Supplementary information

Synthesis of discrete bottlebrush polymers via the iterative convergent growth technique and post-functionalization

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1. Materials and Methods.

General. Zinc powder, tetrabutylammonium bromide and dodecanethiol were purchased from Sigma Aldrich. Glyoxylic acid monohydrate (97+%), allyl bromide, tert-butyldimethylchlorosilane (97%), lithium hydroxide (anhydrous), morpholine and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Alfa Aesar. Bismuth(III) chloride, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDC·HCl) and boron trifluoride etherate (BF3·Et2O) were purchased from Tokyo Chemical Industry Co. Ltd. Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (99%) were purchased from Acros Organics. Potassium carbonate, imidazole (99.5%) dichloromethane (DCM), dimethylformamide (DMF), tetrahydrofuran (THF), and magnesium sulfate ($MgSO_4$) were purchased from Samchun Chemicals. DCM was dried over CaH_2 under N_2 and THF was refluxed over a mixture of Na and benzophenone under N_2 and distilled before use. All reactions were performed under N_2 unless otherwise noted.

Methods. ^1H and ^{13}C NMR spectra were recorded on a Varian/Oxford As-500 and Agilent 400-MR DD2 magnetic resonance system using CD_2Cl_2 and $CDCl_3$ as solvents.

Molecular weights and polydispersity index (PDI) of linear backbone and discrete brush polymers were measured by gel permeation chromatography (GPC) system. The first GPC was performed on an Agilent 1260 Infinity equipped with a PL gel 5 μm mixed D column and differential refractive index detectors. HPLC-grade THF (inhibitor free) was used as a mobile phase with a flow rate of 0.3 ml min^{-1} at 35 ºC. The dn/dc values which were obtained for each injection by assuming 100% mass elution from the column, were used for the PLA brush homopolymer (0.0422). A narrow PS standard kit (Agilent Technologies) was used for calibration. The samples were filtered over a 0.2 μm PTFE filter prior to injection.

The second GPC was equipped with Waters 515 pump, Wyatt Optilab refractive index detector, Wyatt Dawn8 multi-angle static light scattering (MALS) detector, and Shodex SEC LF-804 column eluted with chloroform. HPLC-grade chloroform (inhibitor free) was used as a mobile phase with a flow rate of 1 ml min^{-1} at 35 ºC. The dn/dc values which were obtained for each injection by assuming 100% mass elution from the column, were used for the PLA brush homopolymer (0.0422). The samples were filtered over a 0.2 μm PTFE filter before injection into the GPC.

Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker Ultraflex III TOF-TOF mass spectrometer equipped with a nitrogen laser (335 nm). T*rans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malono-nitrile (DCTB) and 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA) were used as matrix. All samples were dissolved in THF. The obtained mixture was loaded on the MALDI plate and dried before measurement.

2. Synthetic Procedures

2.1 Synthesis of copolyester backbone

2-Hydroxy-4-pentenoic acid (1) was synthesized by following the literature methods procedure.[1] Glyoxylic acid monohydrate (20.0 g, 0.217 mol, 1.0 mol. eq.) was dissolved in THF (300mL) in a 1L schlenk flask and the solution was cooled to 0 °C. Zn powder (29.8 g, 0.456mol, 2.1 mol. eq.) was added to THF and added to the cooled solution of glyoxylate acid monohydrate. Bismuth chloride (95.9 g, 0.304 mol, 1.4 mol. eq.) was dissolved in THF and transferred to the mixture of glyoxylic acid monohydrate and Zn powder in THF. Allyl bromide (36.8 g, 0.304 mol, 1.4 mol. eq.) was added dropwise at 0 °C and the solution was allowed to

proceed from 0˚C to ambient temperature. After 17h, the reaction was quenched by addition of 1N HCl. After stirring for 3h at room temperature, the formed precipitate (Zn-salts) was removed by filtration over filter paper. Extraction of the water/THF phase was done with diethyl ether three times. The combined organic phases were dried over $MgSO_4$ followed by filtration and evaporation in vacuo, which yielded 2-hydroxy-4-pentenoic acid as yellow oil.

^{1}H NMR (δ = ppm, 500 MHz, DMSO-d_6) 12.66-6.27 (m, 1H), 5.88-5.71 (m, 1H), 5.12-4.98 (t, 2H), 4.03-3.92 (q, 1H), 3.55-3.12 (d, 1H), 2.45-2.23 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.13, 134.43, 117.15, 69.61, 38.49.

Allyl 2-hydroxy-4-pentenoate (2) was synthesized by following the literature methods procedure.[2] 2-hydroxypent-4-enoic acid (20.0 g, 0.172 mol, 1.0 mol. eq.) were dissolved in DMF (350 mL). Tetrabutyl ammonium bromide and potassium carbonate were added to the solution of **1**. Then, allyl bromide (5.56 g, 0.017 mol, 0.1 mol. eq.) were added and the reaction was followed by TLC. After 4h stirring at room temperature, the reaction mixture was evaporated under reduced pressure and the product was dissolved in diethyl ether. The organic phases were washed with 5% aq. citric acid solution (300 mL) and water (100 ml). The aqueous phases were separated and extracted with diethyl ether. The combined organic phases were washed twice with 5% $NaHCO_3$(aq) and brine. The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, then the mixture was purified by flash column chromatography using silica gel (Ethyl acetate/Hexane, 1:9 v/v). The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 5.98-5.86 (m, 1H), 5.86-5.75 (m, 1H), 5.38-5.31 (d, 1H), 5.30-5.24 (d, 1H), 5.19-5.1 (d, 2H), 4.3-4.26 (t, 1H), 2.89-2.73 (br, 1H), 2.64-2.55 (m, 1H), 2.50-2.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.25, 132.50, 131.53, 119.31, 119.02, 70.11, 66.36, 38.82.

Ethyl ((*tert*-butyldimethylsilyl)oxy) propanoate (3) was synthesized by following the literature methods.[3] Ethyl lactate (25.0 g, 0.212 mol, 1.0 mol. eq.) was dissolved in dichloromethane (300 mL) and the solution was cooled to 0 °C. *Tert*-butyldimethylsilyl chloride (33.5 g, 0.222 mol, 1.05 mol. eq.) and imidazole were added to the solution of ethyl lactate. The reaction was allowed to proceeded at room temperature and stirred overnight under a nitrogen atmosphere. The reaction mixture was then diluted with water and extracted with dichloromethane (x3). The combined organic phases were washed with ice cold 5% HCl(aq) and brie (x1). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, which yielded colorless oil.

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 4.33-4.28 (q, 1H), 4.23-4.11 (m, 2H), 1.42-1.37 (d, 3H), 1.30-1.25 (t, 3H), 0.94-0.88 (s, 9H), 0.12-0.05 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.26, 68.61, 60.88, 25.86, 21.45, 18.47, 14.34, -4.79, -5.12.

2-((*Tert*-butyldimethylsilyl)oxy)propanoic acid (4) Lithium hydroxide (6.61 g, 0.276 mol, 2.0 mol. eq.) was dissolved in water (0.4 M, 345 mL). The **3** (32.0 g, 0.138 mol, 1.0 mol. eq.) was dissolved in THF (345 mL) and cooled to 0 °C. The solution of lithium hydroxide was transferred dropwise. The reaction mixture was stirred for 2h at room temperature. After the

color of the reaction mixture change to transparent, THF was removed by a rotary evaporator and then the resulting aqueous solution was extracted with diethyl ether (x3). The combined organic phases were washed with a saturated NaHCO3(aq). The combined aqueous phases were acidified to pH 4 with KHSO4 and extracted with diethyl ether. The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, which yielded colorless oil without further purification.

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 9.91-9.04 (br, 1H), 4.41-4.31 (q, 1H), 1.48-1.42 (d, 3H), 0.96-0.88 (s, 9H), 0.18-0.12 (s, 6H).

t-LP-a (5) A schlenk flask was charged with EDC·HCl (3.62 g, 0.012 mol, 0.2 mol. eq.), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) (3.62 g, 0.012 mol, 0.2 mol. eq.) and dichloromethane. The **2** (9.6 g, 0.062 mol, 1.0 mol. eq.) and **4** (15.1 g, 0.074 mol, 1.2 mol. eq.) were added to the reaction mixture at 0 °C. After 30min, the ice bath was removed and the reaction was stirred at ambient temperature and monitored by TLC. At completion the reaction was quenched, the reaction mixture was washed with water (x2) and brine (x1). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, then the mixture was purified by flash column chromatography using silica gel (Ethyl acetate/Hexane, 3:7 v/v). The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 5.95-5.83 (m, 1H), 5.83-5.71 (m, 1H), 5.38-5.28 (d, 1H), 5.28-5.22 (d, 1H), 5.20-5.10 (m, 3H), 4.68-4.57 (t, 2H), 4.47-4.35 (q, 1H), 2.72-2.54 (m, 2H), 1.48-1.38 (t, 3H), 0.96-0.85 (s, 9H), 0.14-0.05 (d, 6H). ^{13}C NMR (101 MHz, cdcl3) δ 174.65, 167.67, 131.42, 118.94, 71.98, 68.28, 66.01, 35.62, 25.86, 21.55, 18.41, -4.89, -5.05.

HO-LP-a (6) The 5 (8.1 g, 0.024 mol, 1.0 mol. eq.) was dissolved in dichloromethane and cooled to 0 °C. Boron trifluoride etherate (13.4 g, 0.095 mol, 4.0 mol.eq.) was added to the solution dropwise at 0 °C and monitored by TLC. After the reaction was complete, the reaction was quenched with saturated a saturated NaHCO3(aq) followed by dilution with water. The organic layer was separated and washed with brine. The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure.

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.97-5.83 (m, 1H), 5.82-5.68 (m, 1H), 5.39-5.30 (d, 1H), 5.30-5.24 (d, 1H), 5.23-5.11 (m, 3H), 4.70-4.58 (m, 2H), 4.45-4.31 (m, 1H), 2.81-2.57 (m, 3H), 1.51-1.42 (d, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.82, 168.70, 131.60, 131.42, 119.36, 119.30, 72.42, 66.86, 66.27, 35.59, 20.68, 20.33.

t-LP-COOH (7) A schlenk flask was charged with $Pd(PPh_3)_4$ (2.70 g, 0.0023 mol, 0.1 mol. eq.) and THF under a nitrogen atmosphere. The **5** (8.00 g, 0.023 mol, 1.0 mol. eq.) was added into the reaction mixture. The reaction mixture was stirred at 0 °C. Morpholine (2.14 g, 0.025 mol, 1.05 mol. eq.) was added to the solution dropwise at 0 °C and monitored by TLC. After the reaction was complete, the solvent was removed under reduced pressure. The crude was dissolved in dichloromethane and washed three times with 1M HCl(aq). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The crude was filtered through a Celite cake. The product was obtained by removing the solvent from the filtrates under reduced pressure.

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.85-5.71 (m, 1H), 5.22-5.08 (m, 3H), 4.47-4.35 (m, 1H), 2.74-2.57 (m, 2H), 1.49-1.39 (t, 3H), 0.96-0.83 (s, 9H), 0.14-0.03 (d, 6H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 173.78, 167.87, 135.15, 112.49, 73.34, 66.94, 66.63, 37.28, 25.76, 20.41, 18.07, -3.48.

t-LP2-a (8) A schlenk flask was charged with EDC·HCl (6.81 g, 0.036 mol, 1.5 mol. eq.), DPTS (1.39 g, 0.005 mol, 0.2 mol. eq.) and dichloromethane. The **6** (5.4 g, 0.024 mol, 1.0 mol. eq.) and **7** (7.15 g, 0.024 mol, 1.0 mol. eq.) were added to the reaction mixture at 0 °C. After 30min, the ice bath was removed and the reaction was stirred at ambient temperature and monitored by TLC. At completion the reaction was quenched, the reaction mixture was washed with water (x2) and brine (x1). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, then the mixture was purified by flash column chromatography using silica gel (Ethyl acetate/Hexane, 3:7 v/v). The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.95-5.84 (m, 1H), 5.83-5.69 (m, 2H), 5.36-5.30 (d, 1H), 5.28-5.24 (d, 1H), 5.24-5.11 (m, 7H), 4.69-4.57 (m, 2H), 4.45-4.36 (m, 1H), 2.80-2.58 (m, 4H), 1.62-1.50 (m, 3H), 1.48-1.38 (dd, 3H), 0.93-0.87 (s, 9H), 0.11-0.05 (dd, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.52, 168.59, 131.54, 119.23, 72.37, 71.56, 69.94, 69.35, 69.04, 68.12, 66.21, 35.37, 25.86, 21.34, 18.34, 16.77, -4.78, -5.16.

t-LP4-a, t-LP8-a, t-LP16-a, t-LP32-a were synthesized by repeated procedures.

t-LP4-a (9) Colorless oil; ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.95-5.84 (m, 1H), 5.83-5.68 (m, 4H), 5.37-5.29 (d, 1H), 5.28-5.23 (d, 1H), 5.22-5.09 (m, 14H), 4.70-4.58 (m, 2H), 4.46-

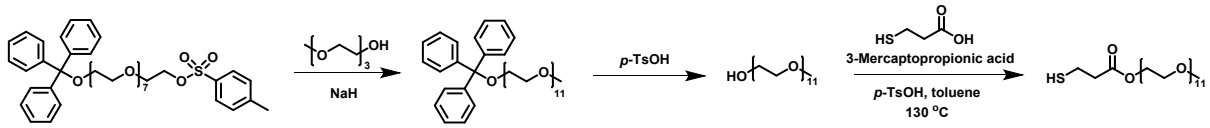
4.35 (m, 1H), 2.80-2.55 (m, 8H), 1.63-1.48 (m, 9H), 1.47-1.38 (t, 3H), 0.94-0.86 (s, 9H), 0.13-0.04 (dd, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.97, 169.65, 131.65, 131.44, 119.17, 72.33, 71.95, 68.11, 35.38, 25.85, 25.75, 16.76, 11.67, -4.56, -5.18.

t-LP8-a (10) Viscous oil; ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.96-5.84 (m, 1H), 5.84-5.68 (m, 8H), 5.36-5.29 (d, 1H), 5.28-5.24 (d, 1H), 5.24-5.08 (m, 31H), 4.69-4.57 (m, 2H), 4.45-4.35 (m, 1H), 2.79-2.57 (m, 16H), 1.62-1.50 (m, 21H), 1.48-1.38 (t, 3H), 0.93-0.87 (s, 9H), 0.11-0.05 (dd, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44-169.04, 168.82-168.33, 168.21-167.79, 132.14-131.55, 131.40-131.23, 119.27-118.71, 72.35-71.29, 69.50-68.80, 68.22-67.81, 66.03-66.03, 35.57-34.91, 25.73, 21.34, 18.27, 16.93-16.60, -4.89, -5.29.

t-LP16-a (11) Viscous oil; ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.96-5.84 (m, 1H), 5.84-5.68 (m, 16H), 5.36-5.30 (d, 1H), 5.28-5.09 (m, 64H), 4.69-4.57 (m, 2H), 4.45-4.35 (m, 1H), 2.81-2.57 (m, 32H), 1.62-1.50 (m, 45H), 1.46-1.40 (t, 3H), 0.93-0.87 (s, 9H), 0.11-0.05 (dd, 6H). ^{13}C NMR (101 MHz, cdcl3) δ 169.73-167.82, 131.94-131.42, 119.41-118.96, 72.45-71.84, 69.58-69.04, 53.50, 35.59-35.04, 25.78, 17.19, 16.75, -4.06, -5.21

t-LP32-a (12) Viscous oil; ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.96-5.84 (m, 1H), 5.84-5.69 (m, 32H), 5.37-5.06 (d, 1H), 5.28-5.09 (m, 129H), 4.67-4.60 (m, 2H), 4.43-4.37 (m, 1H), 2.80-2.56 (m, 64H), 1.62-1.50 (m, 93H), 1.46-1.40 (t, 3H), 0.92-0.88 (s, 9H), 0.11-0.06 (dd, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.52-169.13, 168.55-167.96, 131.94, 131.30, 119.45, 119.11, 72.47, 71.92, 69.55, 69.09, 68.12, 35.55, 35.07, 25.89, 25.69, 17.14, 16.74, -4.85, -5.66.

2.2 Synthesis of thiol-functionalized side chain



Monomethoxy PEG_{11} trityl ether ($mPEG_{11}$-OTrt) (13) was synthesized by following the literature methods procedure.[4–6] A two neck was charged with sodium hydride (60% dispersion in paraffin oil, 0.235 g, 0.006 mol) and dry THF under a nitrogen atmosphere. The mixture was cooled to 0 °C on an ice bath. Monomethoxy triethylene glycol ($mPEG_3$-OH) (1.93 g, 0.012 mol, 3.0 mol. eq.) was added dropwise to the solution of sodium hydride. Then a solution of TrtO-PEG8-OTs (3.0 g, 0.004 mol, 1.0 mol. eq.) in THF was added dropwise. Then the ice bath was removed, the flask was equipped with condenser and the mixture was stirred vigorously at 60 °C on oil bath overnight. After the reaction completed, the mixture was cooled to room temperature and washed with brine and water. The organic layer was separated and the aqueous layer was extracted with diethyl ether. Combined organic extracts were washed with brine. The absence of $mPEG_3$-OH was confirmed by TLC. The solution was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure, then the mixture was purified by flash column chromatography using silica gel (Ethyl acetate/Methanol, 9:1 v/v). The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 7.50-7.42 (d, 6H), 7.34-7.21 (dt, 9H), 3.68-3.47 (m, 42H), 3.36-3.32 (s, 3H), 1.60-1.54 (dd, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.75, 129.19, 128.31, 127.48, 93.06, 72.43, 71.04, 63.99, 59.17.

Monomethoxy PEG11 ($mPEG_{11}$-OH) (14) A schelenk RBF was charged with mPEG11-OTrt (1.42 g, 1.9 mmol, 1.0 mol. eq.) and methanol. p-Toluenesulfonic acid monohydrate (0.036 g, 0.2 mmol, 0.1 mol. eq.) was added into the mixture and stirred for at room temperature. The reaction progress is monitored by TLC. After the reaction completed, the $NaHCO_3$ (0.16 g, 1.9 mmol, 1.0 mol. eq.) was added. Then the crude solution was filtered. The filtrate was concentrated under reduced pressure. The remaining crude mixture was purified by flash column chromatography using silica gel (Dichloromethane/Methanol, 94:6 v/v). The solvent was removed under vacuum to yield a colorless liquid.

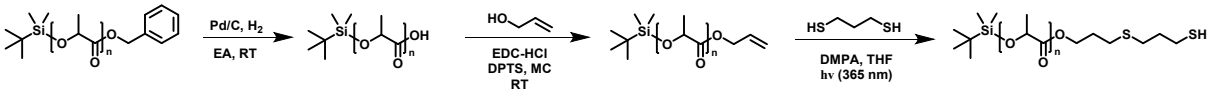
^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 3.81-3.40 (m, 42H), 3.36-3.31 (s, 3H), 2.60-12.38 (br, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 71.05, 62.15, 59.15.

Thiol functionalized monomethoxy PEG_{11} (15) 3-Mercaptopropionic acid (0.66 g, 6.2 mmol, 5.0 mol. eq.), p-toluenesulfonic acid monohydrate (0.024 g, 0.1 mol, 0.1 mol. eq.), $mPEG_{11}$-OH (0.65 g, 1.2 mmol, 1.0 mol. eq.) and toluene were charged in two-neck RBF. Using a Dean–Stark apparatus the reaction was subsequently heated to 130 °C and stirred overnight. When the reaction completed, the solvent was removed under reduced pressure, then the mixture was purified by flash column chromatography using silica gel (Dichloromethane/Methanol, 94:6 v/v). The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 4.30-4.23 (dd, 2H), 3.86-3.44 (m, 42H), 3.40-3.34 (s, 3H), 2.82-2.73 (dd, 2H), 2.72-2.65 dd, 2H), 1.71-1.64 (t, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.69, 72.07, 70.71, 70.66, 69.19, 63.90, 59.18, 38.55, 19.87.

Polydispersed thiol-terminated poly(ethylene glycol) (16) 3-Mercaptopropionic acid (4.83 g, 45.5 mmol, 5.0 mol. eq.), p-toluenesulfonic acid monohydrate (0.173 g, 0.9 mol, 0.1 mol. eq.), $mPEG_{11}$-OH (5.00 g, 9.1 mmol, 1.0 mol. eq.) and toluene were charged in two-neck RBF. Using a Dean–Stark apparatus the reaction was subsequently heated to 130 °C and stirred overnight. When the reaction completed, the solvent was removed under reduced pressure, then the mixture was purified by flash column chromatography using silica gel (Dichloromethane/Methanol, 94:6 v/v). The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 4.27-4.24 (dd, 2H), 3.79-3.59 (m, 50H), 3.37-3.35 (s, 3H), 2.80-2.73 (dd, 2H), 2.70-2.65 dd, 2H), 1.70-1.64 (t, 1H).



TBDMS-LA_8-COOH (17) TBDMS-LA_8-Bz (1.80 g, 2.3 mmol, 1.0 mol. eq.) which was synthesized by following the literature methods procedure[7] was dissolved in EA. Palladium on activated charcoal (10% Pd/C, 0.072 g, 0.07 mmol, 0.03 mol. eq.) was added to the solution, and the suspension was purged with argon for 15 minutes. The argon atmosphere was then replaced with hydrogen atmosphere, and the reaction mixture was stirred at room temperature. The reaction was monitored by thin layer chromatography (TLC) analysis. Upon completion of the reaction, the suspension was filtered through a celite cake to remove Pd/C. The product was obtained by removing the solvent from the filtrates under reduced pressure.

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.31-5.09 (m, 7H), 4.43-4.33 (q, 1H), 1.65-1.50 (m, 21H), 1.49-1.40 d, 3H), 0.92-0.86 (s, 9H), 0.11-0.05 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58-169.34, 69.33- 69.02, 68.97, 68.11, 25.83, 21.40, 18.42, -4.79, -5.18.

TBDMS-LA$_8$-OAllyl (18) A schlenk flask was charged with EDC·HCl (0.523 g, 2.7 mmol, 1.2 mol. eq.), DPTS (0.100 g, 0.3 mmol, 0.15 mol. eq.) and dichloromethane. The **17** (1.61 g, 2.3 mmol, 1.0 mol. eq.) and allyl alcohol (0.34 mL, 5.0 mmol, 2.2 mol. eq.) were added to the reaction mixture at 0 °C. After 30min, the ice bath was removed and the reaction was stirred at ambient temperature and monitored by TLC. At completion the reaction was quenched, the reaction mixture was washed with water (x2) and brine (x1). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum to yield a colorless liquid.

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.93-5.83 (m, 1H), 5.35-5.29 (d, 1H), 5.27-5.23 (d, 1H), 5.23-5.09 (m, 7H), 4.67-4.58 (m, 2H), 4.43-4.36 (d, 1H), 1.60-1.50 (d, 21H), 1.46-1.42 (d, 3H), 0.92-0.88 (s, 9H), 0.12-0.06 (d, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.77, 131.38, 118.90, 69.38, 69.11, 68.95, 68.13, 66.17, 25.84, 21.37, 16.90, -4.77, -5.16.

TBDMS-LA$_8$-SH (19) A schlenk RBF was purged with dry N_2 and charged with DMPA (6.9 mg, 0.027 mmol, 0.02 mol. eq.), **18** (1.1 g, 1.48 mmol, 1.0 mol. eq.) dissolved in 7 mL THF and 1,3-dipropanedithiol (0.8 g, 7.37 mmol, 5.0 mol. eq.) were added dropwise, the reaction was complete after irradiation by 365 nm UV light for 2 h. THF was evaporated under a reduced

pressure and the crude product was purified by column chromatography on a silica gel (EA/ Hexane, 30:70 v/v)).

^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.24-5.06 (m, 7H), 4.42-4.33 (q, 1H), 4.25-4.18 (t, 2H), 2.65-2.58 (m, 4H), 2.57-2.50 (m, 2H), 1.95-1.81 (d, 4H), 1.61-1.47 (d, 21H), 1.45-1.40 (d, 3H), 0.91-0.85 (s, 9H), 0.11-0.04 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.19-169.50, 69.40, 69.28, 69.15, 69.10, 68.99, 68.94, 68.10, 64.16, 33.33, 30.48, 28.65, 28.35, 25.84, 23.50, 21.42, 17.03, 16.94, 16.89, 16.83, 14.34, -4.76, -5.16.

TBDMS-LA$_{16}$-SH were synthesized by same procedures for TBDMS-LA$_8$-SH.

TBDMS-LA$_{16}$-COOH (20) ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.29-5.08 (m, 17H), 4.44-4.33 (q, 1H), 1.62-1.50 (m, 45H), 1.48-1.40 d, 3H), 0.94-0.86 (s, 9H), 0.14-0.05 (d, 6H).

TBDMS-LA$_{16}$-OAllyl (21) ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.94-5.81 (m, 1H), 5.38-5.08 (d, 2H), 5.23-5.09 (m, 15H), 4.68-4.56 (m, 2H), 4.44-4.33 (d, 1H), 1.66-1.48 (d, 45H), 1.47-1.38 (d, 3H), 0.97-0.84 (s, 9H), 0.15-0.02 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58-169.43, 69.33-69.22, 66.25, 25.88, 21.56, 16.80, -2.51, -4.82.

TBDMS-LA$_{16}$-SH (22) ^{1}H NMR (δ = ppm, 500 MHz, CD_2Cl_2) 5.26-5.07 (m, 15H), 4.44-4.35 (q, 1H), 4.28-4.19 (t, 2H), 2.68-2.50 (m, 4H), 2.59-2.52 (m, 2H), 1.95-1.81 (d, 4H), 1.67-1.49 (d, 45H), 1.45-1.40 (d, 3H), 0.96-0.86 (s, 9H), 0.15-0.04 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.71-169.27, 69.42-68.91, 68.11, 64.16, 60.52, 33.34, 30.35, 28.31, 25.86, 23.37, 21.08, 16.77, 14.50, 9.08, -4.77, -5.16.

2.3 Post-functionalization

t-LP(ET)32-ET (23) A vial was charged with charged with DMPA (18.9 mg, 0.07 mmol, 16.5 mol. eq.), **12** (25 mg, 0.005mmol, 1.0 mol. eq.) dissolved in THF. Ethanethiol (73.3 mg, 1.18 mmol, 264 mol. eq.) were added to the mixture. The solution was sparged with N_2. The reaction was complete after irradiation by 365 nm UV light for 2h. THF was evaporated under a reduced pressure and the crude product was purified by prep-SEC).

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 5.24-5.04 (m, 64H), 2.81-2.65 (m, 132H), 1.78-1.54 (t, 66H), 1.46-1.31 (m, 96H), 1.29-1.18 (m, 66H), 1.02-0.94 (s, 9H), 0.16-0.03 (d, 6H).

t-LP(PEG550)32-PEG550 (24) A vial was charged with charged with DMPA (22.6 mg, 0.09 mmol, 16.5 mol. eq.), **12** (30 mg, 0.005 mmol, 1.0 mol. eq.) dissolved in THF. **16** (1.56 g, 1.76 mmol, 330 mol. eq.) were added to the mixture. The solution was sparged with N_2. The reaction was complete after irradiation by 365 nm UV light for 12h. THF was evaporated under a reduced pressure and the crude product was purified by prep-SEC).

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 5.26-5.19 (m, 64H), 5.18-5.05 (m, 232H), 4.44-4.34 (q, 32H), 4.29-4.18 (m, 64H), 2.64-2.49 (m, 264H), 2.13-1.97 (m, 64H), 1.97-1.89 (t, 64H), 1.88-1.79 (t, 64H), 1.78-1.64 (m, 64H), 1.62-1.48 (m, 853H), 1.47-1.41 (d, 99H), 0.97-0.84 (s, 306H), 0.16-0.03 (d, 204H).

t-LP(LA$_8$)32-LA$_8$ (25) A vial was charged with charged with DMPA (27.1 mg, 0.11 mmol, 33 mol. eq.), **12** (18 mg, 0.003 mmol, 1.0 mol. eq.) dissolved in THF. **19** (1.09 g, 1.27 mmol, 396 mol. eq.) were added to the mixture. The solution was sparged with N_2. The reaction was complete after irradiation by 365 nm UV light for overnight. THF was evaporated under a reduced pressure and the crude product was purified by prep-SEC).

^{1}H NMR (δ = ppm, 500 MHz, $CDCl_3$) 5.26-5.19 (m, 64H), 5.18-5.05 (m, 232H), 4.44-4.34 (q, 32H), 4.29-4.18 (m, 64H), 2.64-2.49 (m, 264H), 2.13-1.97 (m, 64H), 1.97-1.89 (t, 64H), 1.88-1.79 (t, 64H), 1.78-1.64 (m, 64H), 1.62-1.48 (m, 853H), 1.47-1.41 (d, 99H), 0.97-0.84 (s, 306H), 0.16-0.03 (d, 204H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.45, 170.12, 169.86, 169.43, 169.38, 169.28, 69.30, 69.26, 69.14, 69.08, 68.97, 68.91, 68.09, 64.17, 31.43, 30.99, 29.22, 28.61, 28.40, 25.83, 21.40, 18.41, 17.00, 16.95, 16.88, 16.81, -4.77, -5.16.

2.4 Synthesis of bottlebrush diblock copolymers

t-LP32-COOH (26) A schlenk flask was charged with $Pd(PPh_3)_4$ (3.99 mg, 0.003 mmol, 0.1 mol. eq.) and THF under a nitrogen atmosphere. The **12** (100 mg, 0.035 mmol, 1.0 mol. eq.) was added into the reaction mixture. The reaction mixture was stirred at 0 °C. Morpholine (3.16 mg, 0.036 mol, 1.05 mol. eq.) was added to the solution dropwise at 0 °C and monitored by TLC. After the reaction was complete, the solvent was removed under reduced pressure. The crude was dissolved in dichloromethane and washed three times with 1M HCl(aq). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The crude was filtered through a Celite cake. The product was obtained by removing the solvent from the filtrates under reduced pressure and purified by prep-SEC.

t-LP(DDT)16-COOH (27) A vial was charged with charged with DMPA (51.7 mg, 0.2 mmol, 8.0 mol. eq.) and **26** (71.9 mg, 0.025 mmol, 1.0 mol. eq.) dissolved in THF. Dodecanethiol (816 mg, 4.03 mmol, 160 mol. eq.) was added to the mixture. The solution was sparged with N_2. The reaction was complete after irradiation by 365 nm UV light for overnight. THF was evaporated under a reduced pressure and the crude product was purified by prep-SEC.

HO-LP32-a (28) The **12** (188 mg, 0.065 mmol, 1.0 mol. eq.) was dissolved in dichloromethane and cooled to 0 °C. Boron trifluoride etherate (55.3 mg, 0.39 mmol, 6.0 mol.eq.) was added to the solution dropwise at 0 °C and monitored by TLC. After the reaction was complete, the reaction was quenched with saturated a saturated $NaHCO_3$(aq) followed by dilution with water. The organic layer was separated and washed with brine. The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure.

t-LP(DDT)16-*b*-LP16-a (29) A schlenk flask was charged with EDC·HCl (5.61 mg, 0.03 mmol, 2.5 mol. eq.), DPTS (0.689 mg, 0.002 mmol, 0.2 mol. eq.) and dichloromethane. The **27** (71.2 mg, 0.012 mol, 1.0 mol. eq.) and **28** (149.5 mg, 0.054 mol, 5.0 mol. eq.) were added to the reaction mixture at 0 °C. After 30min, the ice bath was removed and the reaction was stirred at ambient temperature and monitored by TLC. At completion the reaction was quenched, the reaction mixture was washed with water (x2) and brine (x1). The extracted organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was purified by prep-SEC.

t-[LP(DDT)16]-*b*-[LP(PEG11)16]-PEG11 (30) A vial was charged with charged with DMPA (8.64 mg, 0.03 mmol, 8.5 mol. eq.), **29** (35.1 mg, 0.004 mmol, 1.0 mol. eq.) dissolved in THF. **15** (407 mg, 0.67 mmol, 170.0 mol. eq.) were added to the mixture. The solution was sparged with N_2. The reaction was complete after irradiation by 365 nm UV light for overnight. THF was evaporated under a reduced pressure and the crude product was purified by prep-SEC.

^{1}H NMR (δ = ppm, 500 MHz, CD2Cl2) 5.24-5.02 (m, 64H), 4.25-4.18 (m, 66H), 3.79-3.31 (m, 1650H), 3.38-3.31 (m, 99H), 2.79-2.68 (m, 66H), 2.68-2.60 (m, 128H), 2.07-1.09 (m, 66H), 1.76-1.62 (m, 66H), 1.59-1.48 (m, 96H), 0.99-0.72 (m, 9H), 0.12-0.06 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.93, 72.05, 70.68, 69.17, 63.88, 59.14, 37.20, 34.74, 32.80, 32.03, 31.55, 30.14, 29.81, 29.76, 29.47, 27.19, 26.87, 22.80, 14.23, -2.72, -5.79.

3. NMR spectra

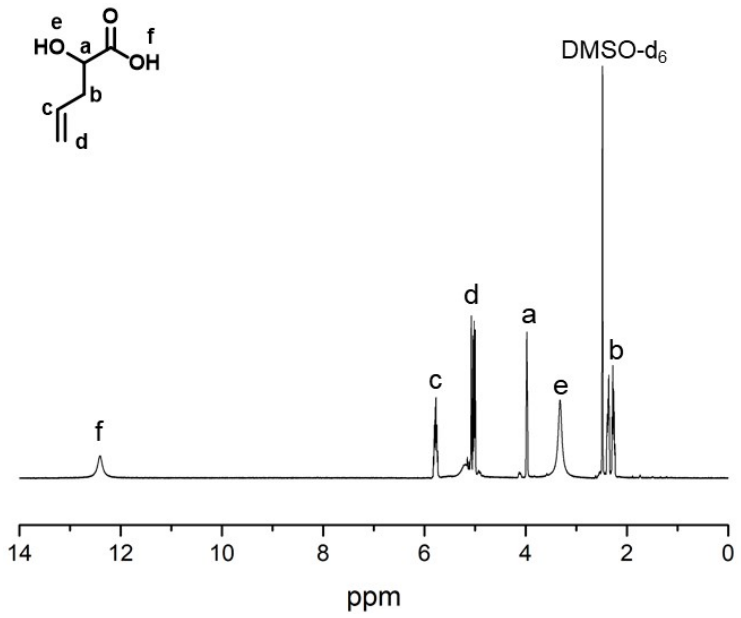


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2-hydroxy-4-pentenoic acid.

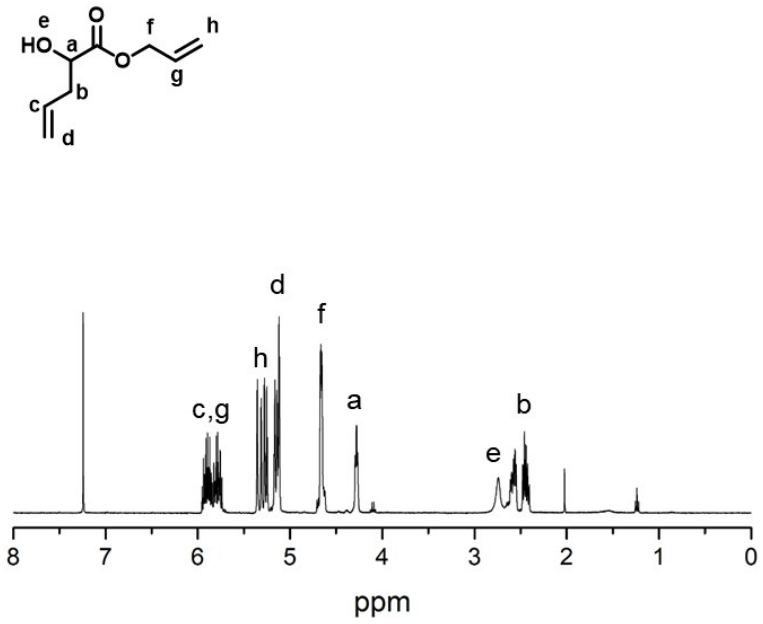


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of allyl 2-hydroxy-4-pentenoate.

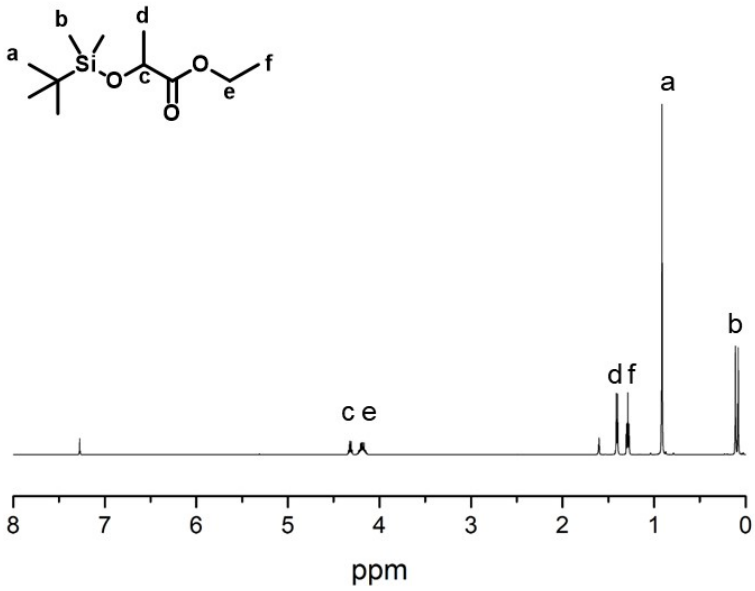


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethyl ((*tert*-butyldimethylsilyl)oxy) propanoate.

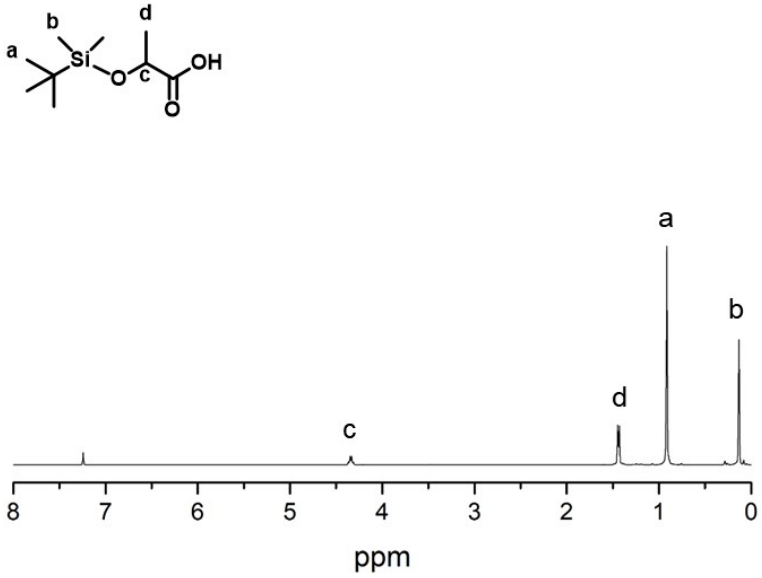


Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ((*tert*-butyldimethylsilyl)oxy) propanoic acid.

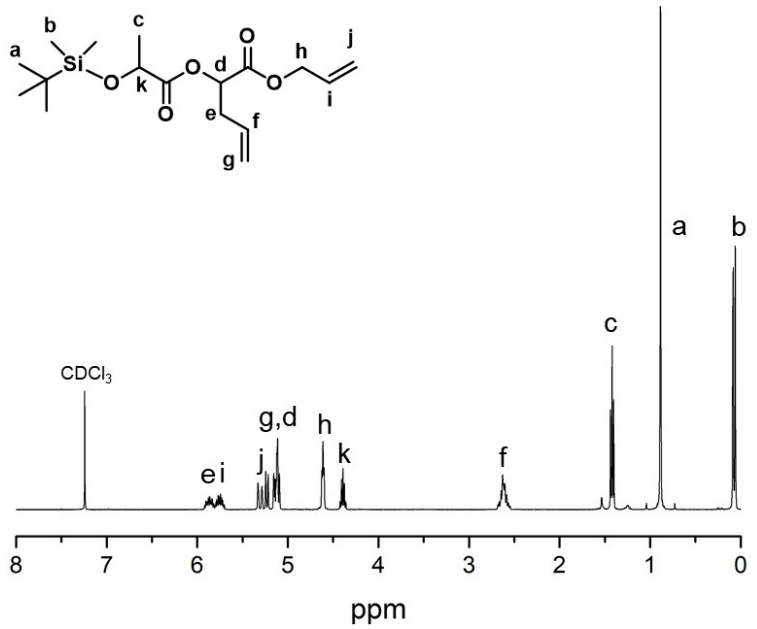


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP-a.

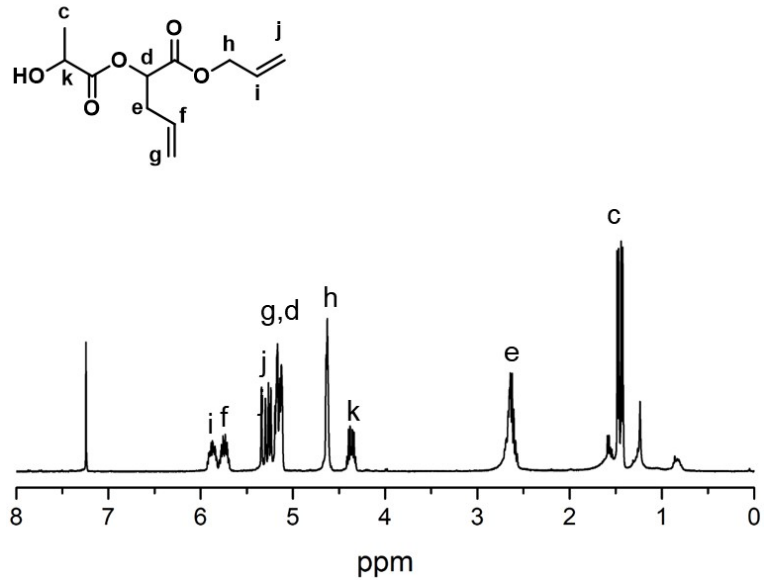


Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of HO-LP-a.

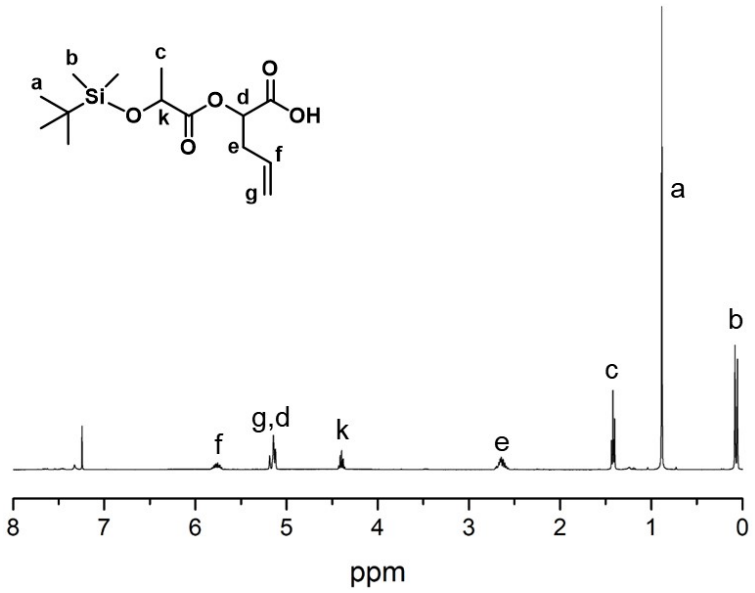


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP-COOH.

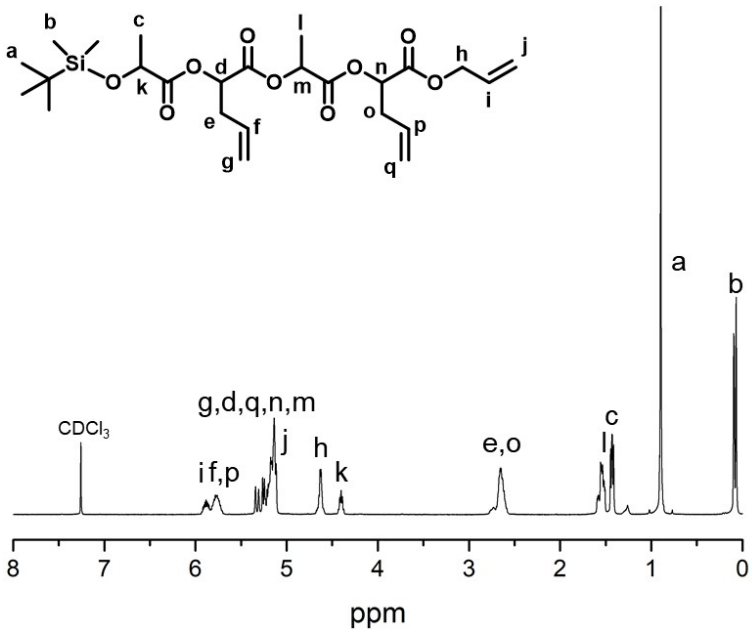


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP2-a.

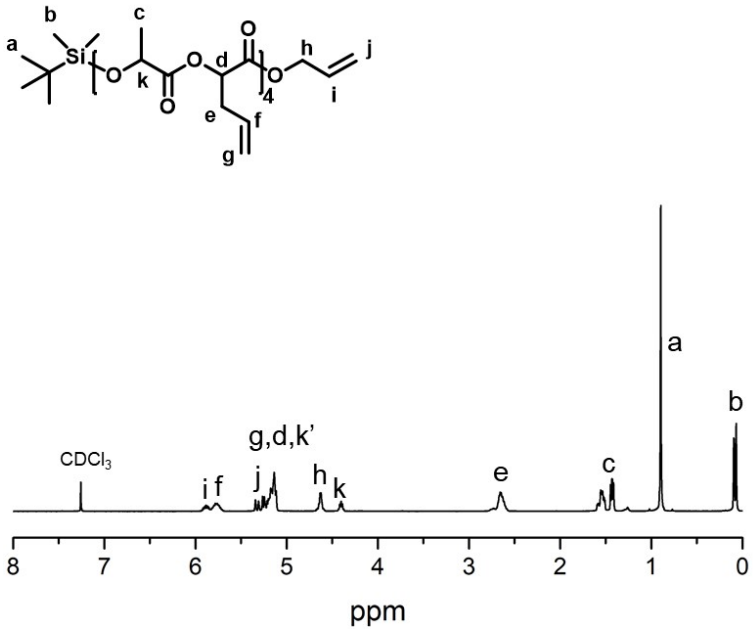


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP4-a.

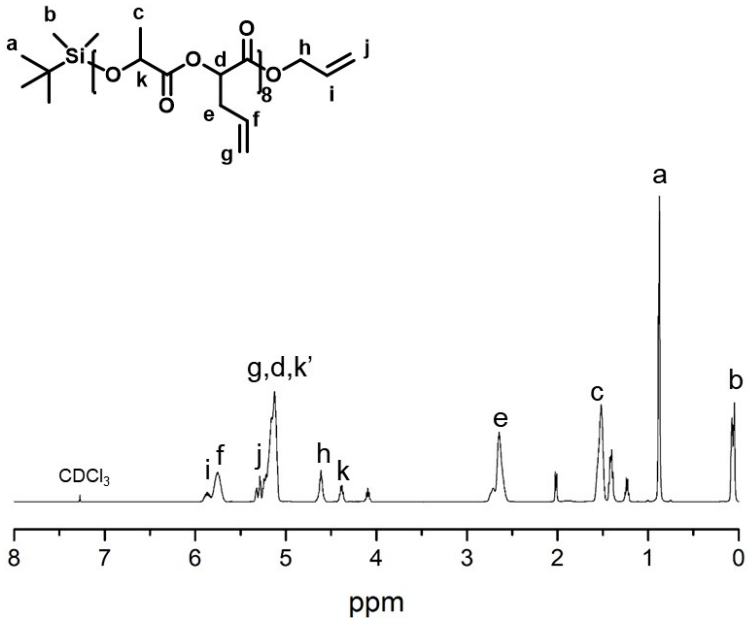


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP8-a.

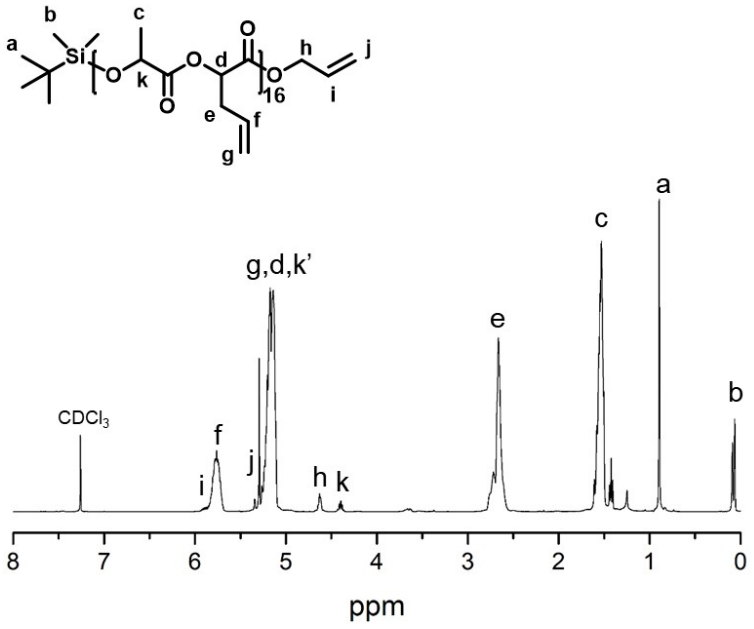


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP16-a.

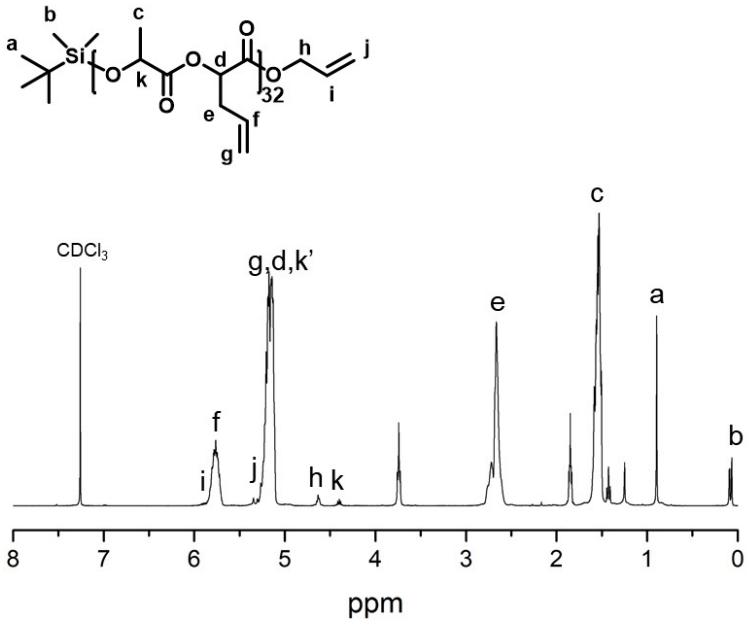


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP32-a.

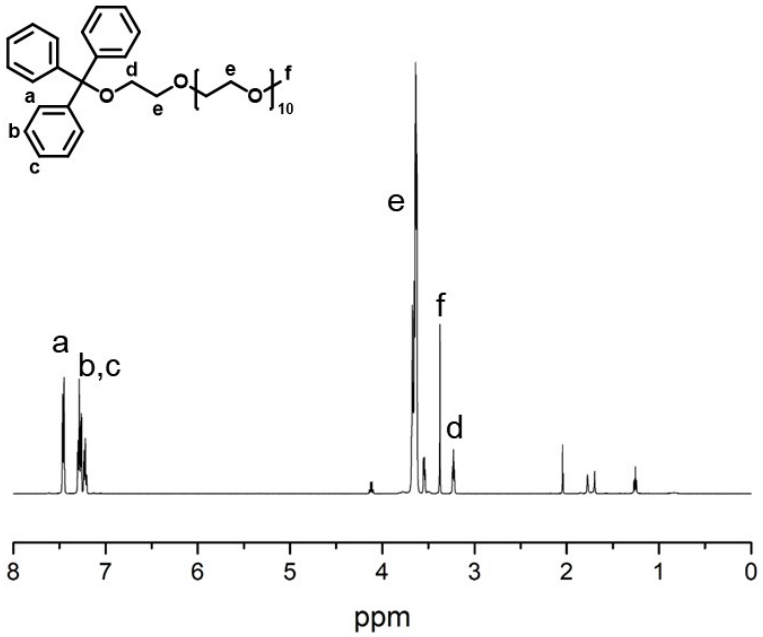


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of monomethoxy PEG_{11} trityl ether ($mPEG_{11}$-OTrt).

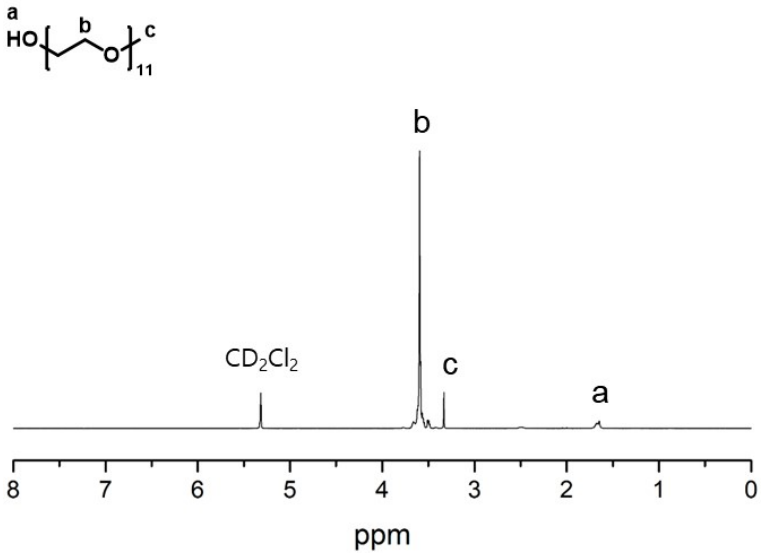


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of monomethoxy PEG_{11} ($mPEG_{11}$-OH).

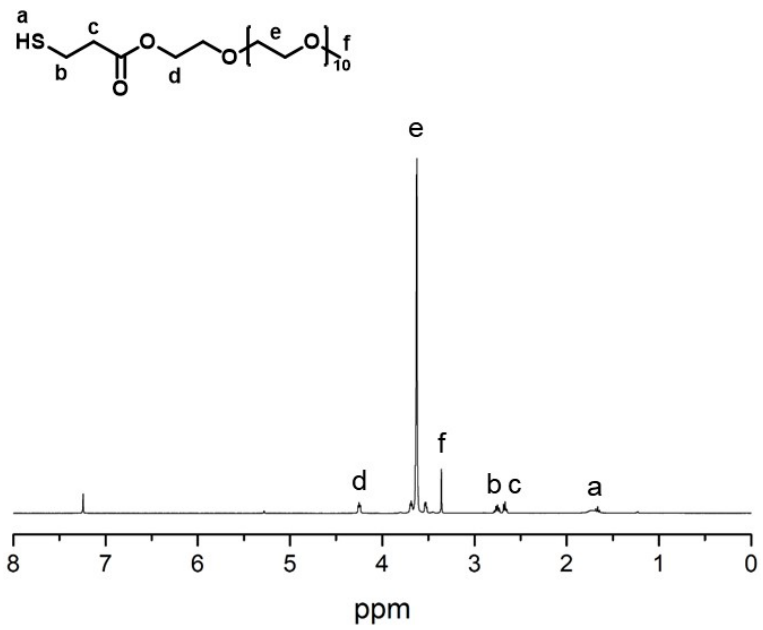


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thiol functionalized monomethoxy PEG_{11}.

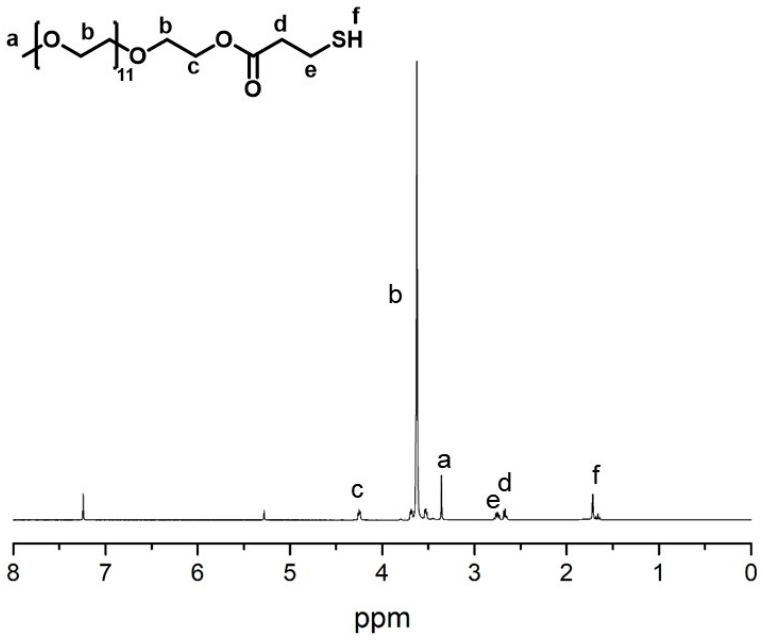


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thiol functionalized PEG550.

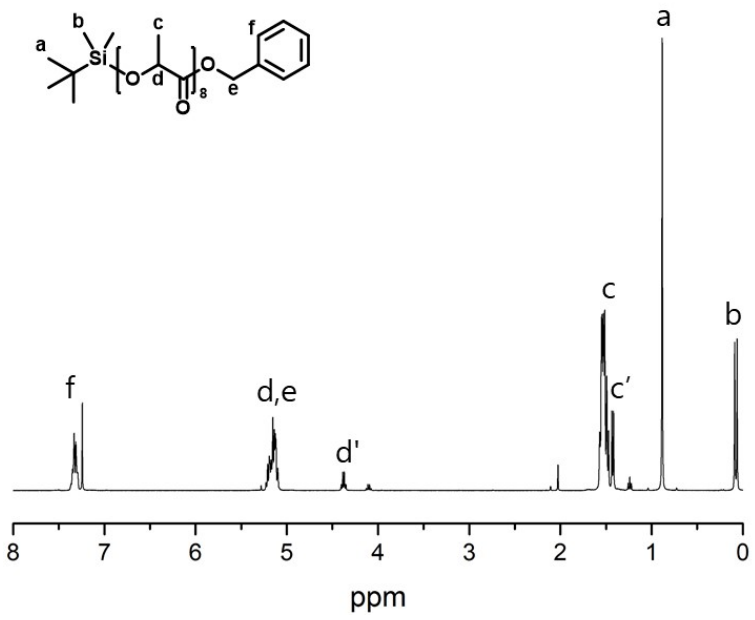


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_8-Bz.

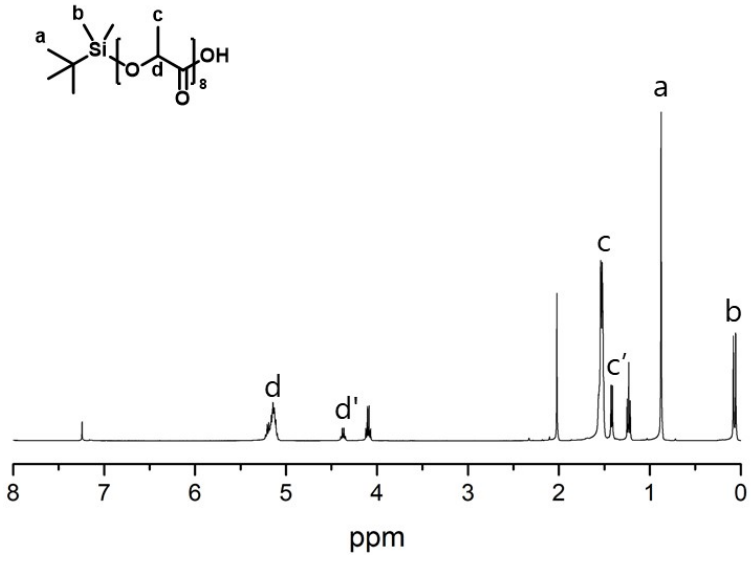


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_8-COOH.

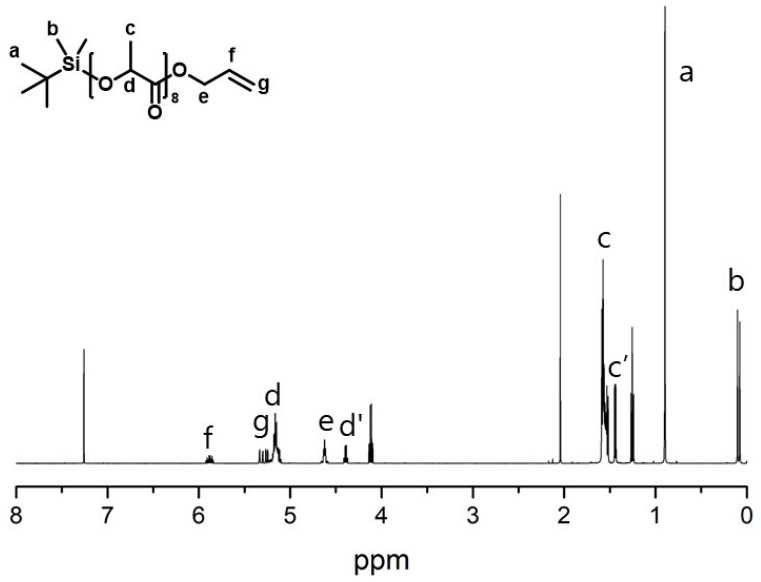


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_8-OAllyl.

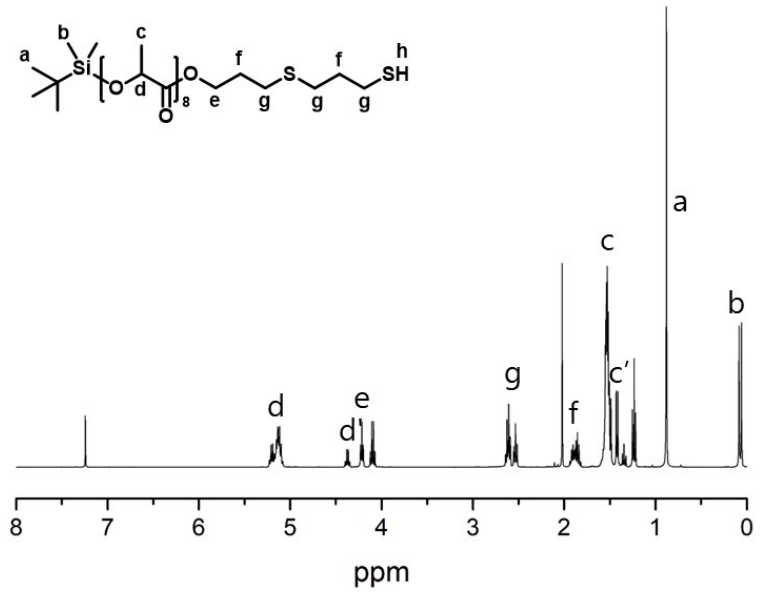


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thiol-functionalized PLA_8 (TBDMS-LA8-SH).

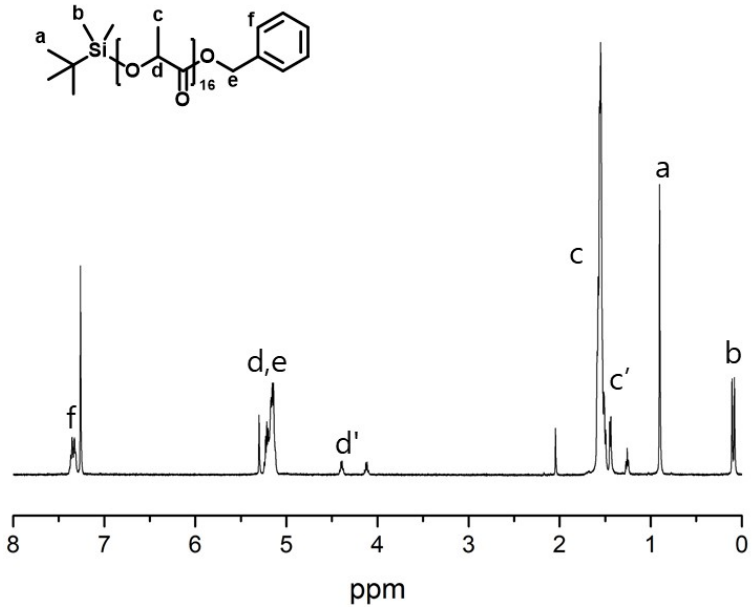


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_{16}-Bz.

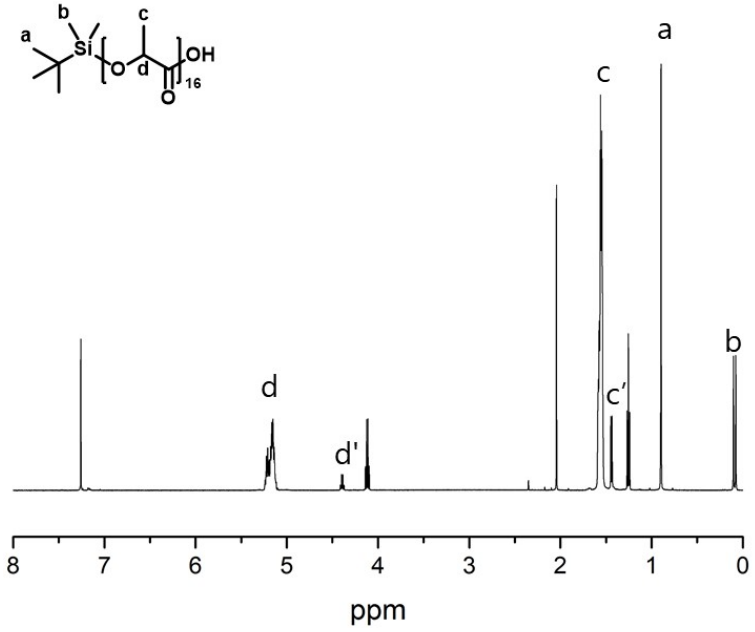


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_{16}-COOH.

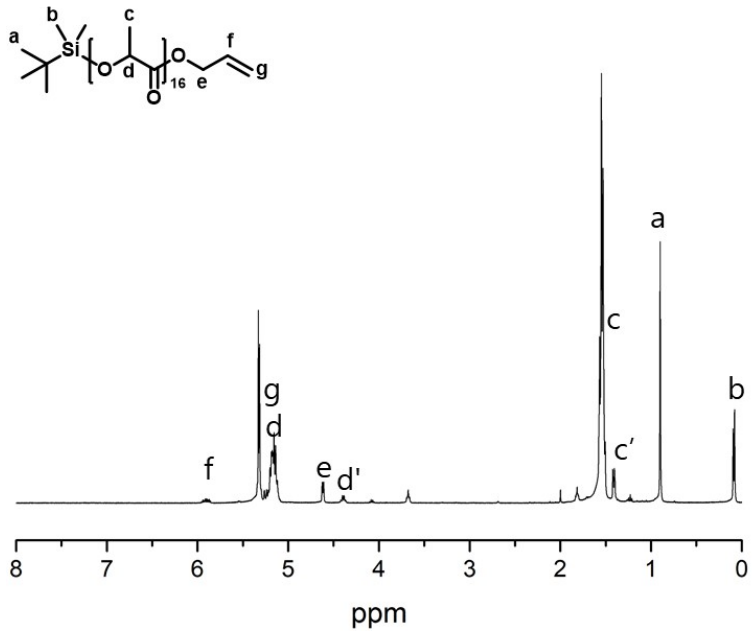


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_{16}-OAllyl.

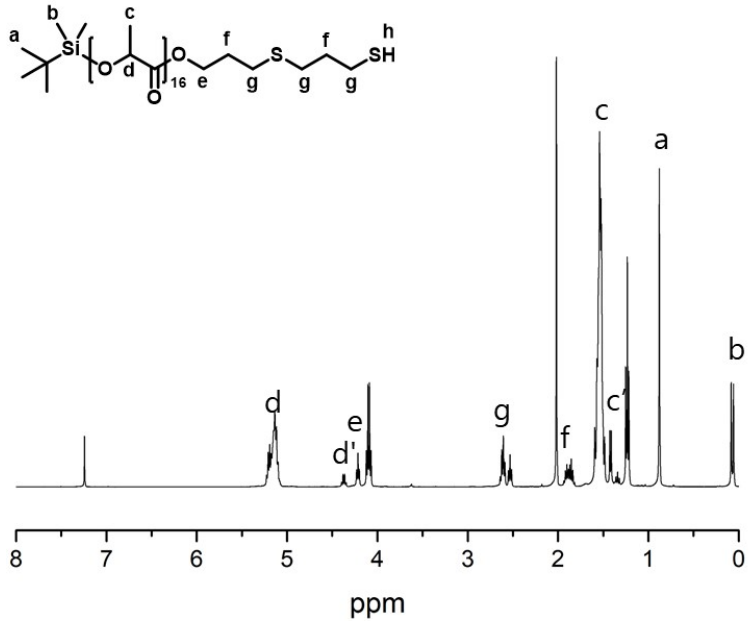


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TBDMS-LA_{16}-SH.

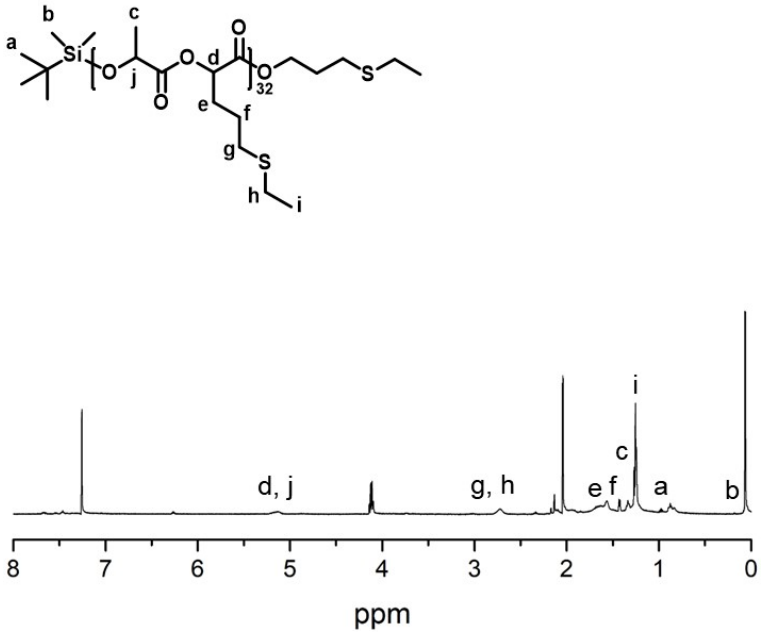


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP(ET)32-ET.

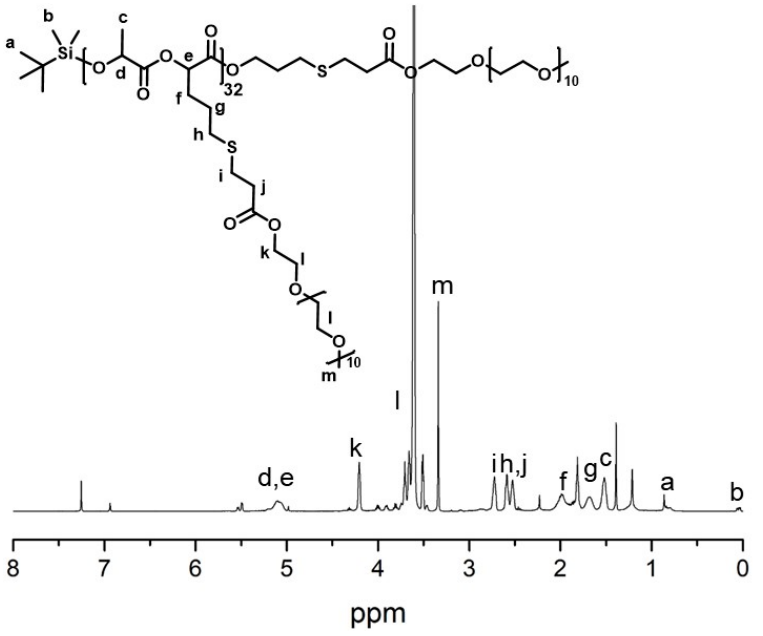


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP(PEG550)32-PEG550.

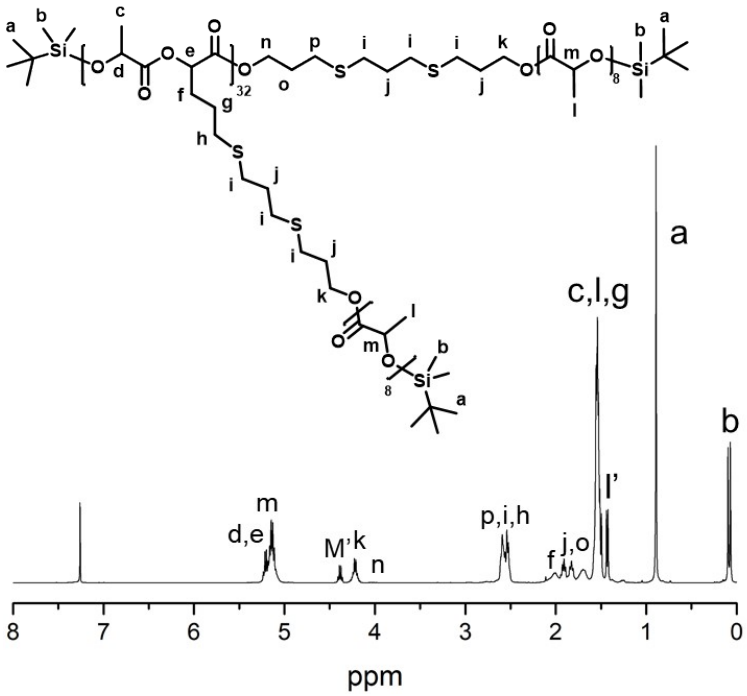


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-LP(LA_8)32-LA_8.

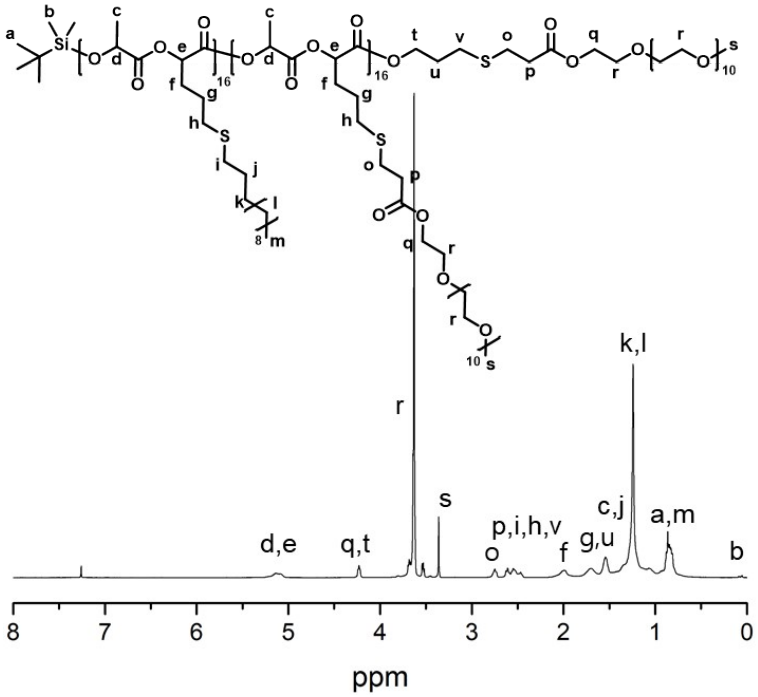


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of t-[LP(DDT)16]-*b*-[LP(PEG_{11})16]-PEG_{11}.

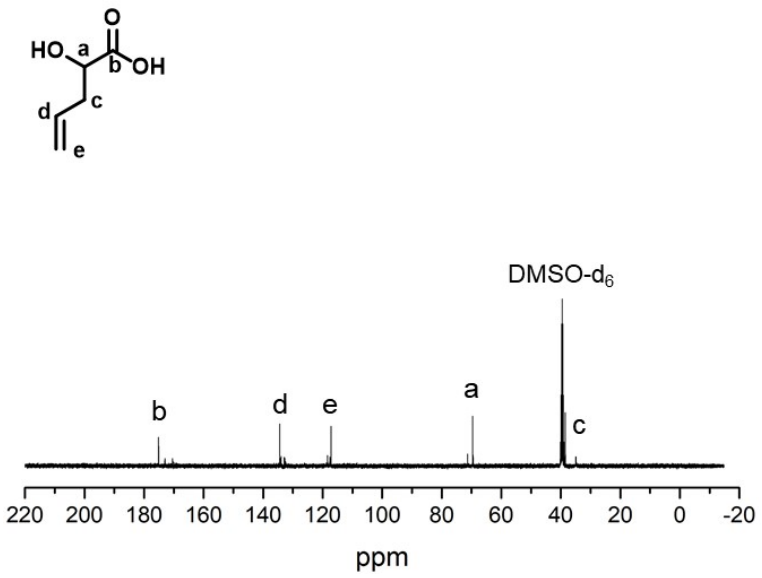


Figure S29. ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of 2-hydroxy-4-pentenoic acid.

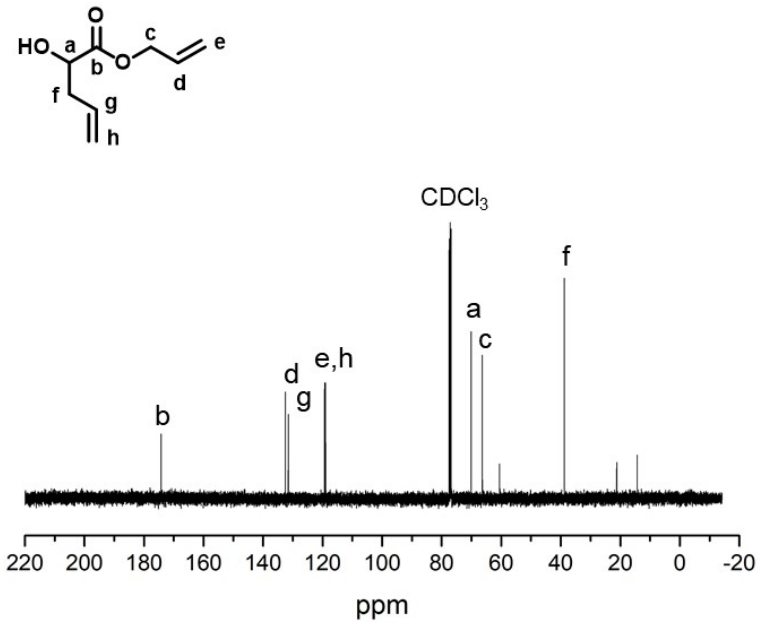


Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of allyl 2-hydroxy-4-pentenoate.

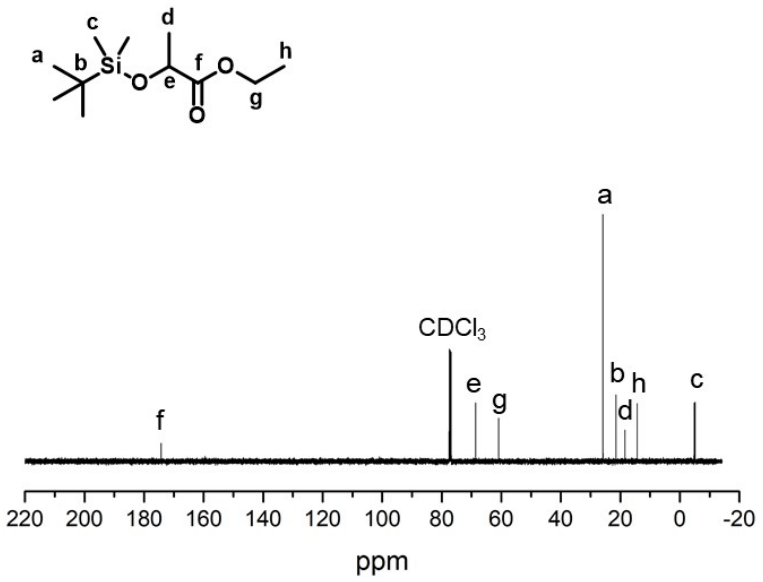


Figure S31. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of ethyl ((tert-butyldimethylsilyl)oxy) propanoate.

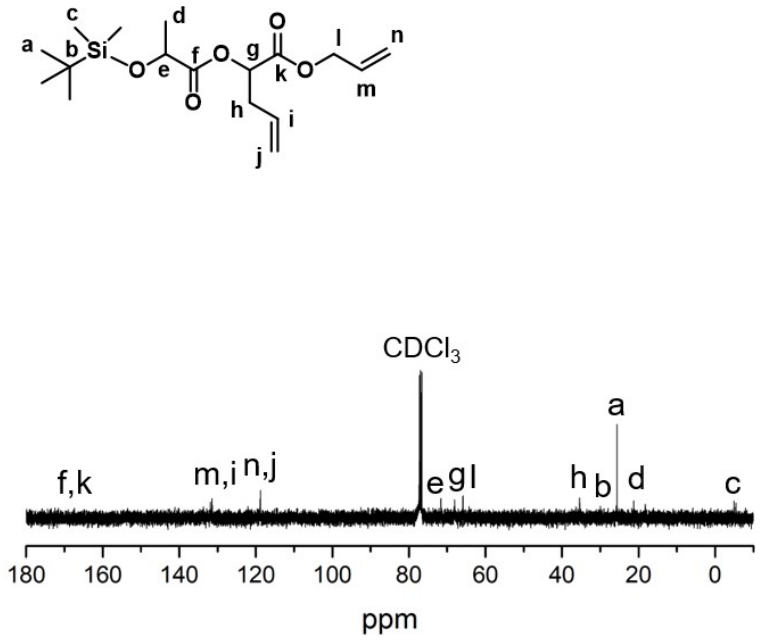


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP-a.

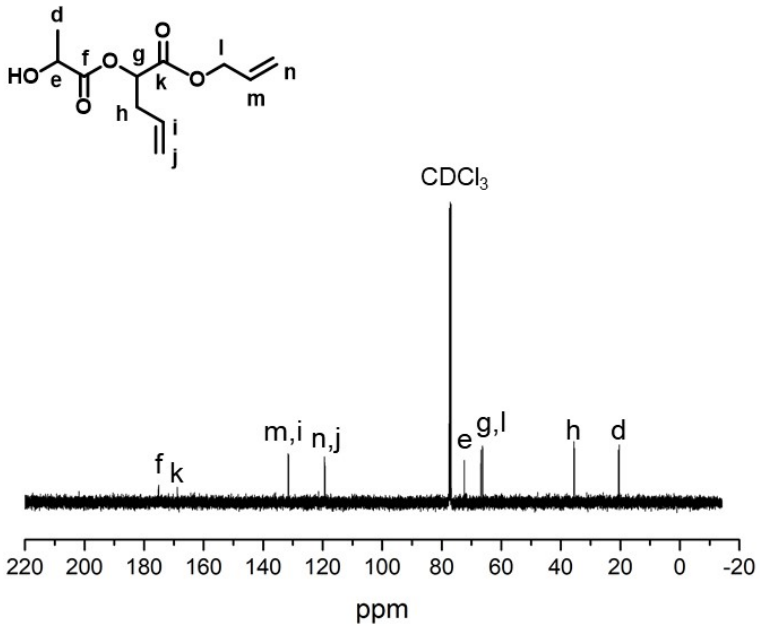


Figure S33. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of HO-LP-a.

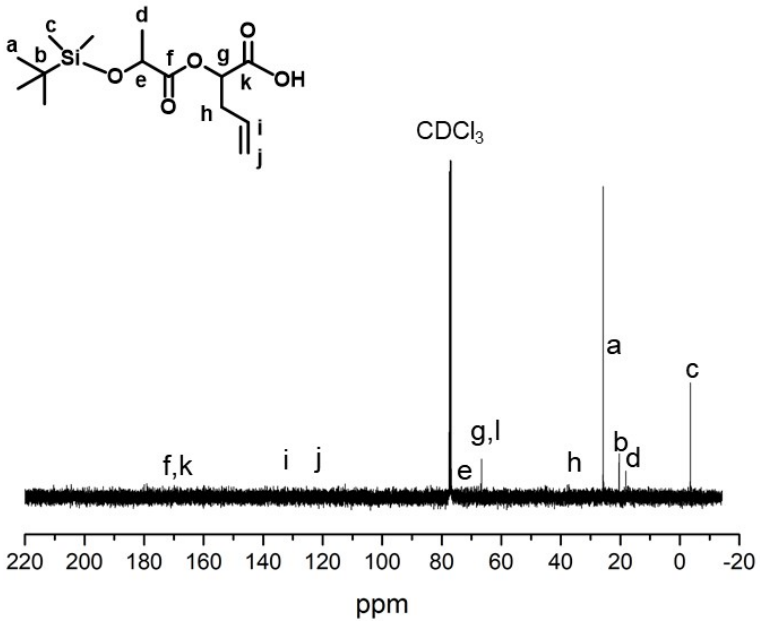


Figure S34. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP-COOH.

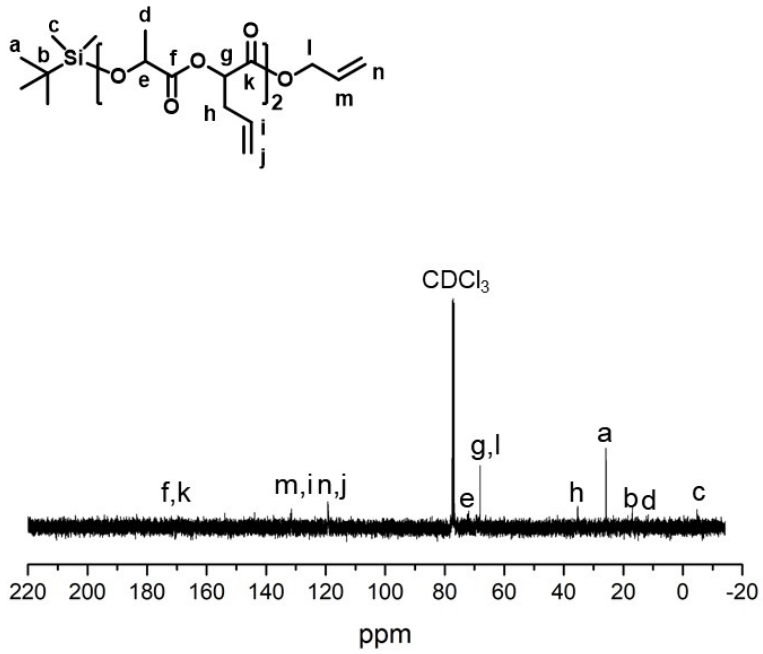


Figure S35. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP2-a.

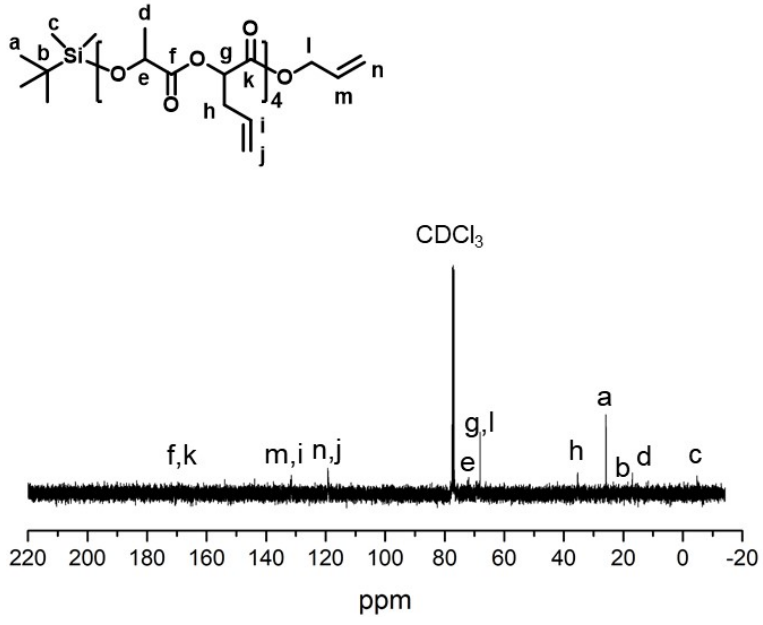


Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP4-a.

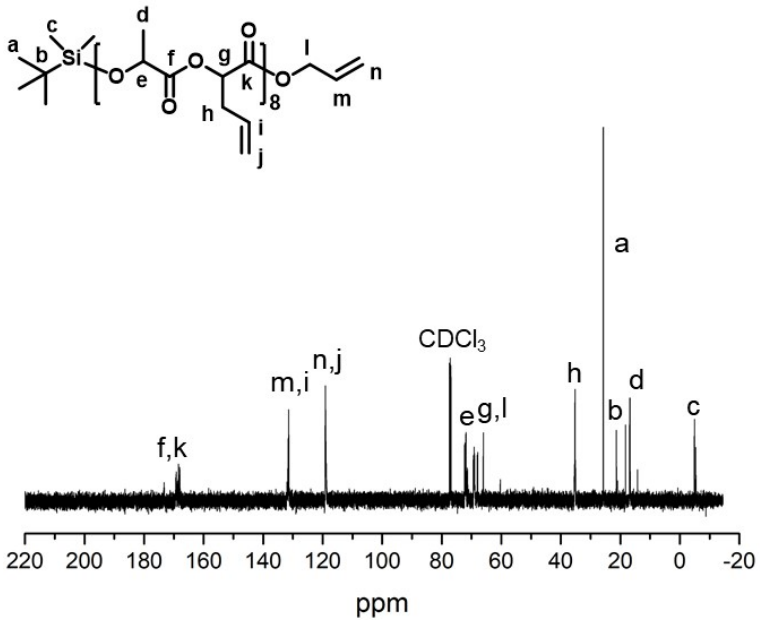


Figure S37. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP8-a.

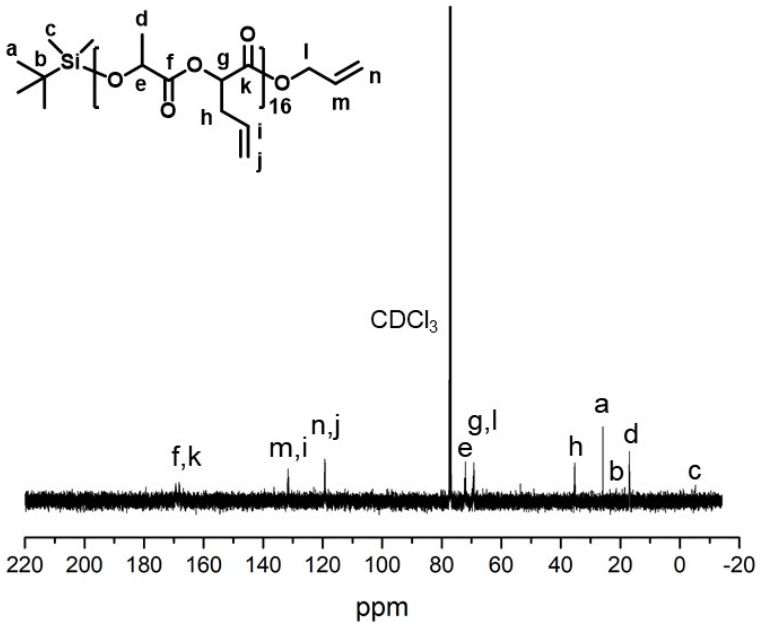


Figure S38. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP16-a.

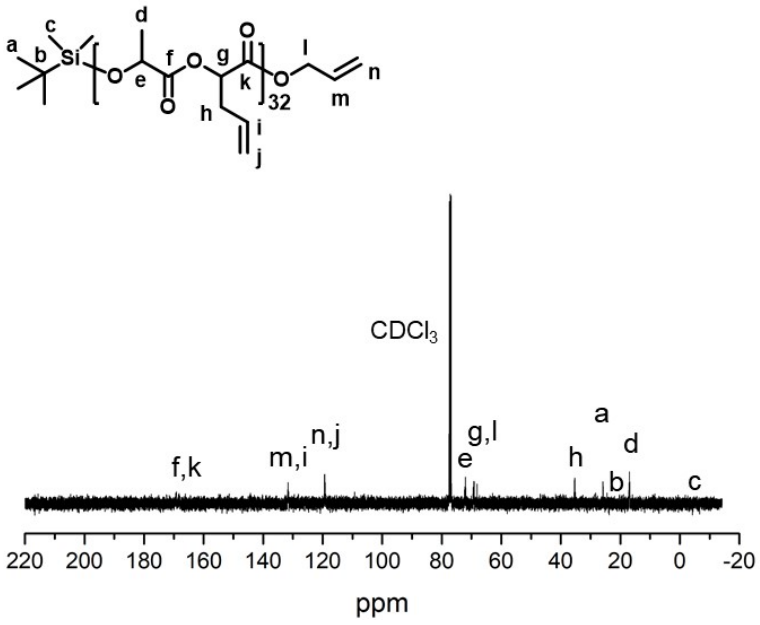


Figure S39. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP32-a.

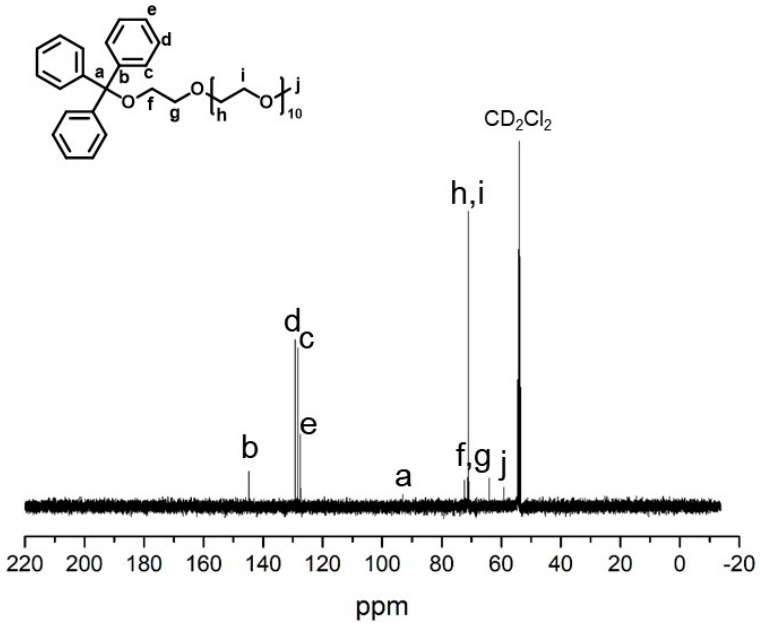


Figure S40. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of monomethoxy PEG_{11} trityl ether ($mPEG_{11}$-OTrt).

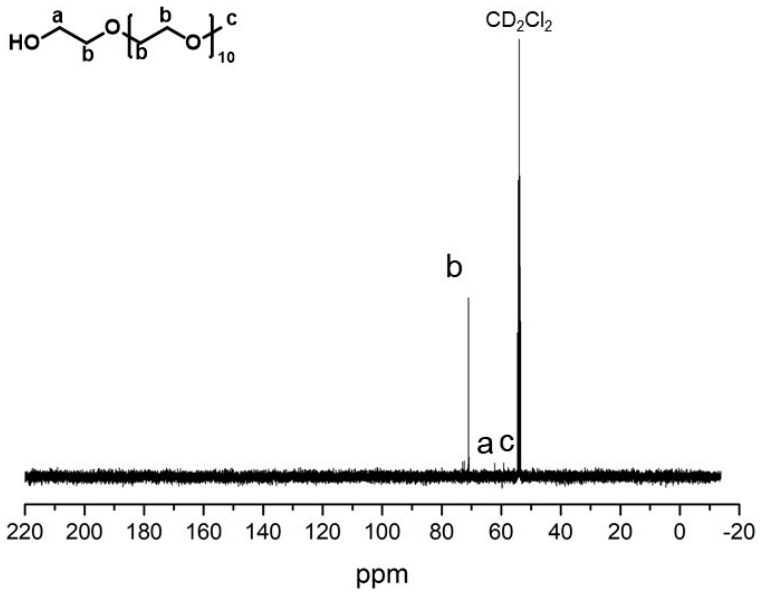


Figure S41. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of monomethoxy PEG_{11} ($mPEG_{11}$-OH).

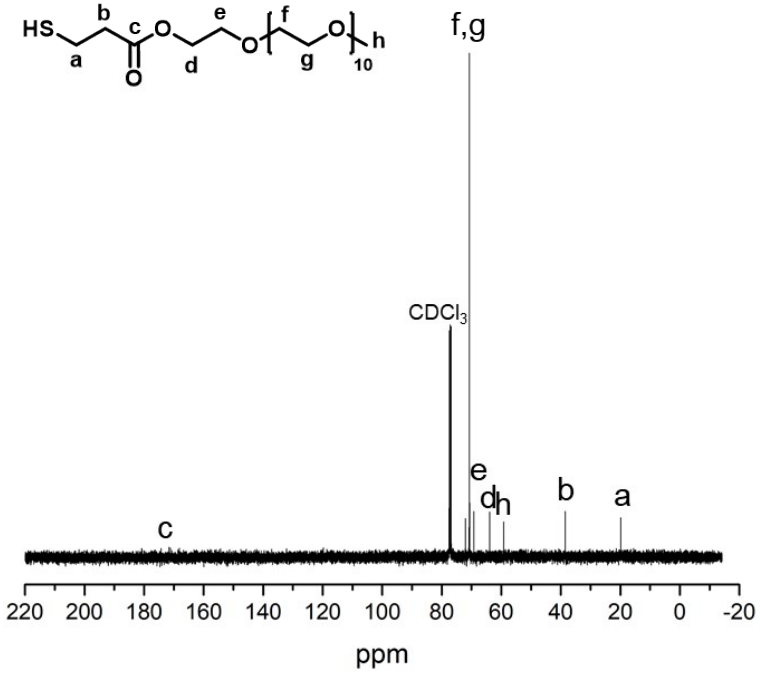


Figure S42. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of thiol functionalized monomethoxy PEG_{11}.

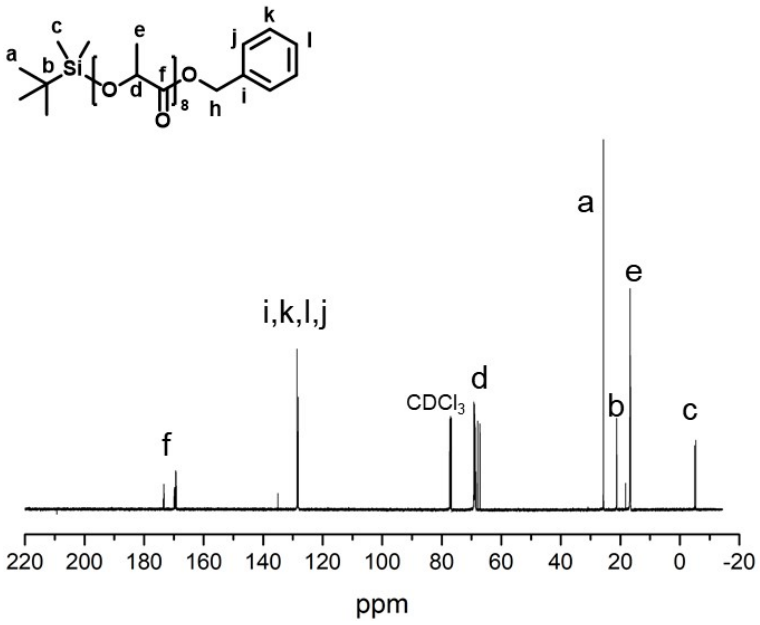


Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of TBDMS-LA_8-Bz.

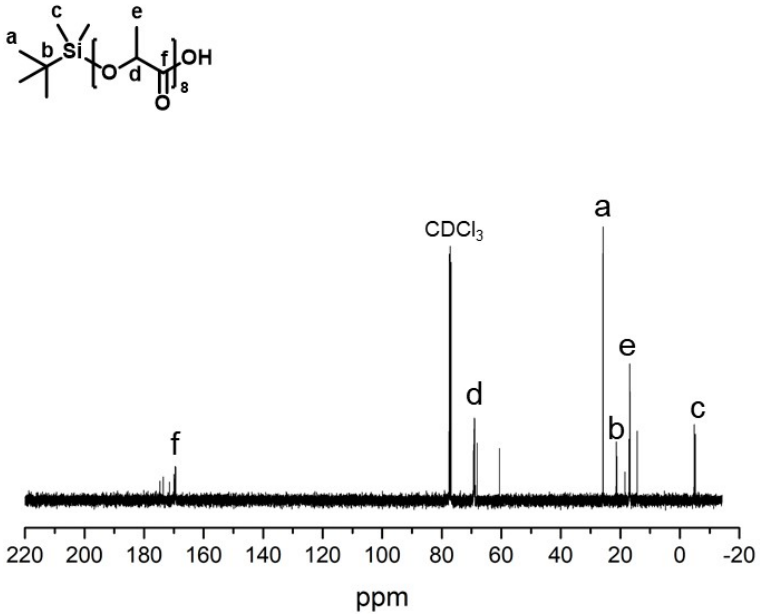


Figure S44. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of TBDMS-LA_8-COOH.

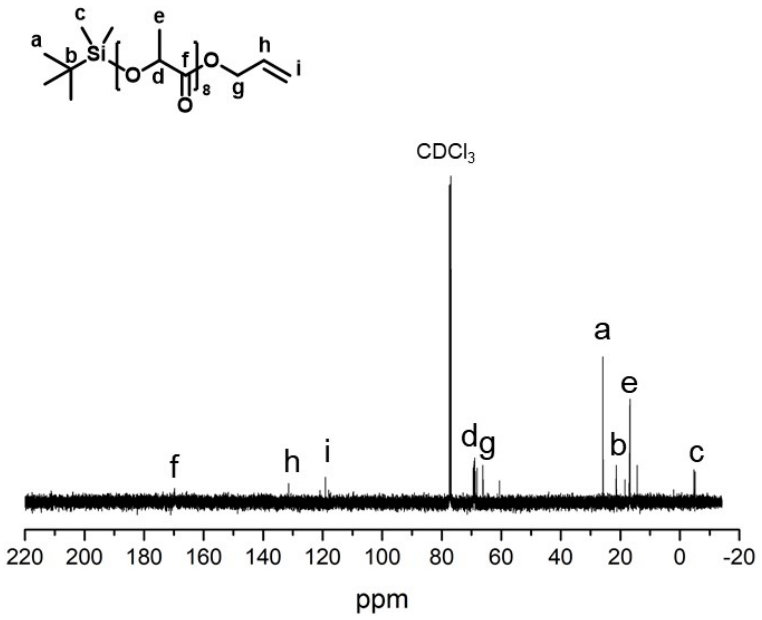


Figure S45. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of TBDMS-LA_8-OAllyl.

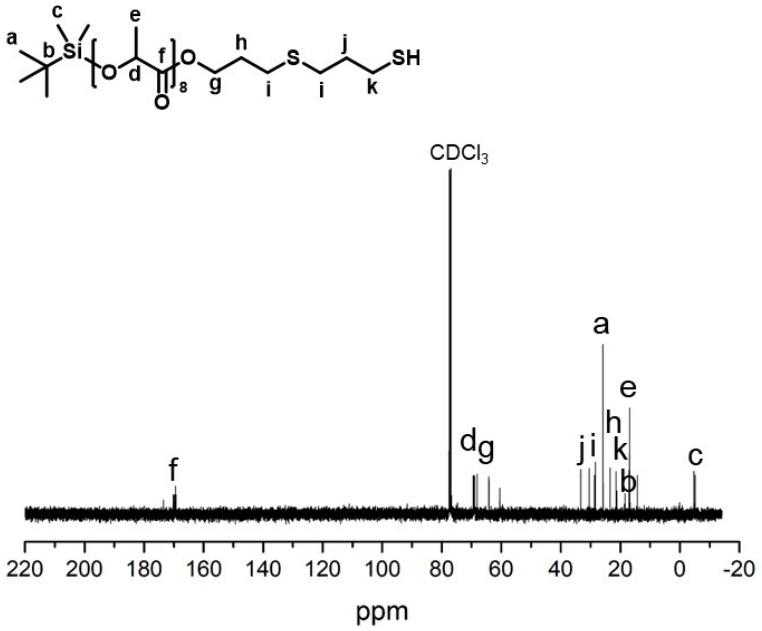


Figure S46. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of thiol-functionalized PLA_8 (TBDMS-LA_8-SH).

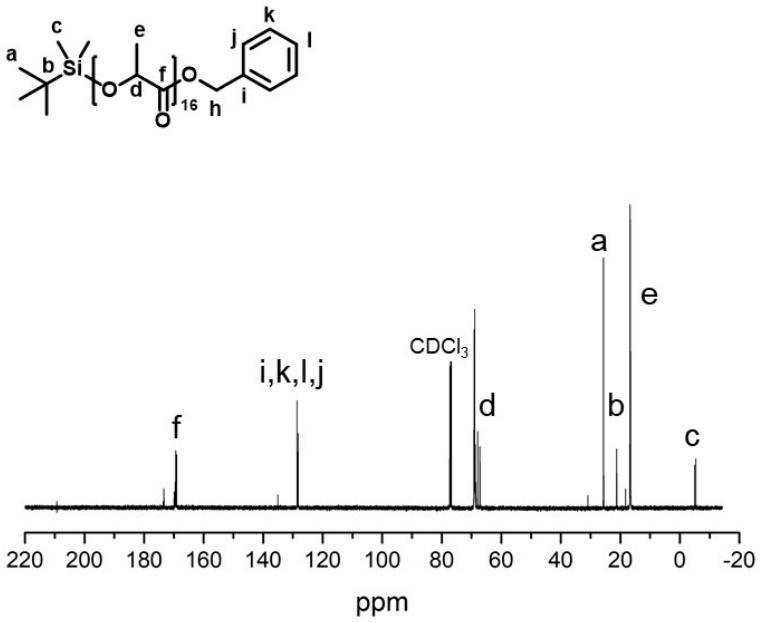


Figure S47. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of TBDMS-LA_{16}-Bz.

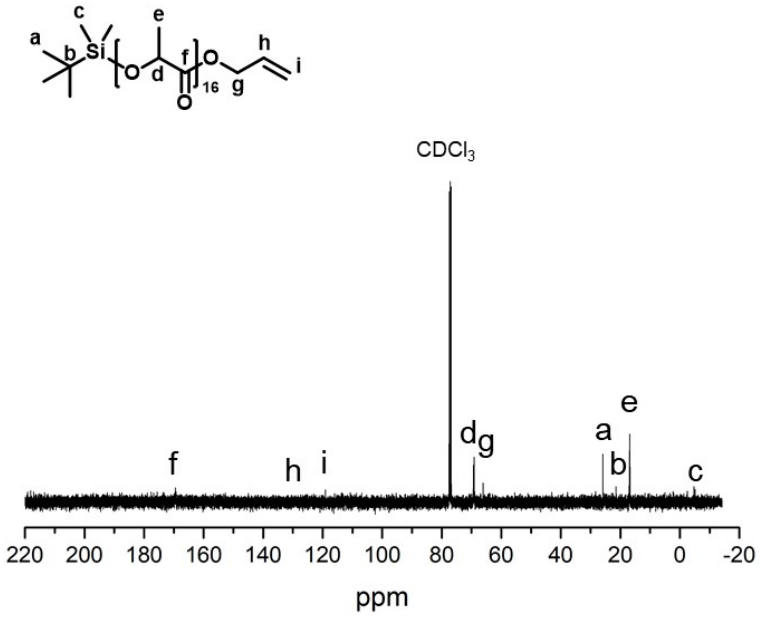


Figure S48. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of TBDMS-LA_{16}-OAllyl.

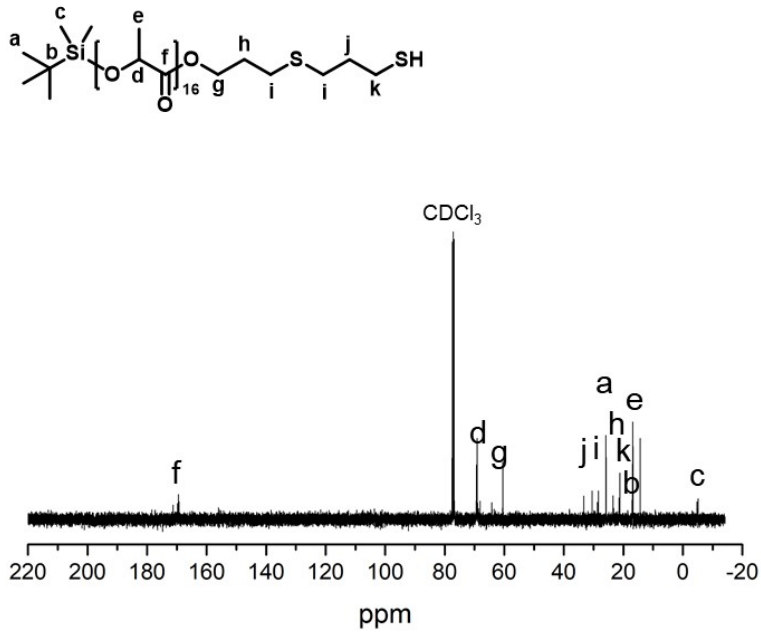


Figure S49. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of thiol-functionalized PLA_{16} (TBDMS-LA_8-SH).

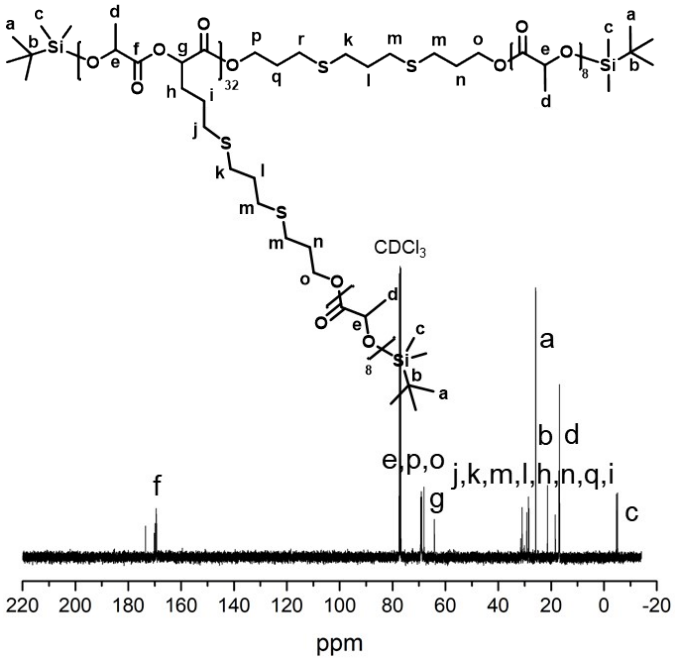


Figure S50. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-LP(LA_8)32-LA_8.

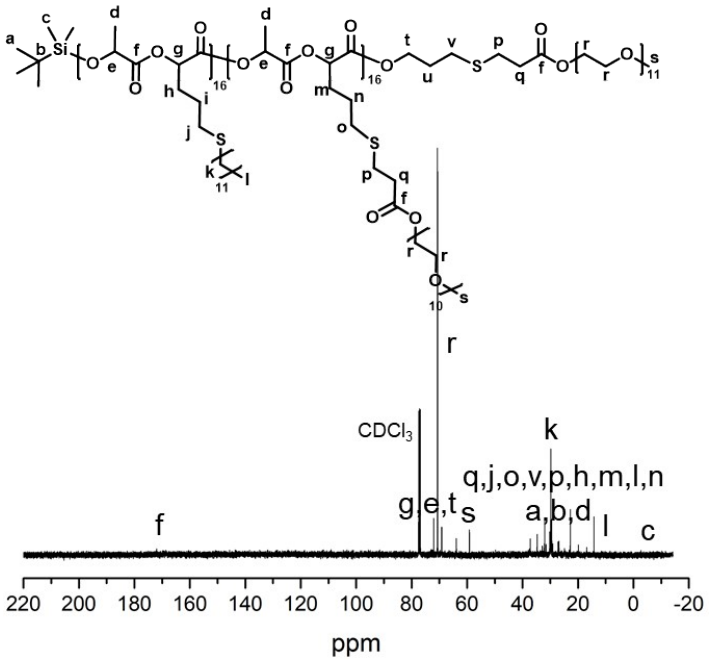


Figure S51. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of t-[LP(DDT)16]-*b*-[LP(PEG_{11})16]-PEG_{11}

4. Table

Table 1. Characterization of α-Hydroxy Acid Backbone

Compound	MALDI[a]		GPC[d]		
	MW (Da) (Cal.)[b] $[M+Na]^+$	MW (Da) (Exp.)[c] $[M+Na]^+$	M_n (Da)	M_w (Da)	PDI
LP8	875.35	875.69	972	995	1.02
LP16	1,555.58	1555.50	1,878	1,909	1.02
LP32	2916.04	2916.01	3,933	3,955	1.03
LP64	5636.97	5638.73	7,867	8,166	1.05

[a]2-(4-Hydroxybenzeneazo)benzoic acid (HABA) was used as a matrix. [b]Theoretical molecular weight of Na^+ adducts of the compound. [c]Experimental molecular weight of Na^+ adducts of the compound. [d]The molecular weight of copolyester backbone was determined by GPC equipped with dRI detector (Eluent = THF).

Table 2. Characterization of Bottlebrush Polymers

Compound	MALDI[a]		GPC[d]		
	MW (Da) (Cal.)	MW (Da) (Exp.)	M_n (kDa)	M_w (kDa)	PDI
t-LP(PEG550)32-PEG550	27,163.48[b]	27135.93[c]	25.7	27.2	1.06
t-LP(LA_8)32-LA_8	33,979.89[b]	33912.41[c]	43.9	46.7	1.06
t-[LP(DDT)16]-*b*-[LP(PEG_{11})16]-PEG_{11}	19145.10[e]	19148.08[f]	17.8	18.5	1.04

[a]Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as a matrix. [b]Theoretical molecular weight of Ag^+ adducts of the compound. [c]Experimental molecular weight of Ag^+ adducts of the compound. [d]The molecular weight of brush polymers was determined by GPC/MALS (Eluent = Chloroform). [e]Theoretical molecular weight of Na^+ adducts of the compound. [f]Experimental molecular weight of Na^+ adducts of the compound.

5. MALDI spectra

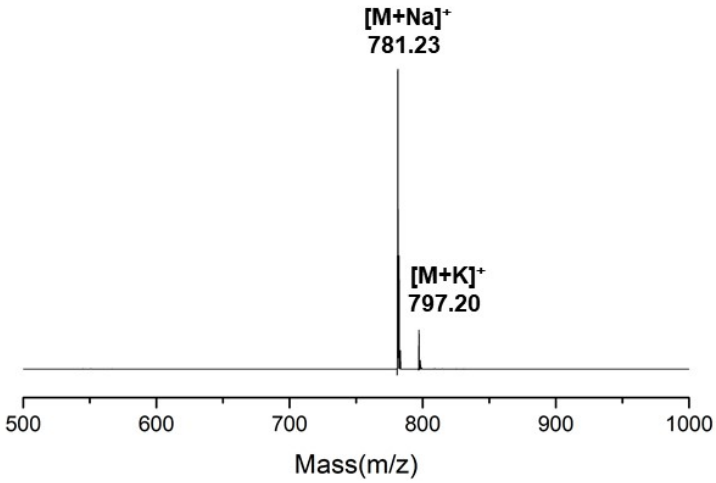


Figure S52. MALDI-TOF mass spectrum of monomethoxy PEG_{11} trityl ether ($mPEG_{11}$-OTrt) ($[M+Na]^+$(cal.): 781.41).

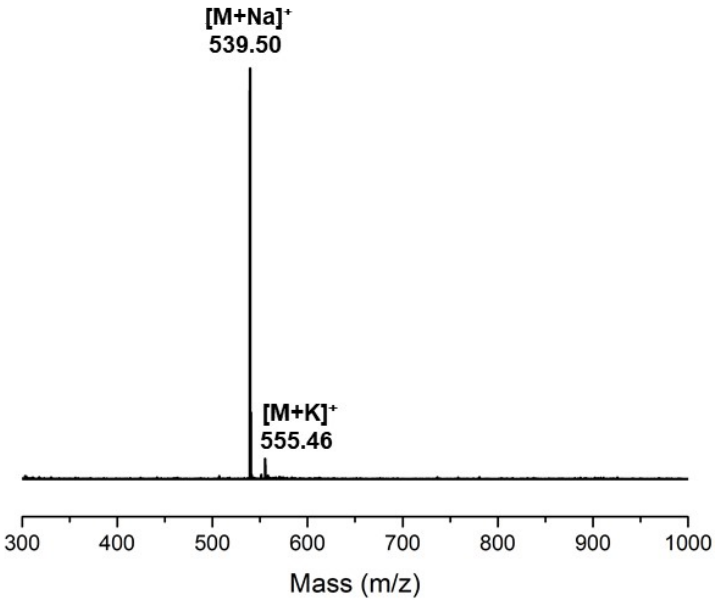


Figure S53. MALDI-TOF mass spectrum of monomethoxy PEG_{11} ($mPEG_{11}$-OH) ($[M+Na]^+$(cal.): 539.30).

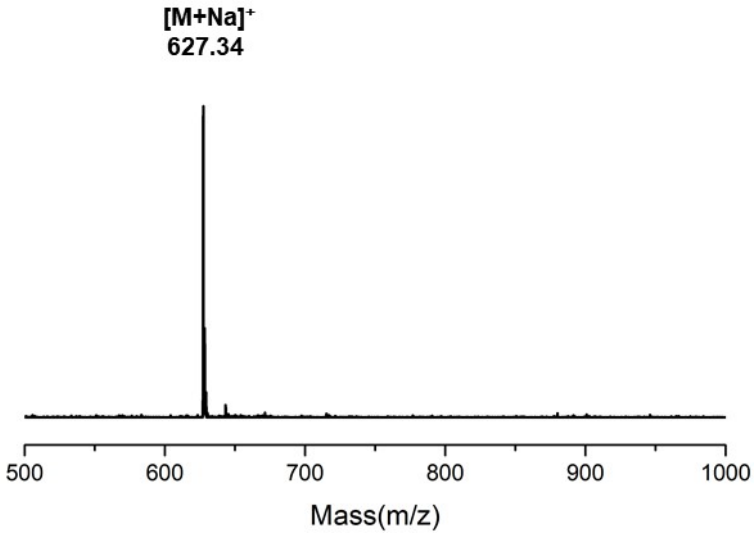


Figure S54. MALDI-TOF mass spectrum of thiol functionalized $mPEG_{11}$ ($[M+Na]^+$(cal.): 627.30).

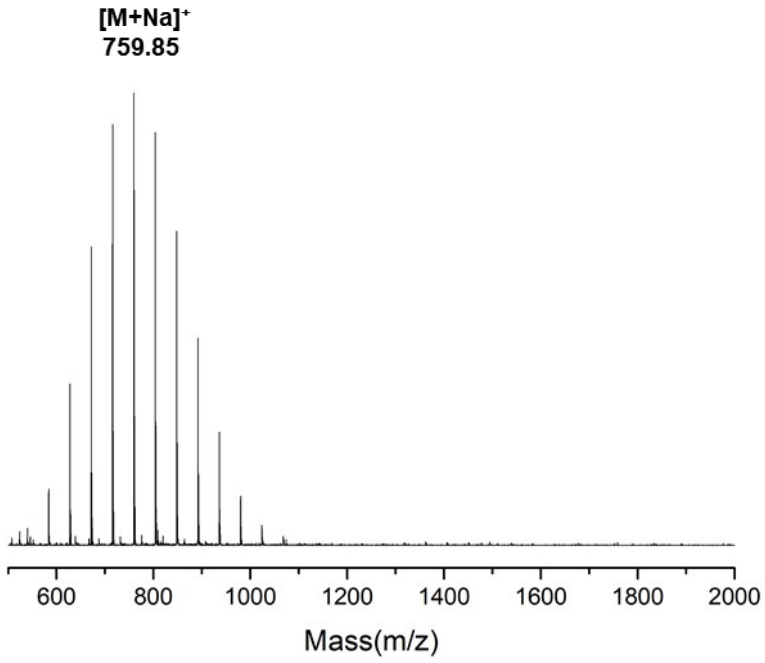


Figure S55. MALDI-TOF mass spectrum of thiol functionalized PEG550.

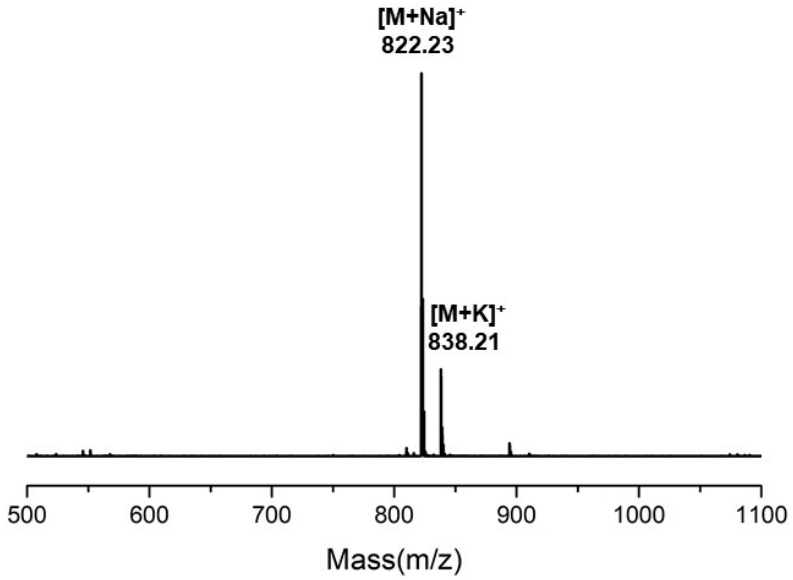


Figure S56. MALDI-TOF mass spectrrum of TBDMS-LA_8-Bn ([M+Na]$^+$(cal.): 821.90).

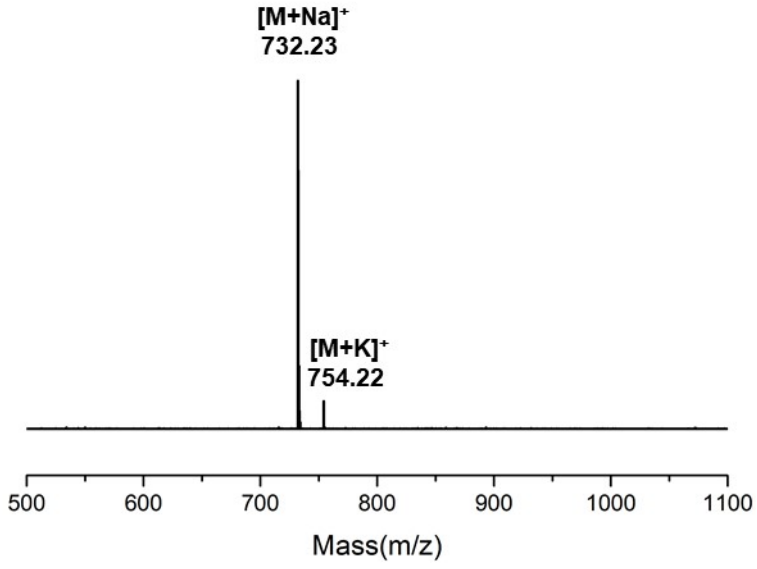


Figure S57. MALDI-TOF mass spectrum of TBDMS-LA_8-COOH ([M+Na]$^+$(cal.): 731.77).

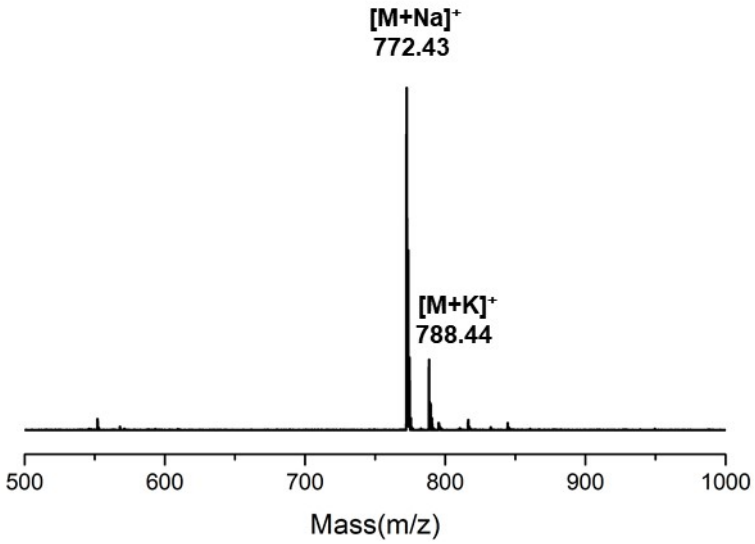


Figure S58. MALDI-TOF mass spectrum of TBDMS-LA_8-OAllyl ($[M+Na]^+$(cal.): 771.84).

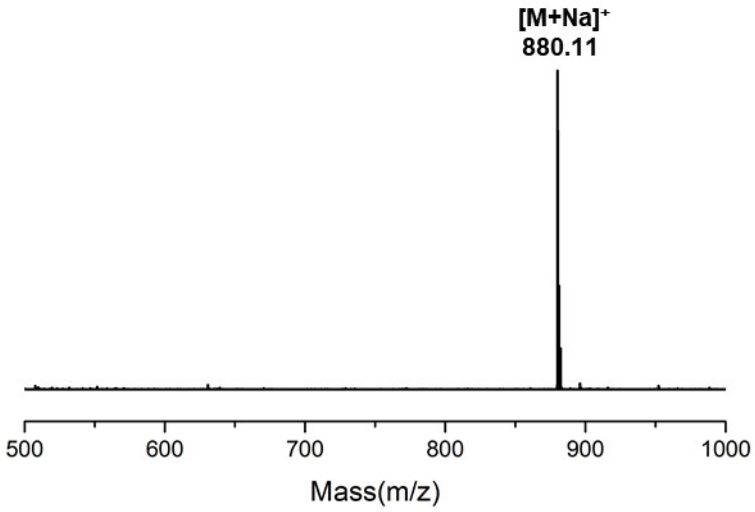


Figure S59. MALDI-TOF mass spectrum of thiol-functionalized PLA_8 ($[M+Na]^+$(cal.): 880.05).

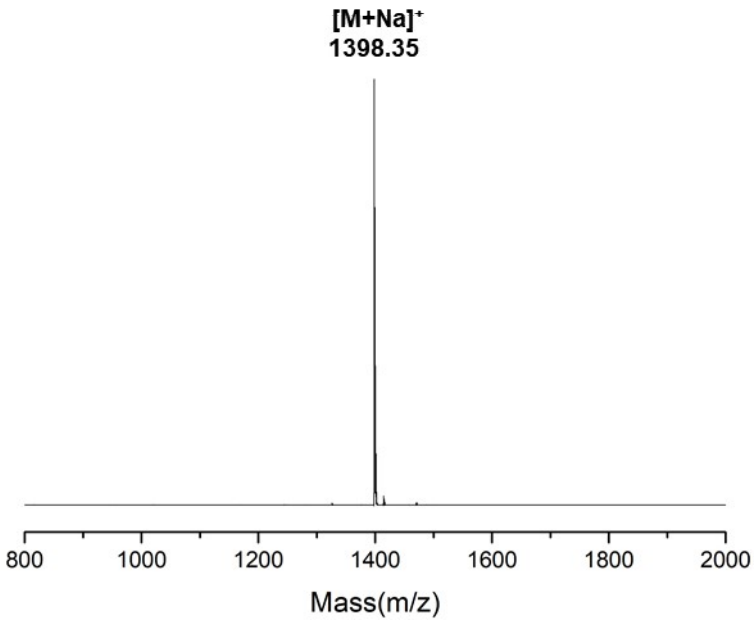


Figure S60. MALDI-TOF mass spectrrum of TBDMS-LA_{16}-Bn ($[M+Na]^+$(cal.): 1398.40).

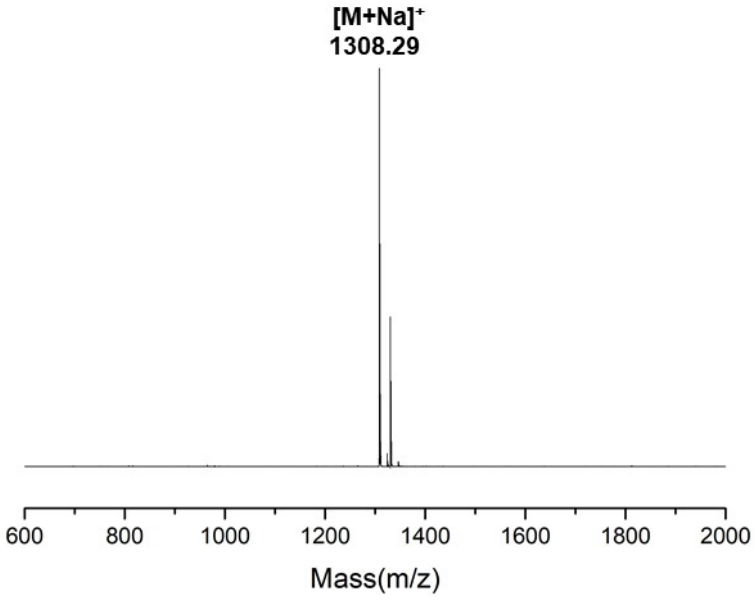


Figure S61. MALDI-TOF mass spectrum of TBDMS-LA_{16}-COOH ($[M+Na]^+$(cal.): 1308.28).

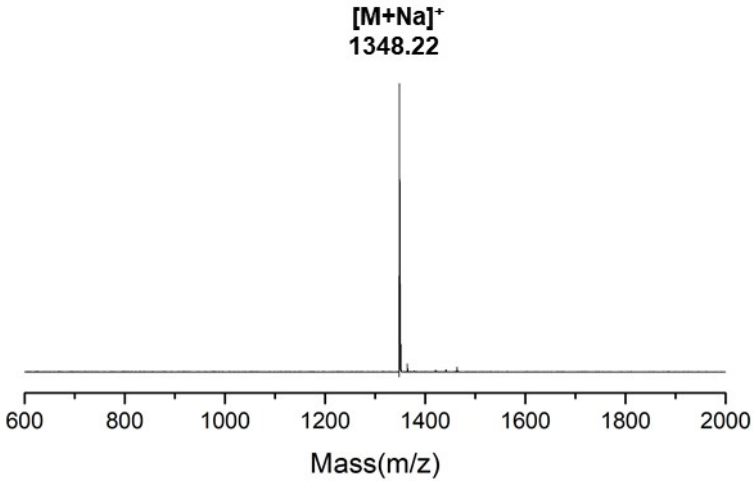


Figure S62. MALDI-TOF mass spectrum of TBDMS-LA_{16}-OAllyl ($[M+Na]^+$(cal.): 1348.34).

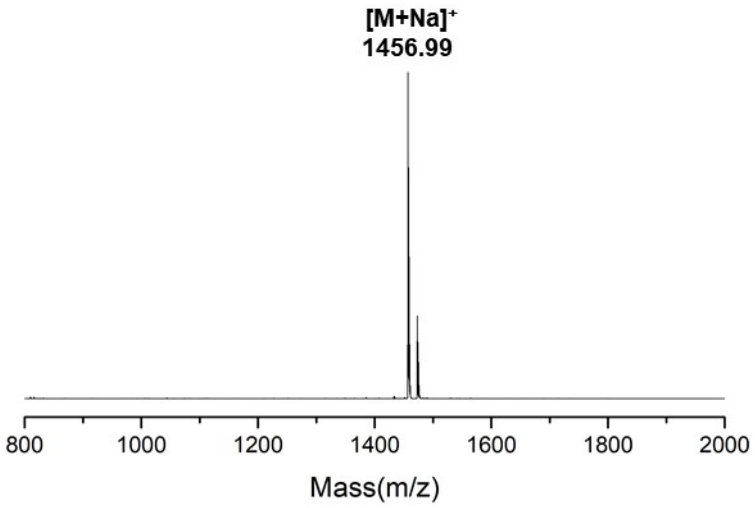


Figure S63. MALDI-TOF mass spectrum of thiol-functionalized PLA_{16} ($[M+Na]^+$(cal.): 1456.56).

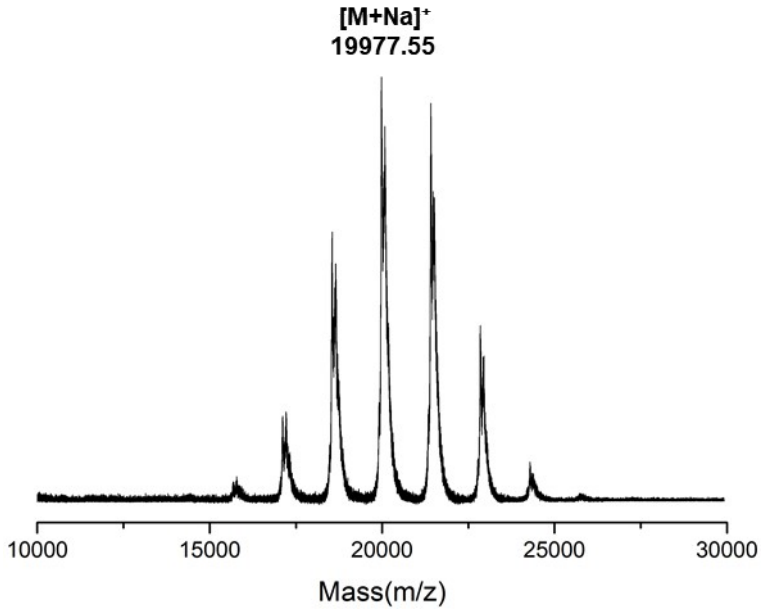


Figure S64. MALDI-TOF mass spectrum of thiol-ene reaction of t-LP(PLA_{16})16-PLA_{16} for 6h ($[M+Na]^+$(cal.): 27268.08).

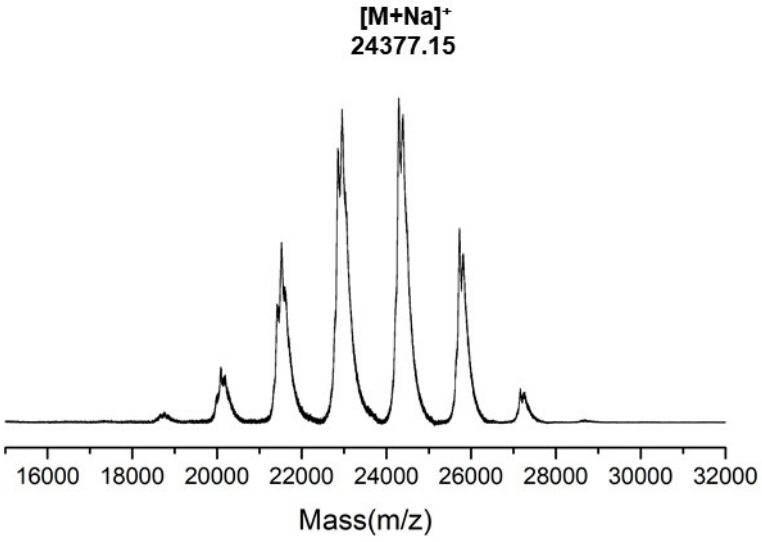


Figure S65. MALDI-TOF mass spectrum of thiol-ene reaction of t-LP(PLA_{16})16-PLA_{16} for 10h ($[M+Na]^+$(cal.): 27268.08).

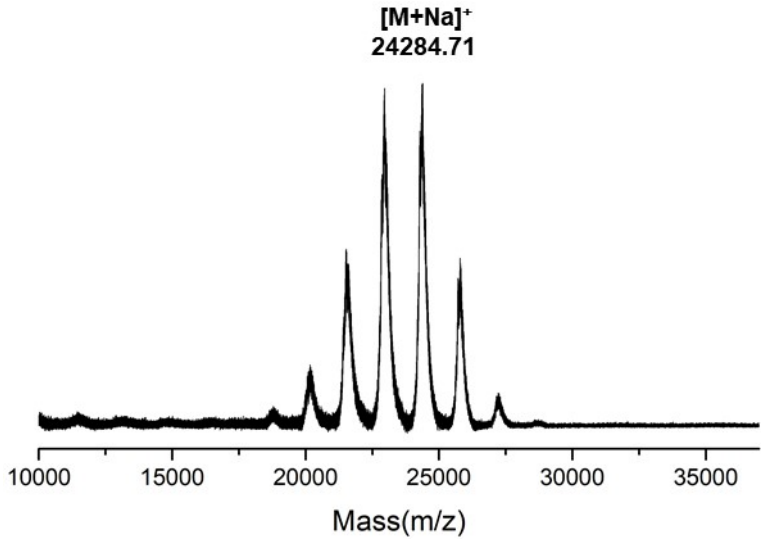


Figure S66. MALDI-TOF mass spectrum of thiol-ene reaction of t-LP(PLA_{16})16-PLA_{16} for 12h. Though we added an excess amount of t-PLA_{16}-SH, this reaction did not proceed to full conversion because of the higher steric hindrance ($[M+Na]^+$(cal.): 27268.08).

6. GPC spectra

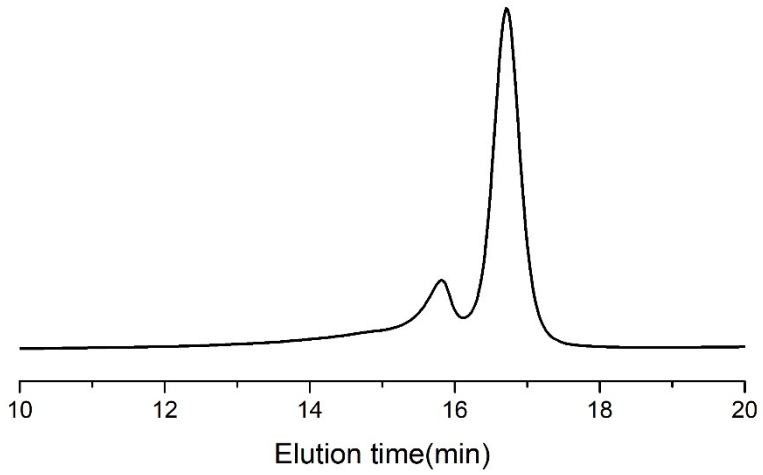


Figure S67. GPC trace of t-LP(PEG550)32-PEG550 detected by GPC/MALS (Eluent = Chloroform). The hump was observed due to the interaction between PEG-SH and column material.

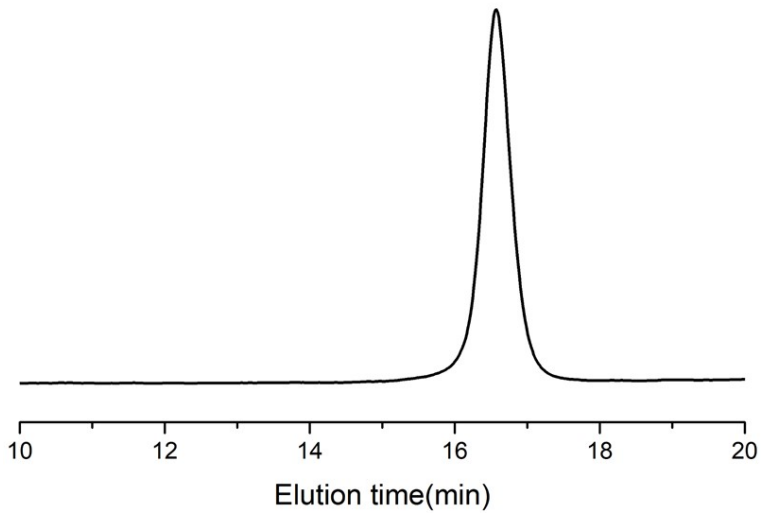


Figure S68. GPC trace of PLA-functionalized LP 64 homopolymers detected by GPC/MALS (Eluent = Chloroform).

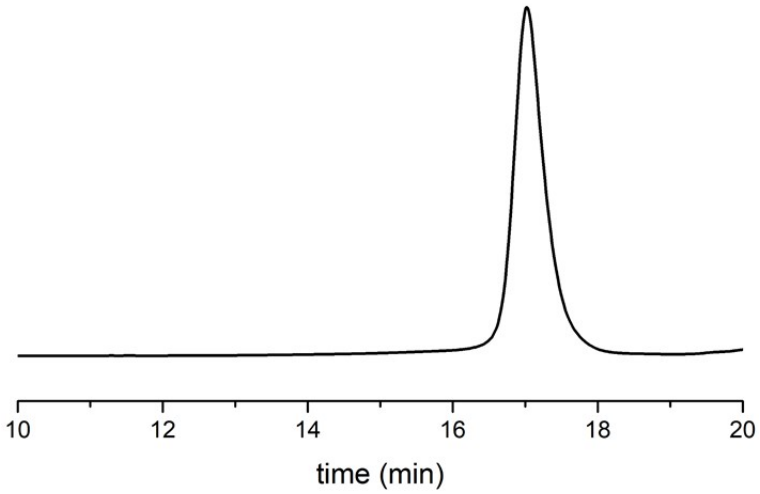


Figure S69. GPC trace of **LP 32**(dodecane)-*b*-**LP 32**(PEG) detected by GPC/MALS (Eluent = Chloroform).

7. Dynamic light scattering (DLS) size plots

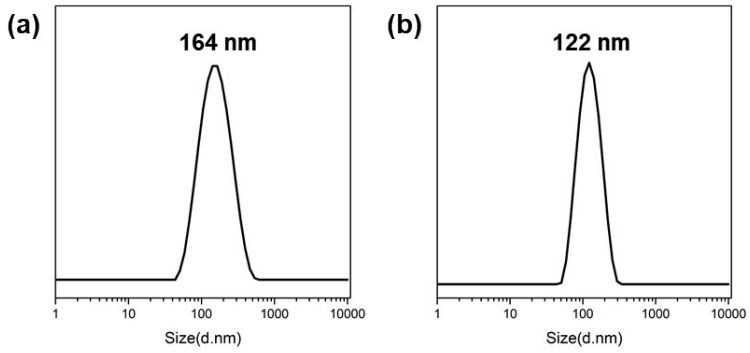


Figure S70. Dynamic light scattering (DLS) size plots of self-assembled structures of BBCP in (a) THF and (b) 1,4-dioxane.

8. References

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