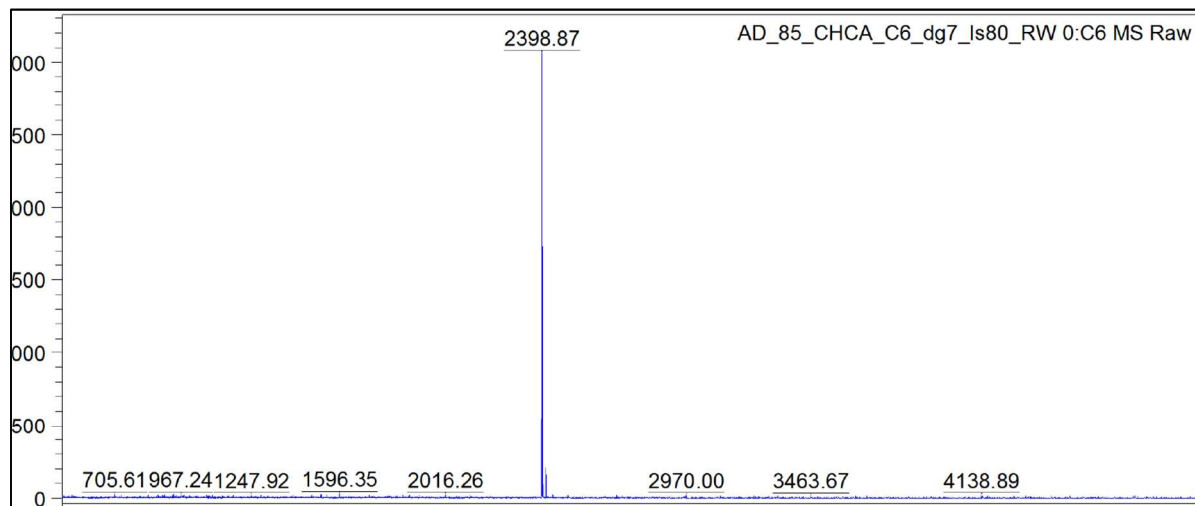
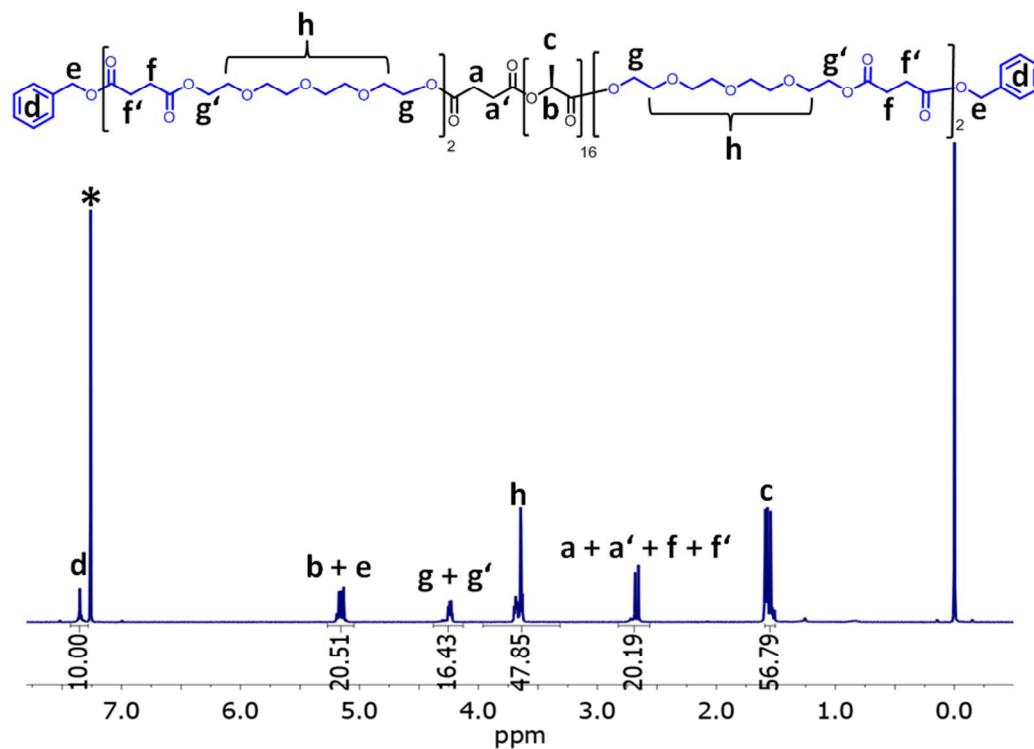
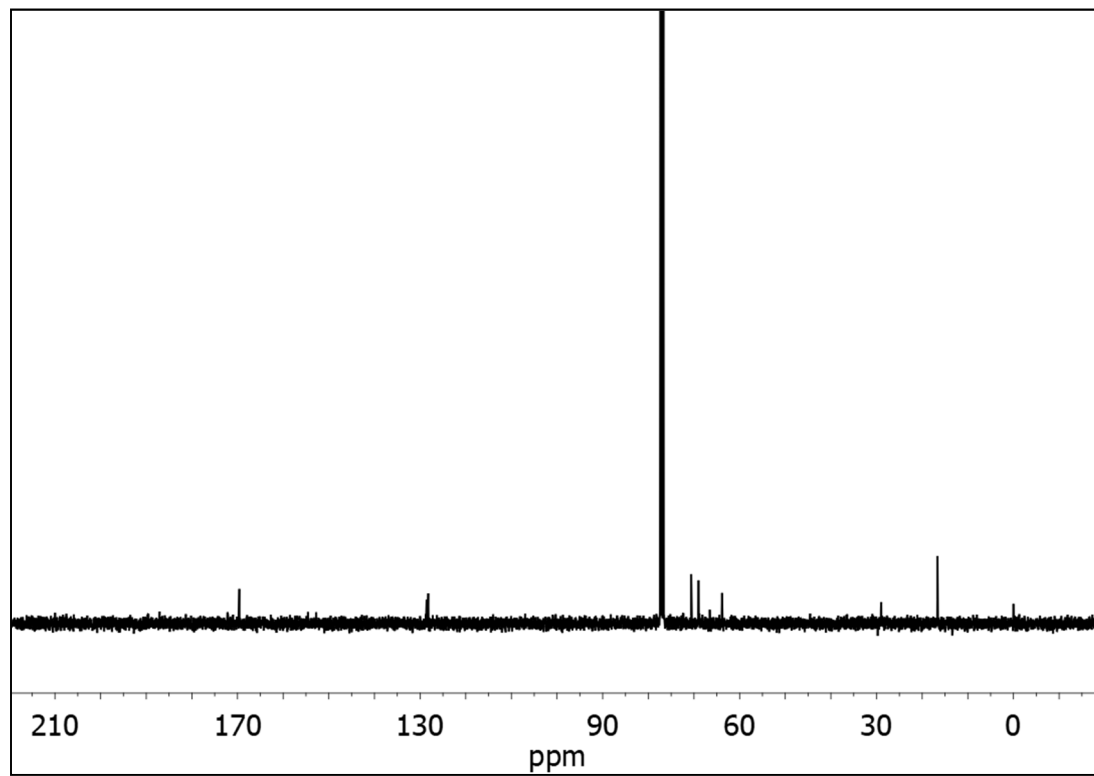


Figure S4: Molecular characterization of $P2^{discrete}$: a) 1H -NMR and b) ^{13}C -NMR and c) MALDI-TOF-MS spectrum.

a) 1H NMR spectrum of $P2^{disperse}Bn$



b) ^{13}C NMR spectrum of $\text{P2}^{\text{disperse}}\text{Bn}$



c) MALDI-TOF MS spectrum of $\text{P2}^{\text{disperse}}\text{Bn}$

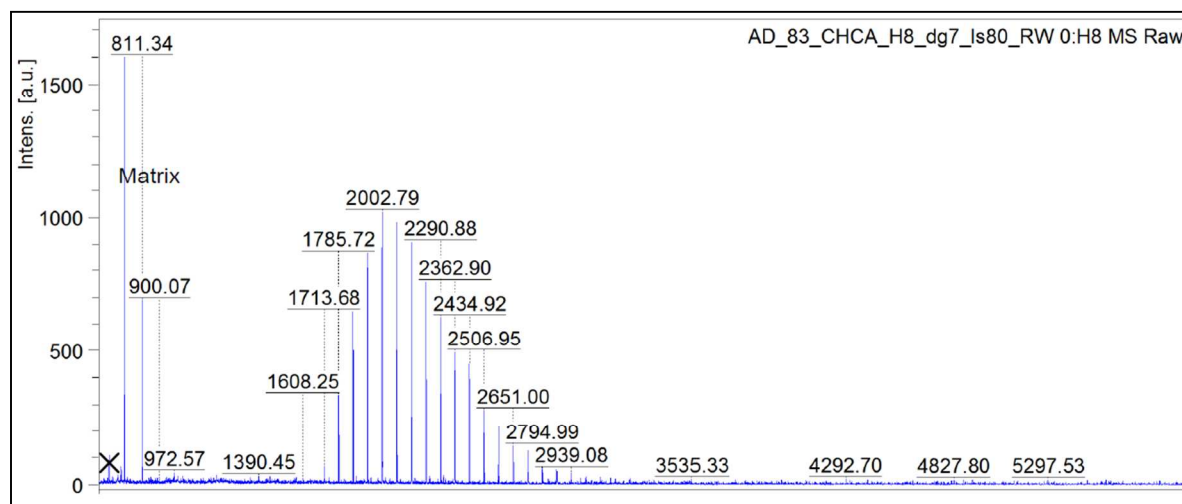
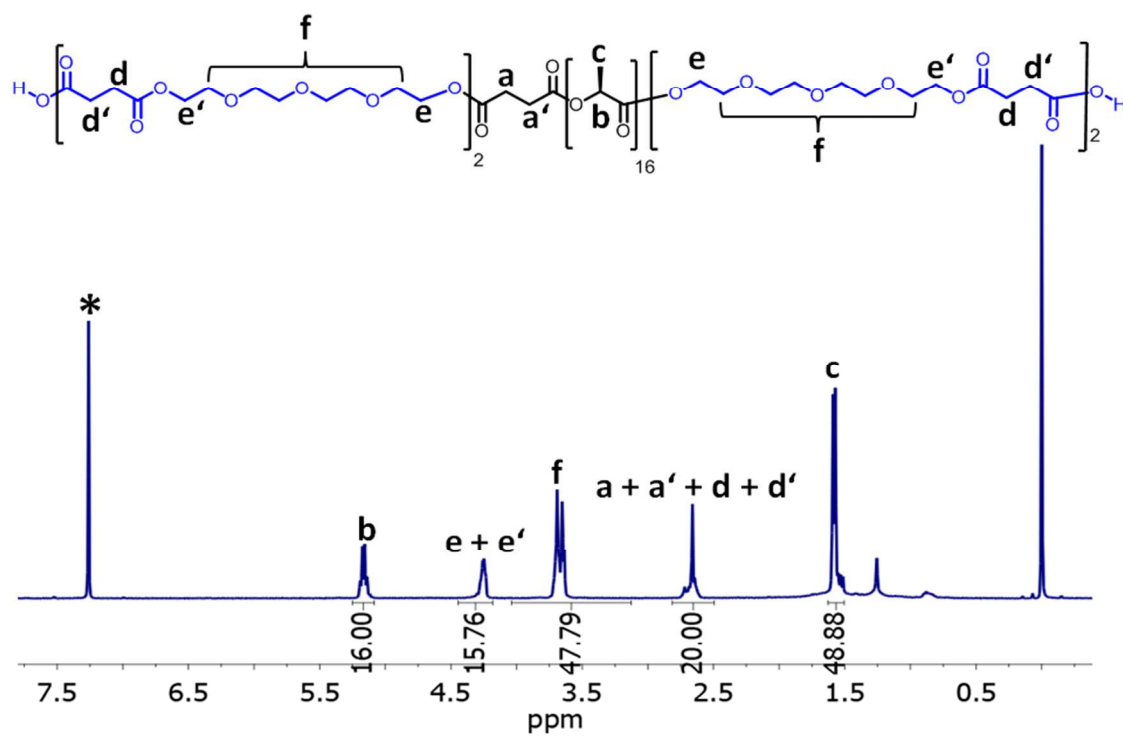
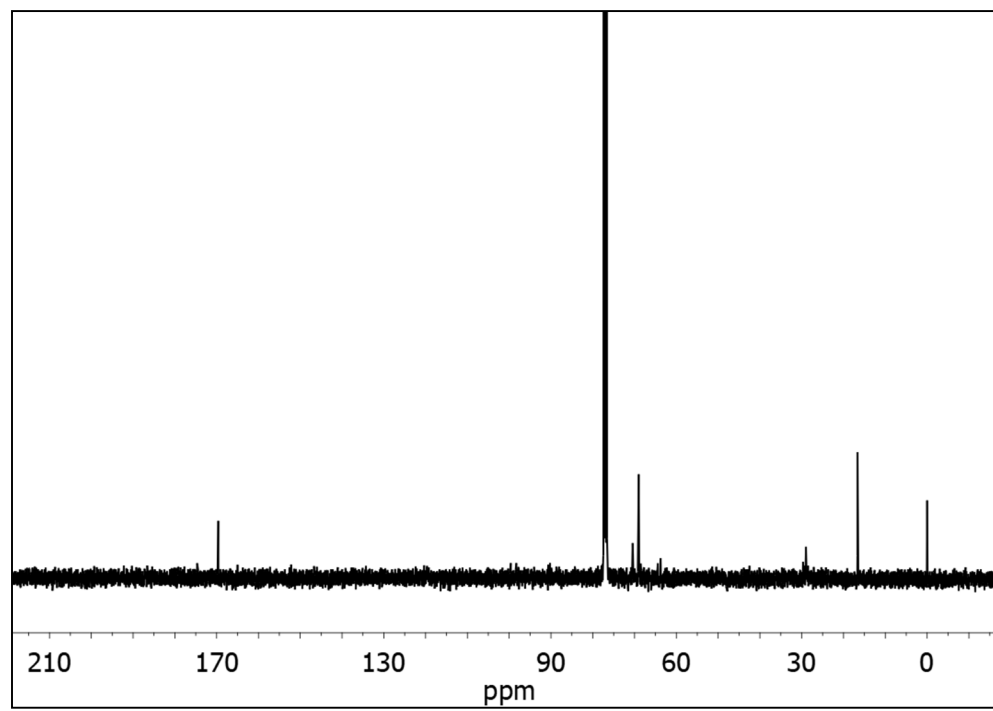


Figure S5: Molecular characterization of $\text{P2}^{\text{disperse}}\text{Bn}$: a) ^1H -NMR and b) ^{13}C -NMR and c) MALDI-TOF-MS spectrum.

a) ^1H NMR spectrum of $\text{P2}^{\text{disperse}}$



b) ^{13}C NMR spectrum of $\text{P2}^{\text{disperse}}$



c) MALDI-TOF MS spectrum of $P2^{disperse}$

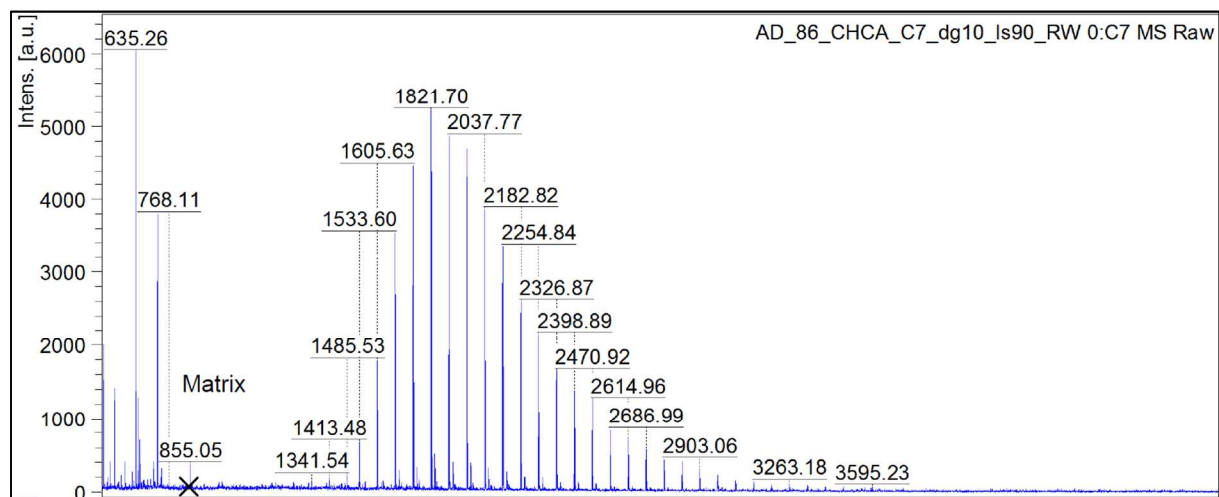
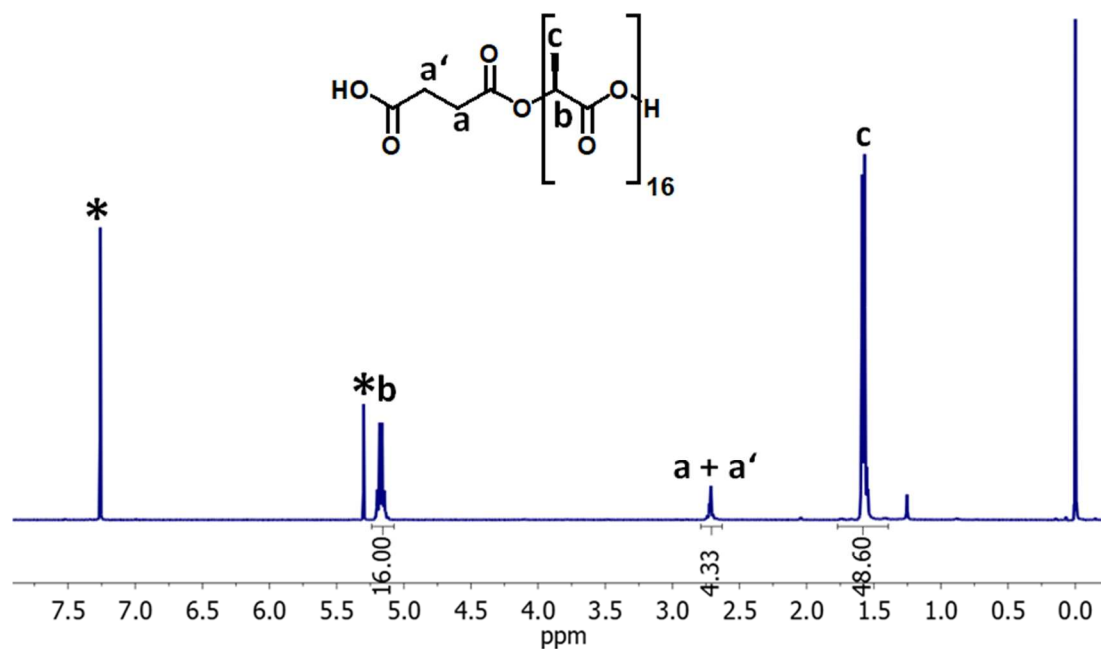


Figure S6: Molecular characterization of $P2^{disperse}$ **Bn:** a) ^1H -NMR and b) ^{13}C -NMR and c) MALDI-TOF-MS spectrum.

a) ^1H NMR spectrum of $\text{HOOC-SA-LLA}_{16}\text{-COOH}$



b) MALDI-TOF spectrum of HOOC-SA-LLA₁₆-COOH

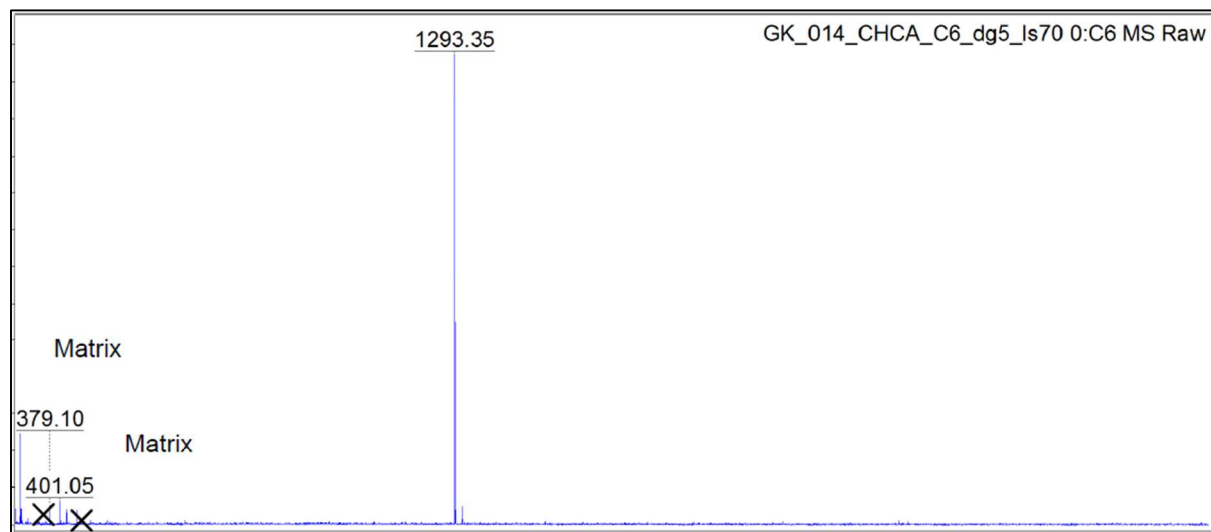
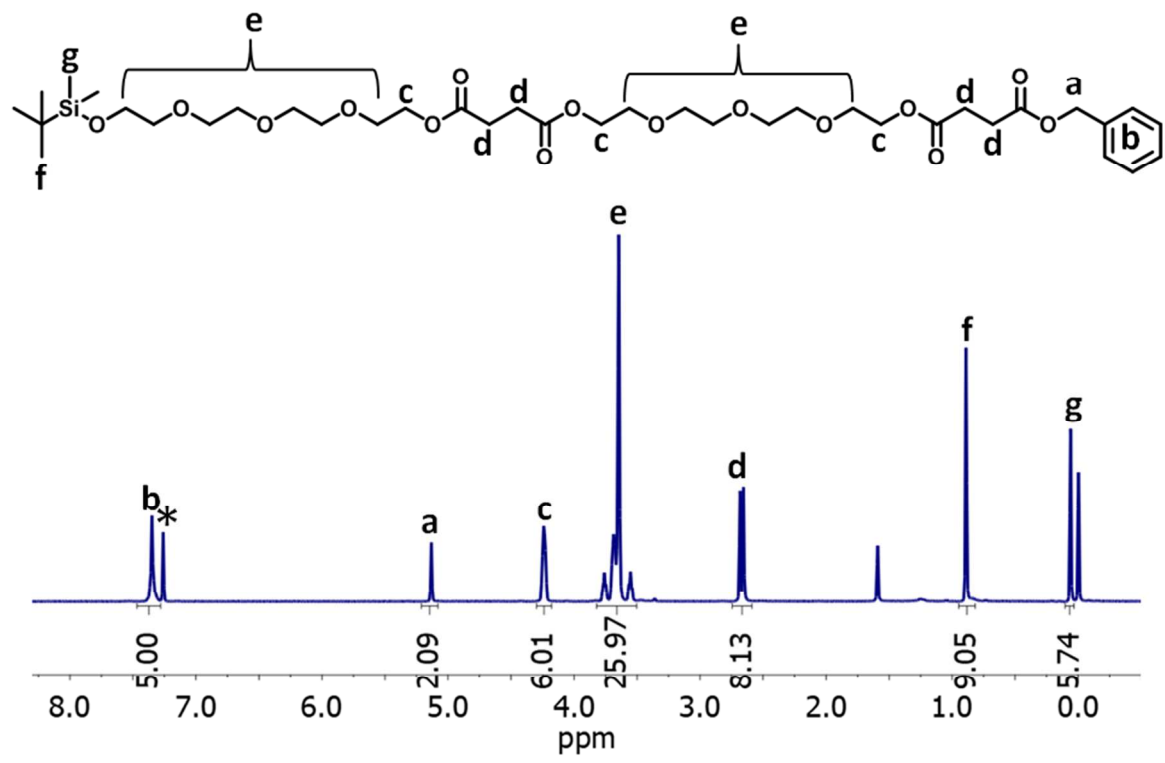


Figure S7: Molecular characterization of discrete HOOC-SA-LLA₁₆-COOH: a) ¹H-NMR and b) MALDI-TOF-MS spectrum.

a) ¹H NMR spectrum of (TEGSuc)₂



b) MALDI-TOF MS spectrum of (TEGSuc)₂

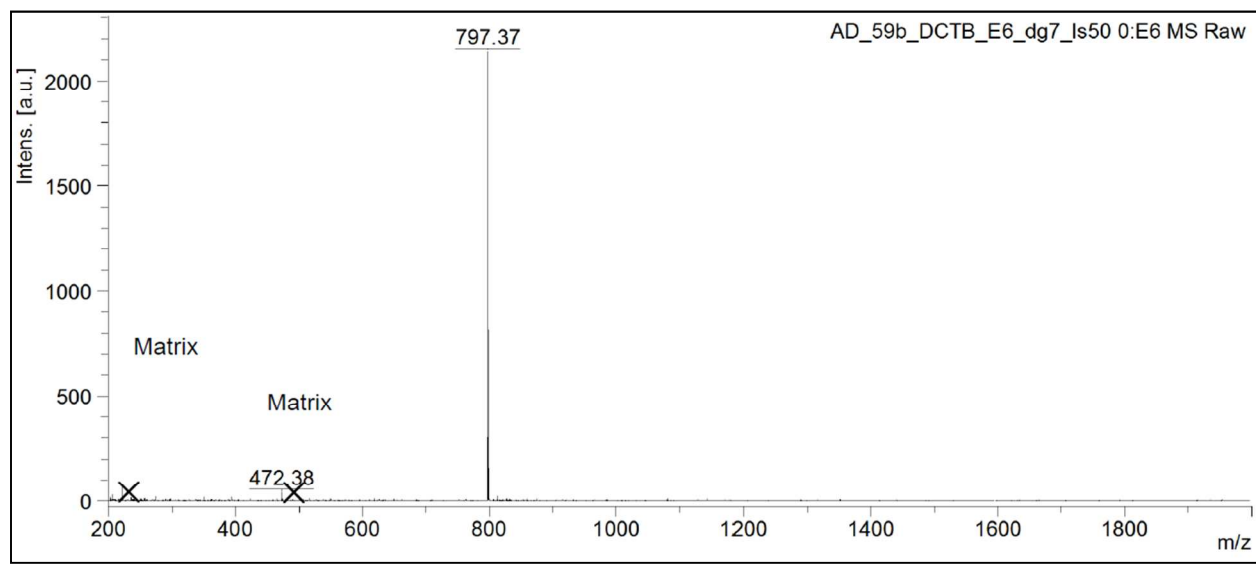
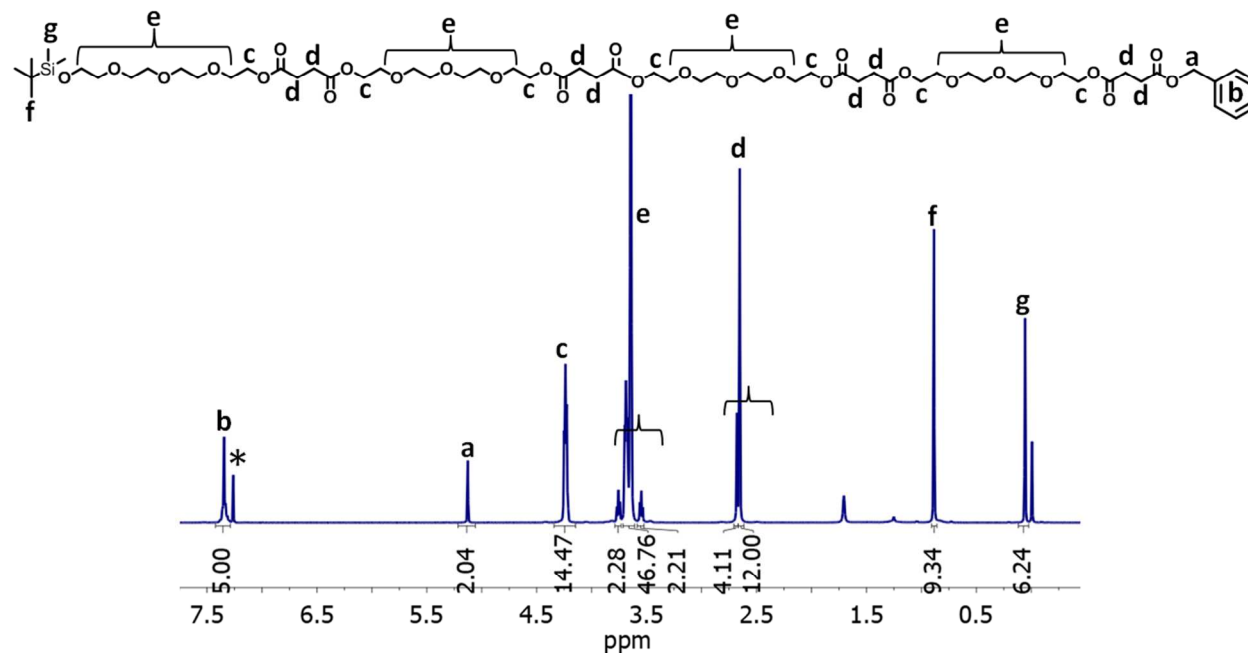


Figure S8: Molecular characterization of discrete (TEGSuc)₂ dimer: a) ¹H-NMR and b) MALDI-TOF-MS spectrum.

a) ¹H NMR spectrum of (TEGSuc)₄



b) MALDI-TOF MS spectrum of (TEGSuc)₄

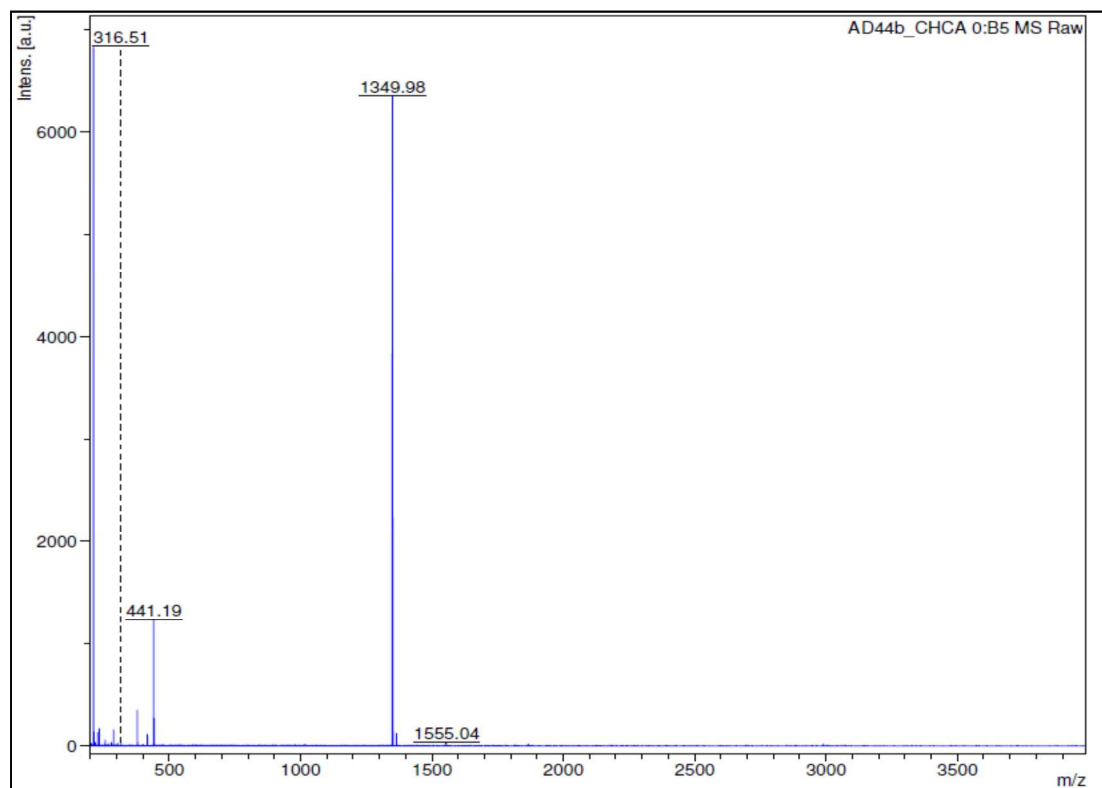


Figure S9: Molecular characterization of discrete (TEGSuc)₄ tetramer: a) ¹H-NMR and b) MALDI-TOF-MS spectrum.

4. Self-assembly in bulk:

First the bulk properties of ABCOs were investigated using differential scanning calorimetry (DSC) and small angle X-Ray scattering (SAXS). To study the effect of oLLA chain length and the nature of the hydrophilic block on the thermal transitions of ABCOs, the samples were heated from $-60\text{ }^{\circ}\text{C}$ to $180\text{ }^{\circ}\text{C}$ and cooled down to $-60\text{ }^{\circ}\text{C}$ at the rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The heating and cooling runs were repeated to check for degradation. For all comparative studies, the second heating and cooling runs were monitored. Sharp melting ($T_m = 41^{\circ}\text{C}$) and crystallization ($T_c = 19^{\circ}\text{C}$) peaks were observed in the 2nd heating/cooling run for discrete **P1^{discrete}** (Figure S10a). Contrarily, the disperse **P1^{disperse}** shows the first sharp melting at a very low temperature ($T_{m1} = 1.7\text{ }^{\circ}\text{C}$), followed by a cold crystallization ($T_{cc} = 66\text{ }^{\circ}\text{C}$) and a 2nd broad melting ($T_{m2} = 98\text{ }^{\circ}\text{C}$) in the heating run. While the cooling run shows an opposite trend i.e. a sharp crystallization ($T_c = 32\text{ }^{\circ}\text{C}$) at a temperature $13\text{ }^{\circ}\text{C}$ higher than that of **P1^{discrete}**. This suggests that the dispersity in LLA₋₁₆ block nucleates crystallization at a higher temperature, but the crystalline packing is not as rigid as in **P1^{discrete}**, leading to low melting. This is also reflected from the lower enthalpy of crystallization for **P1^{disperse}** compared to **P1^{discrete}**. This suggests that the PEG chains helps in better ordering of the LLA block in the disperse oligomer compared to TEGSuc segments.

Comparison between **P2^{discrete}Bn** and **P2^{disperse}Bn** also showed dramatic differences in the DSC runs (Figure S10b). In the 2nd heating/ cooling run, no transition other than $T_g - 10\text{ }^{\circ}\text{C}$ was observed for **P2^{discrete}Bn**. Interestingly, the melting peak for oLLA block at $41\text{ }^{\circ}\text{C}$ reappears (Figure S10c) when the same DSC pan was aged for two months and the measurement was repeated. This suggests slower rate of crystallization of **P2^{discrete}Bn** with respect to **P1^{discrete}**, possibly due to the complete amorphous nature of the TEGSuc block compared to semi-crystalline PEG chain (Figure S11). Notably, for **P2^{disperse}Bn**, no melting at $41\text{ }^{\circ}\text{C}$ (Figure S10b) was observed in the 2nd heating, nor even for the aged sample (Figure S10d). The glass transition temperature was similar to that of **P2^{discrete}Bn** (T_g around $-10\text{ }^{\circ}\text{C}$). However, the heating run showed multiple weak transitions at higher temperature. A cold crystallization ($T_{cc} = 78\text{ }^{\circ}\text{C}$) followed by a melting ($T_m = 103\text{ }^{\circ}\text{C}$). This was attributed to the ordering and disordering of the LLA block with $\text{DP} > 16$ in the disperse oligomer.

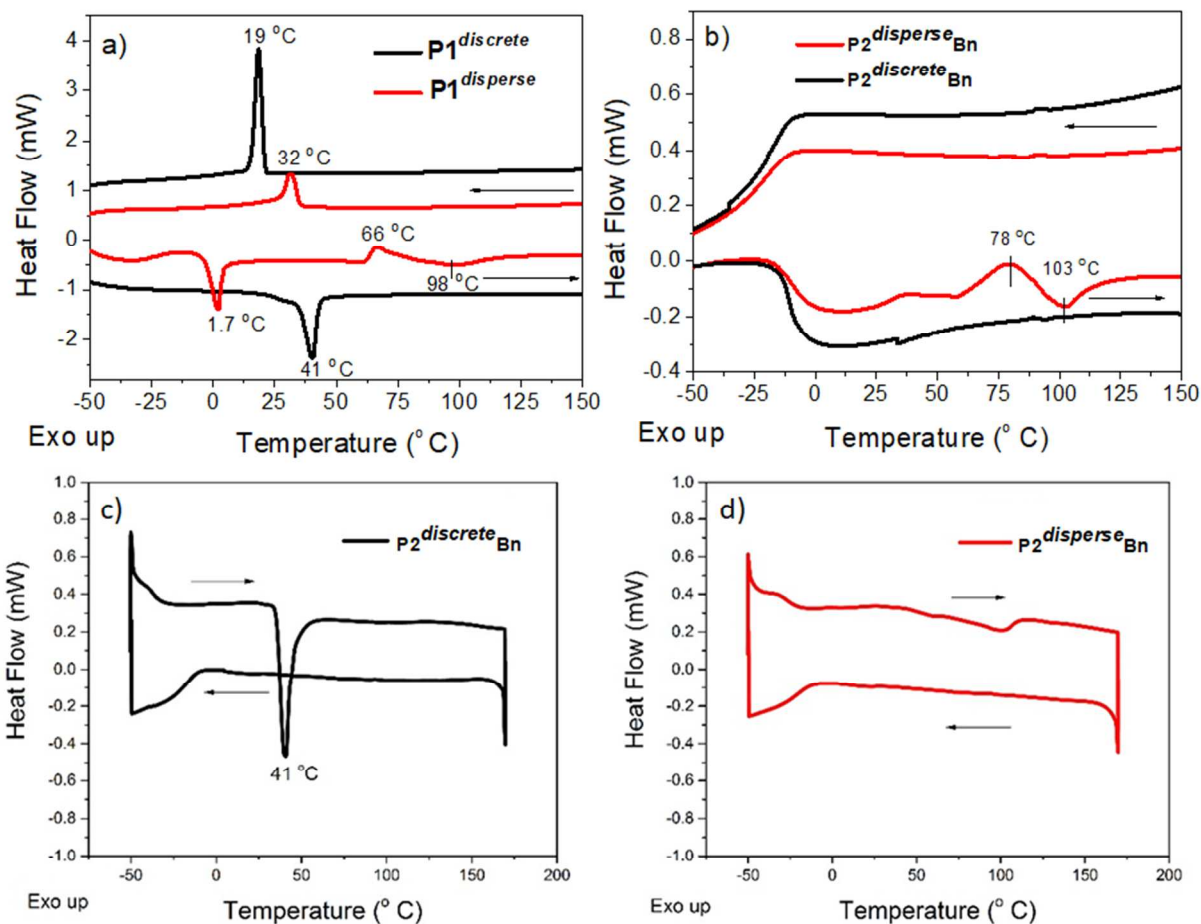


Figure S10: DSC 2nd heating/cooling traces of a) $P1^{discrete}$ and $P1^{disperse}$ and b) $P2^{discrete}_{Bn}$ and $P2^{disperse}_{Bn}$ in the bulk; DSC traces of the two months old aged pan of c) $P2^{discrete}_{Bn}$ and d) $P2^{disperse}_{Bn}$.

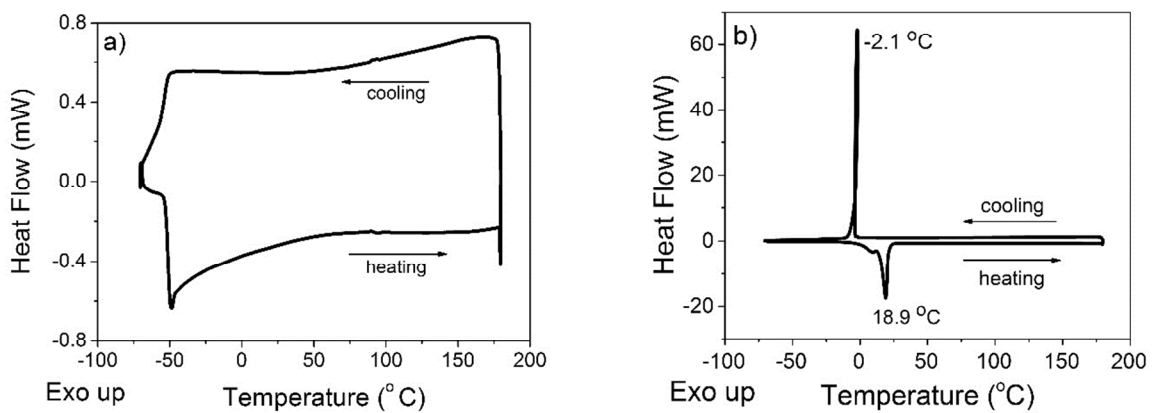


Figure S11: DSC 2nd heating/cooling traces of a) (TEGSuc)₂-OH and of b) MeOoEG₁₁-OH; No crystallization or melting transitions are observed in (a) suggesting amorphous nature of (TEGSuc)₂-OH compared to crystalline MeOoEG₁₁-OH.

SAXS and WAXS in the bulk corroborate with the DSC data. Both discrete $\mathbf{P1}^{discrete}$ and $\mathbf{P2}^{discrete}\mathbf{Bn}$ showed primary reflection peak corresponding to $d = 6.5$ and $d = 10.5$ nm, respectively (Figure S12). The domain size of PEG functionalized $\mathbf{P1}^{discrete}$ was found to be smaller than that of $\mathbf{P2}^{discrete}\mathbf{Bn}$. Higher order reflections with $d = 5.2$ nm for $\mathbf{P2}^{discrete}\mathbf{Bn}$ suggests lamellar packing. While both $\mathbf{P2}^{discrete}$ and $\mathbf{P1}^{discrete}$ showed multiple scattering peaks in the WAXS region corresponding to the inter chain packing of the LLA_{16} block (Figure S12a & S12b, insert). Such transitions are symbolic of the crystalline packing of the lactic acid chain. The disperse sample also showed weak reflection peaks in the WAXS region corresponding to crystallization of the disperse $\text{LLA}_{\sim 16}$ block, which perhaps arise from the chains with $\text{DP} > 16$. This is also in line with the T_{cc} and T_m observed in the heating run of the disperse $\mathbf{P1}^{disperse}$ and $\mathbf{P2}^{disperse}\mathbf{Bn}$.

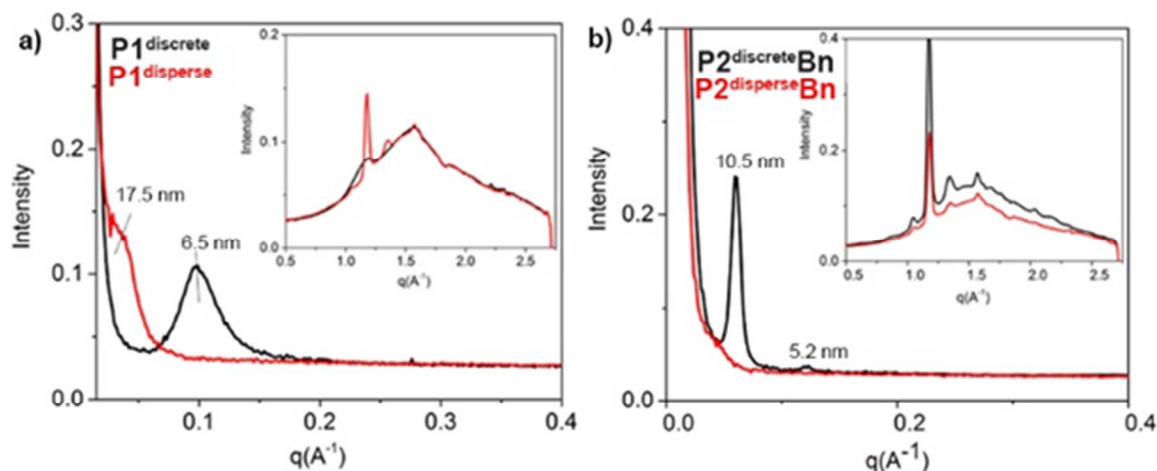


Figure S12: Bulk SAXS profiles of a) $\mathbf{P1}^{discrete}$ / $\mathbf{P1}^{disperse}$; inset shows their WAXS traces and b) of $\mathbf{P2}^{discrete}\mathbf{Bn}$ / $\mathbf{P2}^{disperse}\mathbf{Bn}$; inset shows their WAXS traces.

5. Self-assembly in solution:

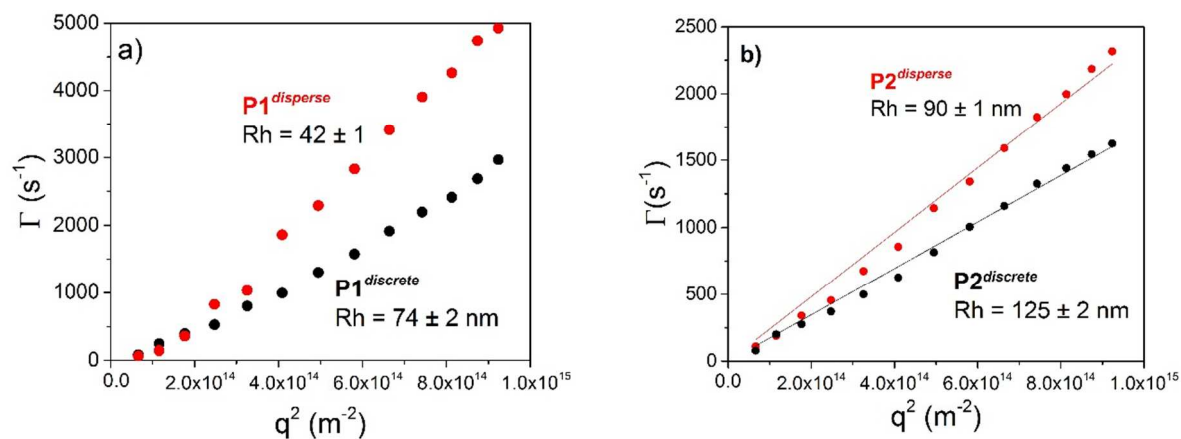


Figure S13: Multi-angle light scattering: Gamma (Γ) vs q^2 plot of a) **P1^{disperse}/P1^{discrete}** and b) of **P2^{disperse}/P2^{discrete}**; where Γ is the decay rate and q is the scattering vector.

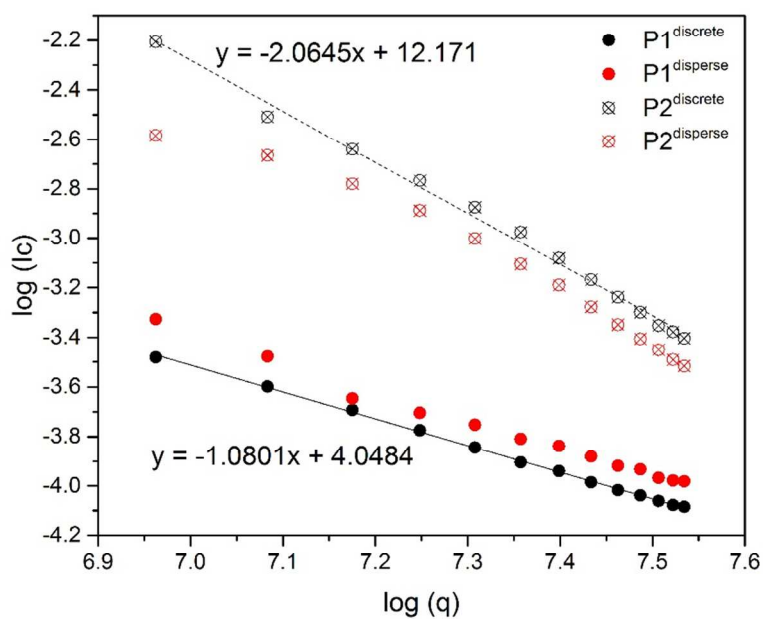


Figure S14: Scattering intensity vs q plot: slope of -2 indicates the formation of vesicles; slope of -1 indicates the formation of cylinders.

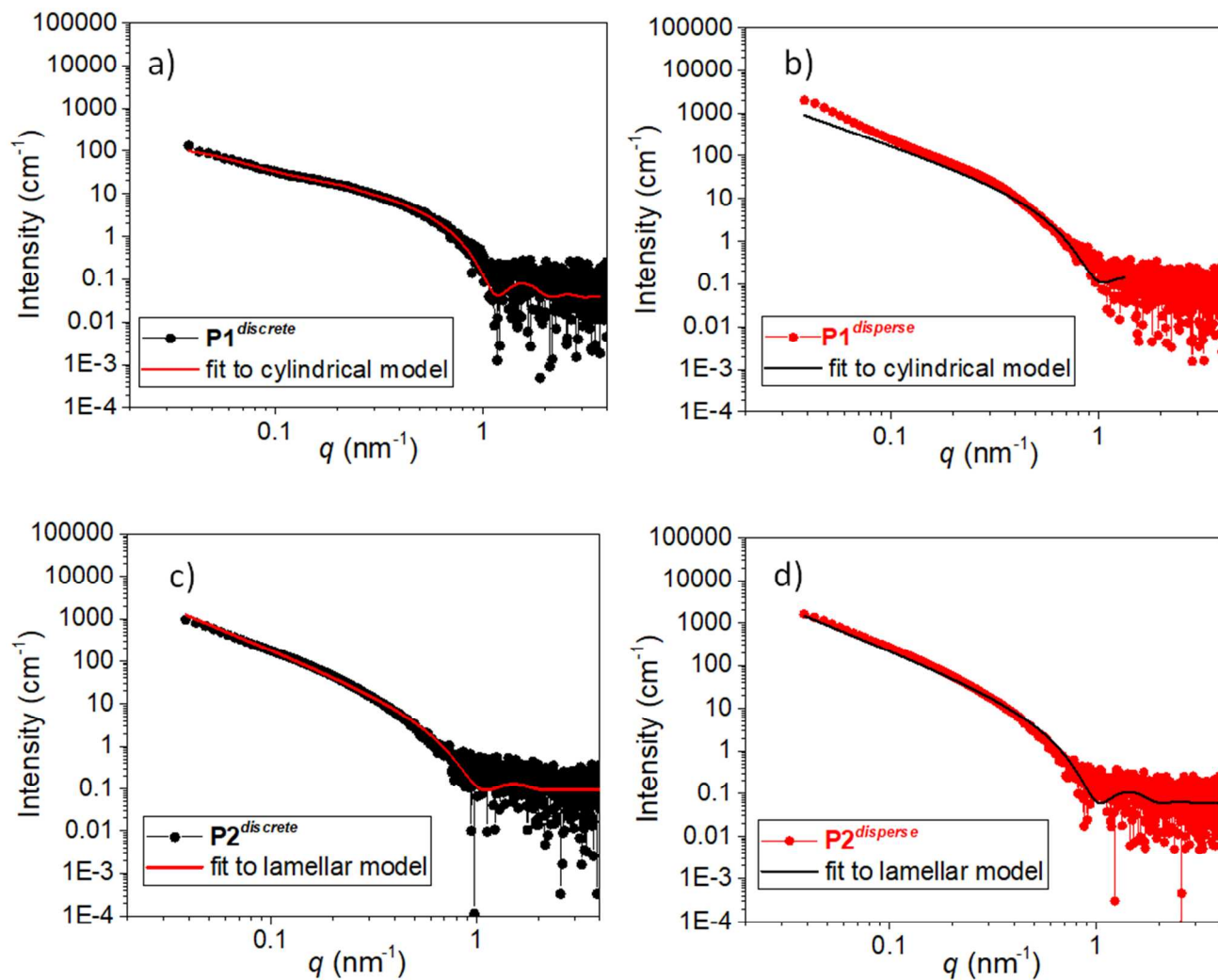


Figure S15: Solution SAXS traces of a) $\text{P1}^{discrete}$ (0.5 mg mL^{-1}), b) $\text{P1}^{disperse}$ (0.5 mg mL^{-1}), c) $\text{P2}^{discrete}$ (0.6 mg mL^{-1}) and d) $\text{P2}^{disperse}$ (0.6 mg mL^{-1}) after self-assembly in water/THF 90/10. The lines represent the best fit to the data using either a flexible cylinder (a,b) or a lamellar (c,d) model.

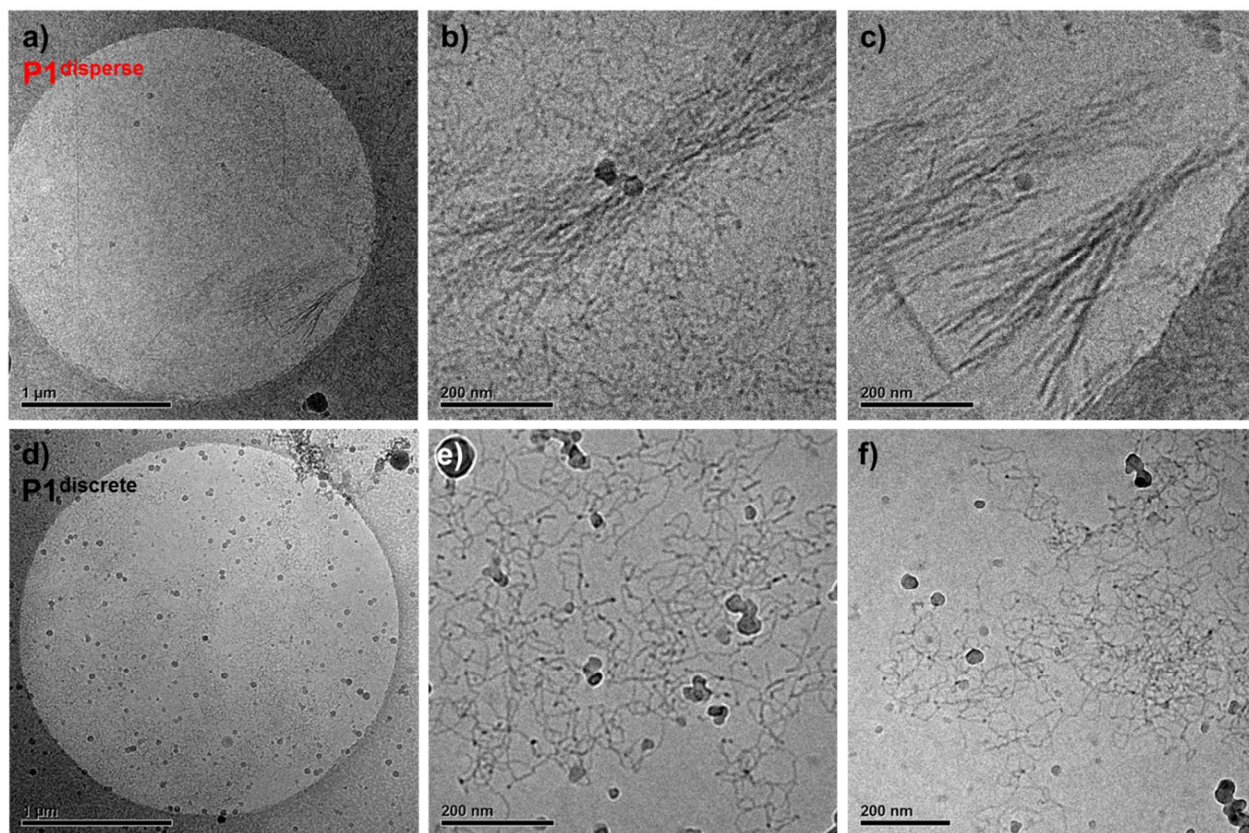


Figure S16: CryoTEM images of aged samples of $P1^{disperse}$ (a-c) and $P1^{discrete}$ (d-f) measured 86 days after sample preparation, at 6500 magnification and 40 μm defocus (a,d), at 25000 magnification and 10 μm (b,c,e) or 12 μm defocus (f). Black dots are crystalline ice particles that are not part of the sample.

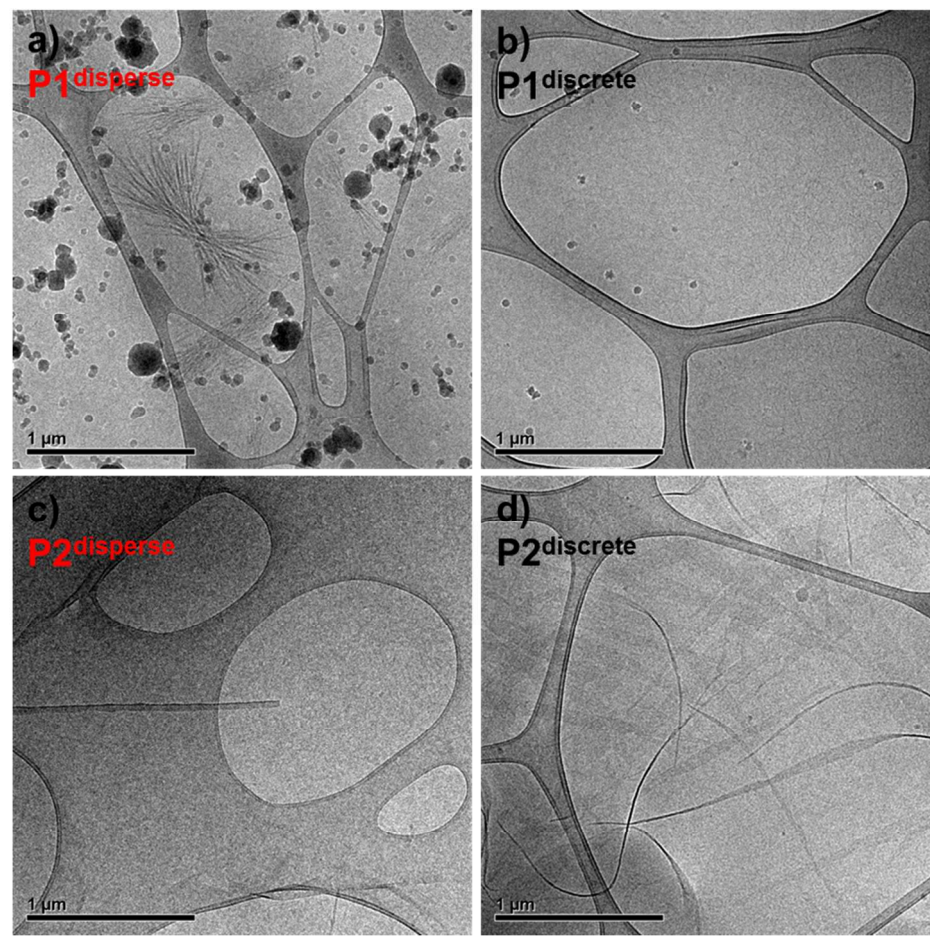


Figure S17: CryoTEM images of a) $P1^{disperse}$, b) $P1^{discrete}$, c) $P2^{disperse}$ and d) $P2^{discrete}$ at a magnification of 6500 and 40 μm defocus. Black dots in a) and b) are crystalline ice particles that are not part of the sample.

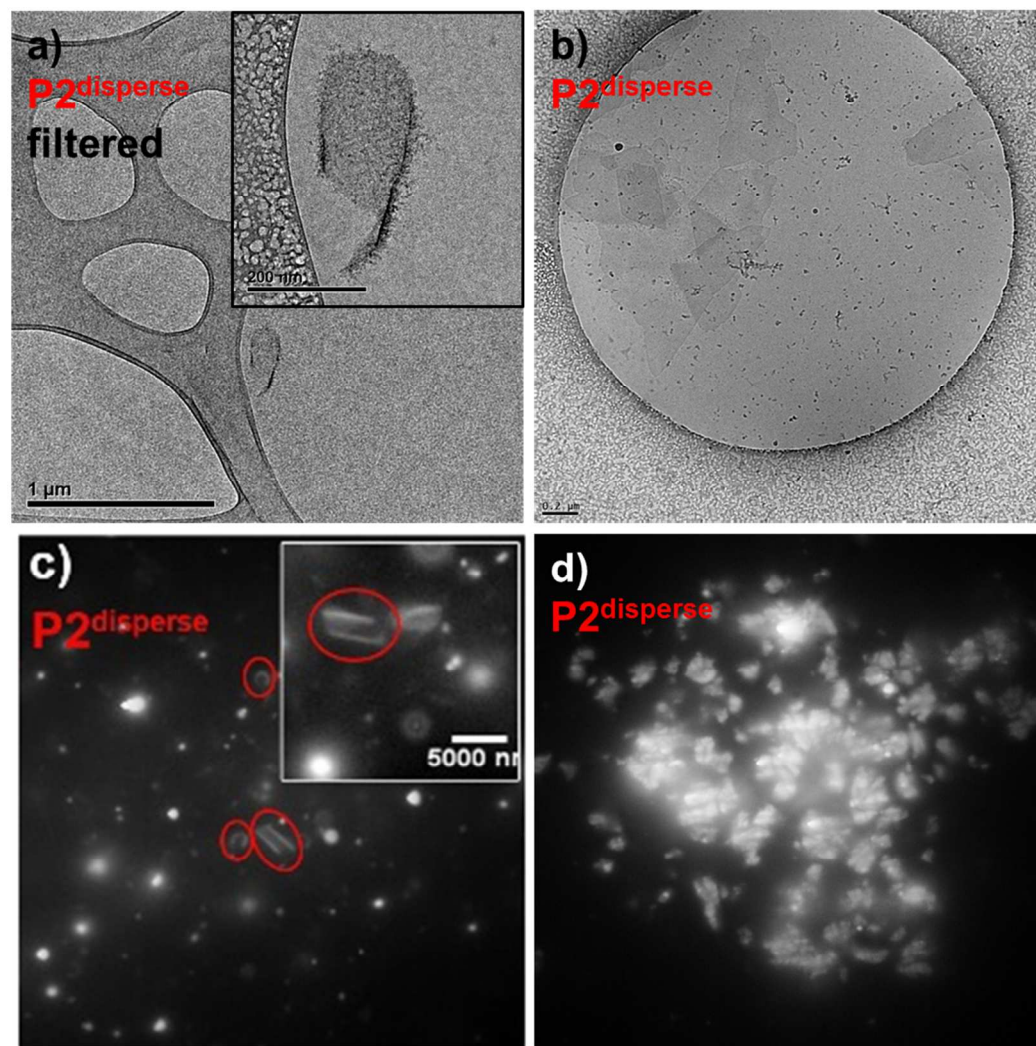


Figure S18: CryoTEM and TIRF microscopy of $P2^{disperse}$ in 1:9 THF:water showing a) U-shaped aggregate for the filtered sample at 6500 magnification and 40 μm defocus (inset: 25000 magnification and 5 μm defocus), b) flat sheets for the sample that was not filtered, including crystalline ice particles, at 6500 magnification and 40 μm defocus, c) uniform sheets rolled into U-shapes (encircled in red), and d) large 2D clusters. The samples in c) and d) were unfiltered.

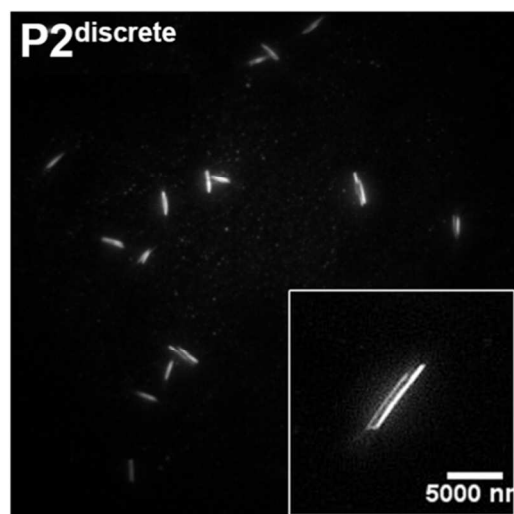


Figure S19: TIRF microscopy of $P2^{discrete}$ at 2 mg/mL in water with 10% THF, showing long and uniform curved sheets that were found only on the glass surface.

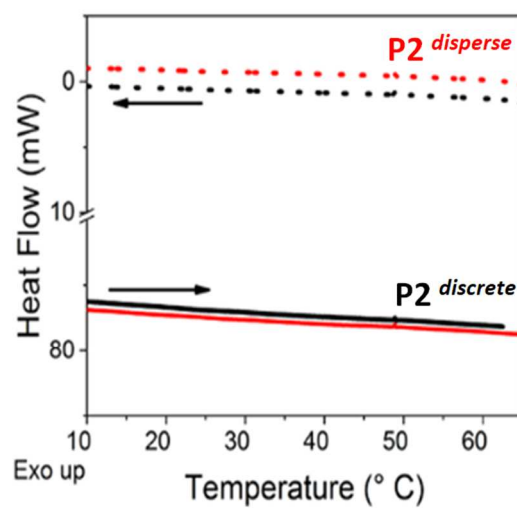


Figure S20: Micro-DSC traces of $P2^{discrete}$ and $P2^{disperse}$ at 2 mg mL⁻¹, after self-assembly in water with 10% THF.

6. References:

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