Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Facile Synthesis of Well-defined Hydrophilic Polyesters as Degradable Poly(ethylene glycol)-like Biomaterials

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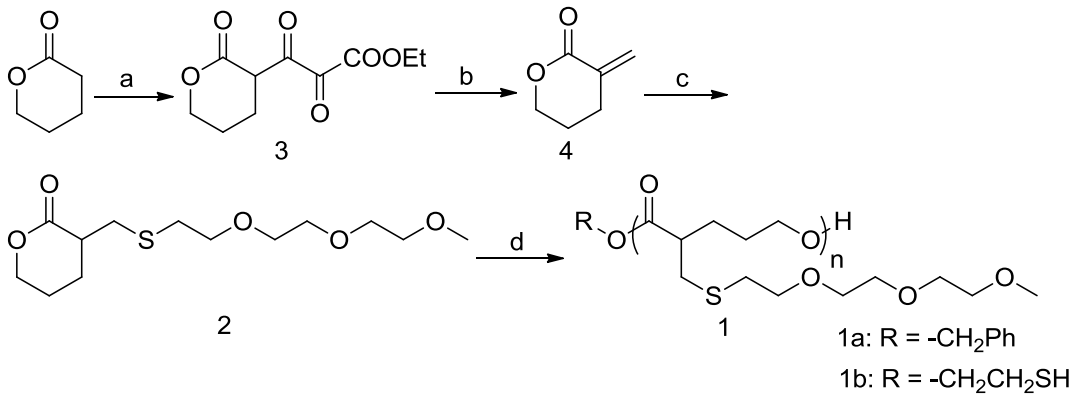
1. Materials and Methods

Chemicals were purchased from commercial sources and used as received. Silica gel for analytical thin layer chromatography (TLC) and column chromatography (200~300 mesh) were purchased from Qingdao Haiyang Chemical Co., Ltd & Special Silica Gel Factory (Qingdao, China). The ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were measured at 100 MHz on a Bruker AV400 spectrometer at ambient temperature. Chemical shifts were reported in parts per million (ppm) downfield from TMS (tetramethylsilane). Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) was performed on a Bruker Reflex III with a UV laser operating at 337 nm and an accelerating voltage of 20 kV. 1, 8, 9- trihydroxyanthracene (dithranol) was used as matrix. Samples were dissolved in THF (10 mg/mL) and mixed with matrix (20 mg/mL in THF) at a mixing ratio of 20 : 5 (v/v, matrix : analyte). ESI mass spectra were performed on a Bruker microTOF-QⅡ instrument. Gel Permeation Chromatography (GPC) was carried out using a PL-GPC 50 Integrated GPC/SEC System with a RI detector (Agilent Technologies, Inc. USA) with polystyrene as standards (American Polymer Standards Corp，USA). The eluant was tetrahydrofuran (THF) and flow rate was set to 1 mL/minute at 35^{o}C. Dialysis was carried out with tubing cellulose membrane (MWCO 1KD, Spectrum Laboratories Inc. USA). Preparation of Mixed Self-Assembled Monolayers (SAMs): The Au substrates and QCM Crystals were cleaned by immersion in piranha solution (3:1, H_2SO_4 : 30% H_2O_2) at room temperature for 10 min, rinsing with Ultra Pure water and then HPLC grade EtOH thoroughly for 1 min, and then dried under N_2 atmosphere. The treated Au substrates and QCM Crystals were immersed in EtOH solution of the polymer **1b** (5364 Da, PDI = 1.01), mPEG-SH and n-Hexadecanethiol for 24 h, and then rinsing with EtOH, followed by drying under N_2 atmosphere. Water contact angle measurements were performed with a video-based optical contact angle measuring instrument (Dataphisics OCA 15EC, DataPhysics Instruments GmbH, Germany). Quartz crystal

microbalance (QCM) assays were carried out using a CHI 420C electrochemical analyzer (Chenhua Instruments, Shanghai, China). The phosphate buffered saline (phosphate 200 mM, pH 7.4, NaCl, 100 mM) used in QCM measurements was prepared at the time of use. Thermal transition data were collected with a Mettler differential scanning calorimeter (DSC) (STAR^e System, Mettler Toledo, Switzerland) equipped with a liquid nitrogen cooling system, calibrated with indium standards. A dry and constant flow of nitrogen (40 mL min^{-1}) was maintained in order to eliminate thermal gradients and ensure the validity of the calibration standard from sample to sample. The sample size ranged from 5 to 8 mg, and each sample was subjected to two cool-heat-cool cycles from -150 °C to 0 °C with a heating and cooling rate 10 °C/min.

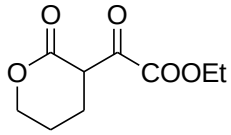
HFF cells and Raw 264.7 cells were obtained from Cell Resource Center (IBMS, CAMS/PUMC) and cultured in Dulbecco's Modified Eagle Medium (DMEM; Thermo Scientific) supplemented with 10% fetal bovine serum (FBS; GIBCO; Invitrogen), and 1% penicillin/streptomycin (Beijing Solarbio Scientific & Technology Co, Ltd). For imaging studies, cells were plated in Class Bottom Cell Culture Dish (Nest) containing 1 mL of complete DMEM and incubated at 37℃ under 5% CO_2 for one day. Bright filed and fluorescence images were taken with a Zeiss Abserver A1 inverted fluorescence microscope equipped with an EM-CCD camera (Hamamatsu) and an X-Cite 120 metal halide lamp (EXFP). Bright field image and fluorescence images were obtained using a 40×objective lens.

2. Synthesis and Characterizations



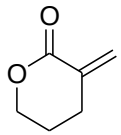
Scheme S1. (a) Ethanol, diethyl oxalate, sodium metal, ice/salt bath 2 h, rt, overnight; (b) THF, NaH, CH_2O, rt, 30 minutes; (c) CH_2Cl_2, **7**, rt, 30 minutes; (d) ROH, diphenyl hydrogen phosphate, rt, 24 hours.

Synthesis of Monomer

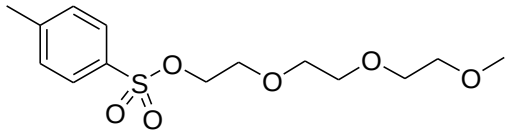


Ethyl 2-oxo-2-(2-oxo-tetrahydro-2H-pyran-3-yl)acetate (**3**)[1]. Sodium metal (3.45 g, 0.15 mol) was cautiously added to 100 mL absolute ethanol. When the solid disappeared, the solution was cooled by an ice/salt bath, and diethyl oxalate (16.06 g, 0.11 mol) was added to the solution. δ-valerolactone (10.00 g, 0.1 mol) dissolved in 20 mL ethanol was added dropwise about 20 minutes. The reaction mixture was stirred at -15^{o}C for 1 hour. Upon removal of the cooling bath, the solution was allowed to warm to room temperature and stirred for 10 hours. The solvent was then removed under reduced pressure. The pasty residue was diluted with 100 mL H_2O, and the aqueous phase was washed with diethyl ether (50 mL) and the organic phase was washed by H_2O (50 mL). The combined aqueous phase was acidified with dilute HCl (2 M), and extracted with DCM (50 mL × 3). The combined organic phases were dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to

give **3** as yellow oil which was used in the next step without any further purification.

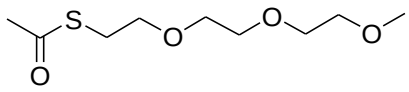


3-Methylene-tetrahydropyran-2-one (4)[1]. Ethyl 2-oxo-2-(2-oxo-tetrahydro-2H-pyran-3-yl)acetate (**3**, 1.00 g, 0.05 mol) dissolved in 10 mL dry THF was added dropwise to a suspension of degreased NaH (1.20 g, 0.05 mol) in 10 mL dry THF. The reaction mixture was stirred at ambient temperature till H_2 evolution ceased. Anhydrous gaseous formaldehyde (generated by thermal cracking of dry paraformaldehyde) was bubbled through the solution by a steam of N_2 carrier gas. After 1 hour at ambient temperature, the reaction mixture was filtered through Celite to remove sodium oxalate and formaldehyde polymer, and the solvent was removed from the filtrate under reduced pressure. The residue was dissolved in 30 mL DCM, and washed with saturated $KHCO_3$, and the organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The isolated residue was purified by column chromatography (SiO2, eluent: EtOAc/*n*-hexane = 1:3) to give 3-methylene-tetrahydropyran-2-one as a colorless oil (0.38 g, 68%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.43(d, 1H, *J* = 1.2 Hz), 5.56(d, 1H, *J* = 1.4 Hz), 4.38(t, 2H, *J* = 1.4 Hz), 2.67(t, 2H, *J* = 6.5 Hz), 1.96(m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 165.48, 134.14, 128.25, 69.67, 28.14, 23.25. ESI MS calculated 112.1, found 135.1 ($M+Na^+$).

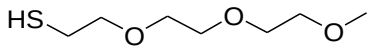


2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (5)[2]. Triethylene glycol monomethyl ether (16.40 g, 0.1 mol) and 4-toluene sulfonyl chloride (19.06 g, 0.102 mol) wrere dissolved in 70 mL DCM. The solution was cooled to 0^{o}C and KOH (22.40 g, 0.4 mol) was added slowly. The reaction mixture was left to stir at ambient temperature for 16 hour, and then, poured it into ice/water and extracted with DCM

(150 mL × 3). The organic phase was washed with H_2O and the aqueous phase was back extracted with DCM (150 mL × 3). The combined organic phases were dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate as a colorless oil (30.21 g, 95%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80(d, 2H, *J* = 8.2 Hz), 7.34(d, 2H, *J* = 8.0 Hz), 4.16(t, 3H, *J* = 4.8 Hz), 3.71-3.50(m, 10H), 3.38(s, 3H), 2.45(s, 3H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 144.73, 133.10, 129.78, 127.95, 71.90, 70.73, 70.53, 69.19, 68.67, 58.98, 21.58; ESI MS calculated 318.4, found 341.1 ($M+Na^+$).

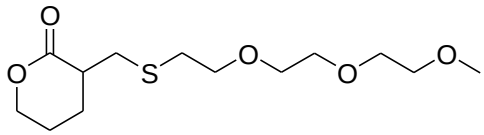


S-2-(2-(2-methoxyethoxy)ethoxy)ethyl ethanethioate (**6**)[2]**.** 2-(2-(2-methoxy-ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate(**5**, 31.83g, 0.1mol) and potassium thioacetate were dissolved in 250 mL CH_3CN and heated to reflux temperature under N_2 for 16 hours. The solvent was then removed under reduced pressure, the atropurpureus residue was diluted with 200 mL DCM, and the organic phase was washed with H_2O(100 mL), dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The isolated residue was purified by column chromatography (SiO2, eluent: EtOAc/*n*-hexane = 1:4) to give S-2-(2-(2-methoxyethoxy)ethoxy)ethyl ethanethioate as a red oil(13.54g, 61%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67-3.54(m, 10H), 3.38(s, 3H), 3.10(t, 2H, *J* = 6.5 Hz), 2.34(s, 3H). ^{13}C NMR(100MHz, $CDCl_3$) δ 195.46, 71.94, 70.57, 70.54, 70.31, 69.75, 59.02, 30.52, 28.84; ESI MS calculated 318.4, found 341.1 ($M+Na^+$).



2-(2-(2-Methoxyethoxy)ethoxy)ethanethiol (**7**)[2]. S-2-(2-(2-methoxyethoxy)ethoxy) ethyl ethanethioate(**6**, 11.15 g, 0.05 mol) was dissolved in MeOH (100 mL)/aq. HCl (10%, 100 mL). The reaction mixture was heated at 100^{o}C for 2.5 h, and then, cooled to ambient temperature, and extracted with DCM (75 mL × 3). The organic phase was

washed with saturated $NaHCO_3$(100 mL), dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The product was further purified by vacuum distillation to give 2-(2-(2-methoxy-ethoxy)ethoxy)ethanethiol as a pale yellow liquid (6.84 g, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67-3.53(m, 10H), 3.38(s, 3H), 2.69(dt, 2H, J_1 = 8.1 Hz, J_2 = 6.5 Hz), 1.58(t, 1H, J = 8.2 Hz). ^{13}C NMR(100 MHz, $CDCl_3$) δ 72.93, 72.00, 70.61, 70.28, 59.04, 24.29; ESI MS calculated 180.1, found 203.1 ($M+Na^+$).



3-((2-(2-(2-Methoxyethoxy)ethoxy)ethylthio)methyl)-tetrahydropyran-2-one (**2**)**.** 3-methylene-tetrahydropyran-2-one (**4**, 1.12 g, 0.01 mol) and tri-n-butylphosphine were dissolved in 50 mL DCM. 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol (**7**, 1.80 g 0.01 mol) dissolved in 20 mL DCM was added dropwise about 10 min. the reaction mixture was stirred at ambient temperature for 30 minutes. The solvent was then removed under reduced pressure. The isolated residue was purified by column chromatography (SiO_2, eluent: EtOAc/*n*-hexane = 1:1) to give 3-((2-(2-(2-methoxyethoxy)ethoxy)ethylthio)methyl)-tetrahydropyran-2-one as a pale yellow oil (2.39 g, 82%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.34(m, 2H), 3.68-3.53(m, 10H), 3.38(s, 3H), 3.16-3.10(m, 1H), 2.78-2.70(m, 4H), 2.27(m, 1H), 1.94(m, 2H), 1.67(m, 1H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 71.93, 70.91, 70.61, 70.57, 70.35, 68.75, 59.05, 40.58, 34.12, 32.47, 24.17, 22.06; ESI MS calculated 292.1, found 315.1 ($M+Na^+$)

General Procedure of Polymerization.

A typical procedure for the polymerization is as follows: In a glove box, 3-((2-(2-(2-Methoxyethoxy)ethoxy)ethylthio)methyl)-tetrahydropyran-2-one (**2**, 0.162 g, 0.55 mmol) was added to a stock solution of ROH (11.2 μL, 11.2 μmol) in DCM at 25^{o}C. A CH_2Cl_2 stock solution of diphenyl hydrogen phosphate (DPP) (11.2 μL, 11.2 μmol) were added to the solution to initiate the polymerization under an argon

atmosphere. The reaction mixture was stirred at 25^{o}C for 24 h (until the conversion of monomer **2** monitored by ^{1}H NMR spectroscopy was higher than 80%). The mixture was then treated with basic alumina in order to eliminate the catalyst and concentrated under vacuum. The mixture was dissolved in methanol (5 mL), then put in a dialysis tube (MWCO = 1000) and dialyzed against methanol (100 mL). The solvent was replaced every 12 hours. After 2 days, the polymer was then concentrated and residue solvent was removed via vacuum pump overnight.

3. Kinetic Study of the Polymerization

Entry	Time (h)	Conv (%)[a]	$M_{n,\,theo}$[b]	$M_{n,\,NMR}$[a]	PDI[c]
1	1	6	1633	5240	1.06
2	2	12	2869	5328	1.07
3	3	17	4133	6046	1.10
4	4	28	6766	8636	1.11
5	6	40	9533	100758	1.19
6	8	48	11388	110408	1.10
7	10	58	13737	131768	1.19
8	12	65	15250	142588	1.16
9	24	79	18498	16755	1.12

Table S1. Data of Figure 3. [a] Determined by ^{1}H NMR. [b] $M_{n,theo}$ = $[M]_0/[BnOH]_0$ × conv. ×(M_w of **2**) + (M_w of BnOH). [c] Determined by GPC in THF with polystyrene as standards (1 mL/min, 35^{o}C). The data was collected with the reactant ratio of $[\mathbf{2}]_0/[BnOH]_0/[DPP]$ = 80/1/1.

4. Examples of ^{1}H NMR Analysis

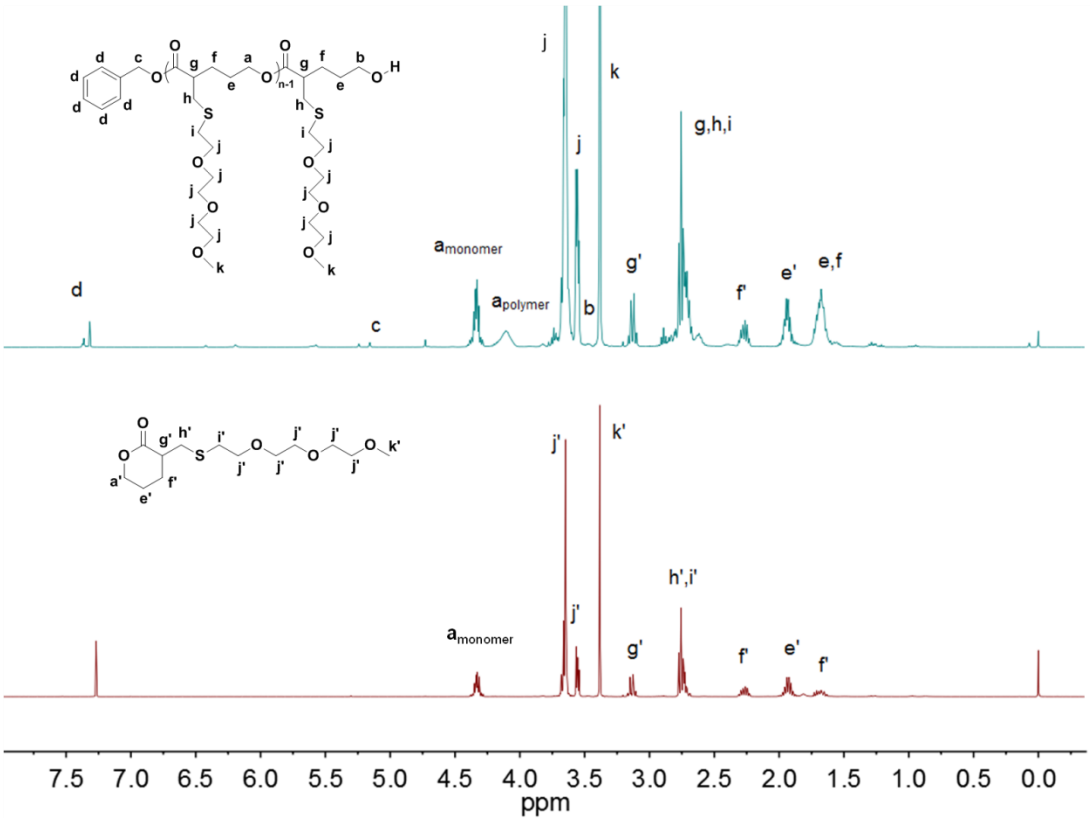


Figure S1. Representative ^{1}H NMR ($CDCl_3$, 400MHz) spectra of the monomer and ROP reaction mixture, entry 5 in Table S1. $M_{n,NMR}$ = ($Ha_{polymer}/Ha_{monomer}$+ 1) × ($M_w$ of **2**) + (M_w of BnOH); Conv. = $Ha_{polymer}/(Ha_{polymer} + Ha_{monomer}) \times 100\%$.

5. Stability evaluation of the monomer by ^{1}H NMR

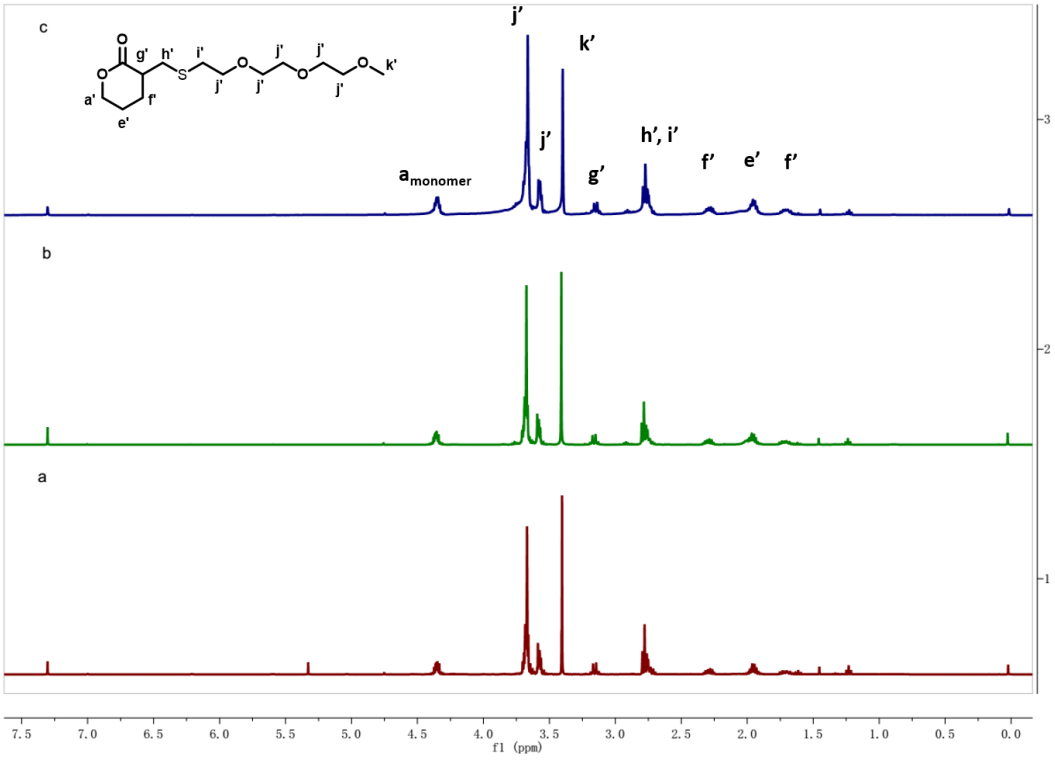


Figure S2. Monomer 2 was isolated and stored on bench top in ambient environment. Samples were taken and checked with ^{1}H NMR in 1(a), 8 (b) and 20 days (c).

6. The ^{1}H-^{1}H COSY NMR spectrum of polymer

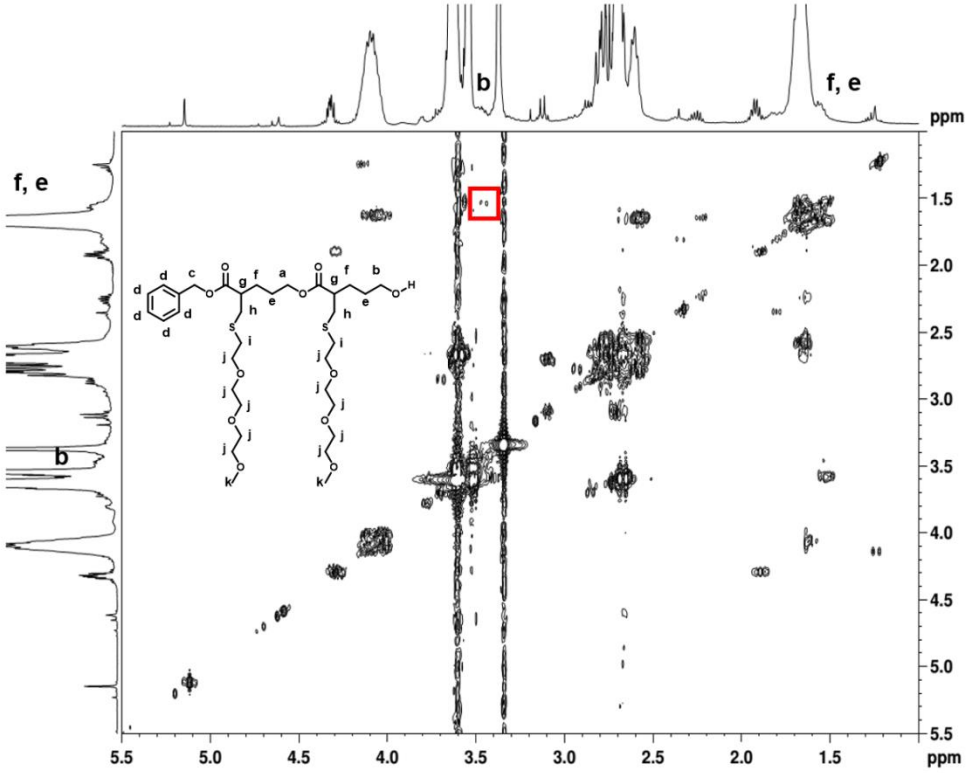


Figure S3. The COSY NMR spectrum of polymer in $CDCl_3$ at 300K (400 MHz).

7. Representative MALDI-TOF Mass Spectra

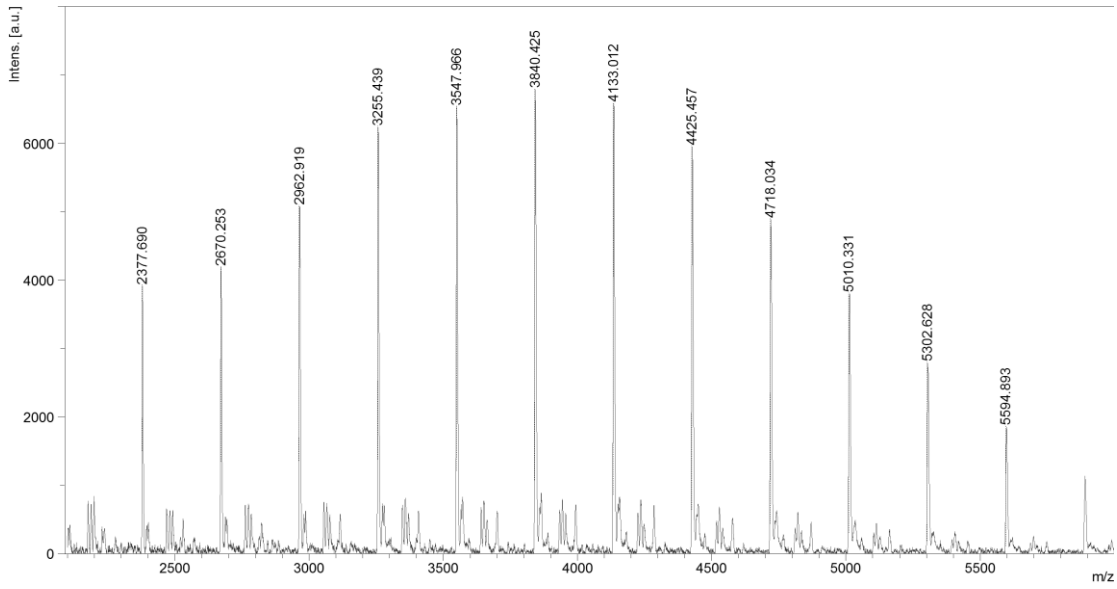


Figure S4. MALDI-TOF MS spectrum in reflector mode of the obtained **1a** ($[\mathbf{2}]_0/[BnOH]_0/[DPP]$ = 20/1/1, reacted for 24 hours, conversion = 78%, $M_{n,NMR}$ = 4663) prepared using a dry drop method with DHB as the matrix.

8. Water Contact Angle Tests

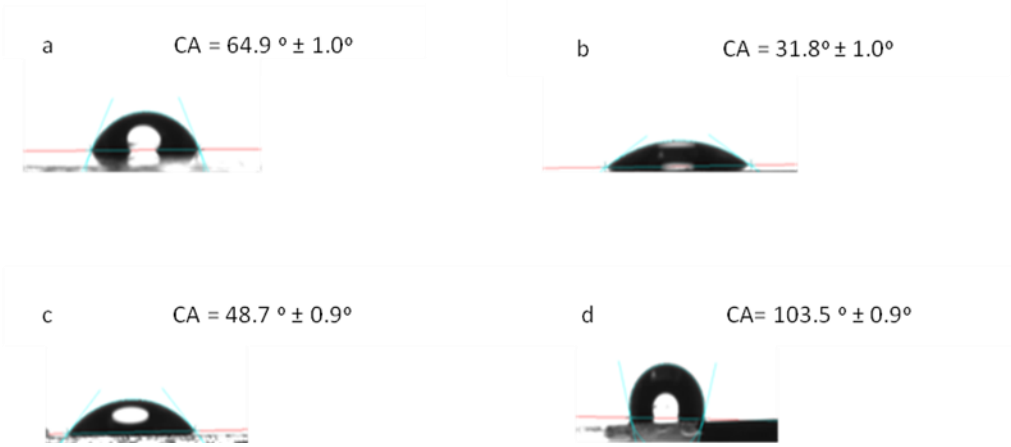


Figure S5. Water contact angle images for (a) blank, (b) mPEG-SH (5000 Da), (c) **1b** (5364 Da, PDI = 1.01), (d) n-Hexadecanethiol.

9. Quartz crystal microbalance (QCM) assays

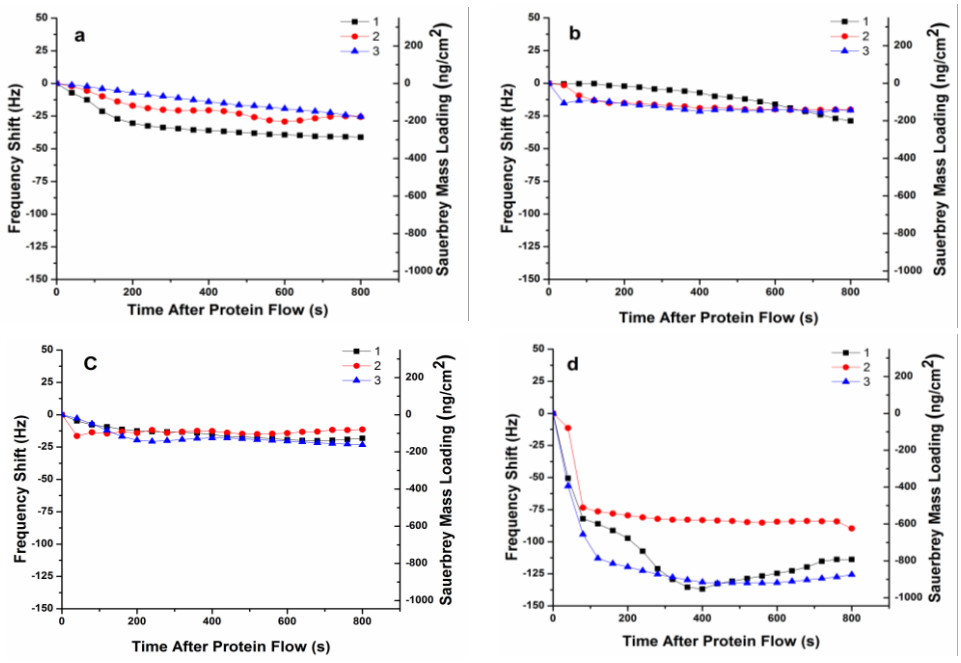


Figure S6. Adsorption profiles of BSA onto QCM Crystal surfaces modified by (a) nothing, (b) mPEG-SH (5000 Da), (c) **1b** (5364 Da, PDI = 1.01), (d) n-Hexadecanethiol. The concentration of Bovine serum albumin Fraction V (BSA)

was /mL in PBS (PH = 7.40).

10. DSC Measurements

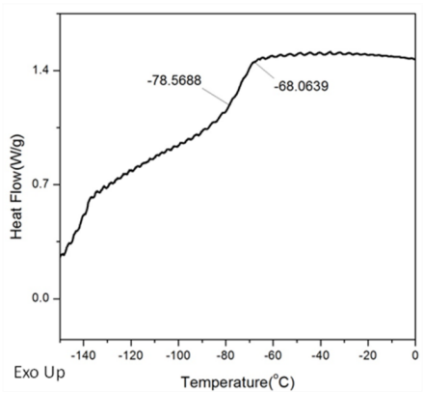


Figure S7. DSC data of **1a** (15234 Da, PDI = 1.23). T_g = 73.3164°C. (10°C/min; -150 ~0 °C; 2 cycles)

11. Degradation of Polymers.

The polyester (M_w 5423, 10 mg) was dissolved in methanol (5 mL). Sodium methoxide (50 mg of a 30 wt % solution in methanol) was added to the solution. The mixture was stirred for 3 h at room temperature, then neutralized with hydrochloric acid (2 M) and evaporated in vacuum. The residue was dispersed in THF, centrifuged and the Supernatant was subject to GPC analysis.

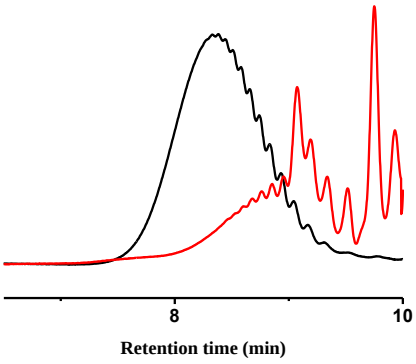


Figure S8. Representative GPC traces of **polymer 1**(M_w 5423) before (black line) and after (red line) degradation.

12. Cell Adhesion Evaluation

Raw 264.7 cells were harvested from culture flasks and suspended in supplemented DMEM. The cells were counted using a haemocytometer and then diluted to a solution of 5×10^5 cells/mL. The SAMs and bare gold substrates were done in triplicates and placed in sterile Petri dishes. The substrates were then immersed in 4mL of DMEM. 1 mL Raw 264.7 cells suspension of 5×10^5 cells/mL was then added to each Petri dish to give a final cell suspension of 1×10^5 cells/mL in each Petri dish. The substrates were incubated for 24 h at 37^oC in 5% CO_2. After incubation the substrates were rinsed in DMEM to ensure loosely bound cells were removed. The cells with Gold substrates stained with Calcien-AM, and then take photoes with Fluorescent microscope as a test for viability. The cells were counted also using the microscope.

13. Cell Cytotoxicity Assay

HFF cells were grown in 96-well plates at an initial density 5×10^3 cells per well for 24 h. Subsequently, the 150 and 200 μg/mL of PEG and polymer **1b** were incubated for 12 h. Cell viability was evaluated using the 3-(4,5-dimethylthiazol-2-yl) 2,5-diphenyl-tetrazoilum bromide (MTT) reduction assay. After incubation, MTT (20 μL, 5 mg mL^{-1}) assay was added to each well for 4 h. DMSO (100 μL) was added to each well after removing media. Absorption at 490 nm was measured on a plate reader.

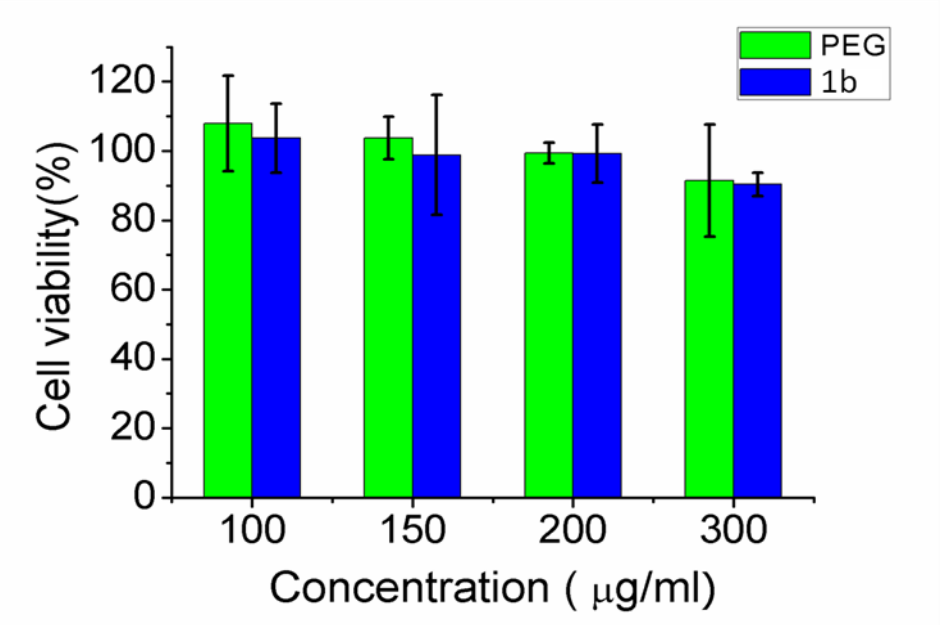


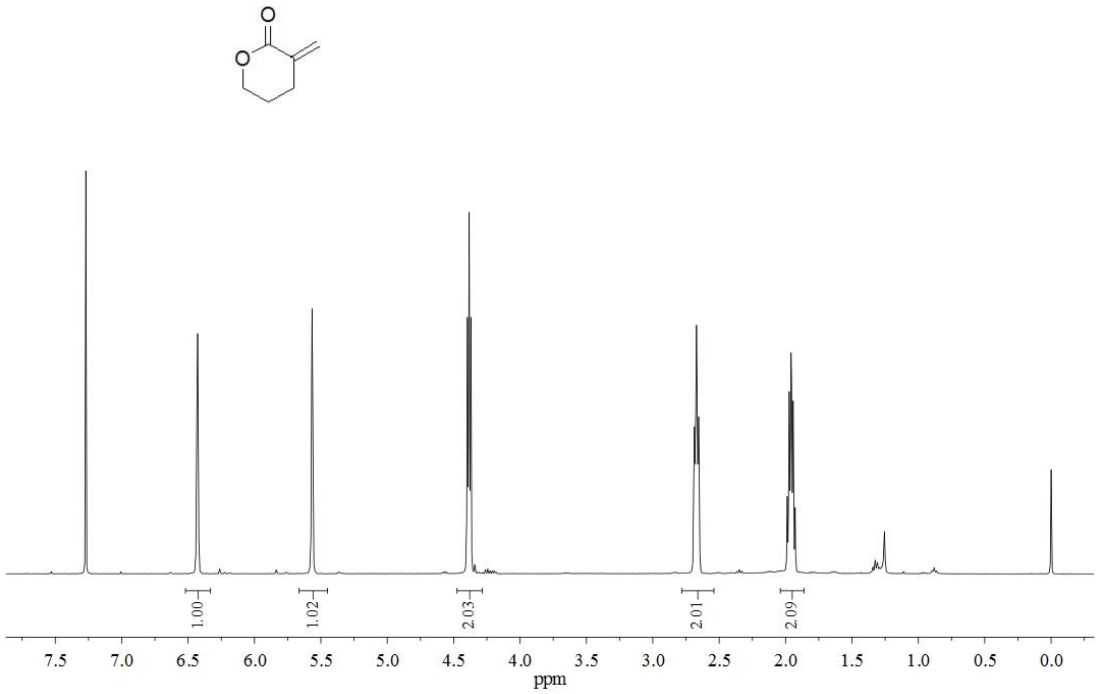
Figure S9. MTT assay of HFF cells treated with (a) PEG (8000 Da), (b) **1b** (5364 Da, PDI = 1.01)

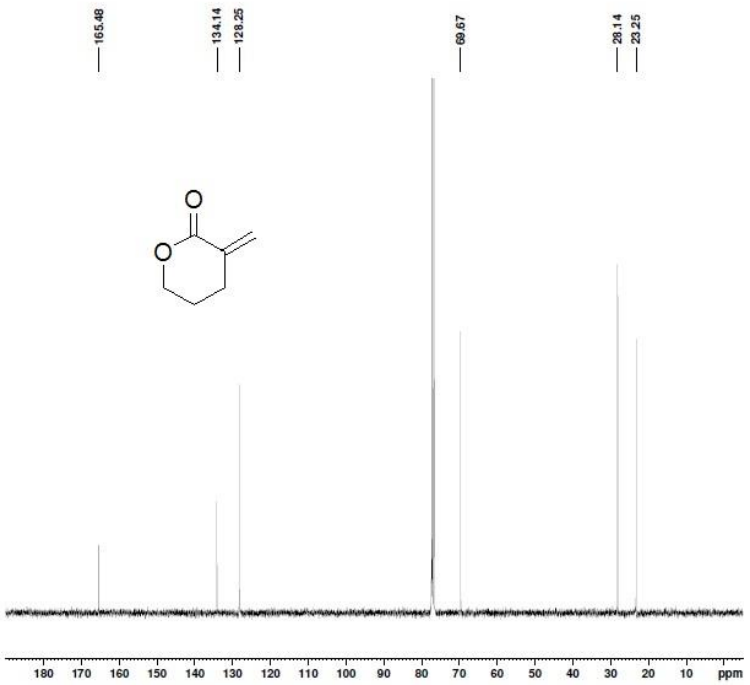
14. References

1. Ksander, G. M.; McMurry, J. E.; Johnson M., *J. Org. Chem.* **1977**, *42*, 1180-1185.

2. Keddie, D.J.; Grande, J. B.; Gonzaga F.; Brook, M. A.; Dargaville, T. R., *Org. Lett.* **2011**, *13*, 6006-6009.

15. Appendix





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DE                   6.50 usec
TE                   295.7 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                         1

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P1                    8.50 usec
PL1                  -2.00 dB
PL1W          57.32743073 W
SFO1          100.6328888 MHz

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NUC2                     1H
PCPD2                80.00 usec
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PL12                 14.26 dB
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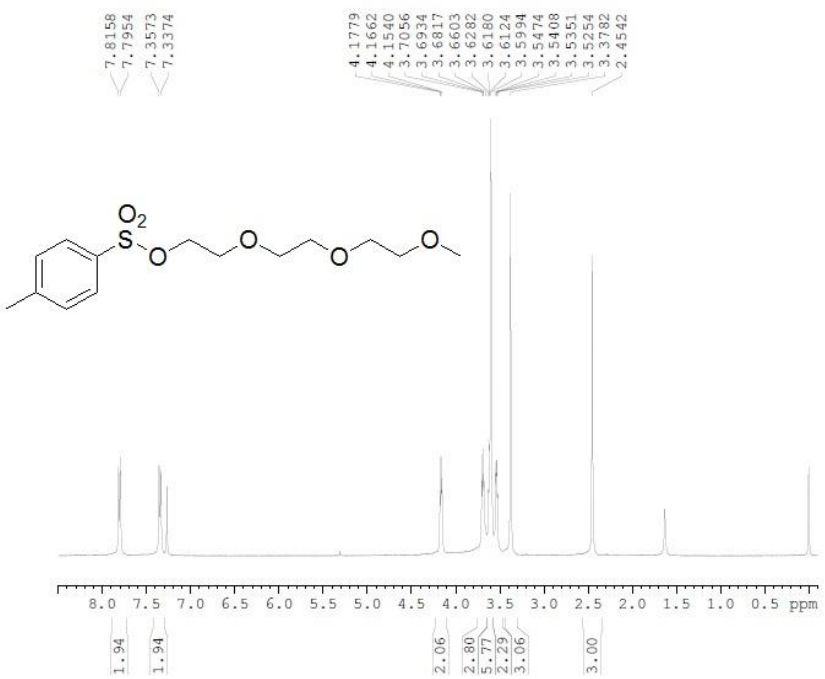

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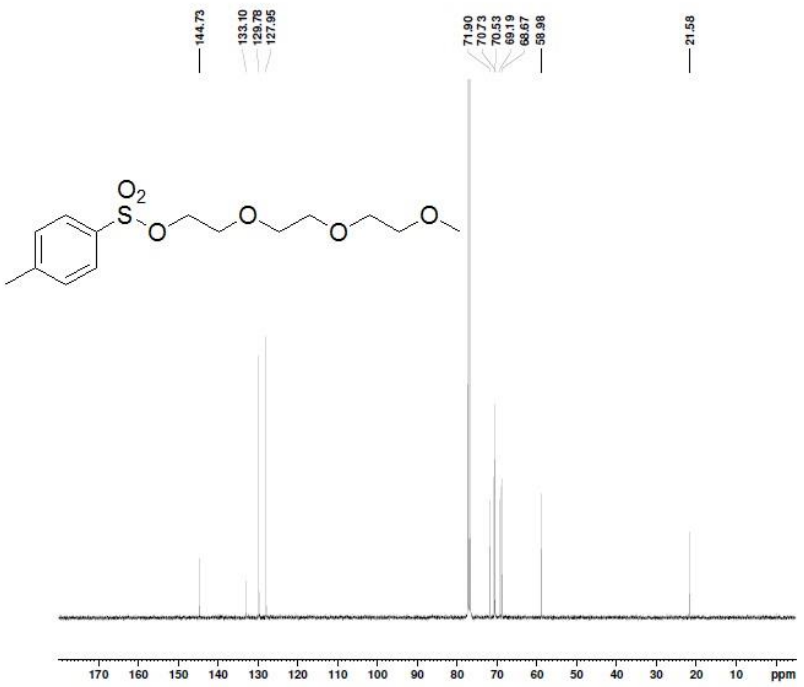
Time                     9.21
INSTRUM                 spect
PROBHD     5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDC13
NS                        16
DS                         0
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       203
DW                    60.800 usec
DE                     6.50 usec
TE                    293.9 K
D1                 1.00000000 sec
TD0                         1

====== CHANNEL f1 ======
NUC1                       1H
P1                      13.80 usec
PL1                     -1.00 dB
PL1W               13.18669796 W
SFO1              400.1724712 MHz
SI                        32768
SF                400.1700005 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

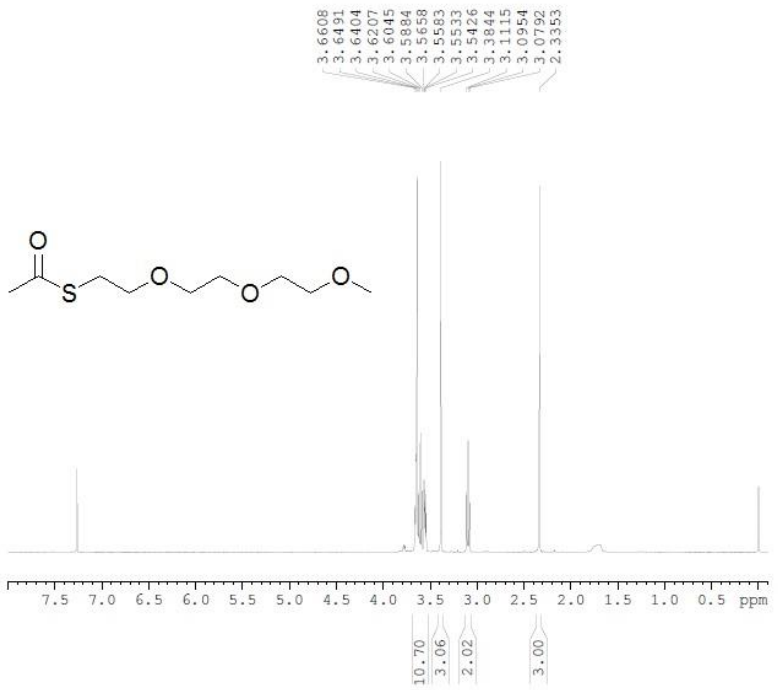


BRUKER

```
NAME           LH-pmsqly-C13
EXPNO                      1
PROCNO                     1
Date_               20120827
Time                   12.19
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDC13
NS                    1020
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     203
DW                  20.800 usec
DE                   6.50 usec
TE                  300.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                        1

====== CHANNEL f1 ======
NUC1                     13C
P1                      8.50 usec
PL1                    -2.00 dB
PL1W            57.32743073 W
SFO1           100.6328888 MHz

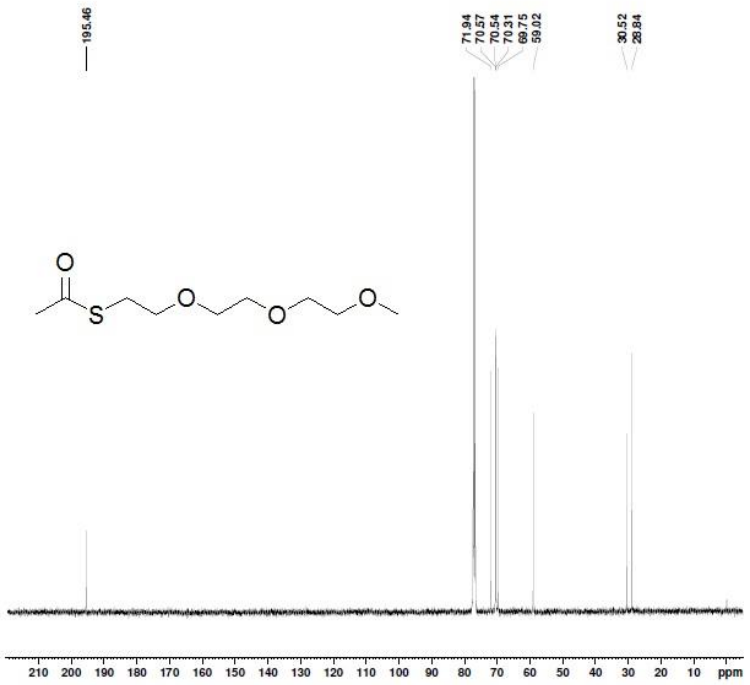
====== CHANNEL f2 ======
CPDPRG2              waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL2                    -1.00 dB
PL12                   14.26 dB
PL13                   14.46 dB
PL2W            13.18669796 W
PL12W            0.39276794 W
PL13W            0.37509048 W
SFO2           400.1716007 MHz
SI                        32768
SF                100.6228270 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



BRUKER

```
NAME                LH-acqly
EXPNO                      1
PROCNO                     1
Date_               20120824
Time                   14.08
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       203
DW                    60.800 usec
DE                     6.50 usec
TE                    300.9 K
D1                 1.00000000 sec
TD0                        1

====== CHANNEL f1 ======
NUC1                      1H
P1                     13.80 usec
PL1                    -1.00 dB
PL1W            13.18669796 W
SFO1           400.1724712 MHz
SI                     32768
SF              400.1700017 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

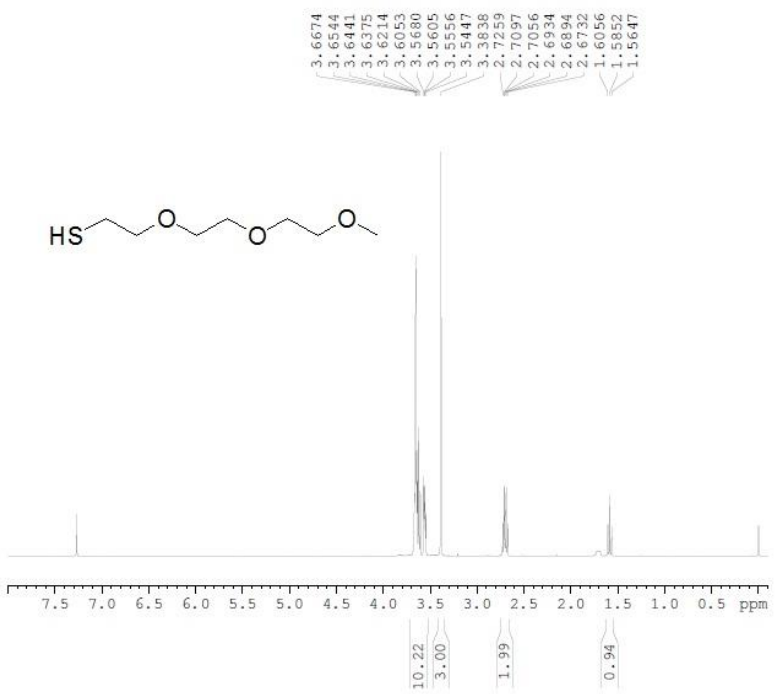


BRUKER

```
NAME            LH-acqly-C13
EXPNO                      1
PROCNO                     1
Date_               20130403
Time                   20.58
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1448
DS                         0
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                       203
DW                    20.800 usec
DE                     6.50 usec
TE                    296.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

====== CHANNEL f1 ======
NUC1                     13C
P1                      8.50 usec
PL1                    -2.00 dB
PL1W           57.32743073 W
SFO1           100.6328888 MHz

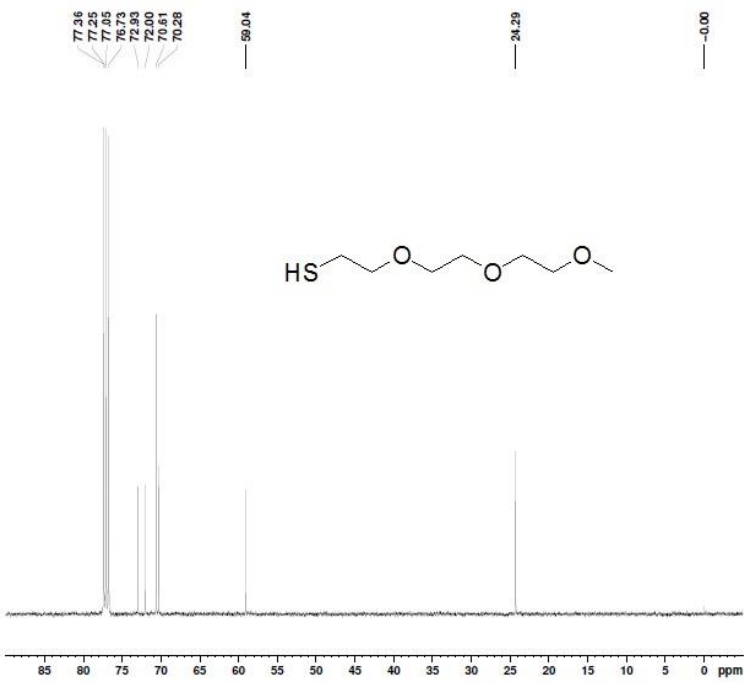
====== CHANNEL f2 ======
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                    -1.00 dB
PL12                   14.26 dB
PL13                   14.46 dB
PL2W            13.18669796 W
PL12W            0.39276794 W
PL13W            0.37509048 W
SFO2           400.1716007 MHz
SI                     32768
SF              100.6228270 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



BRUKER

```
NAME            LH-glythiol
EXPNO                 1
PROCNO                1
Date_          20120824
Time              14.02
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                  181
DW               60.800 usec
DE                6.50 usec
TE               301.1 K
D1            1.00000000 sec
TD0                   1

====== CHANNEL f1 ======
NUC1                 1H
P1                13.80 usec
PL1               -1.00 dB
PL1W        13.18669796 W
SFO1       400.1724712 MHz
SI                32768
SF         400.1700002 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

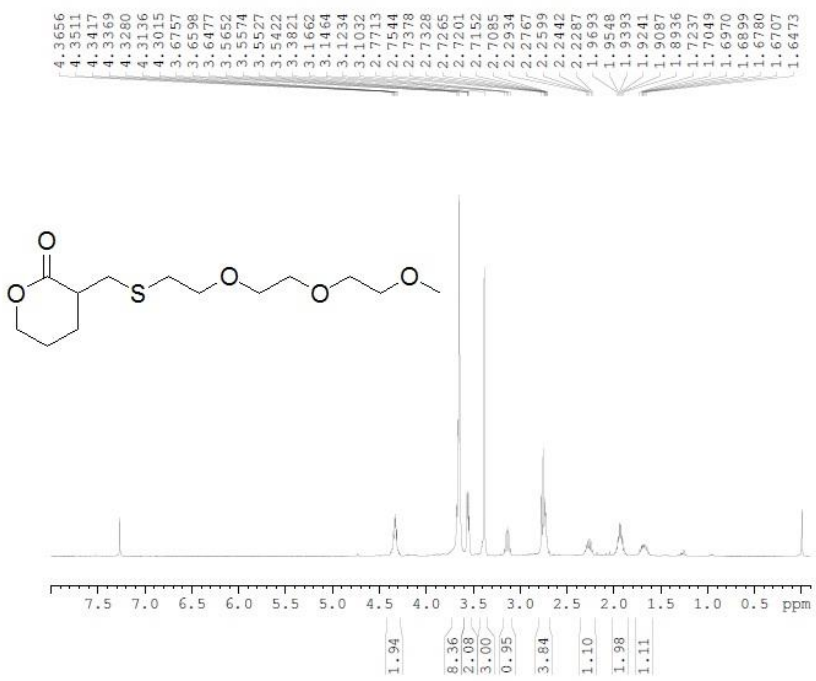


BRUKER

```
NAME       LH-glythiol-C13
EXPNO                 1
PROCNO                1
Date_          20120827
Time              13.11
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  711
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE               300.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

====== CHANNEL f1 ======
NUC1                13C
P1                8.50 usec
PL1              -2.00 dB
PL1W       57.32743073 W
SFO1      100.6328888 MHz

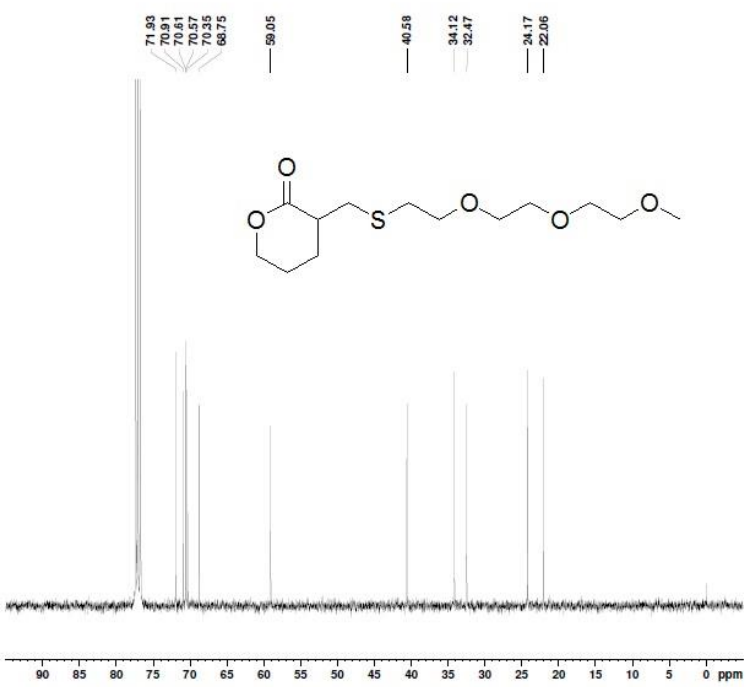
====== CHANNEL f2 ======
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             14.26 dB
PL13             14.46 dB
PL2W        13.18669796 W
PL12W        0.39276794 W
PL13W        0.37509048 W
SFO2      400.1716007 MHz
SI                32768
SF         100.6228224 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



BRUKER

```
NAME          LH-6aneatherthiol-10
EXPNO                            1
PROCNO                           1
Date_                     20130222
Time                          9.19
INSTRUM                      spect
PROBHD     5 mm PABBO BB-
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              0
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                     3.9846387 sec
RG                            144
DW                       60.800 usec
DE                        6.50 usec
TE                       290.9 K
D1                    1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          1H
P1                       13.80 usec
PL1                      -1.00 dB
PL1W                13.18669796 W
SFO1                400.1724712 MHz
SI                          32768
SF                  400.1700005 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```



BRUKER

```
NAME          LH-6aneatherthiol-C13
EXPNO                            1
PROCNO                           1
Date_                     20121213
Time                         13.13
INSTRUM                      spect
PROBHD     5 mm PABBO BB-
PULPROG                   zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                           1000
DS                              4
SWH                   24038.461 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631988 sec
RG                            203
DW                       20.800 usec
DE                        6.50 usec
TE                       293.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                         13C
P1                        8.50 usec
PL1                      -2.00 dB
PL1W                57.32743073 W
SFO1                100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                    80.00 usec
PL2                      -1.00 dB
PL12                     14.26 dB
PL13                     14.46 dB
PL2W                13.18669796 W
PL12W                0.39276794 W
PL13W                0.37509048 W
SFO2                400.1716007 MHz
SI                          32768
SF                  100.6228260 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```