Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Modular amphiphilic copolymer-grafted nanoparticles: "nanoparticle micelle" behavior enhances utility as dispersants

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TABLE OF CONTENTS:

Experimental part and additional experiments made for the characterization of the polymers and the nanoparticles at different stages of the synthesis are presented.

Experimental

Materials. Stannous octanoate ($Sn(Oct)_2$, 95%, Sigma-Aldrich), (3-glycidoxypropyl)triethoxysilane (GPS, Gelest), NaOH (97%, Fisher Scientific), polyethylene glycol) methyl ether (α-hydroxy-ω-methoxy PEG, Sigma-Aldrich), average M_n = 5000 g/mole, Chromium(VI) oxide (CrO_3, 99.9%, Sigma-Aldrich), H_2SO_4 (95-98 w/w %, Fisher Scientific), 4-(dimethylamino)pyridine (DMAP, 99%, Sigma-Aldrich), N,N′-dicyclohexylcarbodiimide (DCC, 99%, Sigma-Aldrich), 4-heptyphenol (Hph, Sigma-Aldrich), tetrahydrofuran (THF, Sigma-Aldrich), pyrene (Sigma-Aldrich, ≥99.0%) and all other reagents were used as obtained from commercial sources. ε-Caprolactone (CL, 99%, Acros Organics) was dried over CaH_2 and vacuum distilled before polymerization. Silica suspension (IPA-ST-ZL) was provided by Nissan Chemical Industries, LTD and consisted of ~30 wt% of colloidal silica particles with an average diameter of ~ 100 nm, in isopropanol. The pristine silica particles were obtained in powdered form from IPA-ST-ZL by centrifugation to collect the particles followed by washing with methanol and finally drying under vacuum overnight at room temperature.

Synthesis

"One-pot" immobilization of the epoxysilane coupling agent onto the silica nanoparticles surface and concurrent hydrolysis of the epoxy groups. The SiO_2NPs were treated with GPS by modification of a previously reported method.[1] The isopropanol solvent from the commercial SiO_2NPs suspension was replaced with water by a solvent-exchange method. The suspension was diluted with water and centrifuged. The collected SiO_2NPs were then dispersed in water and centrifuged again. This cycle was repeated a total of five times yielding a suspension of SiO_2NPs in water.

For the surface functionalization, the SiO_2NPs suspension in water (4.8 g of particles present in 16.0 g of 30 wt% SiO_2NPs) was added to a round bottom flask with a magnetic stir bar and fitted with a reflux condenser. GPS (5.6 g, 0.02 mol) was added and the resultant reaction mixture was diluted with deionized water to reach a concentration of SiO_2NPs of approximately 0.2 g mL^{-1}. This suspension was sonicated for 15 min, at which point the pH was adjusted to 11 by the addition of a 1 M aqueous NaOH solution. The reaction mixture was then refluxed for 36 h to assure both silanol condensation and subsequent epoxy hydrolysis to yield diol functionalized nanoparticles. After cooling the reaction mixture down to room temperature, the SiO_2NPs were repeatedly sonicated in neutral water to disperse them in solution and centrifuged for a period of 30 min at 10,000 rpm to isolate from the solvent, until achieving a neutral pH. The removal of any unattached GPS from the diol functionalized nanoparticles was then achieved by successive centrifuging-redispersion cycles in methanol. Finally, the SiO_2NPs were dried overnight under vacuum at room temperature before pursuing SIROP. After drying, 4.1 g of functionalized nanoparticles were isolated (84% yield based on TGA measurement of 1.2 weight % GPS on SiO_2NP-GPS).

SIROP of CL from the diol functionalized silica nanoparticles (SiO_2NP-OH) to produce SiO_2NP-PCL. 2.1 g of SiO_2NP-OH were dispersed in 60 g of CL (0.526 mol) by sonication in a 100 mL two-neck round bottom flask fitted with a stir bar. After 40 min of Ar purge, 48.00 mg (0.12 mmol) of $Sn(Oct)_2$ was added to the suspension under Ar flow. The flask was placed in a thermostatic oil bath at 130 °C and the suspension was stirred for 7 h under Ar. The polymer-grafted SiO_2NPs were isolated from free polymer by repeatedly dispersing in THF (by sonication), centrifuging, and decanting the THF solution to remove any unbound PCL. The same procedure was followed in the case of the PCL grafting reactions monitored online. After drying under vacuum, 1.8 g of the SiO_2NP-PCL product was isolated (76 % yield based on TGA measurement of 12.1 weight % PCL on SiO_2NP-PCL).

Synthesis of *α*-carboxy-*ω*-methoxy-PEG (HOOC-PEG-OCH_3). The polyethylene glycol (5000 g mol^{-1}), bearing one terminal methyl ether and one carboxylic acid functional group, was prepared as follows.[2] In a round-bottom flask, 47.50 g (9.50×10^{-3} mol, 1 eq.) of *α*-hydroxy-*ω*-methoxy PEG were dissolved in 310 mL of acetone. Jones reagent (10.60 g of CrO_3 dissolved in 9.20 mL of H_2SO_4 and 40 mL of water) was added dropwise until the solution maintained a reddish color for ca. 10 min. The mixture was then diluted with 200 mL of water and washed three times with 300 mL of CH_2Cl_2. Organic phases were combined, washed three times with water and dried with anhydrous $MgSO_4$. The solvent was evaporated and 45.36 g of HOOC-PEG-OCH_3 were obtained (yield 95%). The observed average weight (M_n = 3360 g/ mole) appeared to be slightly reduced, presumably from oxidative scission of the backbone. The reactant (Fig. S18-S21) and final product (Fig. S22-S25) were characterized by ^{1}H NMR, ^{13}C NMR and MALDI mass spectra.

Attachment of HOOC-PEG-OCH_3 on SiO_2NP-PCL-OH by ester coupling to produce SiO_2NP-PCL-PEG. HOOC-PEG-OCH_3 (6.35 g, 1.27 mmol) was dissolved in 45 mL of anhydrous DCM in two-neck round bottom flask under N_2 flow. 1.3~~0~~ g of SiO_2NP-PCL-OH suspended by sonication in 45 mL of anhydrous DCM was charged with the above solution of HOOC-PEG-OCH_3 under N_2 flow and the mixture was cooled to 0 °C while stirring. A solution of 790 mg of DCC (3.83 mmol) and 48.50 mg (0.39 mmol) of DMAP was prepared in 12 mL of

DCM and added dropwise to the above reaction mixture over a period of 15 min. After 1 h, the reaction mixture was allowed to warm to room temperature, at which time the stirring was continued for an additional 36 h. The DCC-urea by-product could be removed by selectively centrifugation of the nanoparticles, and decanting off the urea suspended in solution. The resulting particles were cleaned with a series of different solvents (DCM, THF, acetone, water, and methanol) by redispersion/centrifugation and finally vacuum dried overnight. After drying, 1.1 g of functionalized nanoparticles were isolated (83 % yield based on TGA measurement of 1.8 weight % PEG on SiO_2NP-PCL-PEG).

Synthesis of SiO_2NP-2xPCL-PEG. In the first step 0.7 g of SiO_2NP-PCL were dispersed in 21 g of CL (0.184 mol) by sonication in a 50 mL two-neck round bottom flask fitted with a stir bar. After 40 min of Ar purge, 24.00 mg (0.06 mmol) of $Sn(Oct)_2$ was added to the suspension under Ar flow. The flask was placed in a thermostatic oil bath at 130 °C and the suspension was stirred for 5 h under Ar. The SiO_2NP-PCL with OH terminal ends act as immobilized macroinitiators for SIROP of additional CL. The polymer-grafted SiO_2NP-2xPCL were isolated from free polymer as mentioned above in SIROP of CL from SiO_2NPs-OH. In the second step SiO_2NP-2xPCL were attached with HOOC-PEG-OCH_3 by ester coupling using same protocol as mentioned above for attachment of HOOC-PEG-OCH_3 on SiO_2NP-PCL-OH by ester coupling.

Characterization

The PCL grafting reactions on the functionalized silica nanoparticles via surface-initiated ring opening polymerization (SIROP) were monitored using Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP),[3] a non-chromatographic method that relies on continuous extraction and dilution of a small stream of reactor contents on which measurements are simultaneously made by multiple detectors, as the reaction proceeds. A two-stage dilution with tetrahydrofuran (THF) of a small reactor stream was made throughout the reaction using an ensemble of HPLC pumps. Characterization of the amphiphilic SiO_2NP-PCL-PEG copolymer grafted particles in terms of stability in aqueous media, size, and loading capabilities was made by Automatic Continuous Mixing (ACM).

[4] The technique used a Shimadzu HPLC pump, connected to a mixing unit and a detector train containing multi-angle light scattering (Brookhaven), refractive index and UV detectors (Shimadzu). Particle hydrodynamic diameter, D_h (the intensity-weighted average diameter) was determined by dynamic light scattering (DLS) measurements made using a Brookhaven 90-plus detector (λ = 670 nm) operating at a scattering angle of 90°.[5] Further polymer characterization of the grafted PCL-PEG in terms of molecular weight distribution and polydispersity was made by Size Exclusion Chromatography (SEC), with THF as eluent, at 0.8 mL/min. A SDV linear chromatographic column (100 Å single porosity, 3 μm particle size) from Polymer Standards Service and same detectors as in ACM were employed. Molecular weight determination was based on direct measurements from light scattering (LS) data and/or calibration with PCL standards. The Fourier transform infrared (FTIR) spectroscopy was performed using a NEXUS 670 FT-IR SEP. Analyte was mixed with KBr and ground into a fine powder by mortar and pestle and compacted into a pellet by applying pressure. Thermogravimetric analysis (TGA) data was acquired using TA Instruments TGA 2950 Thermogravimetric Analyzer with heating rate of 20 °C per minute under N_2 atmosphere. Data was processed using TA Instruments Universal Analysis software. Transmission electron (TEM) microscopy data was collected with a FEI G2 F30 Tecnai TEM operated at 200 kV. All the samples were suspend in ethanol and casted on the

TEM grid. Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ (7.26 ppm for ^1H and 77.36 for ^{13}C), as internal reference. MALDI spectra were collected using a Bruker UltraFlex MALDI-TOF MS with a SCOUT-MTP Ion Source (Bruker Daltonics, Bremen), N_2-laser (337nm), and reflector design was used. The intensity of the laser was set to the lowest possible level to acquire high resolution spectra of the product and all spectra were acquired using reflector-positive mode. The instrument was calibrated using SpheriCal™ calibrants purchased from Polymer Factory Sweden AB. The received spectra were analyzed using the software FlexAnalysis from Bruker Daltonics, Bremen, version 2.2. A Bruker Avance 400 MHz NMR instrument was used for ^1H NMR and ^{13}C NMR experiments. Proton NMR spectra were acquired with a spectral window of 20 ppm, an acquisition time of 4 seconds and a relaxation delay of 2 seconds. ^{13}C NMR spectra were acquired with a spectral window of 250 ppm, an acquisition time of 0.7 seconds and a relaxation delay of 5 seconds.

Characterization of the silica nanoparticles. Initial characterization of the commercially available starting material provided by Nissan Chemical Industries, LTD as ~30 wt% of colloidal silica particles in isopropanol was carried out to confirm their well-defined structure.

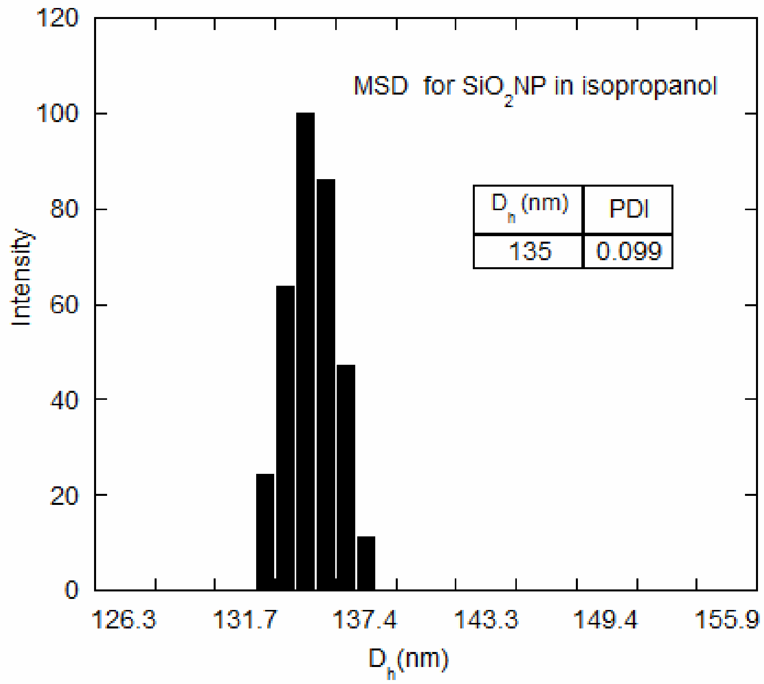


Figure S1. MSD data from DLS experiments for SiO_2NPs in isopropanol.

Results of the DLS measurements made on diluted nanoparticles (SiO_2NPs) in isopropanol give an average D_h value of 135 nm and narrow polydispersity (PDI) ~ 0.1, confirming their excellent dispersibility. Figure S1 shows a graphical representation in terms of multimodal size distribution (MSD), based on the non-negatively constrained least squares (NNLS) algorithm used to fit data.[1]

General procedure for cleavage of (co)polymers from silica nanoparticles.[6,7] SiO_2-polymer nanoparticles (100.0 mg) were suspended in 4 mL of toluene or dichloromethane (DCM) in a Teflon flask. Aliquat 336 (phase transfer catalyst, 50.0 mg) and 48% HF (aq) solution (5 mL) were added to the particle suspension and the reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was washed with aqueous $NaHCO_3$ and water and organic layer containing polymer was separated. Polymer was recovered by evaporation of solvent.

Characterization of the free PCL, grafted PCL cleaved from SiO_2NP-PCL, and grafted PCL-PEG cleaved from SiO_2NP-PCL-PEG. Characterization of the free and grafted polymers obtained during SIROP reactions (and subsequently cleaved from the nanoparticles) in terms of molecular weight was conducted by size exclusion chromatography (SEC) in THF, relative to PCL standards (previously synthesized by ROP with each M_n determined by MALDI). Weight average molecular weight (M_w) values of 7400 g/mole and 12,000 g/mole and rather low polydispersity values (~1.1) for the free and cleaved PCL, respectively, were determined.

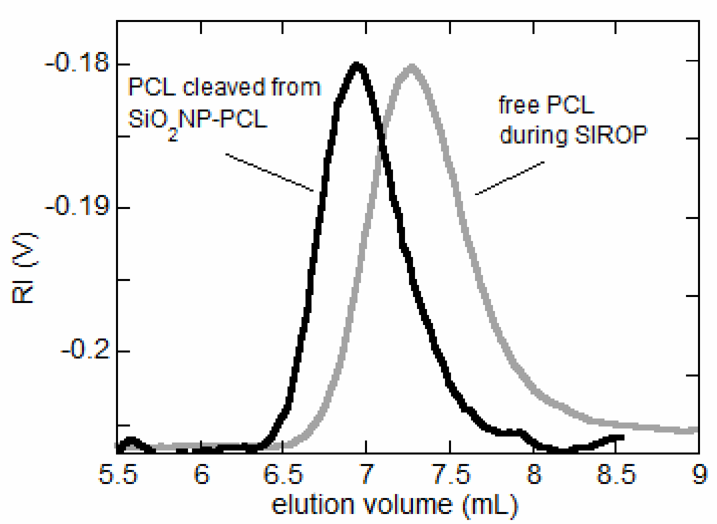


Figure S2. SEC: RI data from PCL cleaved from SiO_2NP-PCL, compared to the free PCL during SIROP led to M_n values of 11243 (Đ=1.1806) and 6894 g/mole (Đ=1.1822) for the cleaved and free PCL, respectively, based on calibration curve with linear PCL

To provide a measure of the accuracy of the molecular weight determination by SEC, MALDI data for the free PCL was also acquired in Figure S3.

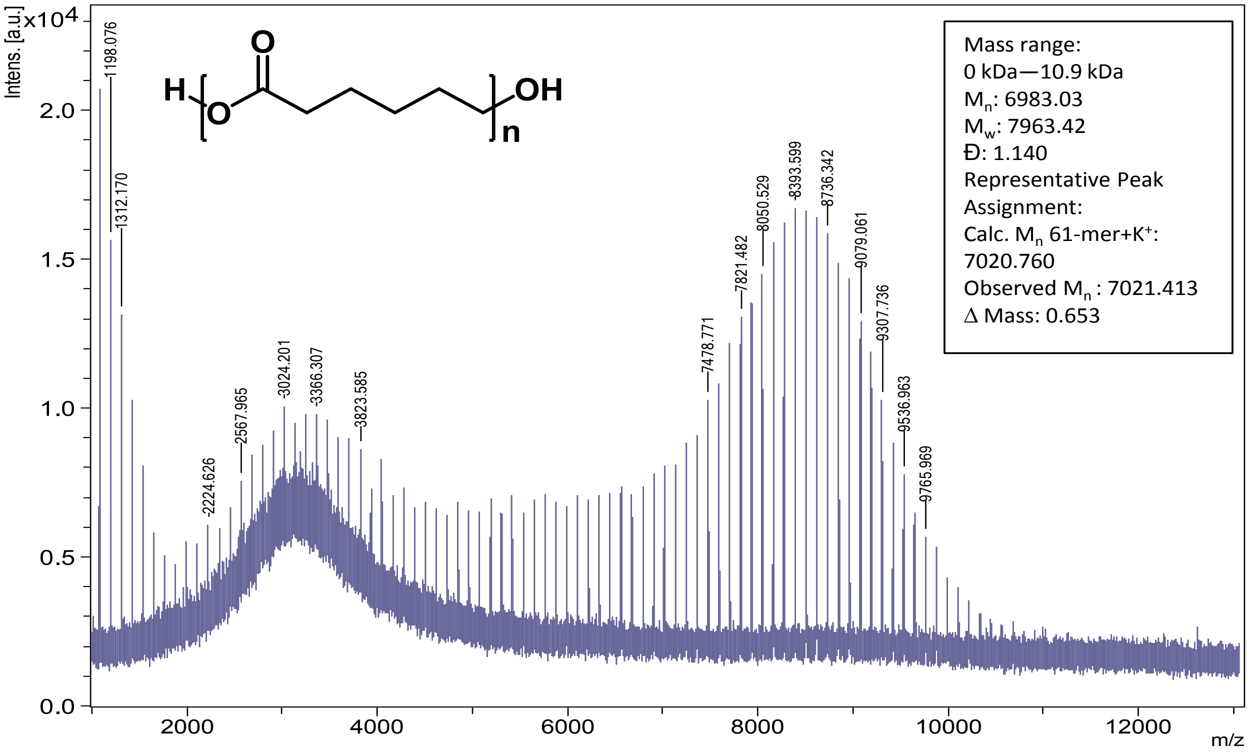


Figure S3. MALDI TOF mass spectrum of free PCL. MS conditions: matrix: 2-mercapto-benzothiazole 10 mg mL^{-1}, analyte: 20 mg mL^{-1}, and added cation: potassium trifluoroacetate 1 mg mL^{-1} [7:7:1], calibrated, reflector mode.

In order to quantify the ratio of PEG to PCL, the SiO_2NP-PCL-PEG were treated with HF to isolate free block copolymer, and the block ratio determined by ^{1}H NMR (Figures S4-S10).

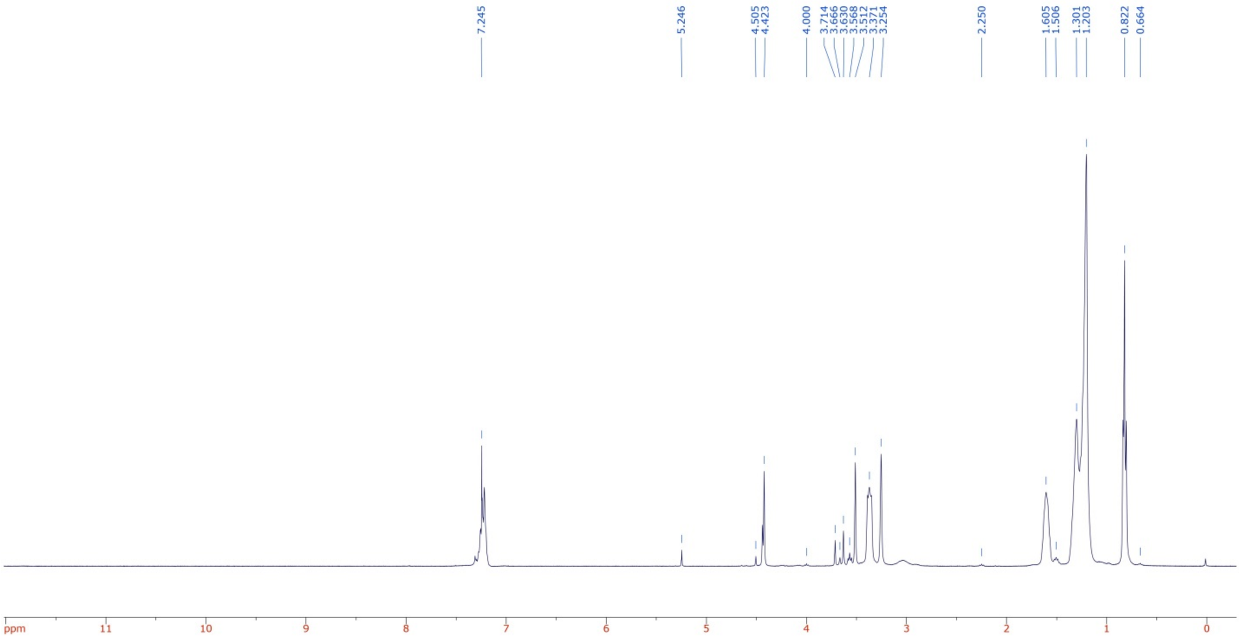


Figure S4. ^{1}H NMR spectrum of product of native silica nanoparticles (without polymer grafting) after treatment with HF/Aliquot 336 catalyst, in $CDCl_3$

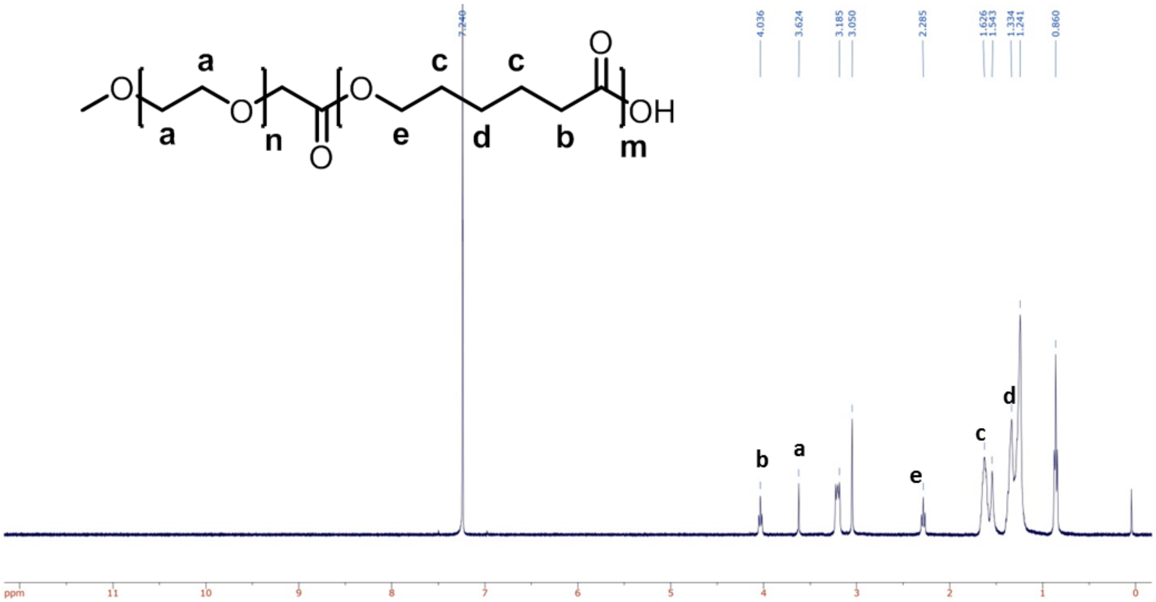
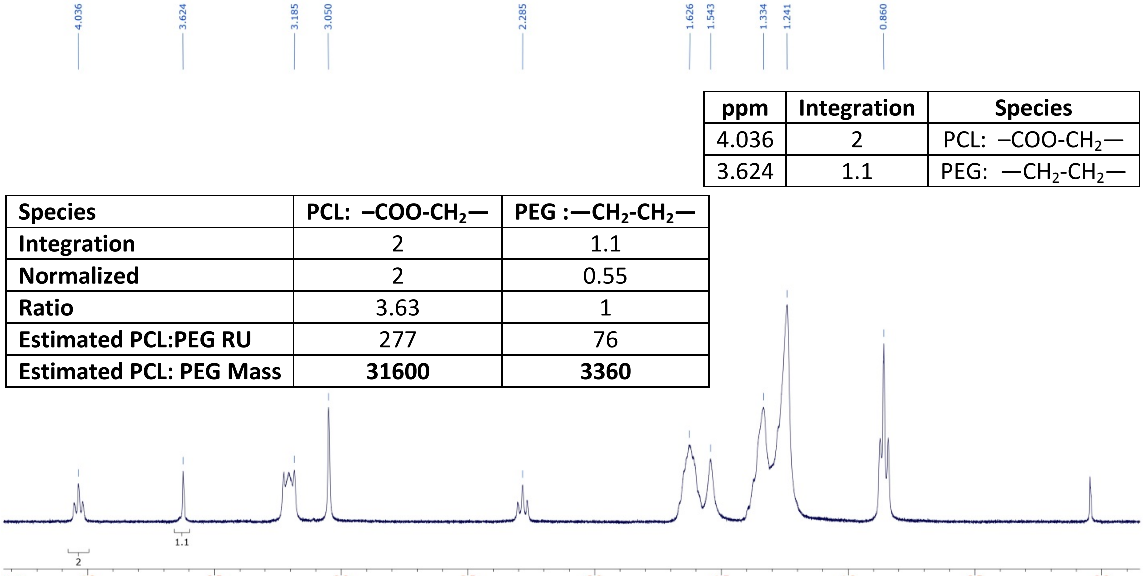


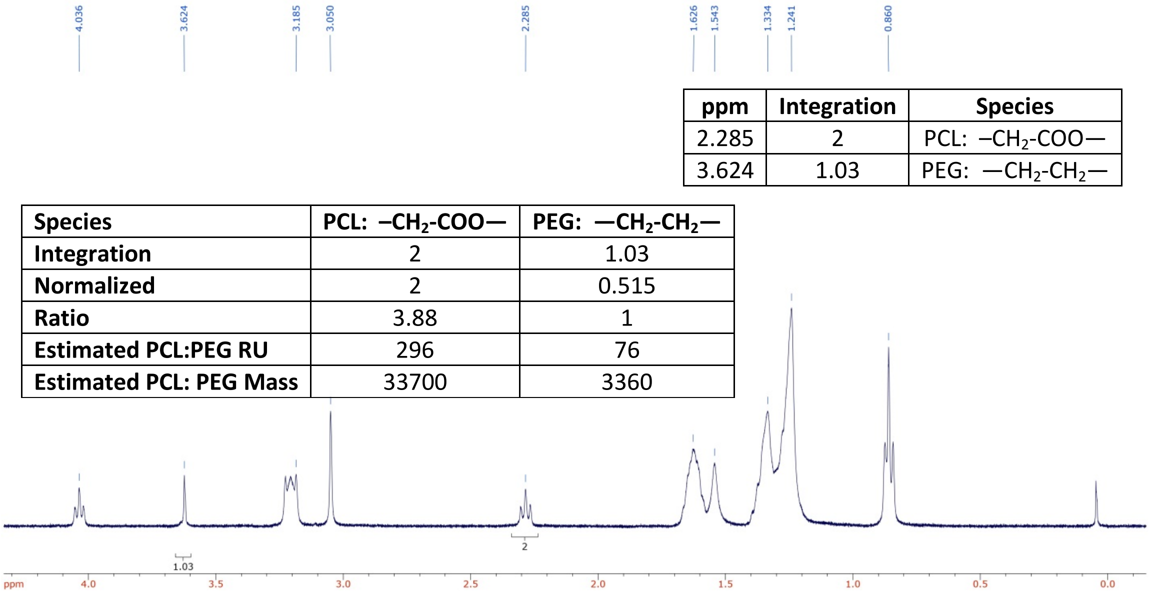
Figure S5. ^{1}H NMR spectrum in $CDCl_3$ of SiO_2NP-PCL-PEG treated with HF/Aliquot 336.



ppm	Integration	Species
4.036	2	PCL: $-COO-CH_2-$
3.624	1.1	PEG: $-CH_2-CH_2-$

Species	**PCL: $-COO-CH_2-$**	**PEG: $-CH_2-CH_2-$**
Integration	2	1.1
Normalized	2	0.55
Ratio	3.63	1
Estimated PCL:PEG RU	277	76
Estimated PCL: PEG Mass	**31600**	**3360**

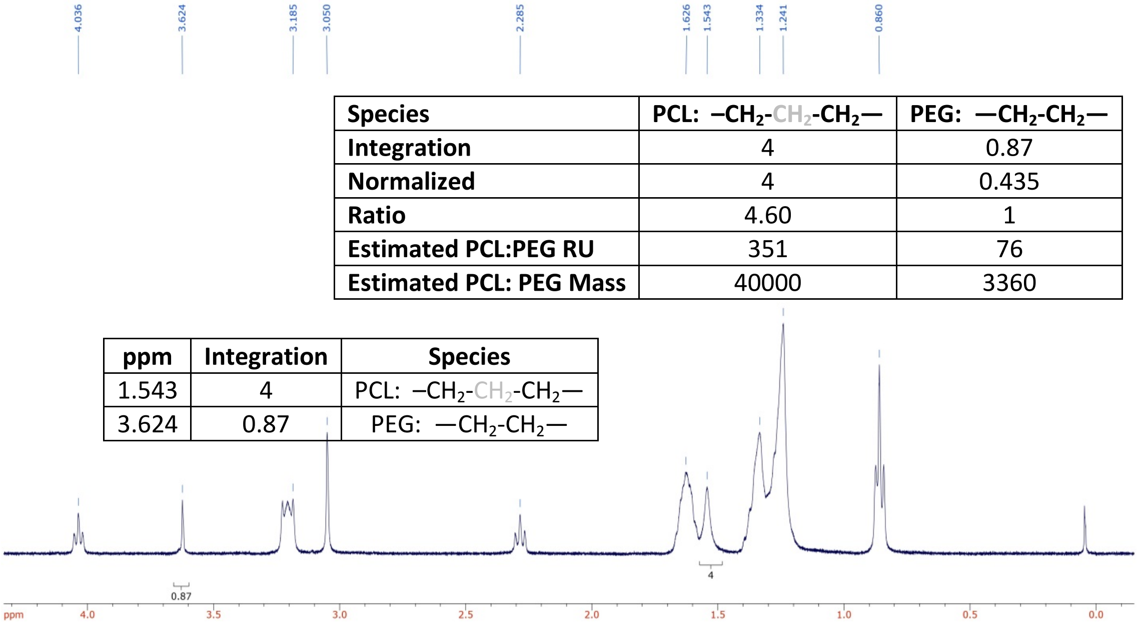
Figure S6. Integration of significant peaks from ^{1}H NMR spectrum in $CDCl_3$ of SiO_2NP-PCL-PEG treated with HF/Aliquot 336; values calculated against PCL ester α-position hydrogens, and molecular weight estimations based on PEG = 3360.



ppm	Integration	Species
2.285	2	PCL: –CH_2-COO—
3.624	1.03	PEG: —CH_2-CH_2—

Species	PCL: –CH_2-COO—	PEG: —CH_2-CH_2—
Integration	2	1.03
Normalized	2	0.515
Ratio	3.88	1
Estimated PCL:PEG RU	296	76
Estimated PCL: PEG Mass	33700	3360

Figure S7. Integration of significant peaks from ^1H NMR spectrum in $CDCl_3$ of SiO_2NP-PCL-PEG treated with HF/Aliquot 336; values calculated against ester ω-position hydrogens, and molecular weight estimation based on PEG = 3360.



Species	PCL: –CH_2-CH_2-CH_2—	PEG: —CH_2-CH_2—
Integration	4	0.87
Normalized	4	0.435
Ratio	4.60	1
Estimated PCL:PEG RU	351	76
Estimated PCL: PEG Mass	40000	3360

ppm	Integration	Species
1.543	4	PCL: –CH_2-CH_2-CH_2—
3.624	0.87	PEG: —CH_2-CH_2—

Figure S8. Integration of significant peaks from ^1H NMR spectrum in $CDCl_3$ of SiO_2NP-PCL-PEG treated with HF/Aliquot 336; values calculated against ester β,δ-position hydrogens, and molecular weight estimation based on PEG =3360.

Table S1. TGA relative mass estimation, based on the assumption that PEG M_n = 3360 for SiO_2NP-PCL-PEG.

Polymer	**Weight Loss (%)**	**Mass Ratio**	**Estimated Mass**	**Estimated Repeat Unit**	**Repeat Unit Ratio**
PCL	12.1	6.72	22600	198	2.59
PEG	1.8	1	3360	76	1

Table S2. ^{1}H NMR relative mass estimation based on the assumption that PEG M_n = 3360 for SiO_2NP-PCL-PEG.

Position	Ratio PEG:PCL	Calculated PCL Repeat Units	Calculated PCL Mass
α	1:3.64	277	31600
ω	1:3.88	296	33700
β, δ	1:4.60	351	40000
Average	**1:4.04**	**308**	**35100**

General procedure for basic hydrolysis of SiO_2NP-PCL-PEG

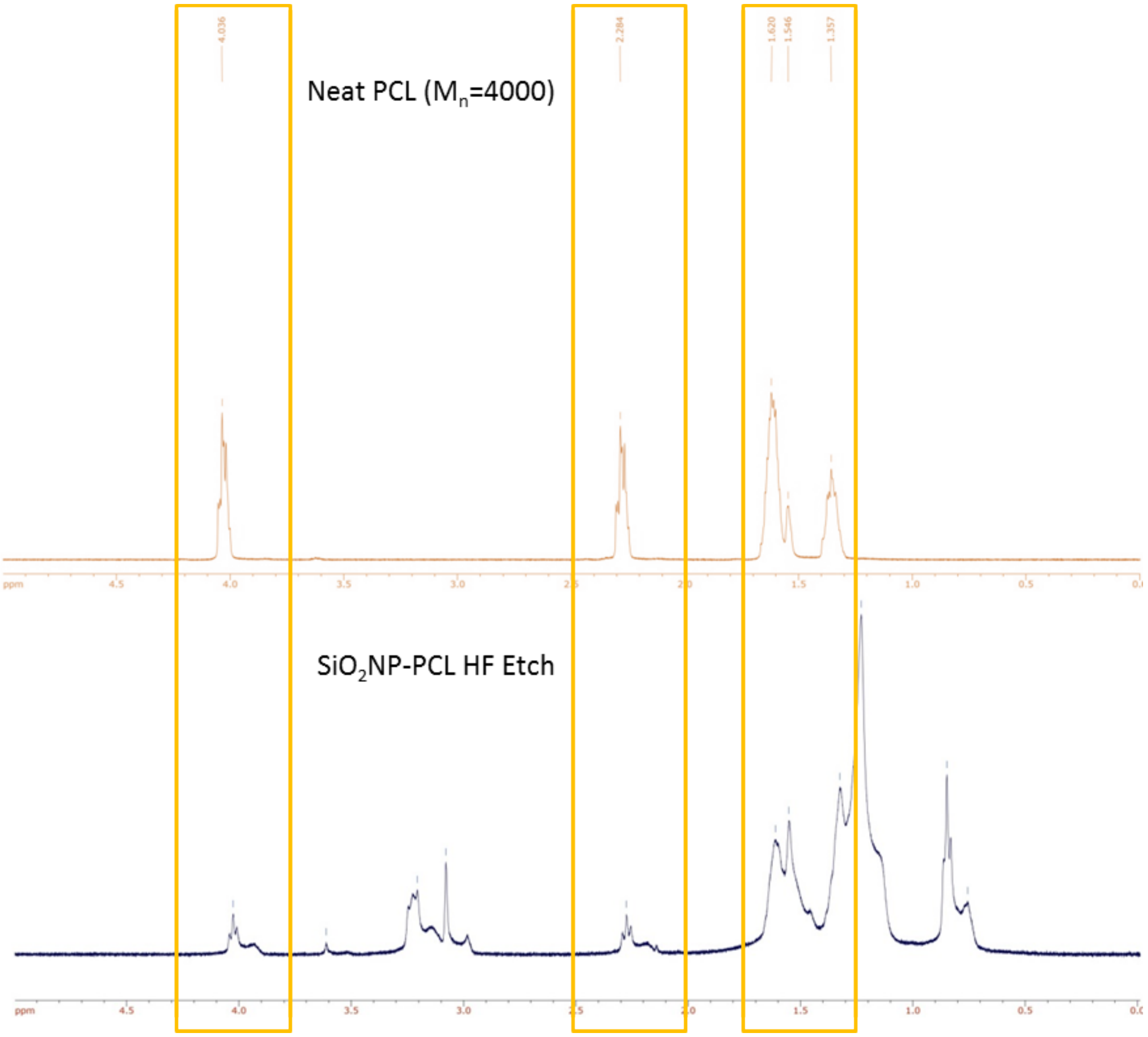


Figure S9. ^{1}H NMR spectrum in $CDCl_3$ of SiO_2NP-PCL treated with HF/Aliquot 336; overlay with neat PCL ^{1}H NMR spectrum to confirm the presence of PCL in the HF treated product.

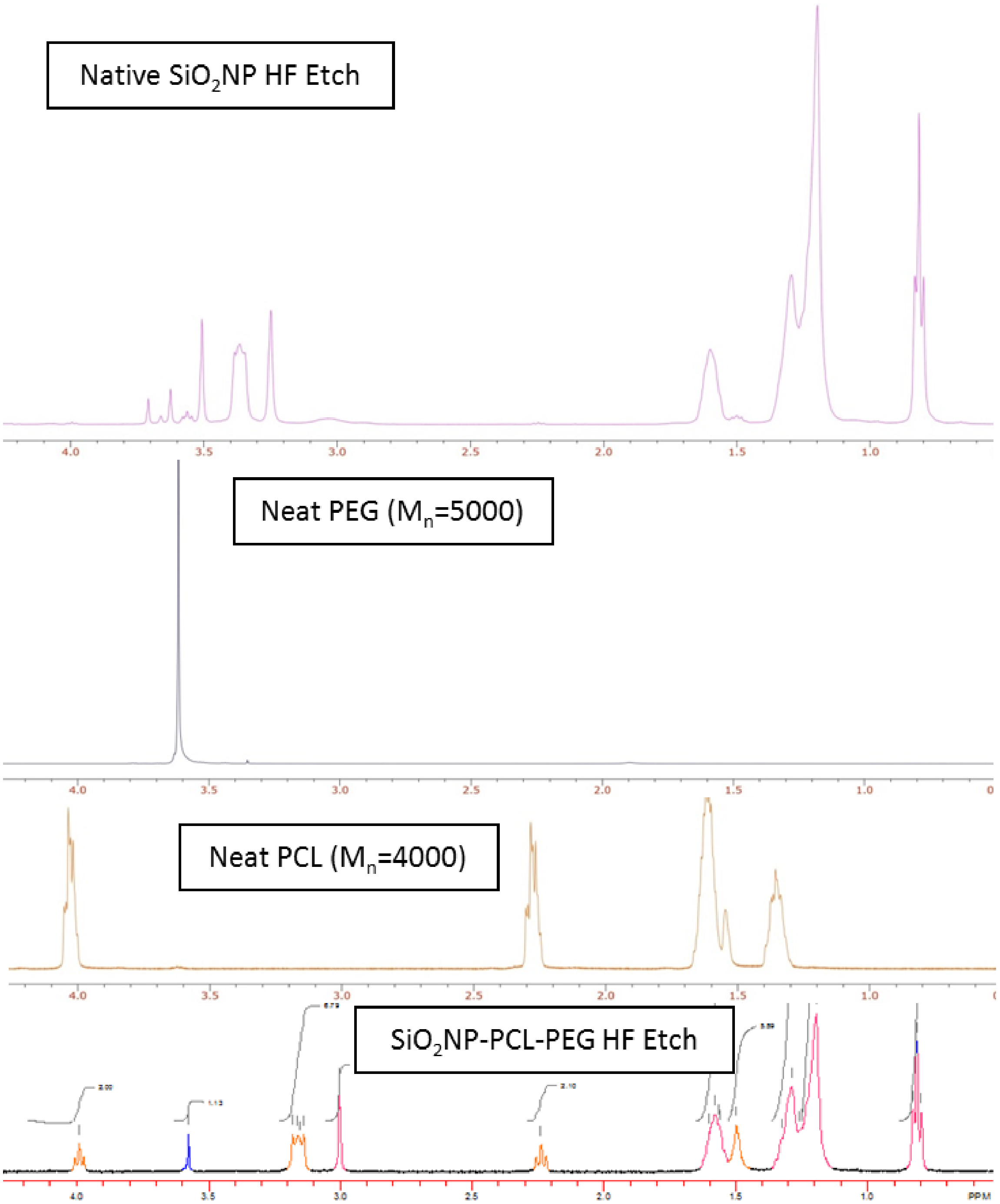


Figure S10. ^{1}H NMR spectrum of SiO_2NP-PCL-PEG treated with HF/Aliquo 336, in $CDCl_3$; overlay with neat PCL, neat PEG and native SiO_2NP after HF/Aliquot 336 etch ^{1}H NMR spectra to confirm the assignment of PEG (purple), PCL (orange), and SiO_2NP/aliquot byproducts (pink).

As an additional confirmation of the attachment of PEG, the PEG-PCL functionalized nanoparticles were reacted with NaOH to complete degrade the PCL, enabling the PEG (and degraded PCL) to be characterized by NMR and MALDI-ToF MS (Figures S11-S13):

General procedure for treatment of silica nanoparticles grafted with PCL and PEG with NaOH. SiO_2-polymer nanoparticles (50.0 mg) were suspended in 15 mL of THF. 3 mL of 0.01 NaOH (aq) solution was added to the above suspension and reaction mixture was allowed to stir at room temperature for 12 h. At this stage, the reaction mixture could be extracted with CH_2Cl_2 to isolate the PEG. Alternatively, the reaction could be acidified to neutrality with 1 M HCl and extracted with $CHCl_3$ in order to isolate PEG along with the degradation product (hydroxyhexanoic acid) of the PDL.

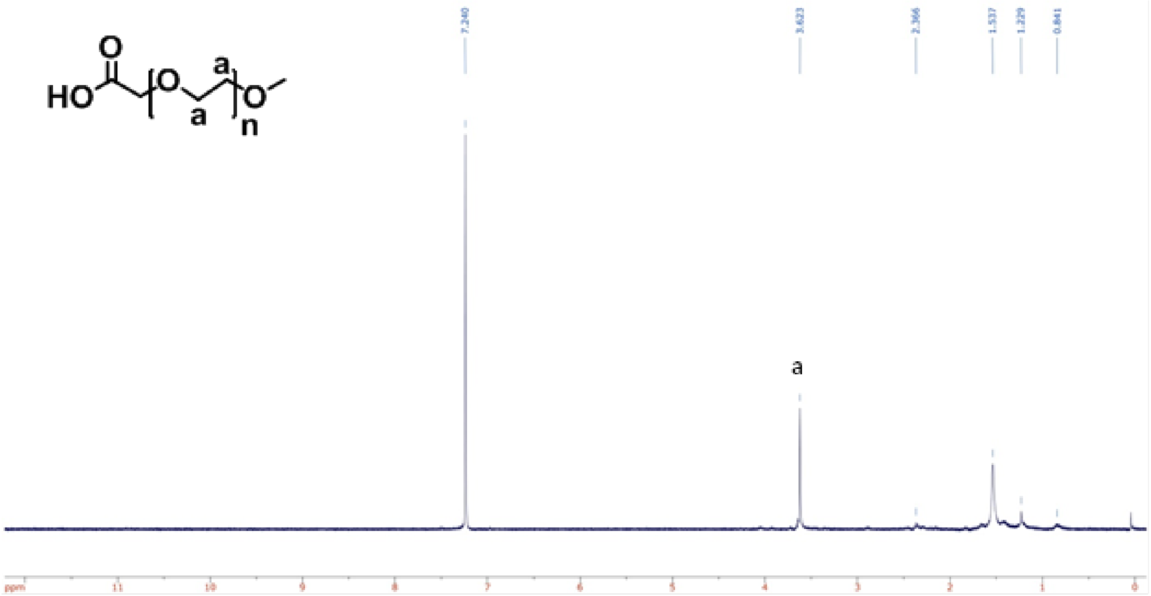


Figure S11. ^1H NMR spectrum in $CDCl_3$ of SiO_2NP-PCL-PEG treated with NaOH, PCL degradation followed by PEG extraction in CH_2Cl_2 (no acid quench).

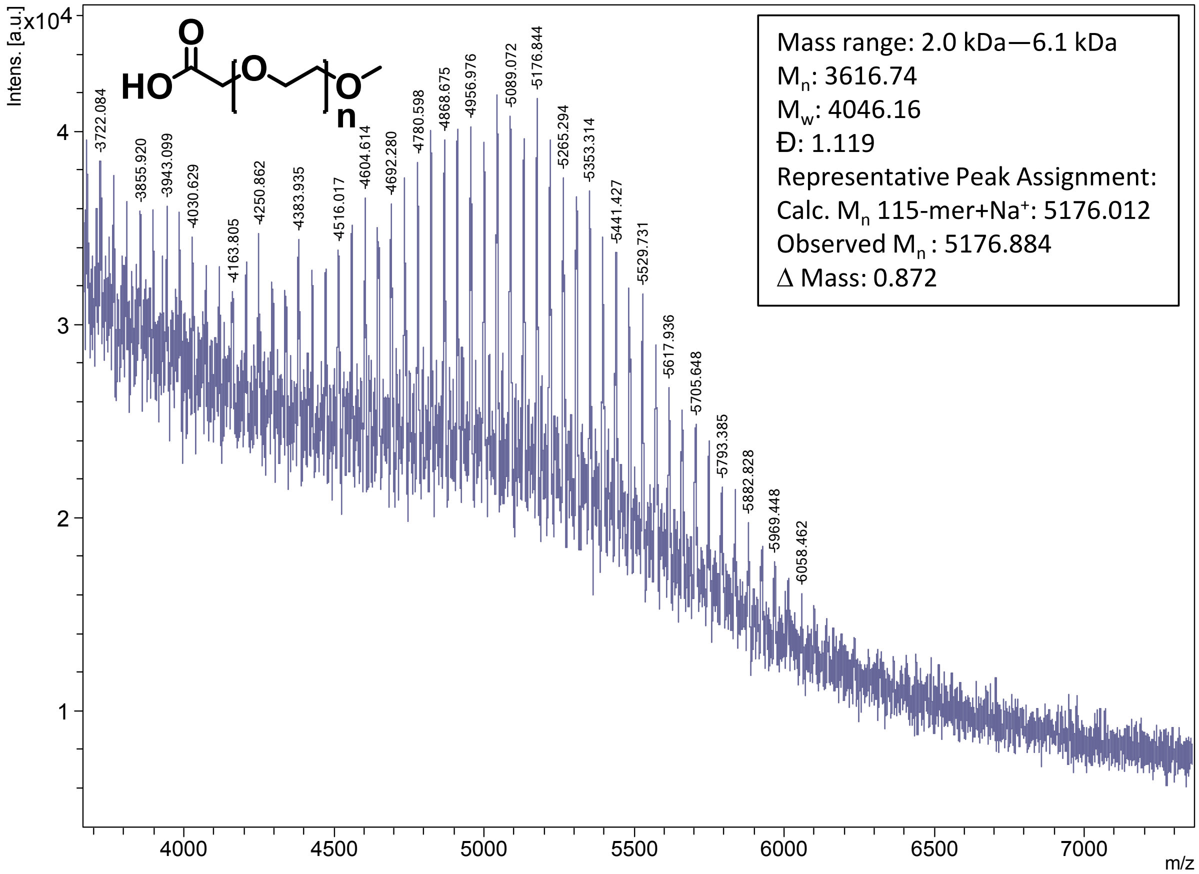


Figure S12. MALDI TOF mass spectrum of PEG carboxylic acid, removed from SiO_2NP-PCL-PEG by treatment with NaOH, (to achieve PCL degradation) followed by acid quench. MS conditions: matrix: trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) 20 mg/mL, analyte: 20 mg/mL, and added cation: sodium trifluoroacetate 2 mg mL^{-1} [3:2:1], calibrated, reflector mode.

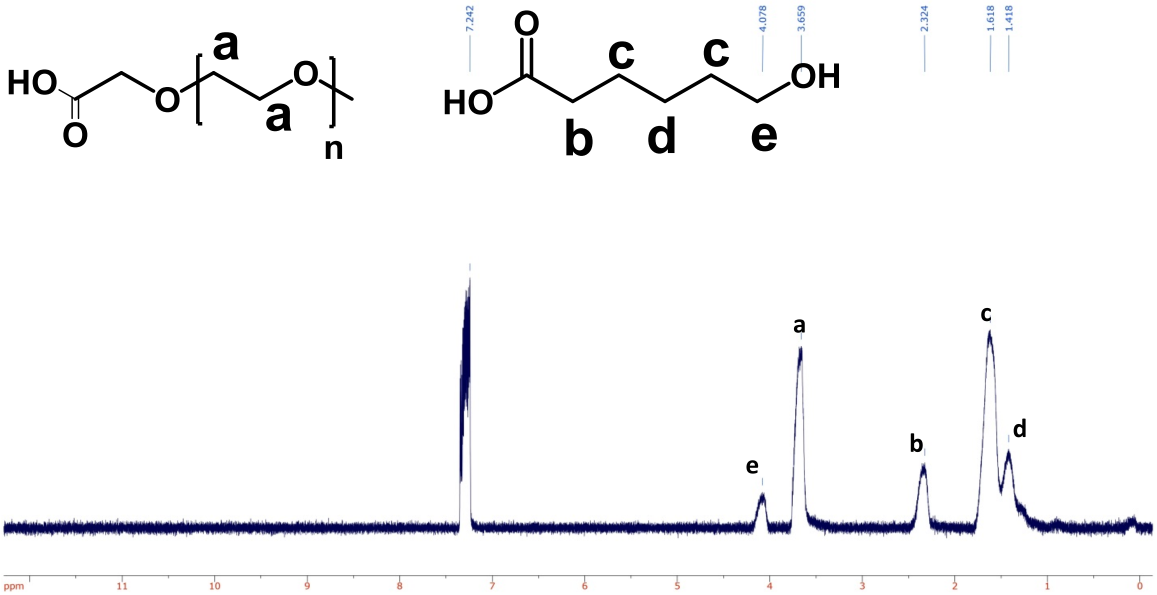


Figure S13. ^{1}H NMR spectrum in $CDCl_3$ of the degraded polymer grafts (hydrolyzed PCL as well as PEG) obtained by treatment of SiO_2NP-PCL-PEG with NaOH, PCL degradation, followed with acid quench and extraction into $CHCl_3$.

Particle size and stability of the nanoparticles in aqueous solutions. DLS experiments made on aqueous solutions containing nanoparticles at different stages of the synthesis: the bare SiO_2NP, the surface-functionalized SiO_2NP-GPS, the hydrophobic, grafted SiO_2NP-PCL, and the amphiphilic copolymer-grafted SiO_2NP-PCL-PEG confirmed that the nanoparticles were rather stable when dispersed in aqueous media and exhibited homogeneous particle distributions, with the notable exception of the hydrophobic PCL grafted nanoparticles which exhibited limited stability and a tendency to aggregate. An illustration of their behavior is shown in Fig. S19 containing multimodal size distribution (MSD) data for all the above types of nanoparticles in aqueous solutions. The number-weighted distributions are shown in the figure. Data for SiO_2NP-PCL are included only to show the presence of aggregated particles, otherwise not quantitatively meaningful.

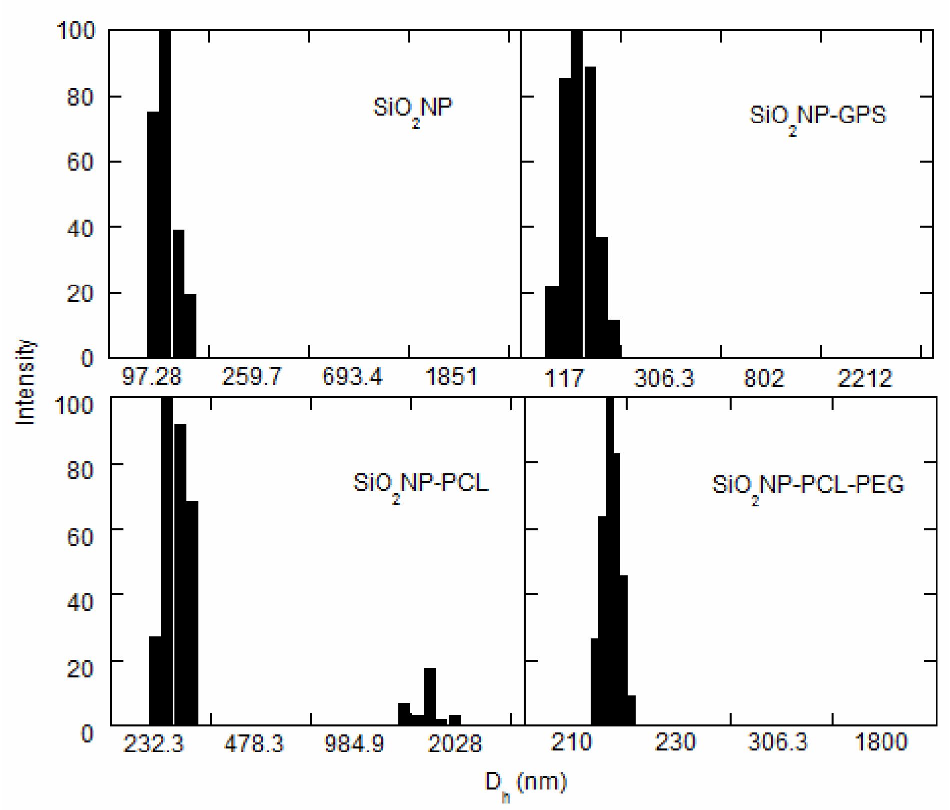


Figure S14. MSD data from DLS experiments for SiO_2NP, SiO_2NP-GPS, SiO_2NP-PCL, and SiO_2NP-PCL-PEG

Results from additional studies shown in Table S3 confirmed that the behavior of the SiO_2NP-PCL-PEG nanoparticles was not significantly affected by variations of the aqueous media, including fresh water, salt water or water samples extracted from the Gulf of Mexico.

Table S3. Intensity-averaged D_h values from multiple DLS measurements made on aqueous SiO_2NPs-PCL-PEG dispersed in fresh water, salt water, and in water samples from the Gulf of Mexico

In water			In 0.6 M NaCl			In sea water		
D_h(nm)	PDI	LS90	D_h(nm)	PDI	LS90	D_h(nm)	PDI	LS90
211	0.129	270.5	203	0.047	235.4	232	0.210	366.1

Shown in Figure S15 are PDI (top) and D_h and LS90° *vs*. temperature for SiO_2NP-PCL-PEG in sea water, indicating no significant effect of the temperature on the physical characteristics studied.

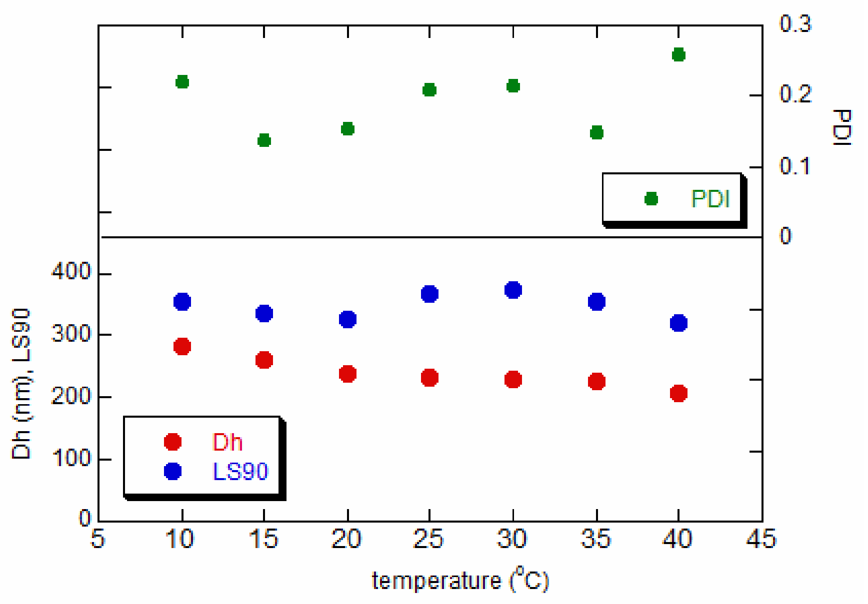


Figure S15. PDI (top) and D_h and LS90 LS *vs*. temperature for SiO_2NP-PCL-PEG in sea water

Small hydrophobic molecule sequestration by SiO_2NPs-PCL-PEG copolymer grafted particles. Additional DLS data – MSD (intensity-weighted distributions) for SiO_2NP-PCL-PEG/Hph aqueous mixtures compared to data for Hph alone - are shown in Figure S16. Narrow

MSDs for the copolymer nanoparticles & Hph mixture contrasts to the bimodal MSD of the aggregated hydrophobic Hph and confirm, by the disappearance of the clustered particles, the Hph sequestration.

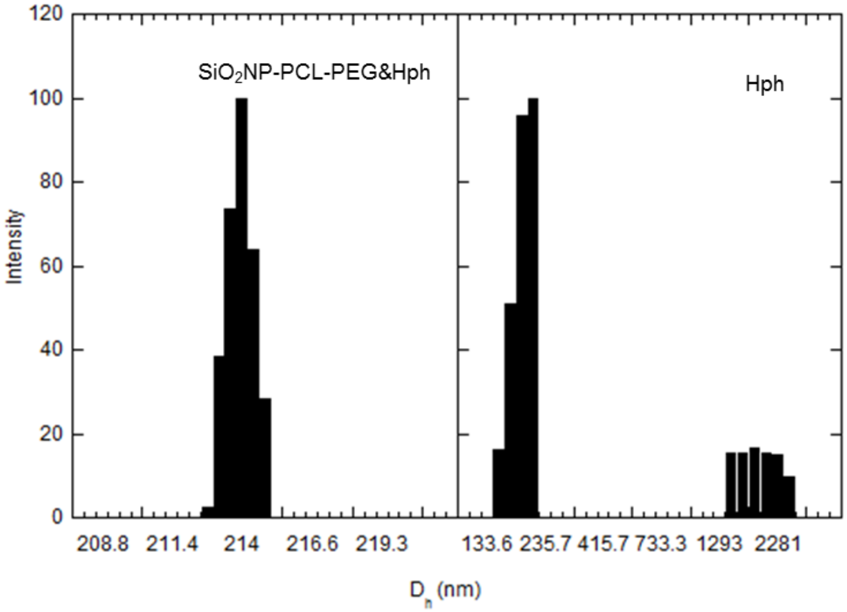


Figure S16. MSD data from DLS experiments for SiO_2NP-PCL-PEG/Hph aqueous mixtures compared to Hph

Discrete UV and fluorescence experiments with pyrene shown in Figure S17 allowed comparing SiO_2NP-PCL-PEG and Corexit loading capabilities. Excess pyrene was added to the aqueous nanoparticle with different PCL layer and Corexit solutions (0.1 mg mL^{-1}) and, after filtering off the undissolved dye, UV spectra were acquired. Based on the UV data at 335 nm, Corexit could load about twice the amount of guest than the single layer SiO_2NP-PCL-PEG and 1.6 times as much as the double layer SiO_2NP-2xPCL-PEG.

The intensity ratio of the two characteristic absorbance peaks at 383 nm and 373 nm (I_3/I_1) from uncalibrated fluorescence experiments, also shown in the figure (top), indicate higher loading capabilities of the SiO_2NP-2xPCL-PEG and Corexit, compared to SiO_2NP-1xPCL-PEG.

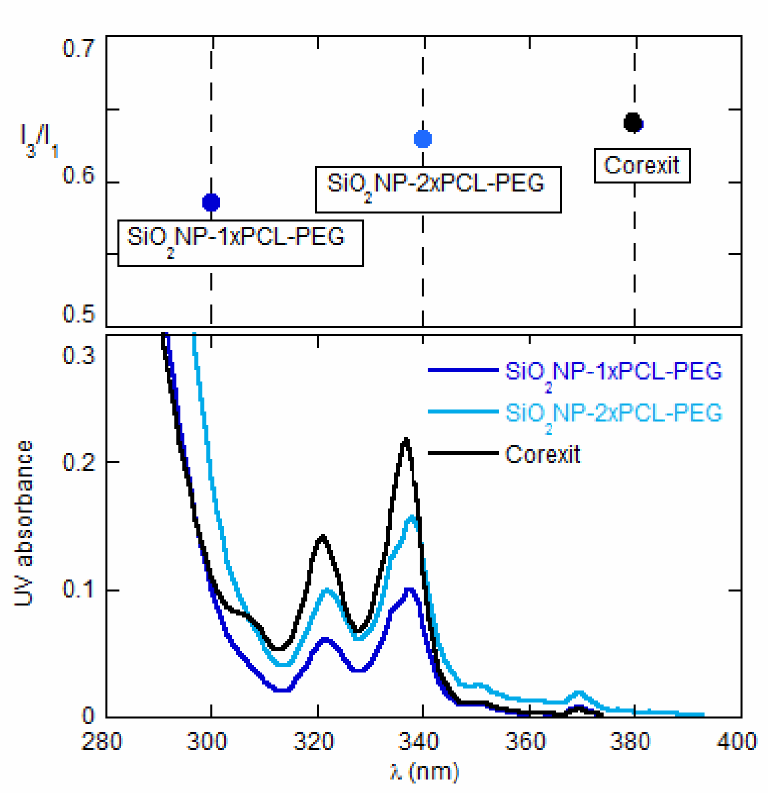


Figure S17. Fluorescence emission spectra (top) and UV spectra (bottom) from pyrene encapsulation for SiO_2NP-PCL-PEG, SiO_2NP-2xPCL-PEG, and Corexit (0.1mg mL^{-1}) in water

Data from the reactant and final product characterization by ^{1}H NMR, ^{13}C NMR and MALDI mass spectra are shown in Figures S18-S21 and Figures S22-S25, respectively.

Characterization of HOOC-PEG-OCH_3 starting material

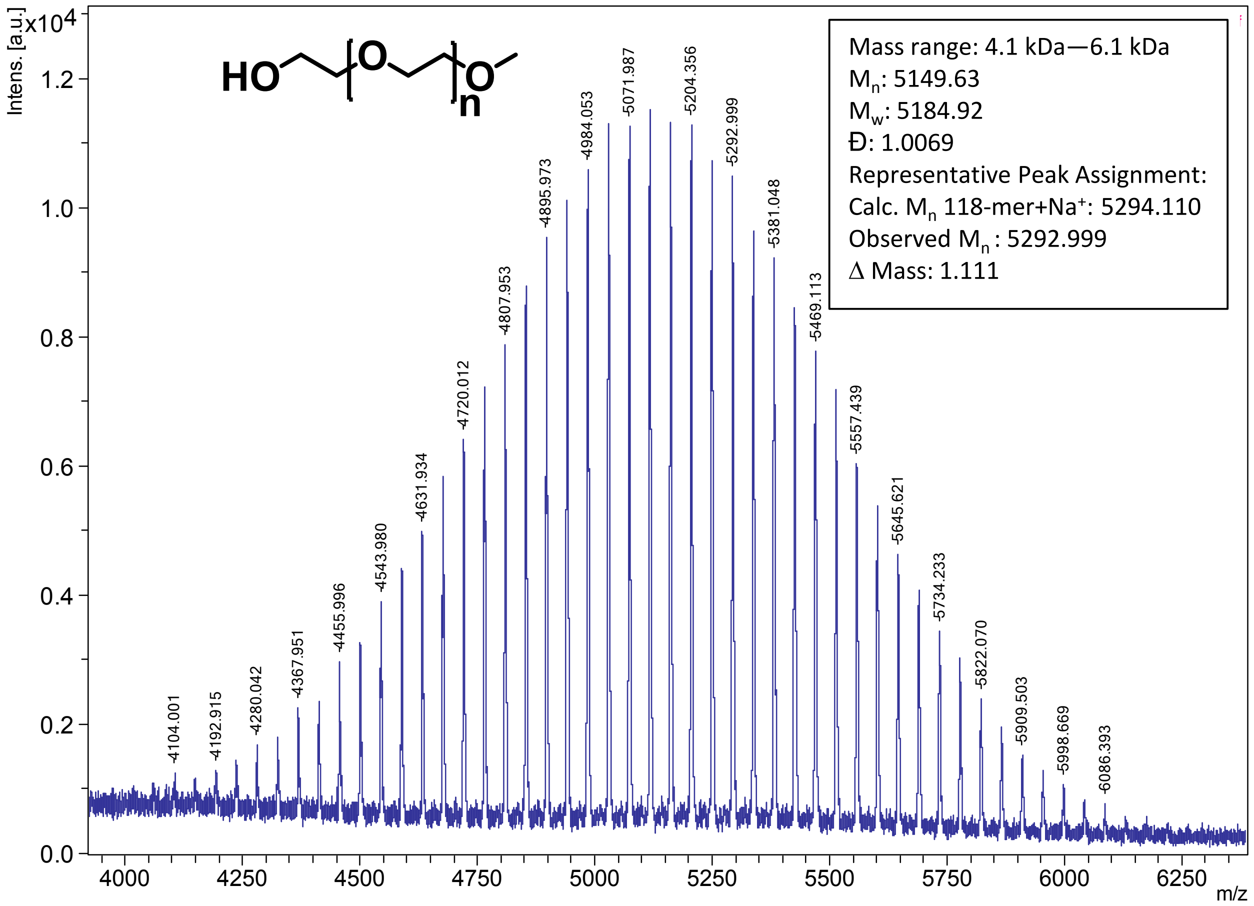


Figure S18. MALDI TOF mass spectrum of *α*-hydroxy-*ω*-methoxy PEG 5000 (MeO-PEG-OH). MS conditions: matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) 20 mg mL^{-1}, analyte: 20 mg mL^{-1}, and added cation: sodium trifluoroacetate 2 mg/ mL [3:2:1], calibrated, reflector mode

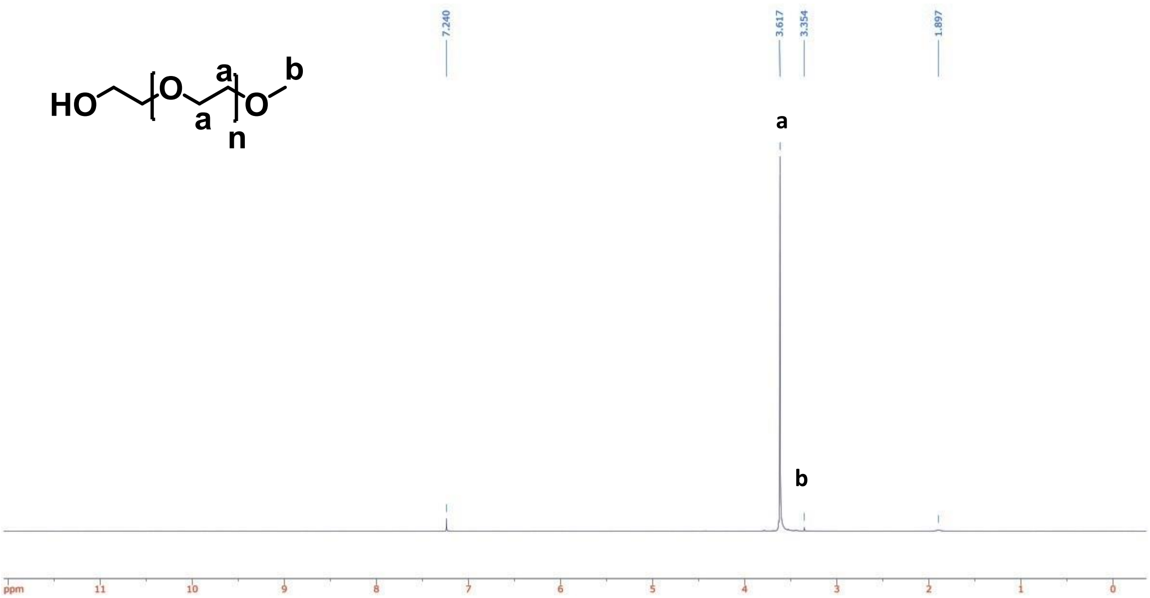
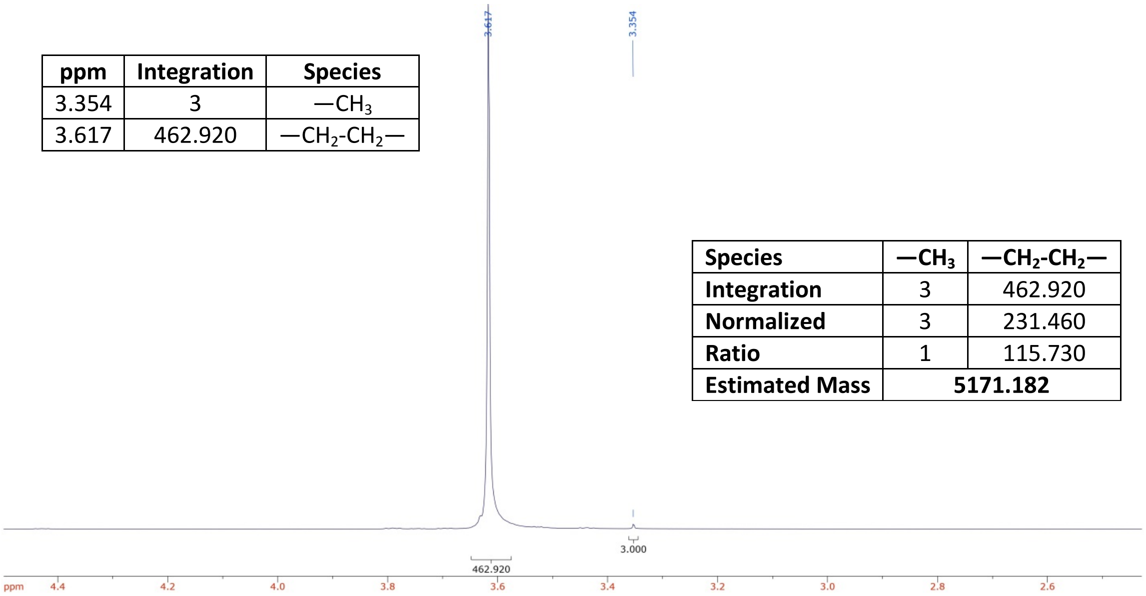


Figure S19. ^{1}H NMR spectrum in $CDCl_3$ of α -hydroxy-ω-methoxy PEG 5000 (MeO-PEG-OH) in $CDCl_3$



ppm	Integration	Species
3.354	3	—CH_3
3.617	462.920	—CH_2-CH_2—

Species	**—CH_3**	**—CH_2-CH_2—**
Integration	3	462.920
Normalized	3	231.460
Ratio	1	115.730
Estimated Mass	**5171.182**	

Figure S20. Integration of significant peaks from ^{1}H NMR spectrum of α-hydroxy-ω--methoxy PEG 5000 (MeO-PEG-OH) in $CDCl_3$; mass calculation

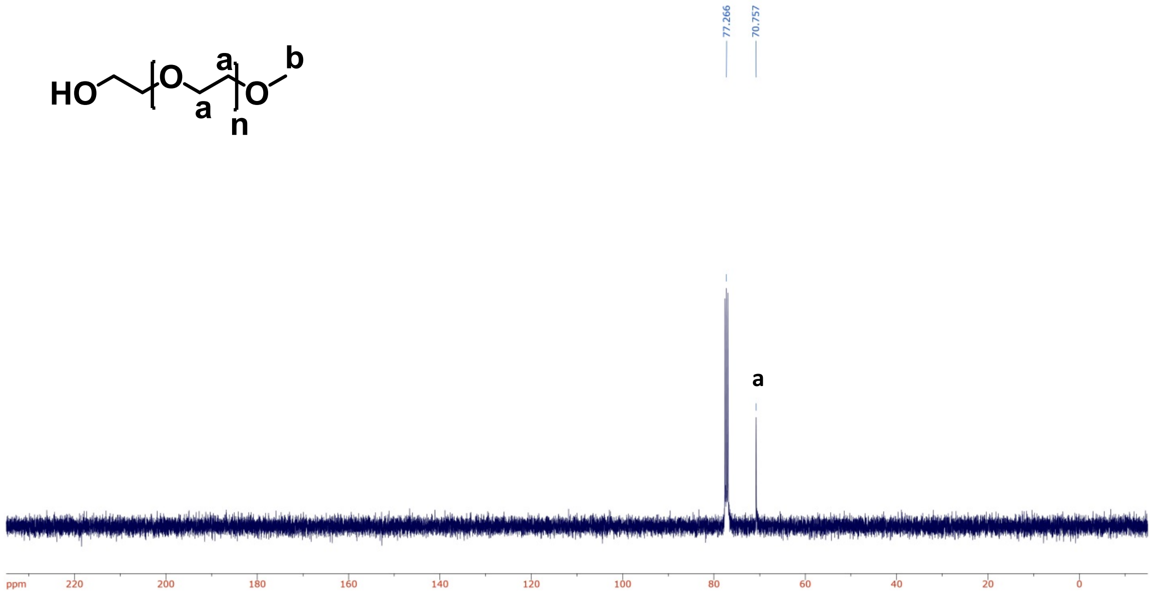
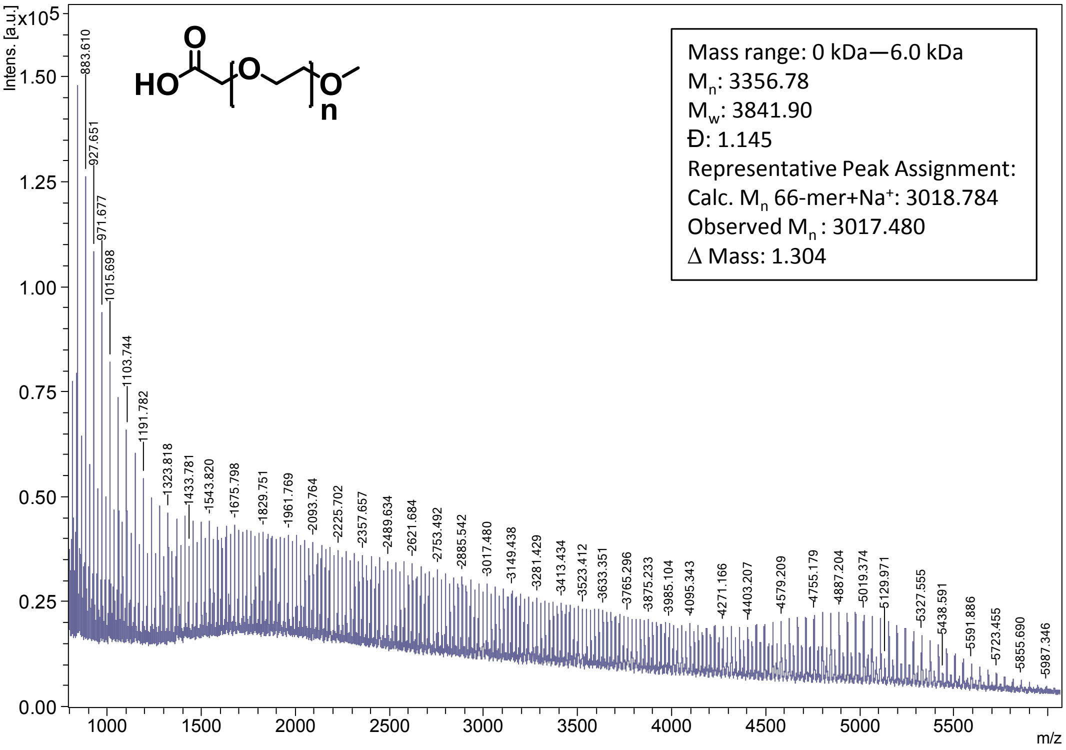


Figure S21. ^{13}C NMR spectrum of α -hydroxy-ω-methoxy PEG 5000 (MeO-PEG-OH) in $CDCl_3$

Characterization of HOOC-PEG-OCH$_3$ product for DCC coupling



Mass range: 0 kDa—6.0 kDa
M_n: 3356.78
M_w: 3841.90
Đ: 1.145
Representative Peak Assignment:
Calc. M_n 66-mer+Na$^+$: 3018.784
Observed M_n : 3017.480
Δ Mass: 1.304

Figure S22. MALDI TOF mass spectrum of α-carboxy-ω-methoxy PEG 3360 (MeO-PEG-COOH). MS conditions: matrix: *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) 20 mg mL^{-1}, analyte: 20 mg/mL, and added cation: sodium trifluoroacetate 2 mg mL^{-1} [3:2:1], calibrated, reflector mode.

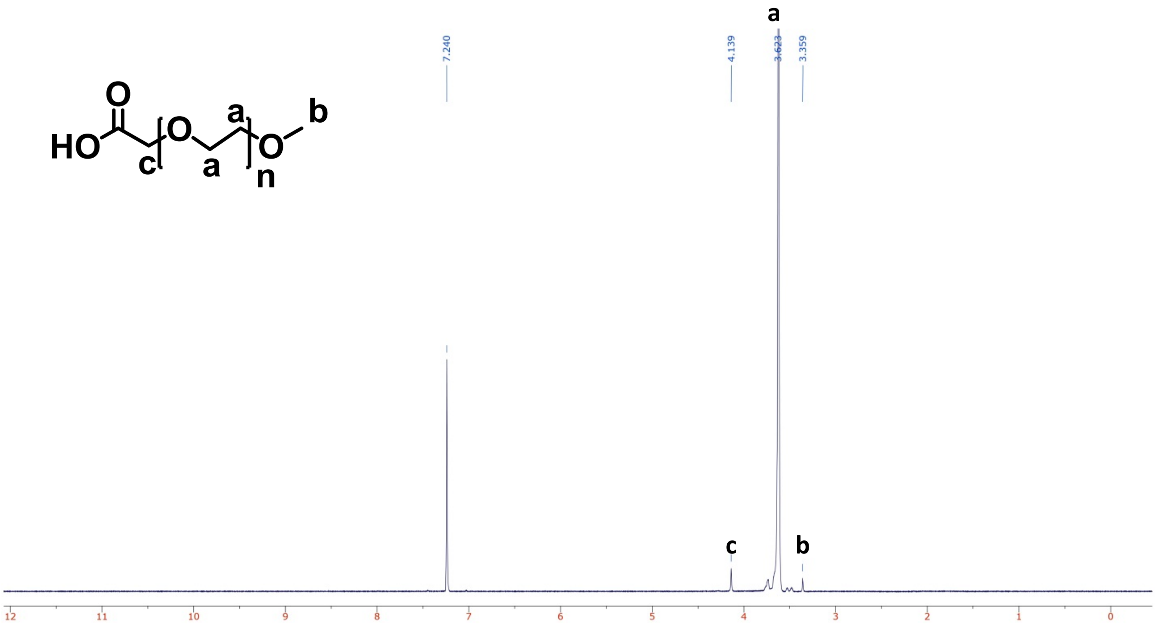
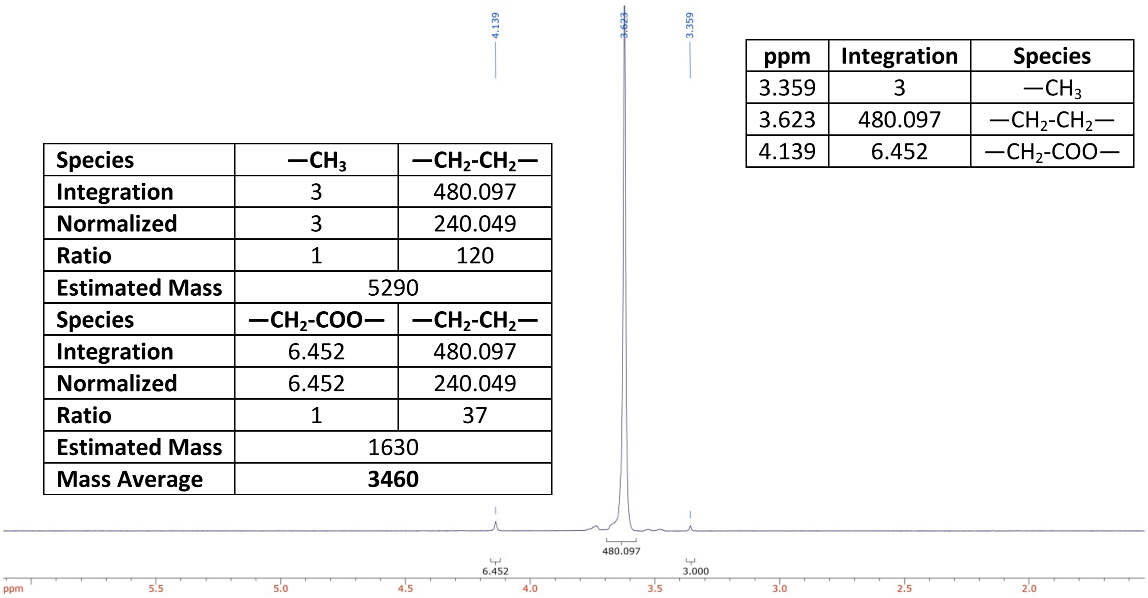


Figure S23. ^{1}H NMR spectrum of α-carboxy-ω-methoxyPEG 3360 (MeO-PEG-COOH) in $CDCl_3$



Species	—CH_3	—CH_2-CH_2—
Integration	3	480.097
Normalized	3	240.049
Ratio	1	120
Estimated Mass	5290	
Species	—CH_2-COO—	—CH_2-CH_2—
Integration	6.452	480.097
Normalized	6.452	240.049
Ratio	1	37
Estimated Mass	1630	
Mass Average	**3460**	

ppm	Integration	Species
3.359	3	—CH_3
3.623	480.097	—CH_2-CH_2—
4.139	6.452	—CH_2-COO—

Figure S24. Integration of significant peaks from ^{1}H NMR spectrum of α-carboxy-ω-methoxy PEG 3360 (MeO-PEG-COOH) in $CDCl_3$; values calculated against methyl and carboxy α-position hydrogens.

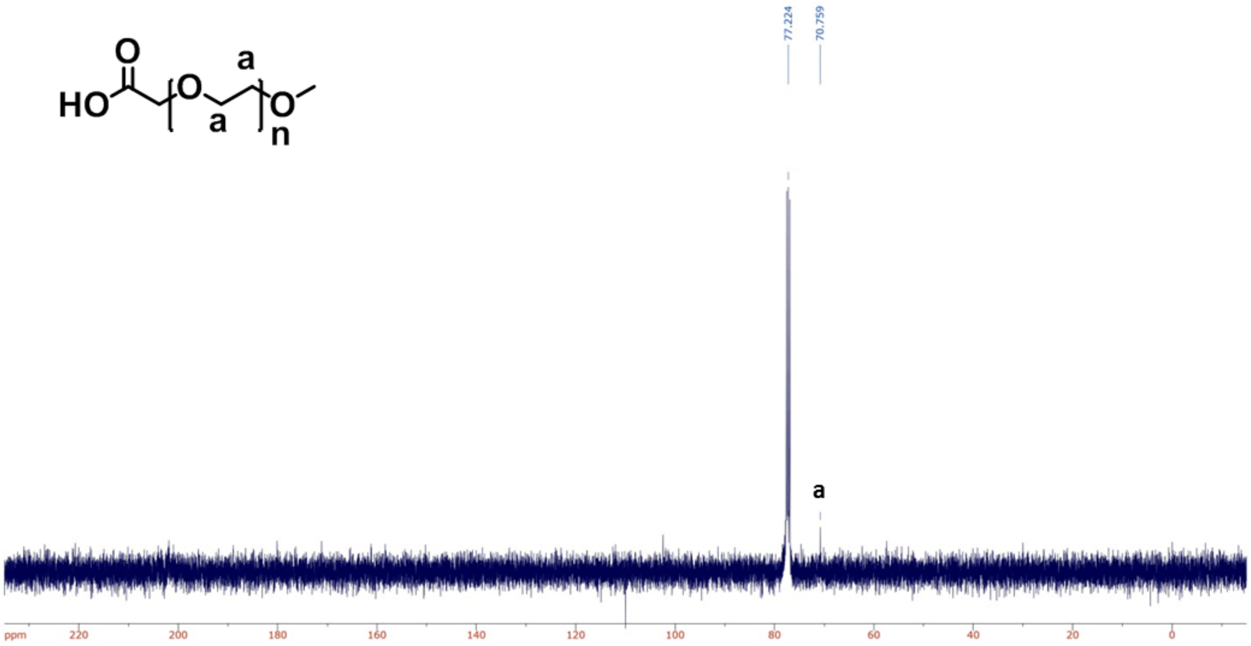


Figure S25. ^{13}C NMR spectrum of α-carboxy-ω-methoxy PEG 3360 (MeO-PEG-COOH) in $CDCl_3$

Additional raw data are available through: https://data.gulfresearchinitiative.org/data-discovery

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