Renewable Thermosets and Thermoplastics from Itaconic Acid

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EXPERIMENTAL DETAIL AND METHODS

General Reagent Information

Ethyl acetate (99.5%, Fisher), hexanes (98.5%, Fisher), methanol (99.8%, Fisher), chloroform (99.8%, J.T. Baker), diethyl ether (Laboratory grade, Fisher), dimethyl sulfoxide (99.9%, Fisher), benzene (99.0%, EMD Millipore), ethanol (200 proof, Decon Labs Inc.), chloroform-D (99.8%, Cambridge Isotope Laboratories, Inc.), dimethyl sulfoxide-d6 (DMSO-d6, 99.9%, Cambridge Isotope Laboratories, Inc.), anhydrous magnesium sulfate (98.0%, EMD Millipore), dimethyl itaconate (DMI, >98.0%, TCI or 99%, Aldrich), isoprene (99.0%, Aldrich), aluminum(III) chloride (≥99.0%, Honeywell), ytterbium(III) trifluoromethanesulfonate ($Y(OTf)_3$, 98%, Sigma), lutetium(III) trifluoromethanesulfonate (Fluka Chemical Corporation), lanthanum(III) trifluoromethanesulfonate (Fluka Chemical Corporation), scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$, 99%, Sigma or >98.0%, TCI), carbonylhydrido(tetrahydroborato)[bis(2-diphenylphosphinoethyl)amino]ruthenium(II) (RuMACHO-BH, min. 98%, Strem), palladium on carbon (Pd/C, 10% Pd basis, Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (>95%, Aldrich), titanium(IV) isoproxide (97+%, Alfa Aesar), 4-methoxyphenol (MEHQ, 99%, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich), 1-dodecanethiol (≥98%, Aldrich), α-bromoisobutyryl bromide (98%, Aldrich), triethyl amine (NEt_3, 100.0%, J.T. Baker), copper(II) chloride (min. 98%, Strem), 2,2'-bipyridine (98%, Alfa Aesar), 2-cyano-2-propyl benzodithioate (97%, Sigma-Aldrich), basic aluminum oxide (alumina, activated, Brockmann Grade I, 58 angstroms, Alfa Aesar), hydrogen (Ultra high purity 5.0 grade, Airgas), and argon (High purity grade 4.8, Airgas) were used as received. Deionized (DI) water was obtained by reverse osmosis. Tetrahydrofuran (THF, 99%, Macron) was degassed by sparging with argon for 30 min and then purified by passing through

two packed columns of neutral alumina on the JC Meyer solvent system. Toluene (PhMe, 99.9%, Fisher) was degassed by sparging with argon for 30 min and then purified by passing through a packed column of neutral alumina followed by a packed column of Q5 reactant, a copper(II) oxide oxygen scavenger on a JC Meyer solvent system. N,N-dimethylformamide (DMF, Macron) was degassed by sparging with argon for 30 min and then purified by passing through two packed columns of activated molecular sieves followed by a packed column of isocyanide on the JC Meyer solvent system. Azobisisobutyronitrile (AIBN, Sigma, 98.0%) was recrystallized from methanol before use. Hydrochloric acid (HCl, Macron) was used as received and diluted with DI water to make a 3.0 M or 0.5 M solution. Copper(I) chloride (97%, Sigma) was purified by being dissolving it in hydrochloric acid and precipitating it by diluting with DI water.[1] The solid was then filtered and washed with ethanol, diethyl ether, dried under high vacuum (40 mTorr) for 24 h, and stored under nitrogen in a desiccator. Mylar sheets (10" x 10" x 0.04") were obtained from Carver, Inc. Quartz tubes were obtained from the Cornell Chemistry Glass Shop (Cornell University, Department of Chemistry and Chemical Biology, S. T. Olin Chemistry Research Wing, Room B66). α-methylene-γ-butyrolactone (MBL, >95.0%, TCI) was passed through a plug of basic alumina to remove radical inhibitor prior to use. 3 M sodium hydroxide was prepared by dissolving sodium hydroxide (NaOH, Macron) in DI water.

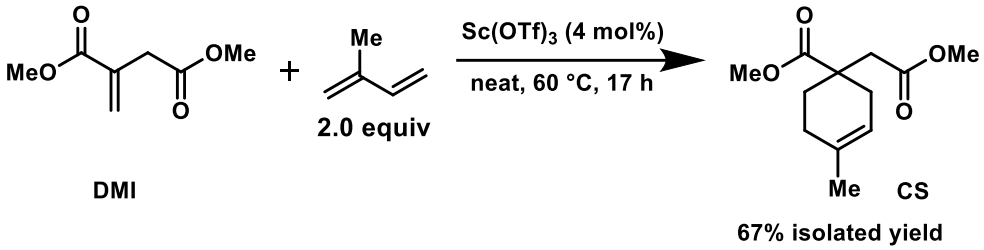
General Analytical Information

Polymers samples were analyzed using size exclusion chromatography (SEC) instruments operating with a THF or DMF eluent. For the SEC with THF eluent, a Tosoh EcoSec HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min at 40 °C was used. Number-average molar masses (M_n), weight-average molar masses (M_w), and dispersities ($Đ$) for polymer samples were determined by light scattering using a Wyatt mini Dawn

Treos multi-angle light scattering detector at 25 °C. The *dn/dc* values of the polymer samples were estimated using size exclusion chromatography with samples of known concentrations in THF. This indirect ("in-line") method uses the total area of the RI signal and the assumption that 100% of the sample mass is recovered to calculate the polymer *dn/dc* values. M_n, M_w, and $Đ$ values were also determined from the refractive index chromatogram against polystyrene (TSKgel) standards. For the SEC with DMF eluent, polymer samples were analyzed using a GPC system composing of a Waters 1515 Isocratic HPLC pump and three PSS GRAM columns (100–1000–3000) in series at a flow rate of 1.0 mL min^{-1} at 35 °C. A 0.1% LiBr solution in DMF was used as the eluent and M_ns, M_ws, and $Đ$s were determined from refractive index chromatograms against polystyrene standards (Polymer Standards Service USA, Inc., Amherst, MA) using a Waters 2414 differential refractive index detector. Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury 300 MHz, a Varian 400 MHz, a Bruker 500 MHz, or a Varian 600 MHz instrument. Mass spectra were obtained on an Exactive Plus Orbitrap Mass Spectrometer with a DART SVP ion source from Ion Sense. The Fourier transform infrared (FTIR) spectra were obtained on a Bruker Alpha Platinum or a Thermo Scientific Smart Orbit Nicolet Avatar 370 DTGS spectrometer equipped with a diamond crystal in attenuated total reflection (ATR) mode at a resolution of 4/cm with 32 scans obtained for each spectrum. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q1000. Samples were prepared in aluminum pans and were analyzed using the following heating program: −50 °C to 150 °C at 30 °C/min, 150 °C to −50 °C at 10 °C/min, and −50 °C to 150 °C at 30 °C/min. The data were processed using Universal Analysis 2000 for Windows software. All reported T_gs were observed on the second heating cycle. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer or an Instruments Q500 Analyzer. Typically, samples were heated at 10 °C/min to 550

°C under nitrogen. Data were processed using Universal Analysis 2000 for Windows software. To melt process the thermoplastics, PMBL-PMBMS-PMBL was placed between two Teflon sheets and melt pressed in a rectangular mold at 2500 lbs and 190 °C and then quenched by cooling to RT using water cooling at a rate of 35 °C/min to yield a 0.5 mm thick film. PMBL was placed between two Teflon sheets and melt pressed in a rectangular mold at 2500 lbs and 235 °C and then quenched by cooling to RT using water cooling at a rate of 35 °C/min. Using 8 mm parallel plates, TA Instruments Rheometric Series ARES instrument was used for dynamic mechanical analysis. Heating was controlled under nitrogen atmosphere, and the samples were equilibrated at the designated temperature for 10 minutes before testing. Thermoset materials were solvent cast into a 0.8 mm thick film and cured under 250 nm light. Dog-bone-shaped tensile bars for both the thermosets and thermoplastics were punched out resulting in samples with approximately 3 mm gauge width and 16 mm gauge length. Samples were tested to the point of break using Shimadzu Autograph AGS-X Tensile Tester and an extension rate of 5 mm/min. Extensional dynamic mechanical thermal analysis was performed on a TA Instruments RSA-G2 in tension mode on rectangular polymer films with 0.5 mm thickness and 3 mm gauge width. DMTA experiments were conducted at a heating rate of 5 °C/min with an oscillating strain of 0.05% and angular frequency of 1 Hz. High-pressure hydrogenations were performed using a 300 mL Parr reactor obtained from Parr Instrument Company (Moline, Illinois). Thermoset and PMBL densities were determined to be 1.16 g/cm^3 and 1.38 g/cm^3, respectively, using a Mettler-Toledo XPE205 DeltaRange equipped with a Mettler-Toledo MS-DNY-54 density kit. The density of PMBMS was estimated to be 1.12 g/cm^3 using sink-or-float tests.

Synthesis of dimethyl 2-(4-methylcyclohex-3-ene)succinate (CS) using catalytic scandium(III) triflate

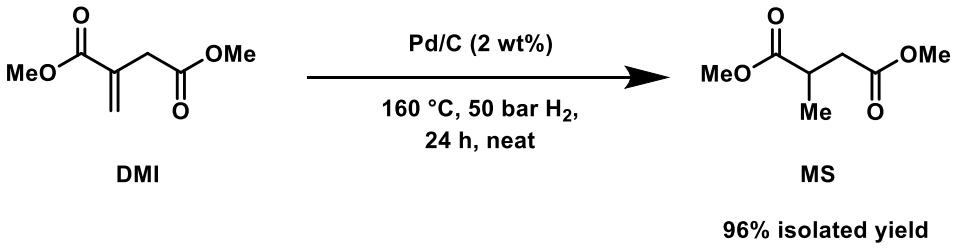


A 250 mL round bottom flask equipped with a stir bar, reflux condenser, and rubber septum was flamed dried and then evacuated and backfilled with nitrogen three times. Following this, DMI (55.31 g, 0.3497 mol, 1.000 equiv) was added under positive pressure of nitrogen, followed by scandium triflate (6.56 g, 0.0133 mol, 3.80 mol%). The system was then again evacuated and backfilled three times with nitrogen. Subsequently, isoprene (70.0 mL, 47.7 g, 0.700 mol, 2.00 equiv) was added by syringe. A nitrogen balloon was then added to the top of the reflux condenser and the system was heated to 60 °C and left to stir overnight. After 17 h, the reaction mixture was cooled to RT. The crude mixture was then diluted with ethyl acetate (ca. 20 mL) and washed three times with DI water (ca. 100 mL x 3), and once with brine (ca. 100 mL). The organic phase was then dried with magnesium sulfate (ca. 10 g), filtered, and concentrated down on a rotary evaporator. Distillation of the crude oil under vacuum (40 mTorr, 150 °C oil bath, 63 °C vapor temperature) gave a clear, colorless liquid with a ~3% DMI impurity; further heating of this mixture under vacuum (40 mTorr, 130 °C oil bath) distilled off the remaining DMI to give the pure product (52.92 g, 0.2339 mol) in 67% isolated yield. Characterization data matched those reported in the literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.31 (s, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 2.63 (q, J = 15.5, 4H), 2.51 (m, 1H), 2.05 – 1.93 (m, 4H) 1.79 (m, 1H), 1.64 (s, 3H).

Recovery of the Scandium Triflate in the synthesis of 2-(4-methylcyclohex-3-ene)succinate (CS)

Following the standard procedure for the synthesis of CS, the aqueous phase obtained by washing the crude organic phase with DI water was concentrated down on a rotary evaporator. The off-white solid was then dried at 90 °C under vacuum (50 – 100 m Torr) for 19 h to afford 3.96 g of $Sc(OTf)_3$ (starting from 4.06 g of $Sc(OTf)_3$ used initial, 97% recovery).

Synthesis of dimethyl 2-methylsuccinate (MS)



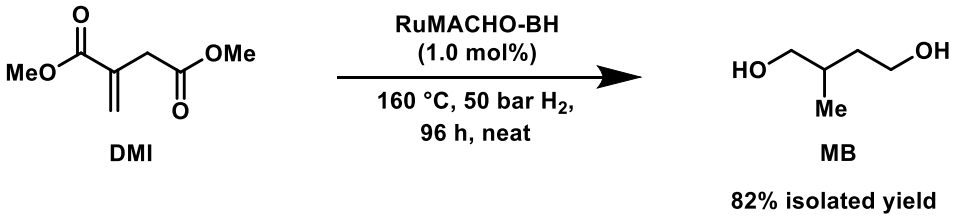
DMI MS

96% isolated yield

DMI (102.94 g, 0.6509 mol, 1.000 equiv) and 2.00 g Pd/C (10% Pd basis, 1.94 wt%) were added to a 300 mL Parr reactor. The reactor was then sealed with an open-ended wrench under atmosphere. The reaction was run behind a blast shield with the hood sash closed in an isolated fume hood. The atmosphere was then replaced with hydrogen gas by pressurizing the reactor with hydrogen and venting it three times before being pressurized one last time with hydrogen (50 bar). The reaction was then stirred and heated in an oil bath at 160 °C, at which point the pressure read 60 bar. After 1 h, the pressure had dropped to 0 bar, and the Parr reactor was allowed to cool to RT. The reactor was then repressurized to 50 bar with hydrogen, and was heated back up to 160 °C where the pressure increased 60 bar. The reaction was then allowed to stir overnight for 14 h, by which point the pressure had not dropped from 60 bar. The Parr reactor was then allowed to cool to RT and was vented. The crude oil was distilled under vacuum (40 mTorr) to give a clear, colorless oil (100.33 g, 0.6265 mol) in 96% isolated yield. Characterization data matched those

reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.70 (s, 3H), 3.68 (s, 3H), 2.93 (m, 1H), 2.74 (dd, 1H, *J* = 8.2, Hz 16.7 Hz), 2.41 (dd, 1H, *J* = 6.1 Hz, 16.5 Hz, 1H), 1.22 (d, *J* = 7.9 Hz, 3H).

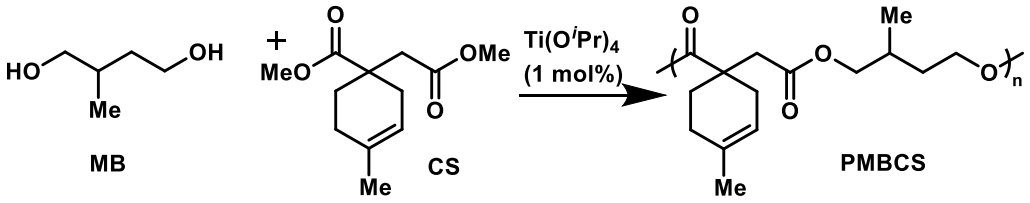
Synthesis of 2-methylbutane-1,4-diol (MB)



In a glovebox, a 300 mL Parr reactor was equipped with a stir bar. Dimethyl itaconate (61.76 g, 0.3905 mol, 1.000 equiv) was added to the reactor, followed by RuMACHO-BH (2.20 g, 0.00375 mol, 0.982 mol%). The Parr reactor was then sealed with an open-ended wrench inside the glovebox. The reaction was run behind a blast shield with the hood sash closed in an isolated fume hood. The Parr reactor was then removed from the glovebox and the nitrogen atmosphere was replaced with hydrogen gas by pressurizing the reactor with hydrogen and venting it a total of three times. The reactor was then pressurized one last time with hydrogen (50 bar). The reaction was then stirred and heated in an oil bath to 160 °C, at which point the pressure read 60 bar. A few hours after the reaction started, the pressure had dropped to 0 bar, and the reaction was cooled to RT, repressurized to 50 bar, and heated back to 160 °C. This process was repeated a total of five times, whenever the hydrogen pressure at 160 °C decreased significantly below 60 bar. After 96 h the reaction was cooled to RT one final time and vented. After venting, the Parr reactor was then opened up, and the crude oil was distilled under reduced pressure to remove dimethyl 2-methylsuccinate (MS) (45 mTorr, 100 °C oil bath, 30 °C vapor temperature). After removal of the MS, the oil bath was heated further (45 mTorr, 130 °C oil bath, 70 °C vapor temperature) to give

2-methyl-1,4-butanediol (MB) as a clear, colorless, viscous liquid (33.23 g, 0.3195 mol) in 82% yield. Characterization data was consistent with that previously reported in the literature.[4] ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.77 (m, 1H), 3.67 (m, 1H), 3.57 (m, 1H), 3.45 (m, 1H), 2.64 (m, 2H), 1.98 (m, 4H), 1.82 (m, 1H), 1.59 (m, 2H, OH), 0.93 (d, 3H, J = 6.8).

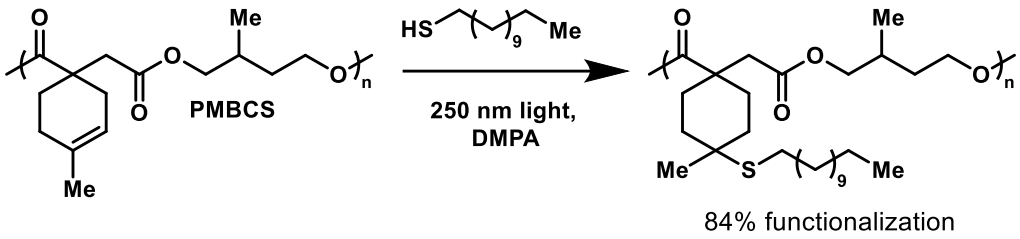
Synthesis of poly(MB-alt-CS) (PMBCS)



The two-stage polycondensation polymerization method was adopted from a known procedure.[5] CS (1.55 g, 6.85 mmol, 1.00 equiv), MB (1.02 g, 9.79 mmol, 1.43 equiv), and 4-methoxyphenol (9.9 mg, 0.38 wt%) were added to a 50 mL round bottom flask equipped with a stir bar, reflux condensder, and rubber septum. Nitrogen gas was then purged through the system for 20 min while stirring to give a clear, colorless liquid. Ti(O^{i}Pr)$_4$ (0.030 mL, 0.10 mmol, 1.5 mol% relative to CS) was then injected and the reaction mixture a turned a clear yellow color and was submerged into a 180 °C oil bath. The reaction was stirred for 3 h with nitrogen gas purging through the system to remove the methanol byproduct. The reflux condenser was then replaced with a short path distillation head, and the vacuum was applied to the system (400 Torr) while the temperature was increased to 200 °C. The vacuum was then steadily lowered over 1 h to 0.05 Torr. After reaching 0.05 Torr, the short path distillation head was periodically heated to encourage distillation of the excess diol. After 5 h, the stirring of the mixture became more difficult at the stirring setting of 50 rpm, and the heat was increased briefly to 240 °C for 0.5 h. The reaciton mixture was still stirring at 50 rpm and the reaction mixture was allowed to cool to RT under vacuum. After cooling, the

crude polymer solid was dissolved in dichloromethane (ca. 10 mL) and precipitated once from –78 °C methanol (ca. 200 mL). The solid was dried under vacuum to give the product (1.09 g) in 60% isolated yield. M_n = 11.7 kg/mol, M_w = 25.7, $Đ$ = 2.19, and *dn/dc* = 0.0867mL/g were determined using a light scattering detector in THF solvent. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.31 (s, 1H), 4.11 (m, 2H), 3.92 (m, 2H), 2.58 (m, 3H), 1.96 (m, 4H) 1.75 (m, 2H), 1.64 (s, 3H), 1.45 (m, 1H), 0.94 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 176.1, 171.5 – 171.4, 132.9, 118.5, 69.2 – 69.0, 62.7 – 62.4, 42.8 – 42.6, 40.3, 33.0, 32.2, 29.8, 27.1, 23.3, 16.7. IR (ATR, cm^{-1}): 2965, 2937, 2878, 1728, 1462, 1344, 1158, 1054, 989, 757.

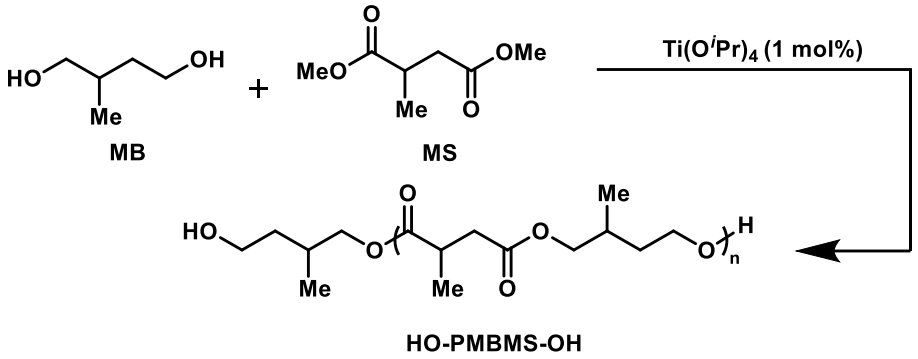
Functionalization of PMBCS with 1-dodecanethiol



PMBCS (100.2 mg, 0.3762 mmol, 1.000 equiv), DMPA (9.7 mg, 0.038 mmol, 0.10 equiv), and dodecanethiol (0.090 mL, 76.1 mg, 0.376 mmol, 1.00 equiv) were dissolved in DCM (1.00 mL, 0.100 g/mL) and solvent cast onto a mylar sheet. The mixture was allowed to dry in air to remove the DCM. The mixture was then covered with another mylar film and was irradiated with 250 nm light for 2 h. The mylar sheet / polymer mixture was then flipped over and irradiated further for 2 h. An aliquot by ^{1}H NMR showed 75% conversion. The mylar sheet / polymer mixture was then irradiated further for 18 h (22 h total). An aliquot by ^{1}H NMR showed 84% conversion. The mylar sheet / polymer mixture was then stirred in chloroform to dissolve the polymer. The resulting solution was concentrated down to give a concentrated solution of polymer in chloroform (ca. 1 mL), and the polymer was then precipitated from − 78 °C methanol (ca. 100 mL) and was dried

under high vacuum to give predominantly dodecanethiol-functionalized PMBCS (74.1 mg, 0.1581 mmol) in 42% isolated yield.

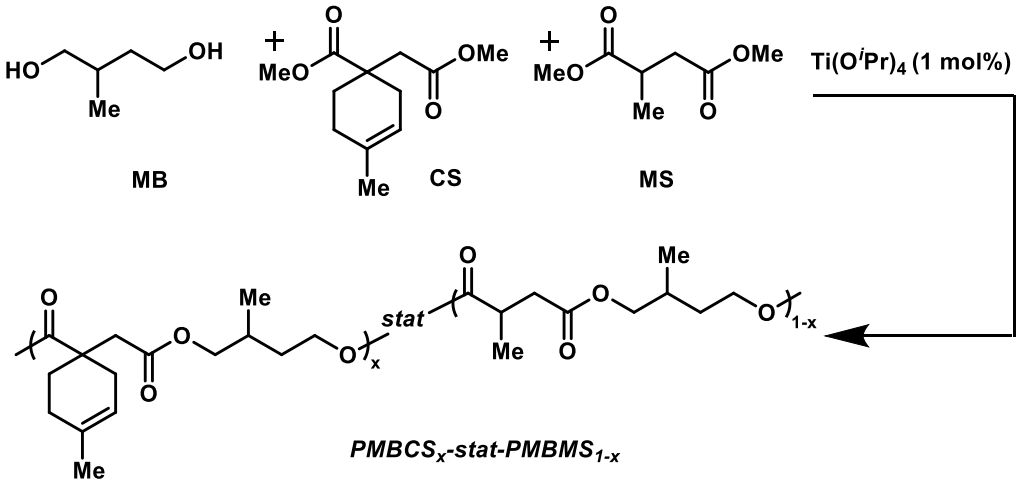
Synthesis of α,ω-hydroxy poly(MB-alt-MS) (HO-PMBMS-OH)



MS (5.87 g, 36.7 mmol, 1.0 equiv), MB (7.60 g, 73.0 mmol, 1.99 equiv), and 4-methoxyphenol (57.6 mg, 0.43 wt%) were added to a 100 mL round bottom flask equipped with a stir bar, reflux condensder, and rubber septum. Nitrogen gas was then purged through the system for 20 min while stirring to give a clear, colorless liquid. Ti(O^{i}Pr)$_4$ (0.140 mL, 0.473 mmol, 1.29 mol% relative to MS) was then injected and the reaction mixture turned a clear yellow color and was submerged into a 180 °C oil bath. The reaction was stirred for 3 h with nitrogen gas purging through the system to remove the methanol byproduct. The reflux condenser was then replaced with a short path distillation head, and the vacuum was applied to the system (400 Torr) while the temperature was increased to 200 °C. The vacuum was then steadily lowered over 1 h to 0.05 Torr. After reaching 0.05 Torr, the short path distillation head was periodically heated to encourage distillation of the excess diol. Within 0.5 h, the reaction mixture was barely stirring when the stirring was set to 50 rpm. After an additional 1.5 h (2.0 h total) the stir bar was stationary at 50 rpm, and the reaction mixture was allowed to cool to RT under vacuum. After cooling, the crude polymer solid was dissolved in dichloromethane (ca. 20 mL) and precipitated twice from –78 °C methanol (ca. 400

mL x 2) and then a final time form –78 °C hexanes (ca. 400 mL), dissolving the precipitated polymer back in dichloromethane (ca. 20 mL x 2) prior to each reprecipitation. The solid was dried under vacuum to give the product (5.62 g) in 76% isolated yield. M_n = 15.7 kg/mol, M_w = 38.9 kg/mol, $Đ$ = 2.48, and *dn/dc* = 0.0660 mL/g were determined using a light scattering detector in THF solvent. M_n = 15.9 kg/mol, M_w = 51.5 kg/mol, and $Đ$ = 3.24 were determined using a refractive index detector in THF solvent calibrated against polystyrene standards. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 4.14 (m, 2H), 3.95 ppm (m, 2H), 3.49 (m, C*H*$_2$OH end groups), 2.91, (m, 1H), 2.74 (m, 1H), 2.41 (m, 1H), 1.93 (m, 1H), 1.75 (m, 1H), 1.49 (m, 1H), 1.22 (m, 3H), 0.97 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 175.3, 173.2, 172.0, 69.1, 62.7, 62.6, 37.6, 35.9 – 35.8, 32.2, 29.9 –29.8, 17.2 – 17.1, 16.7 – 16.6. IR (ATR, cm^{-1}): 2965, 2937, 2878, 1728, 1462, 1344, 1158, 1054, 989, 757.

Synthesis of poly((MB-alt-CS)$_x$-stat-(MB-alt-MS)$_{1-x}$) (PMBCS$_x$-stat-PMBMS$_{1-x}$)

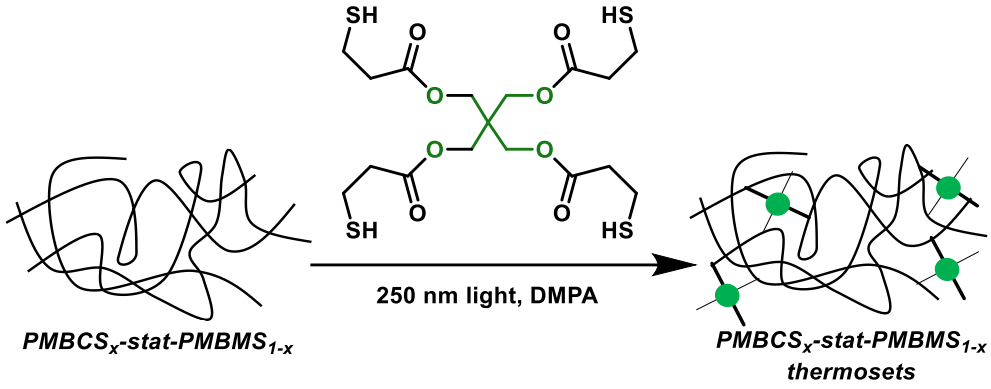


In a typical reaction, the desired amount of CS and MS was weighed out (1.0 equiv of total diester consisting of a mixture of CS and MS) relative to MB (1.4 equiv). For x = 0.2: CS (1.36 g, 6.01 mmol, 0.21 equiv), MS (3.68 g, 22.98 mmol, 0.79 equiv), MB (4.20 g, 40.3 mmol, 1.39 equiv),

and 4-methoxyphenol (53.2 mg, 0.57 wt%) were added to a 100 mL round bottom flask equipped with a stir bar, reflux condensder, and rubber septum. Nitrogen gas was then purged through the system for 20 min to give a clear, colorless liquid. $Ti(O^iPr)_4$ (0.110 mL, 0.37 mmol, 1.3 mol% relative to 1.0 equiv total diester) was then injected and the reaction mixture turned clear, yellow, and was submerged into a 180 °C in an oil bath. The reaction was stirred for 3 h with nitrogen gas purging through the system to remove methanol byproduct. The reflux condenser was then replaced with a short path distillation head, and the vacuum was applied to the system (400 Torr) while the temperature was increased to 200 °C. The vacuum was then steadily lowered over 1 h to 0.05 Torr. After reaching 0.05 Torr, the short path distillation head was periodically heated to encourage distillation of the excess diol. The polymerization was continued until the reaction mixture could no longer stir when the stirring was set 50 rpm (typically 1.0 h). The reaction mixture was then allowed to cool to RT under vacuum. An aliquot was taken of the crude sample for ^{1}H NMR, GPC, and DSC, and the mass was determined by the difference of the crude mixture with polymer and the tared round bottom flask and stir bar; polymer (5.67 g) was obtained in 92% isolated yield. For x = 0.2, M_n = 21.5 kg/mol, M_w = 103 kg/mol, $Đ$ = 4.81, and *dn/dc* = 0.0700 mL/g (calculated from the molar average using F_{MBCS} of the *dn/dc* values of PMBMS and PMBCS) were determined using a light scattering detector in THF solvent. M_n, M_w, and $Đ$ for x = 0.3 and 0.4 are reported in table 3 in the main text. The polymer was then dissolved in DCM and used without purification in the crosslinking experiments. ^{1}H NMR spectra contained all peaks associated with PMBMS and PMBCS. F_{MBCS} (0.19 for x = 0.2) was calculated from the ratio of PMBCS vinyl peak at ~5.3 ppm to PMBMS methyl peak at 1.22 ppm. For x = 0.2, ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.32 (s, 1H), 4.14 (m, 2x 2H), 3.95 ppm (m, 2x 2H), 2.91, (m, 1H), 2.74 (m, 1H), 2.58 (m, 3H), 2.40 (m, 1H), 1.95 (m, 1H and 4H), 1.75 (m, 1H and 2H), 1.64 (s, 3H),

1.50 (m, 1H and 3H), 1.22 (m, 3H), 0.97 (m, 2x 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 176.2, 175.3, 171.9, 171.5, 171.4, 132.9, 118.5, 69.2, 69.0, 62.7, 62.6, 62.5, 42.8, 42.7, 42.6, 40.4, 37.6, 35.9, 33.0, 32.2, 29.9, 27.1, 23.4, 17.2, 16.7. IR (ATR, cm^{-1}): 2965, 2937, 2878, 1728, 1462, 1344, 1158, 1054, 989, 757.

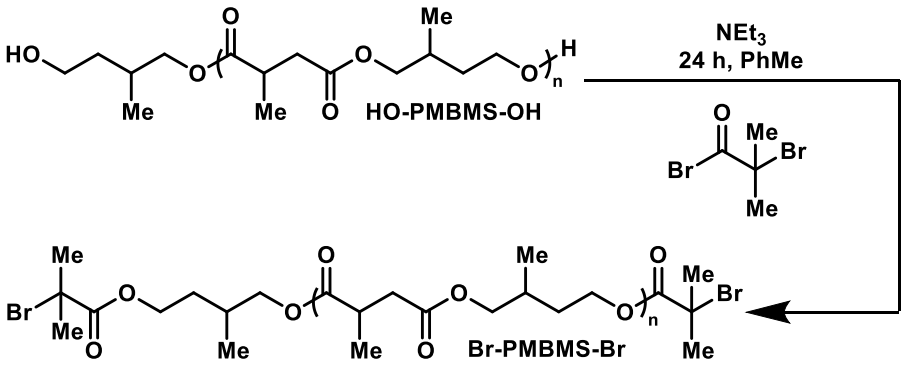
Crosslinking of poly((MB-alt-CS)$_x$-stat-(MB-alt-MS)$_{1-x}$) (PMBCS$_x$-stat-PMBMS$_{1-x}$)



In a typical reaction, PMBCS$_x$-*stat*-PMBMS$_{1-x}$ obtained directly from the crude reaction mixture described in the above section was dissolved in DCM. The desired amount of 2,2-dimethoxy-2-phenylacetophenone (DMPA, 0.10 equiv) initiator and pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol, 0.25 equiv) crosslinker was the added to the polymer solution in DCM. For x = 0.2: PMBCS$_{0.2}$-*stat*-PMBMS$_{0.8}$ (5.67 g, 5.14 mmol olefin) was dissolved in DCM (ca. 10 mL). Tetrathiol (0.45 mL, 1.18 mmol, 0.23 equiv) and DMPA (132.5 mg, 0.525 mmol, 0.102 equiv) was added to the solution. A mylar sheet was then clamped between a metal plate on the bottom and a 5.00” x 2.75” metal plate with a 3.50” x 1.25” rectangular mold cut-out on the top. Approximately one half of the DCM solution was then added to the mylar sheet in the metal plate cut-out until full and allowed to dry at room temperature (RT) overnight. After drying, a mylar sheet was carefully added to the top of the mold while avoiding trapping air between the mylar sheet and the neat mixture. The neat mixture was then irradiated with 250 nm

hν directly, typically for 12 h. The thermoset and mylar films were then flipped over and irradiated further, typically for an additional 12 h. After irradiation, the mylar films were carefully removed from the crosslinked thermoset. The resulting thermoset film was typically dried under high vacuum (0.05 Torr) for 48 h prior to analysis. A second film was also cast in the same manner with the remaining DCM solution, and the combined dried thermoset films (5.13 g) were obtained in 80% isolated yield based on mass recovery. For x = 0.2, IR (ATR, cm^{-1}): 2965, 2937, 2878, 1728, 1462, 1344, 1158, 1054, 989, 757.

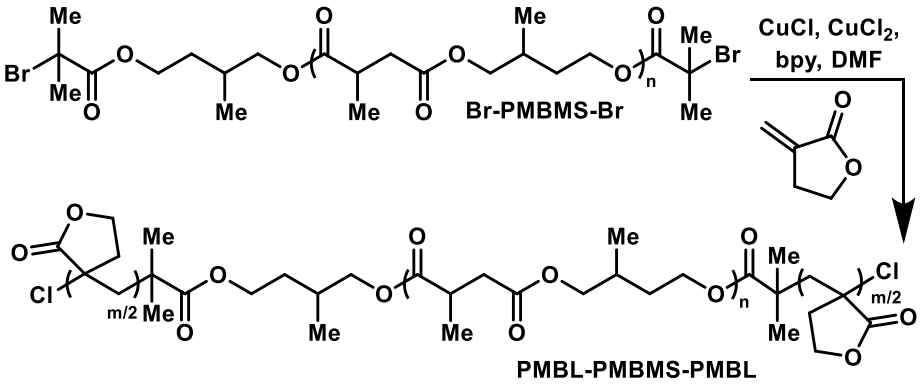
Chain-end functionalization of α,ω-hydroxy-poly(MB-alt-MS) (HO-PMBMS-OH)



The functionalization method was adapted from a known procedure.[6] HO-PMBMS-OH (3.646 g, 18.21 mmol PMBMS repeat unit, M_n = 15.7 kg/mol, degree of polymerization = 78.4, 0.232 mmol HO-PMBMS-OH macroinitiator, 1.00 equiv) was dissolved in toluene (34.0 mL, 0.107 g/mL) in a 100 mL round bottom flask. Triethylamine (0.780 mL, 0.569 g, 5.63 mmol, 24.3 equiv) and α-bromoisobutyrlbromide (0.70 mL, 1.302 g, 5.66 mmol, 24.4 equiv) were added by syringe at RT. The reaction mixture was allowed to stir at RT for 26 h. The cloudy mixture was then filtered through a plug of magnesium sulfate in a fritted funnel and then the toluene was removed by rotary evaporation under reduced pressure. The crude polymer was then dissolved in DCM (ca. 100 mL) and transferred to a separatory funnel, where the organic layer was washed

three times with saturated bicarbonate in DI water (ca. 100 mL x 3), five times with DI water (ca. 100 mL x 5), and three times with 3 M NaOH (ca.100 mL x 3). The organic layer was then dried over anhydrous magnesium sulfate (ca. 50 g), filtered, and concentrated down. The polymer was then dissolved in DCM (ca. 20 mL) precipitated twice from − 78 °C methanol (ca. 400 mL x 2), once from − 78 °C hexanes (ca. 400 mL), dissolving the precipitated polymer back in dichloromethane (ca. 20 mL x 2) prior to each reprecipitation. The polymer was then dried under vacuum to afford Br-PMBMS-Br (1.144 g) in 31% isolated yield (based on the 100% conversion of chain ends and mass recovery). M_n = 19.0 kg/mol, M_w = 159, $Đ$ = 7.42, and *dn/dc* = 0.0650 mL/g were determined using a light scattering detector in THF solvent. M_n = 21.3 kg/mol, M_w = 141 kg/mol, and $Đ$ = 7.44 were determined using a refractive index detector in THF solvent calibrated against polystyrene standards. M_n = 25.7 kg/mol, M_w = 59.1, and $Đ$ = 2.30 were determined using a refractive index detector in DMF solvent calibrated against polystyrene standards. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 4.05 (m, 2H), 3.87 ppm (m, 2H), 2.80, (m, 1H), 2.58 (m, 1H), 2.47 (m, 1H), 1.89 (s, CH_3 end group), 1.88 (s, CH_3 end group), 1.83 (m, 1H), 1.64 (m, 1H), 1.42 (m, 3H), 1.12 (m, 3H), 0.89 (m, 3H).

Chain extension of α,ω-bromo-poly(MB-alt-MS) (Br-PMBMS-Br)



The chain extension of Br-PMBMS-Br was adapted from a known procedure.[7] Br-PMBMS-Br (0.9063 g, 4.527 mmol repeat unit, M_n = 19.0 kg/mol, degree of polymerization = 94.9, 0.0131 mmol Br-PMBMS-Br macroinitiator, 1.00 equiv) was dissolved in DMF (1.80 mL, 0.504 g/mL) in a Schlenk bomb. 2,2'-bipyridine (27.4 mg, 0.180 mmol, 0.0493 equiv), CuCl (33.9 mg, 0.342 mmol, 0.0937 equiv), $CuCl_2$ (9.7 mg, 0.072 mmol, 0.0197 equiv), and MBL (0.320 mL, 0.358 g, 3.65 mmol, 1.00 equiv) were then added to the bomb. The reaction mixture was degassed by three freeze-pump-thaw cycles and then placed in a 60 °C oil bath and stirred for 16 h. Aliquot analysis by ^{1}H NMR showed >99% conversion of MBL. The DMF solution was then precipitated from − 78 °C cold methanol (ca. 100 mL). The polymer was isolated and dissolved in DCM (ca. 10 mL) and then passed through a plug of basic Al_2O_3 on a fritted funnel to remove the copper catalyst. The filtrate was then precipitated three times from − 78 °C methanol (ca. 100 mL x 3) and once from − 78 °C hexanes (ca. 100 mL), dissolving the precipitated polymer back in dichloromethane (ca. 20 mL x 4) prior to each reprecipitation. The polymer was then dried under vacuum to afford PMBL-PMBMS-PMBL (0.8774 g) in 69% isolated yield (based on 100% conversion of MBL and mass recovery). M_n = 33.3 kg/mol, M_w = 60.0, and $Đ$ = 1.80 were determined using a refractive index detector in DMF solvent calibrated against polystyrene standards. ^{1}H NMR (500 MHz,

DMSO-d_6, δ, ppm): 4.36 (m, 2H), 4.05 (m, 2H), 3.87 (m, 2H), 2.79, (m, 1H), 2.58 (m, 1H), 2.48 (m, 1H), 2.07, (m, 4H), 1.84 (m, 1H), 1.65 (m, 1H), 1.41 (m, 1H), 1.12 (m, 3H), 0.89 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 180.2 – 180.0, 174.4, 171.2, 68.2, 65.1, 62.0, 61.9, 44.5 – 44.0, 36.8, 35.3 – 35.2, 31.5, 29.3 –29.2, 167 – 16.6, 16.7 – 16.3.

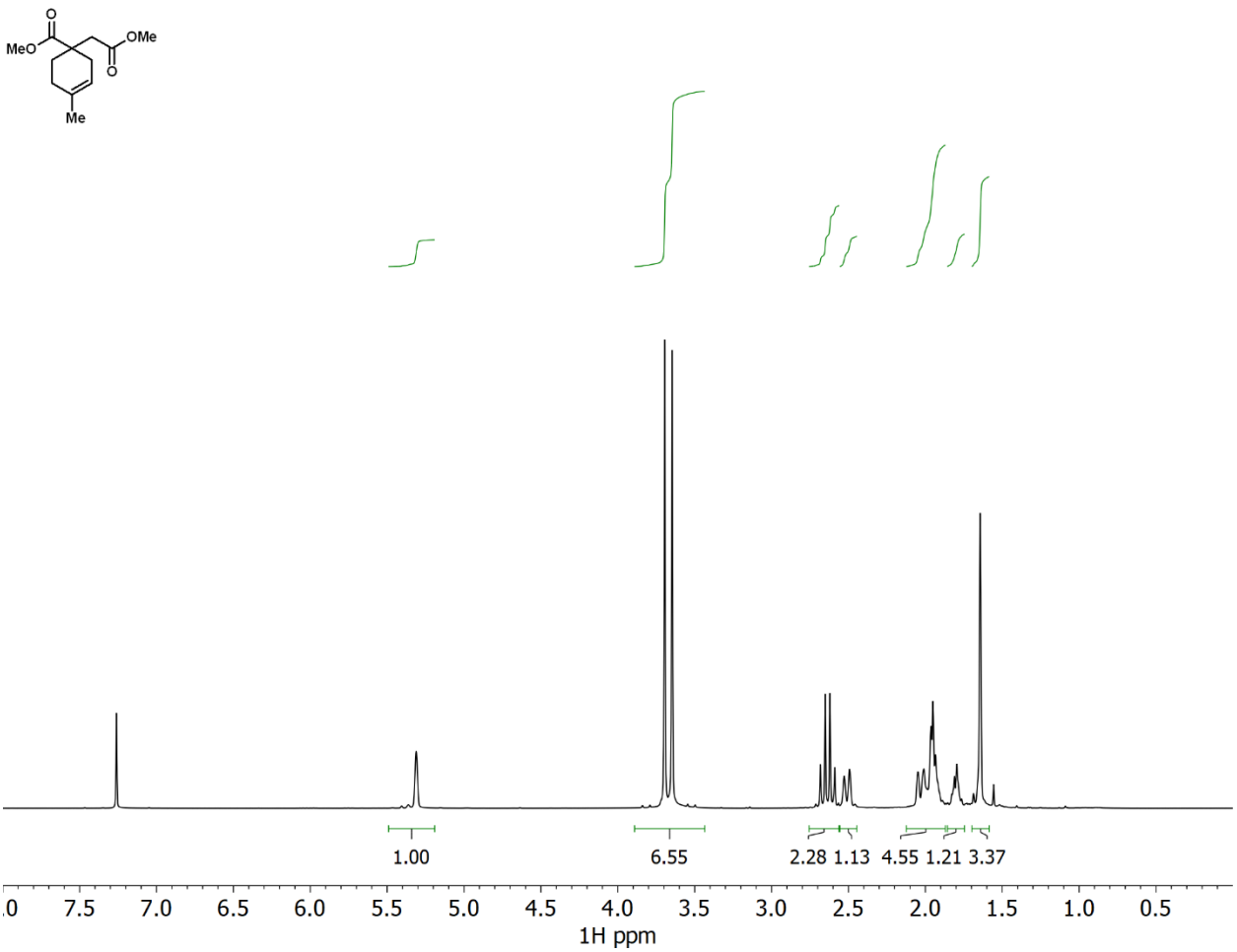


Figure S1. ^{1}H NMR spectra of 2-(4-methylcyclohex-3-ene)succinate (CS) in $CDCl_3$.

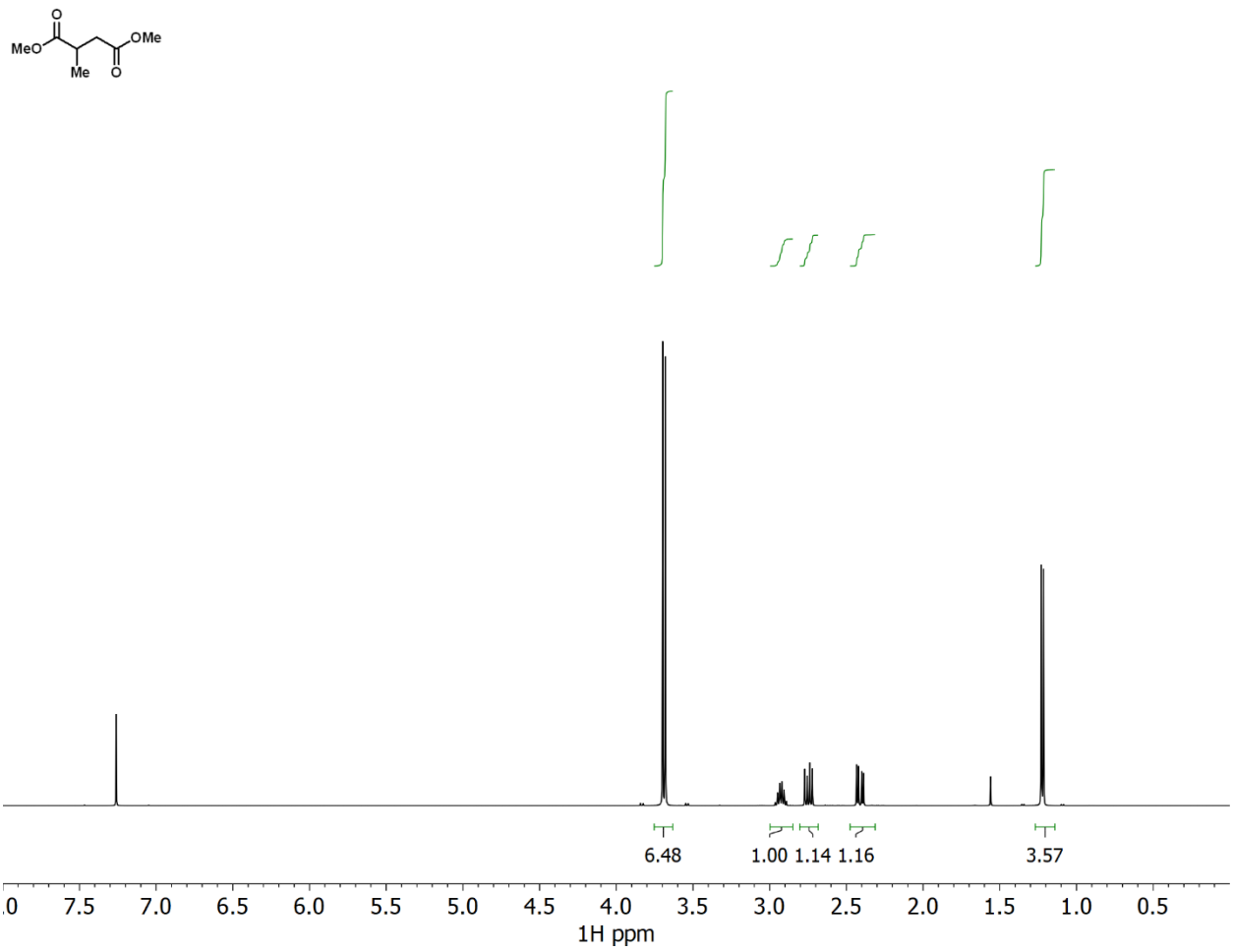


Figure S2. ^{1}H NMR spectra of dimethyl 2-methylsuccinate (MS) in $CDCl_3$.

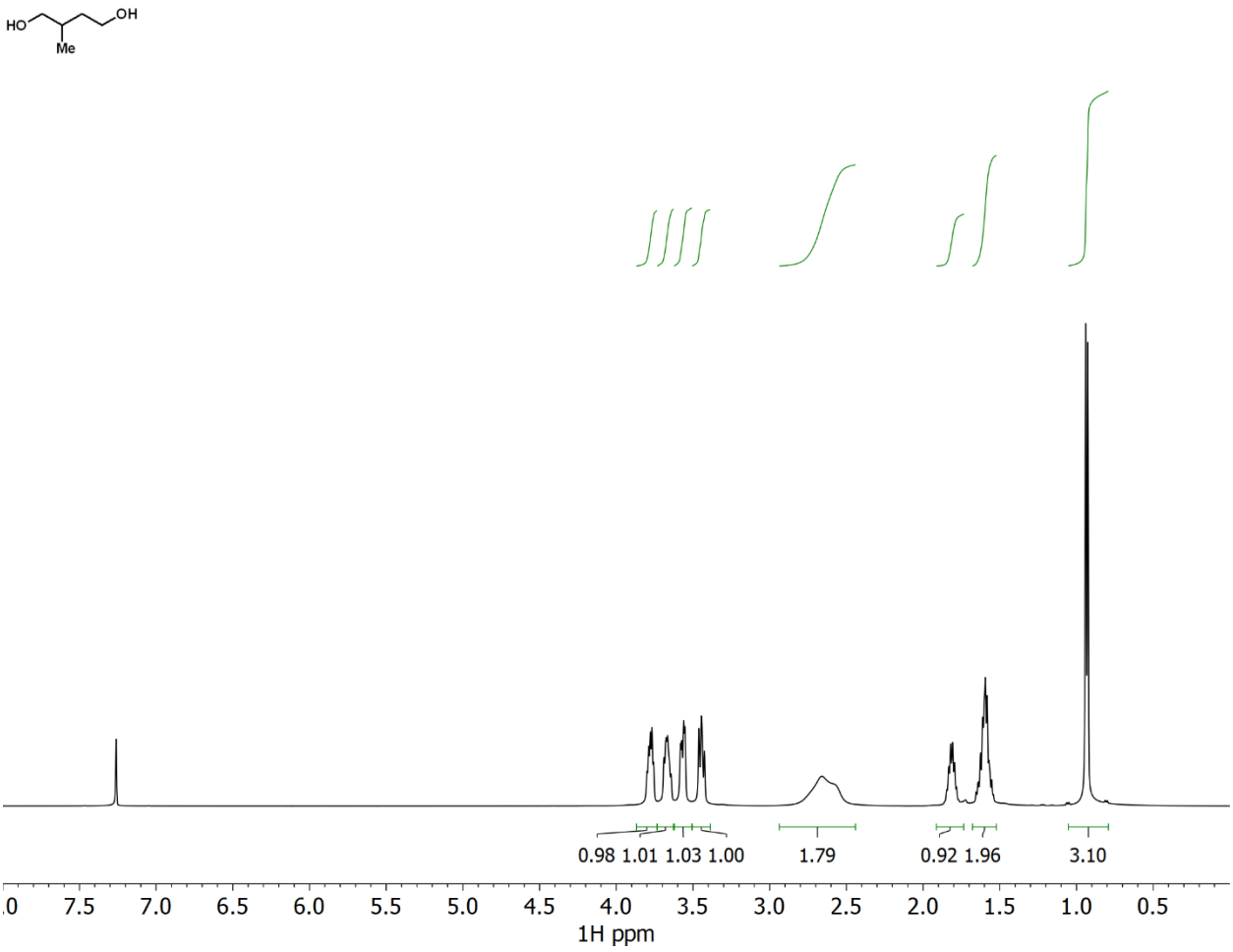


Figure S3. ^{1}H NMR of 2-methyl-1,4-butanediol (MB) in $CDCl_3$.

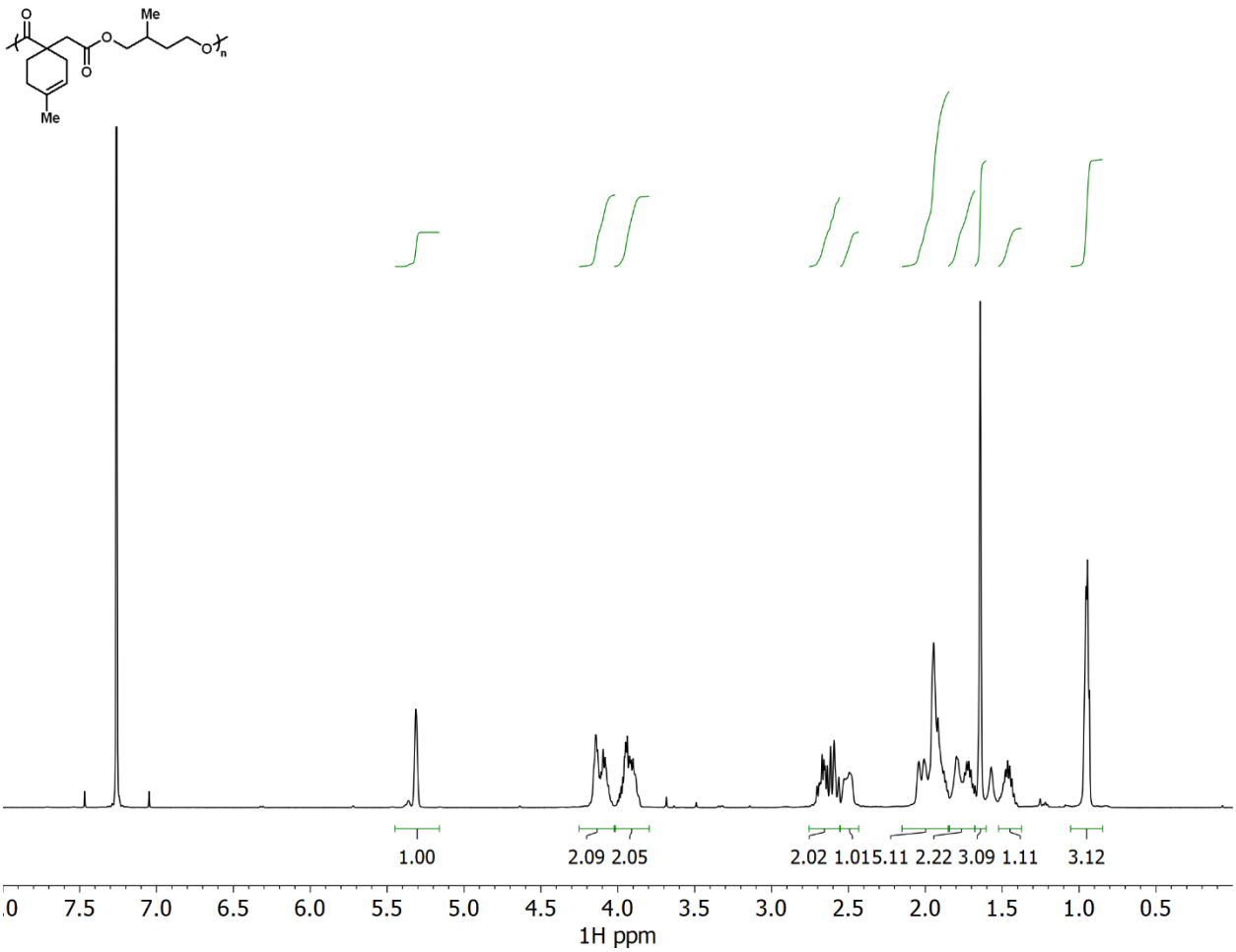


Figure S4. ^{1}H NMR of PMBCS in $CDCl_3$.

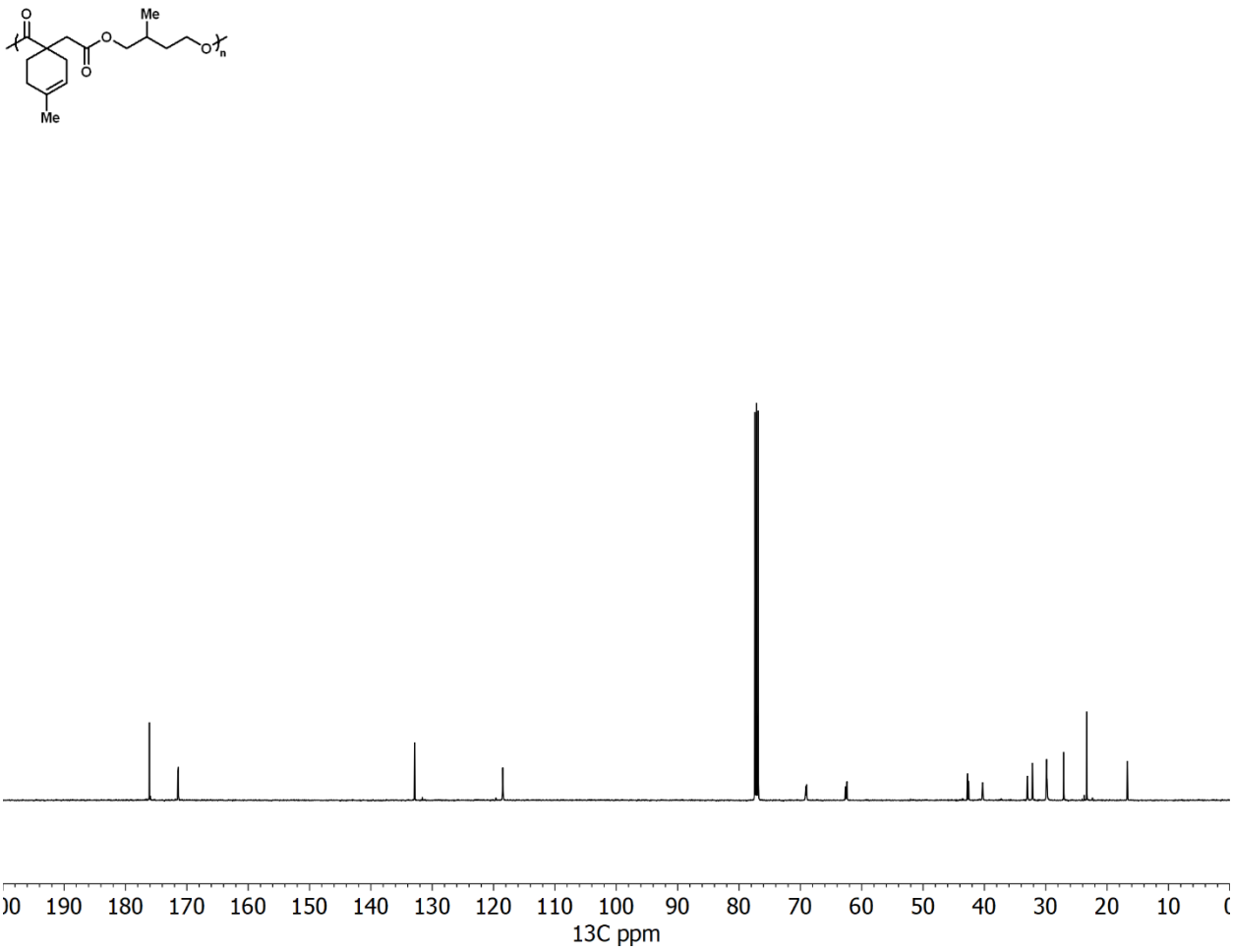


Figure S5. ^{13}C NMR of PMBCS in $CDCl_3$.

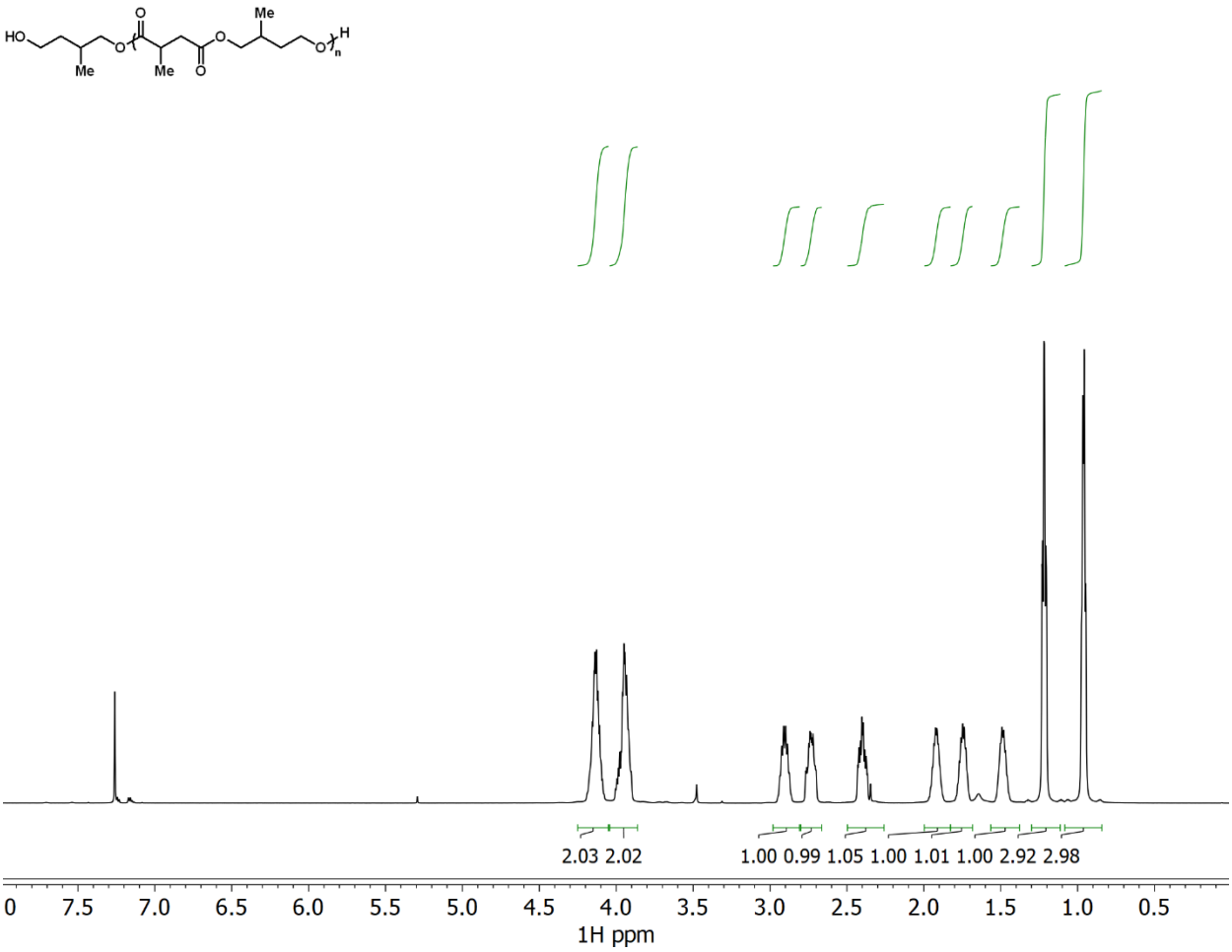


Figure S6. ^{1}H NMR of PMBMS in $CDCl_3$.

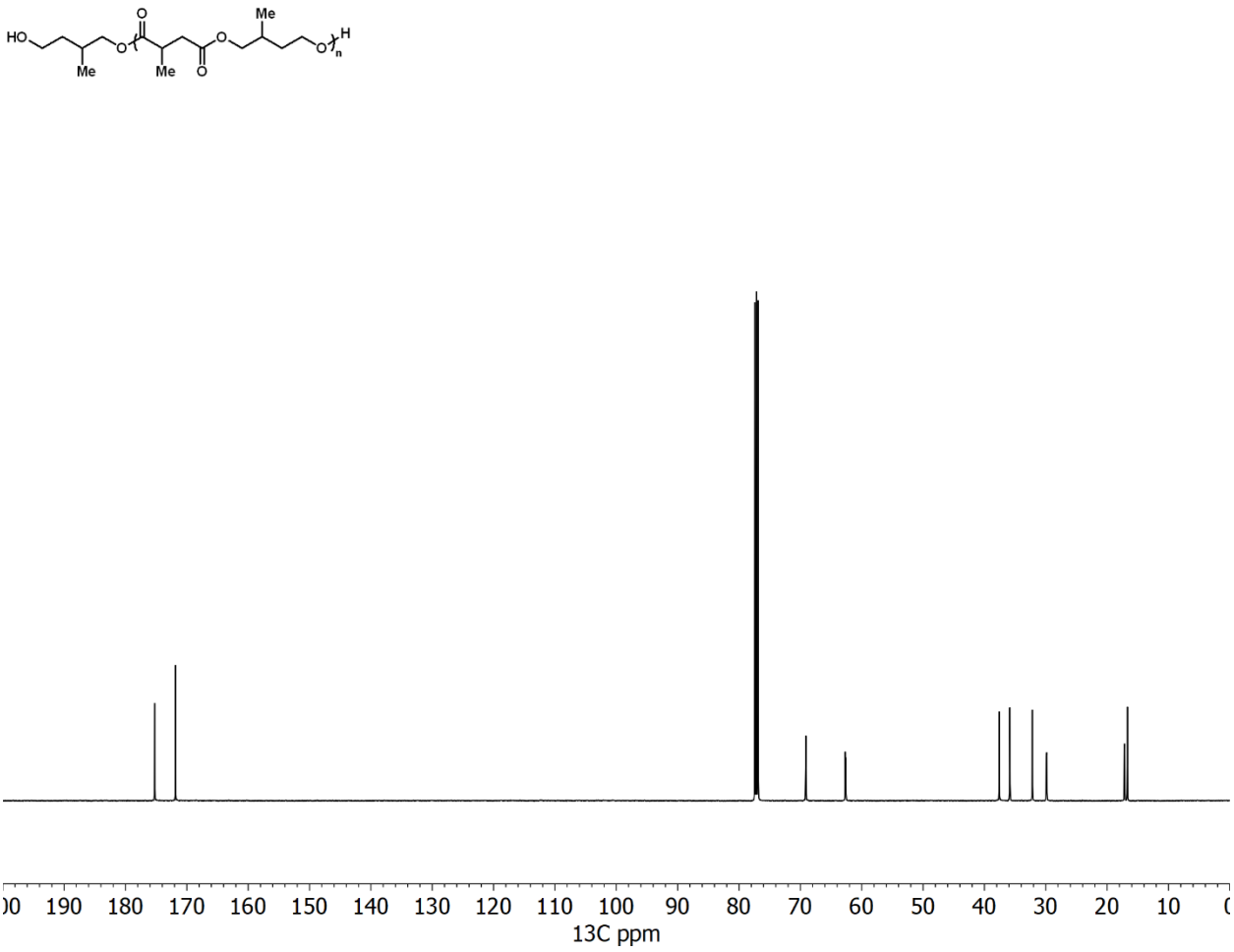


Figure S7. ^{13}C NMR of PMBMS in $CDCl_3$.

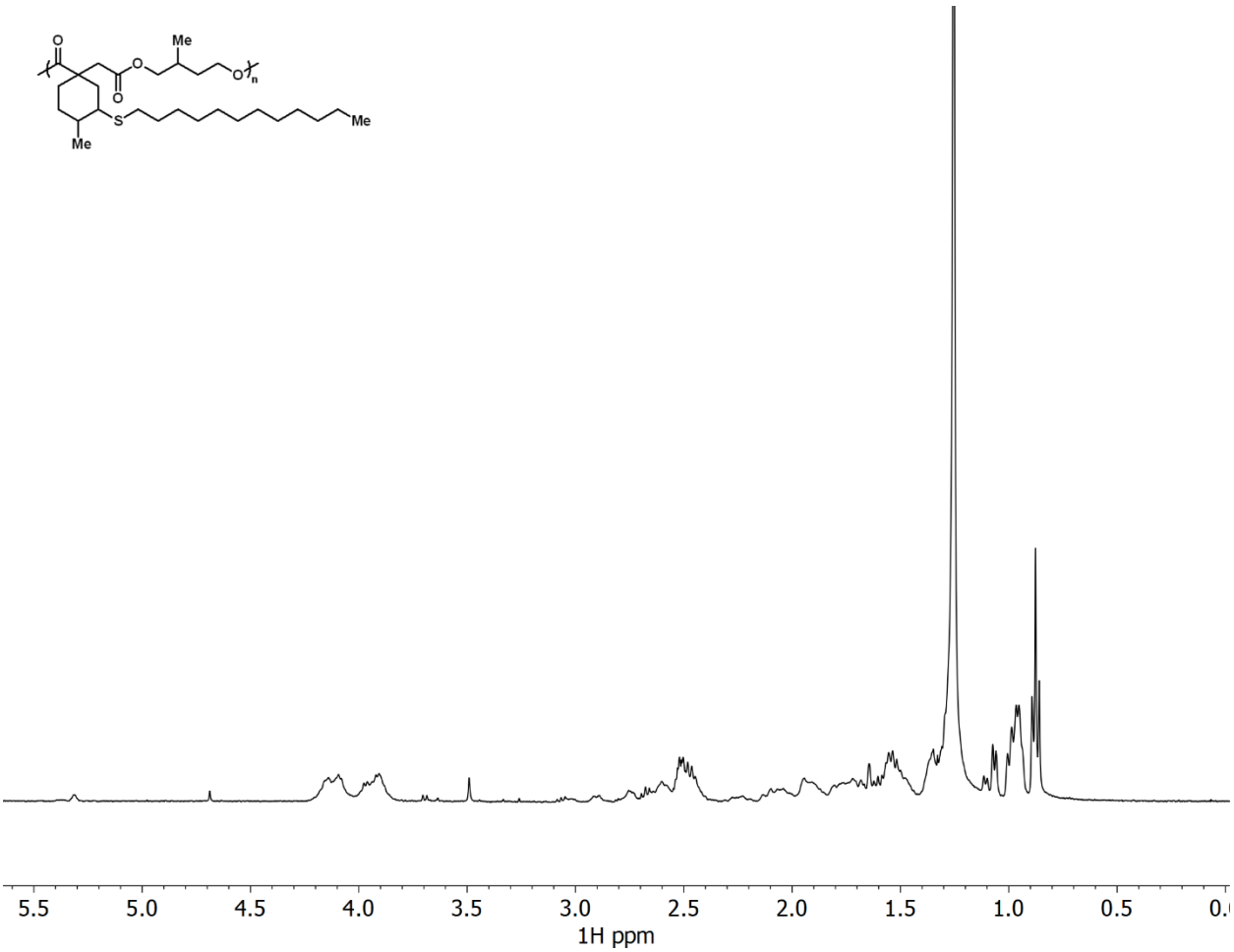


Figure S8. ^{1}H NMR spectra of dodecanethiol-functionalizd PMBCS in $CDCl_3$.

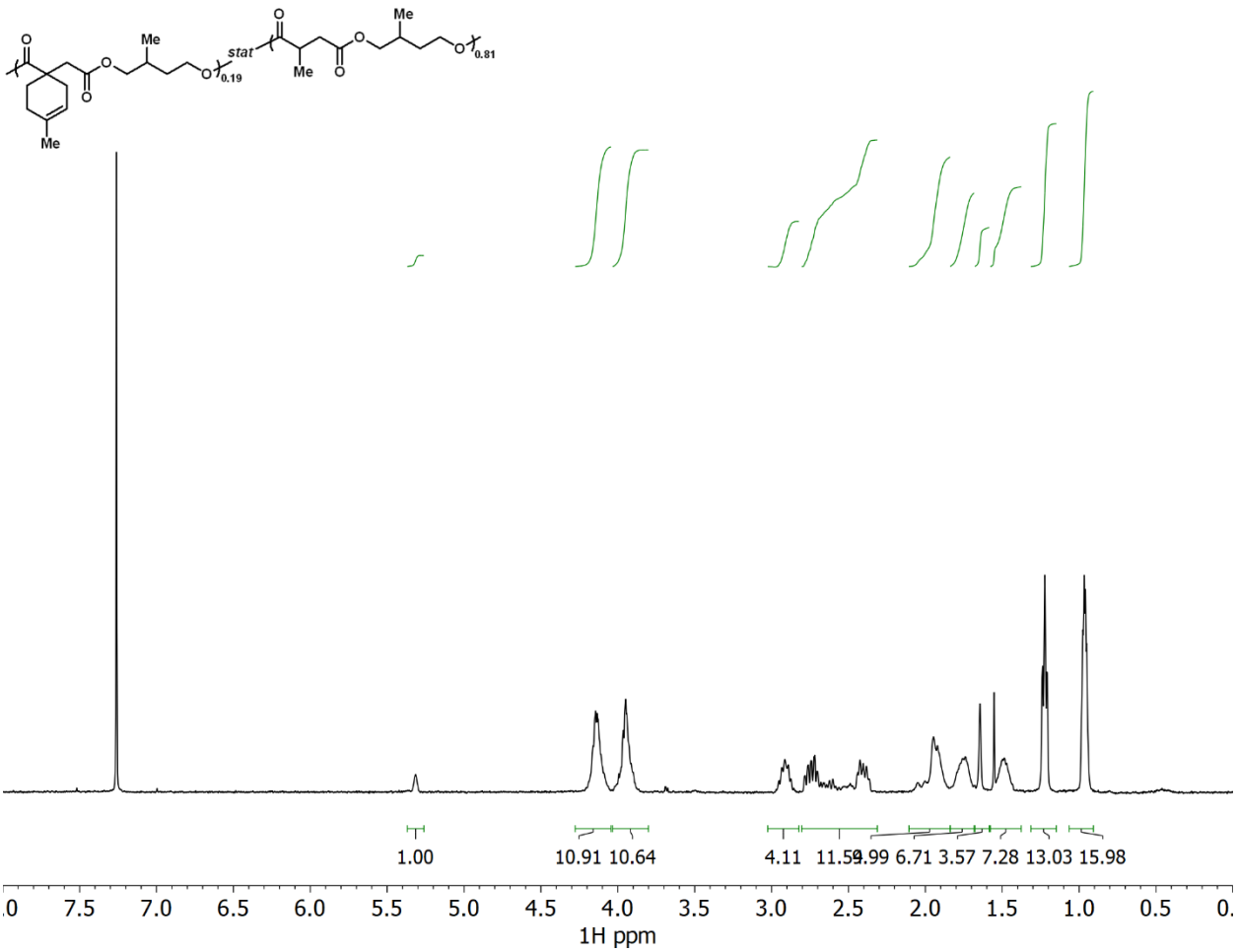


Figure S9. ^{13}H NMR of PMBCS$_x$-*stat*-PMBMS$_{1-x}$ (x = 0.2) in $CDCl_3$.

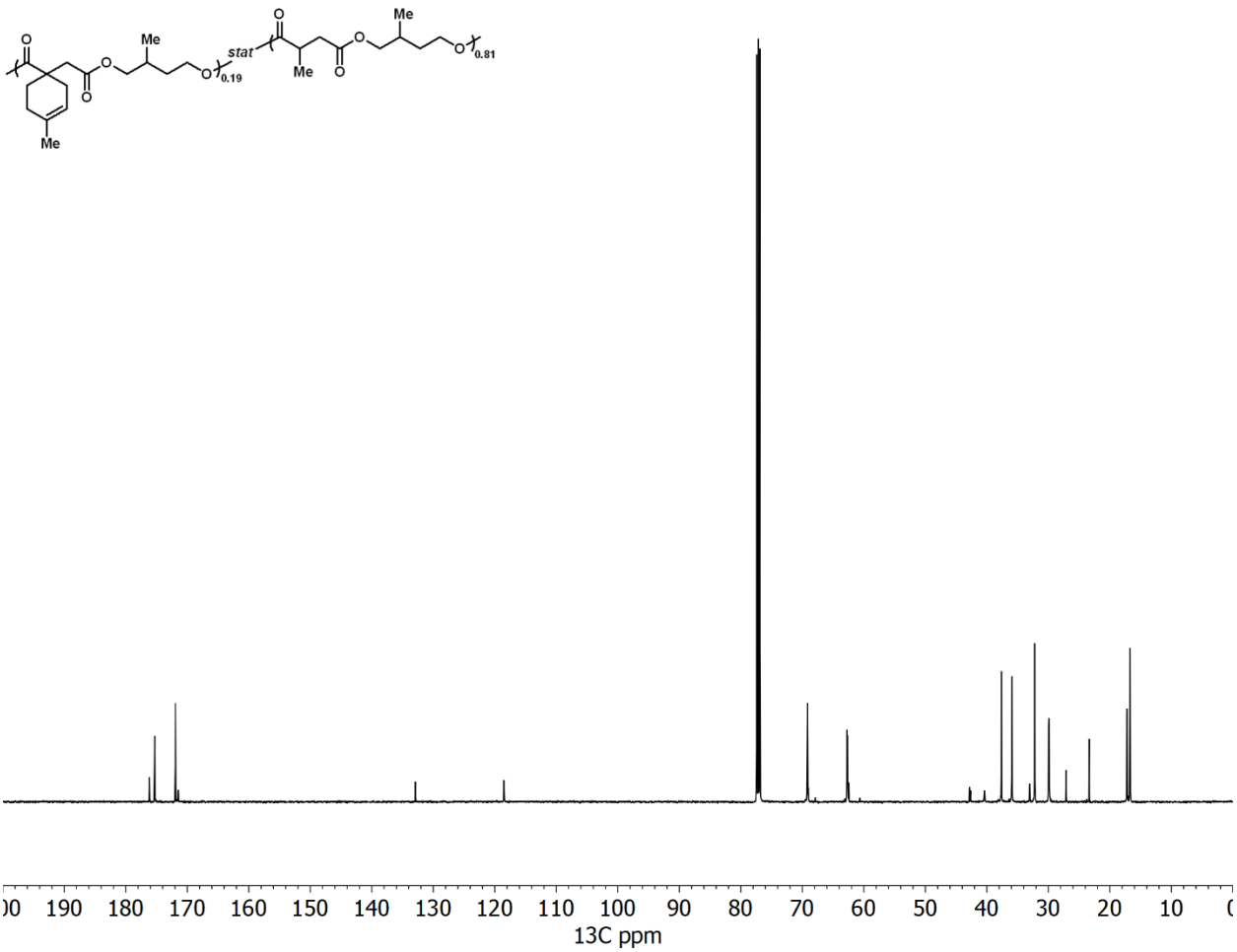


Figure S10. ^{13}C NMR of $PMBCS_x$-*stat*-$PMBMS_{1-x}$ (x = 0.2) in $CDCl_3$.

2D NMR Spectroscopy of PMBCS and PMBMS for regioregularity determination and end-group analysis for PMBMS

The regioregularity of the polymer was determined after assigning individual ^{1}H and ^{13}C peaks for both PMBMS and PMBCS through COSY, HSQC, and HMBC 2D experiments. During this process, multiple peaks integrating to a single carbon from quantitative ^{13}C spectra were observed, with the multiple peaks associated with carbons in different chemical environments resulting from varying regiochemistry. For both PMBMS and PMBCS, line fitting analysis using MestReNova was used to determine the ratio of the α-carbonyl carbon (a quaternary carbon for PMBCS at ~43 ppm or a tertiary carbon for PMBMS at ~36 ppm) interacting with either the head or tail end of the MB comonomer in the polymer repeat unit. The individual peaks associated with a head or tail interaction with MB were not assigned; a 1.0:1.0 ratio was measured, indicating that interaction of MS with the head or tail end of MB occurred in equal amounts.

PMBCS

PMBCS sample analyzed by 2D NMR was synthesized using the general procedure described above (Figures S11 – S15).

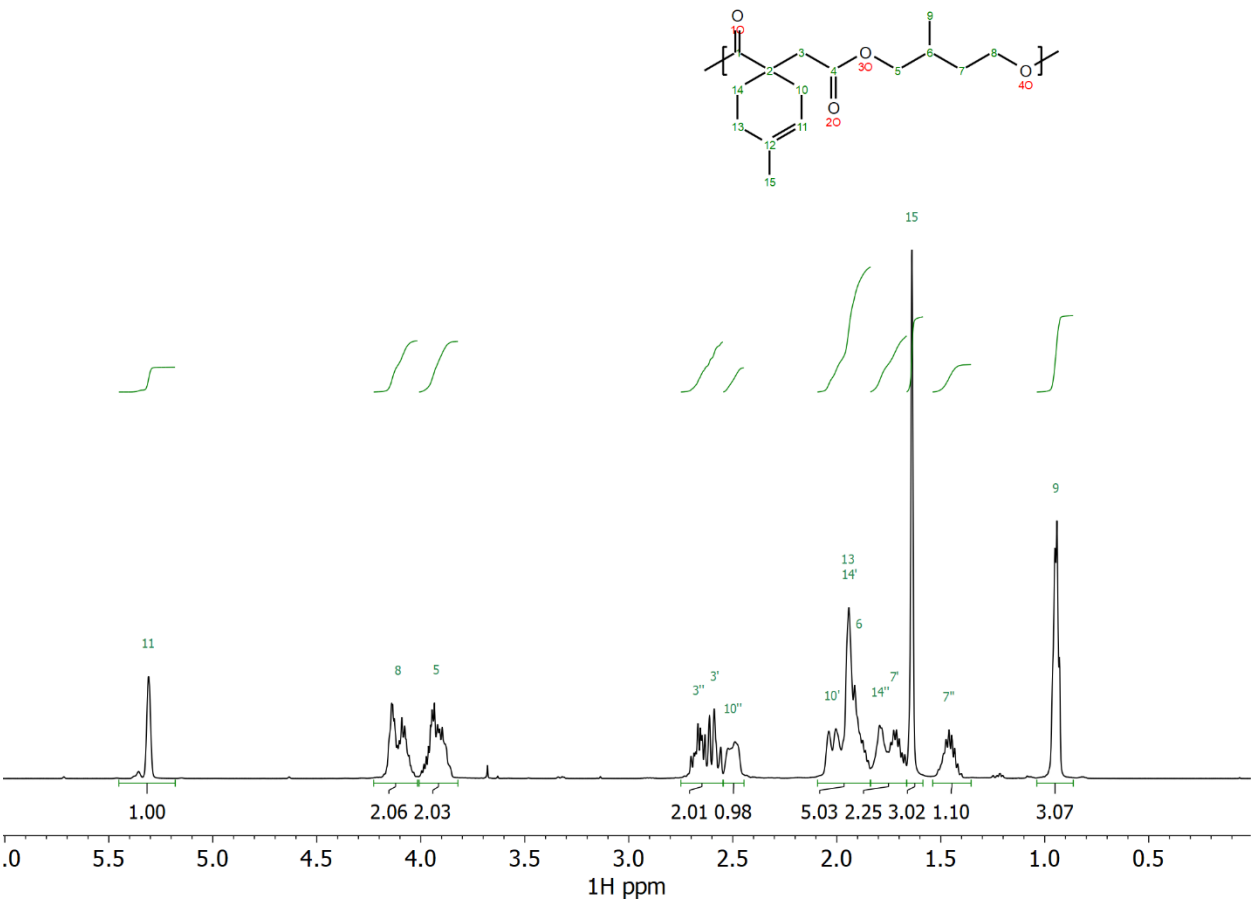


Figure S11. Quantitative ^{1}H NMR spectrum of PMBCS in $CDCl_3$ with assignments.

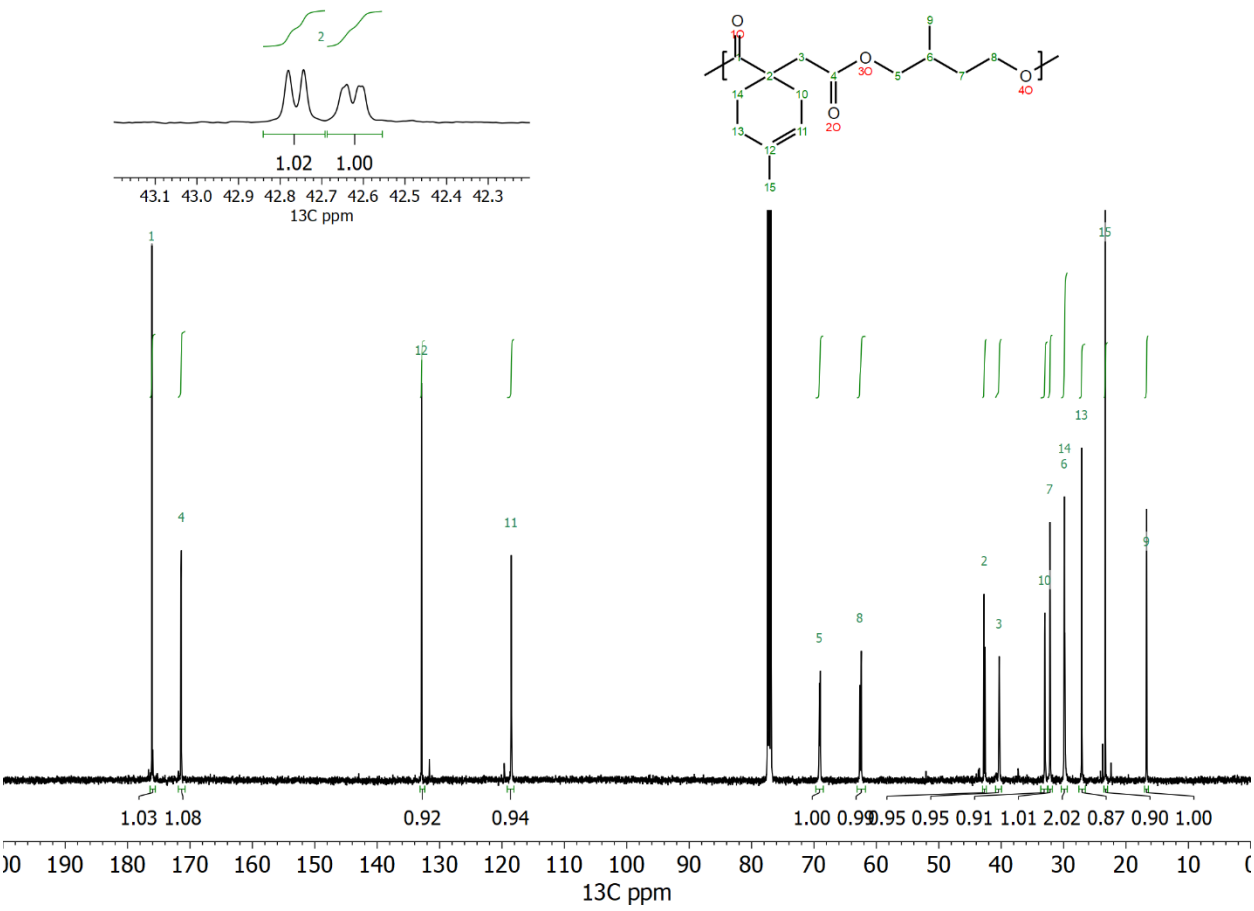


Figure S12. Quantitative ^{13}C NMR spectrum of PMBCS in $CDCl_3$ with assignments. Insert in top-left depicts the peaks associated with the quaternary carbon (carbon 1).

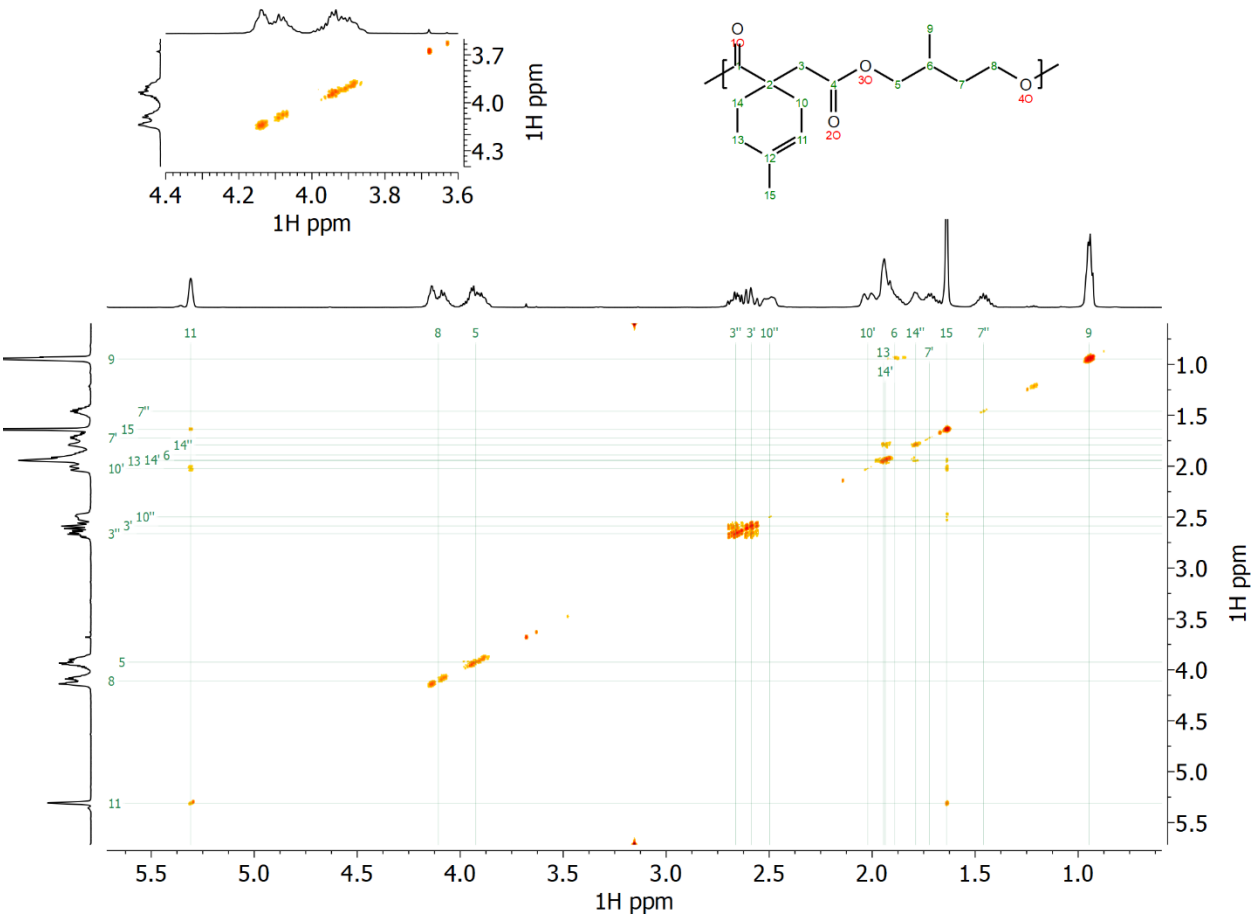


Figure S13. COSY spectrum of PMBCS in $CDCl_3$. Insert in top-left depicts the cross-peaks associated with the methylene protons adjacent to the alcohols (carbons 5 and 8).

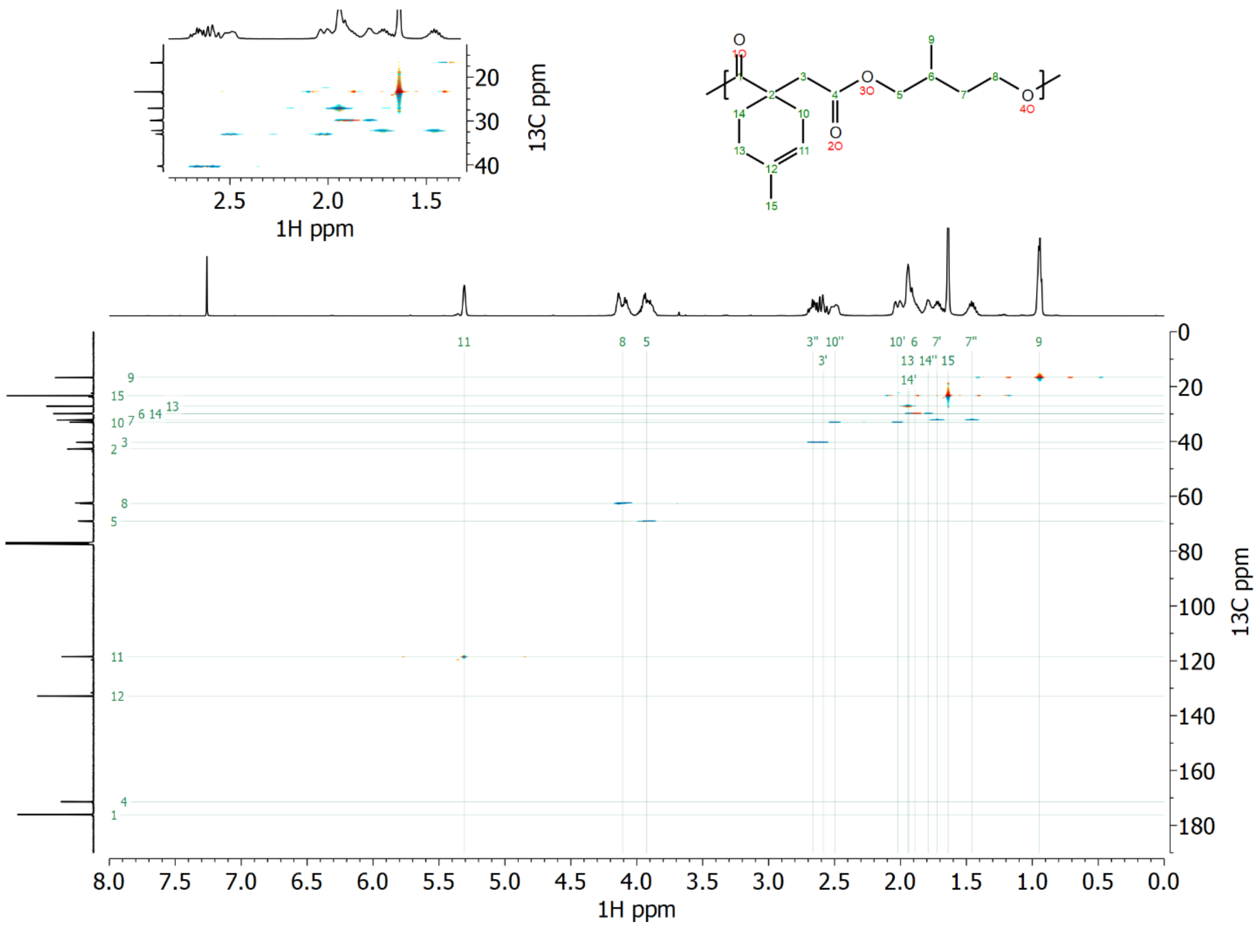


Figure S14. HSQC spectrum of PMBCS in $CDCl_3$. Insert in top-left depicts the cross-peaks associated with the aliphatic protons not adjacent to the alcohols.

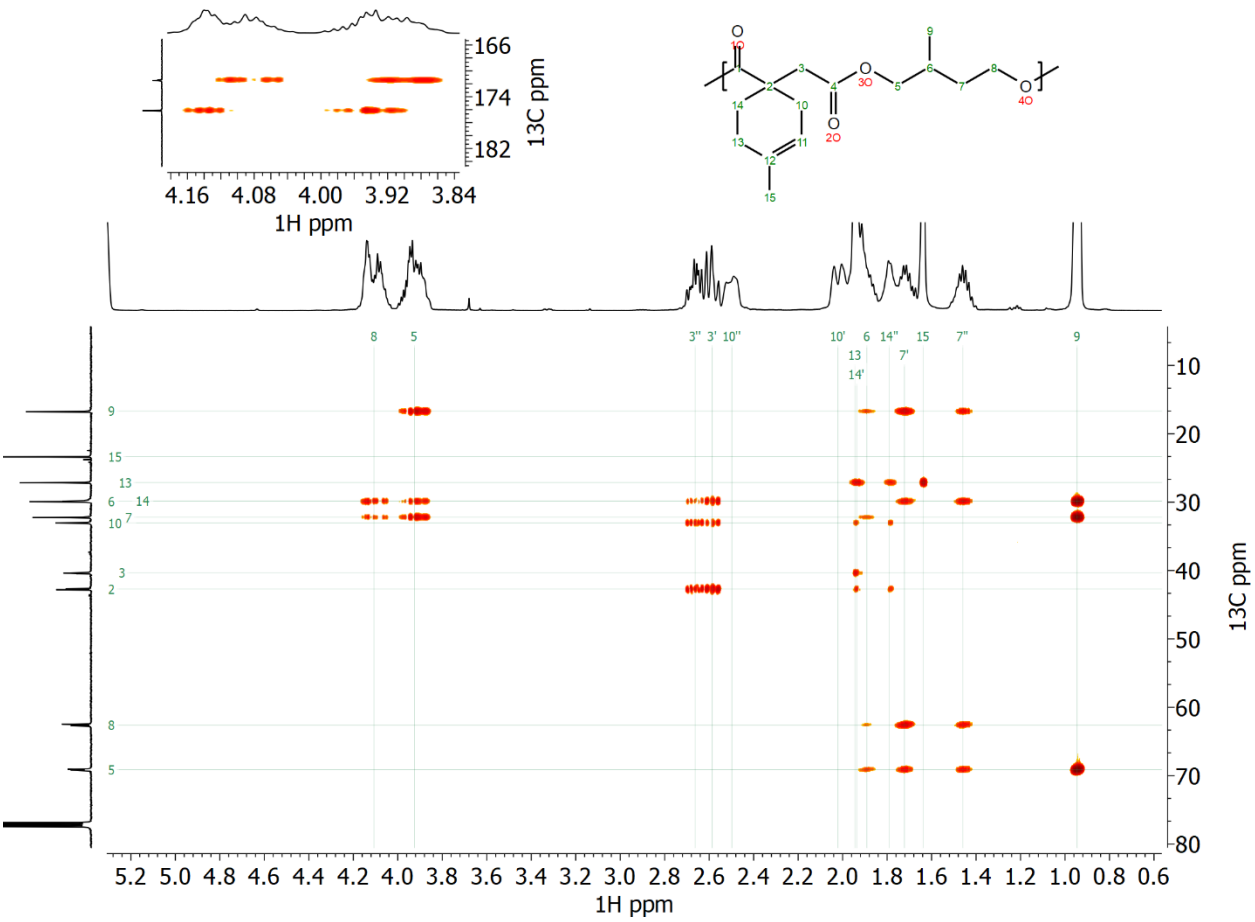


Figure S15. HMBC spectrum of PMBCS in $CDCl_3$. Insert in top-left depicts the cross-peaks associated with the methylene protons adjacent to the alcohols (carbons 5 and 8).

PMBMS

PMBMS analyzed by 2D NMR was synthesized according to the general procedure above, in a 1.0:1.2 MS:MB ratio (Figures S16 – S20).

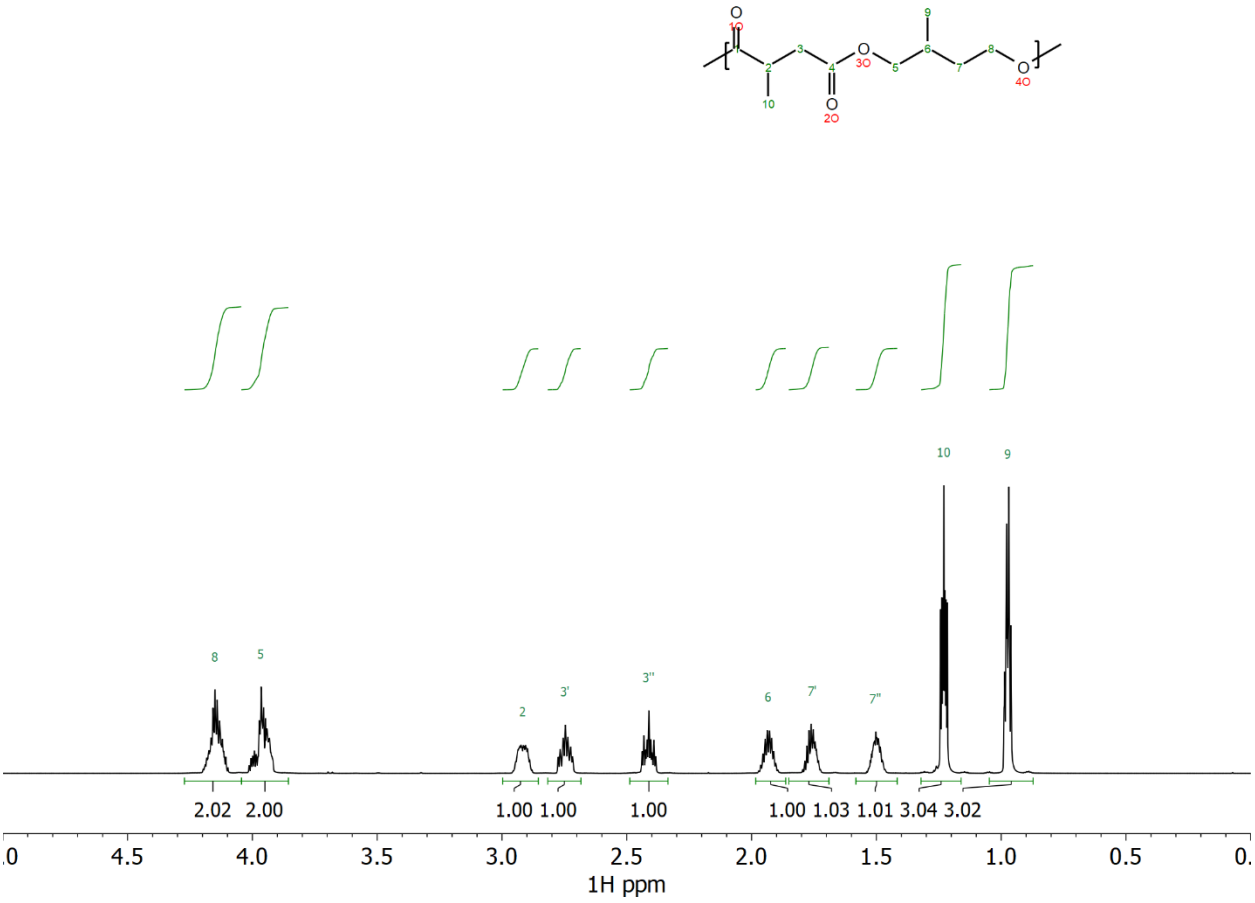


Figure S16. Quantitative ^{1}H NMR spectrum of PMBMS in $CDCl_3$ with assignments.

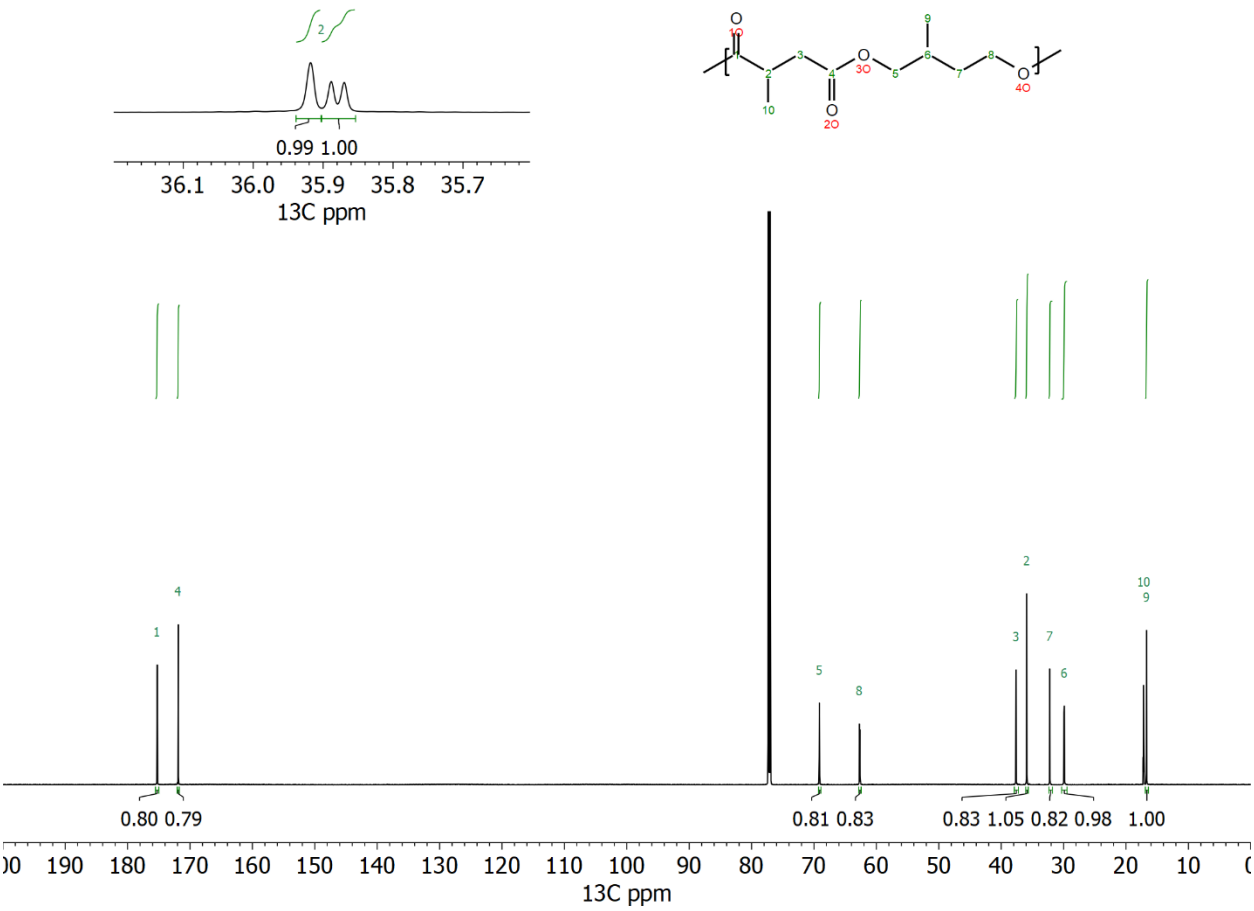


Figure S17. Quantitative ^{13}C NMR spectrum of PMBMS in $CDCl_3$ with assignments.

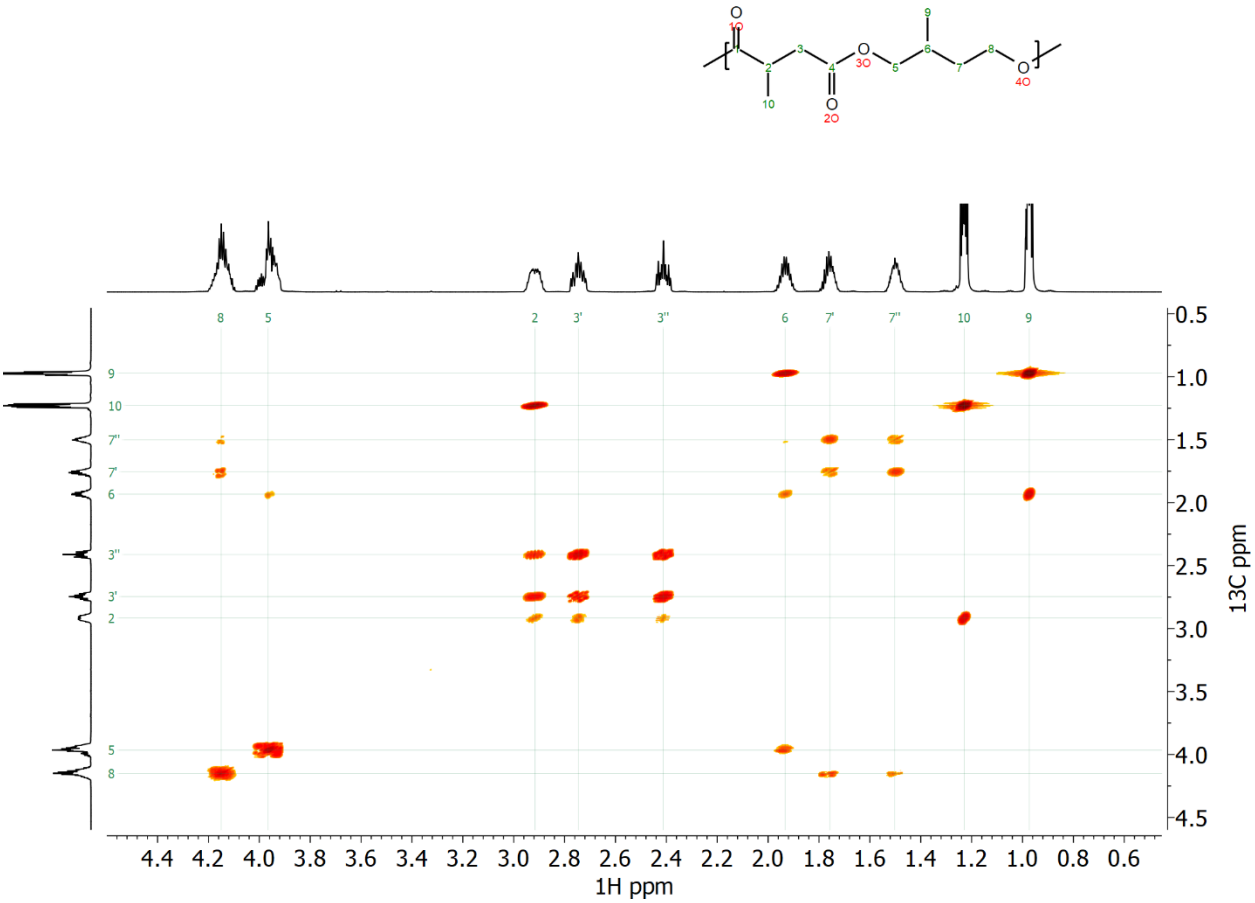


Figure S18. COSY spectrum of PMBMS in $CDCl_3$.

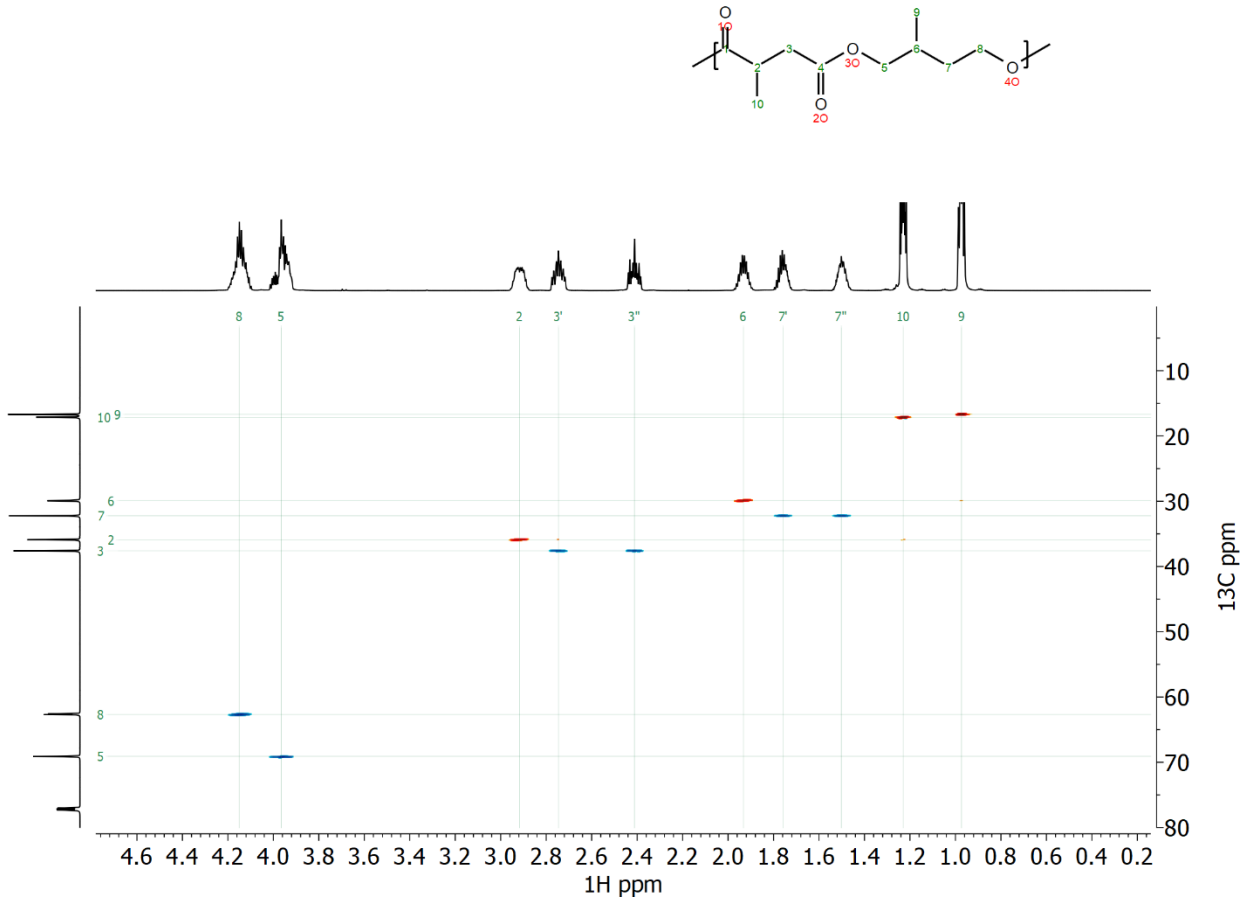


Figure S19. HSQC spectrum of PMBMS in $CDCl_3$.

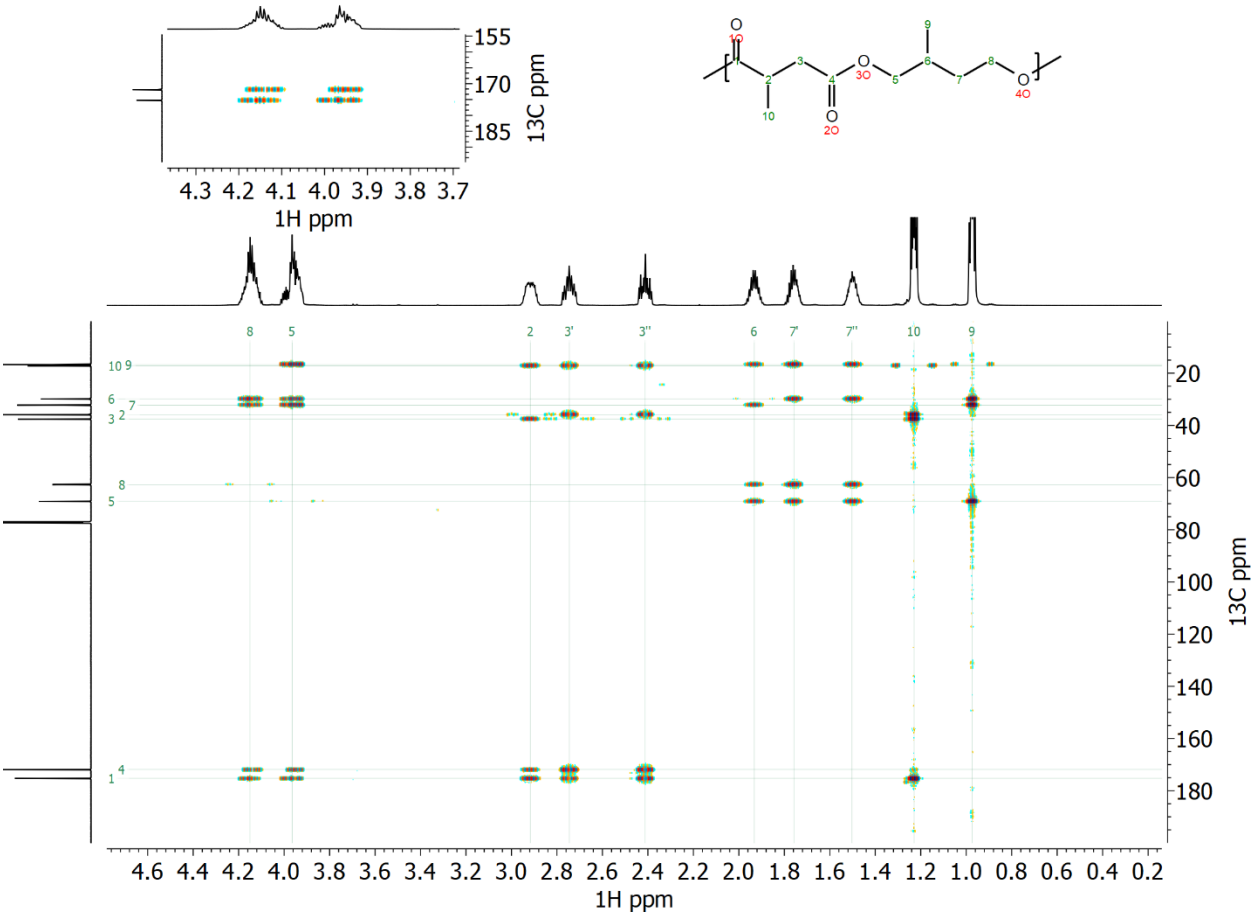


Figure S20. HMBC spectrum of PMBCS in $CDCl_3$. Insert in top-left depicts the cross-peaks associated with the methylene protons adjacent to the alcohols (carbons 5 and 8).

Conversion of MS and MB to PMBMS over time

The PMBMS polymerization was also followed through both stages of the polycondensation method following the general procedure using SEC to determine M_n and $Đ$ and ^{1}H NMR analysis to determine conversion (Figures S21, S22, and Table S1).

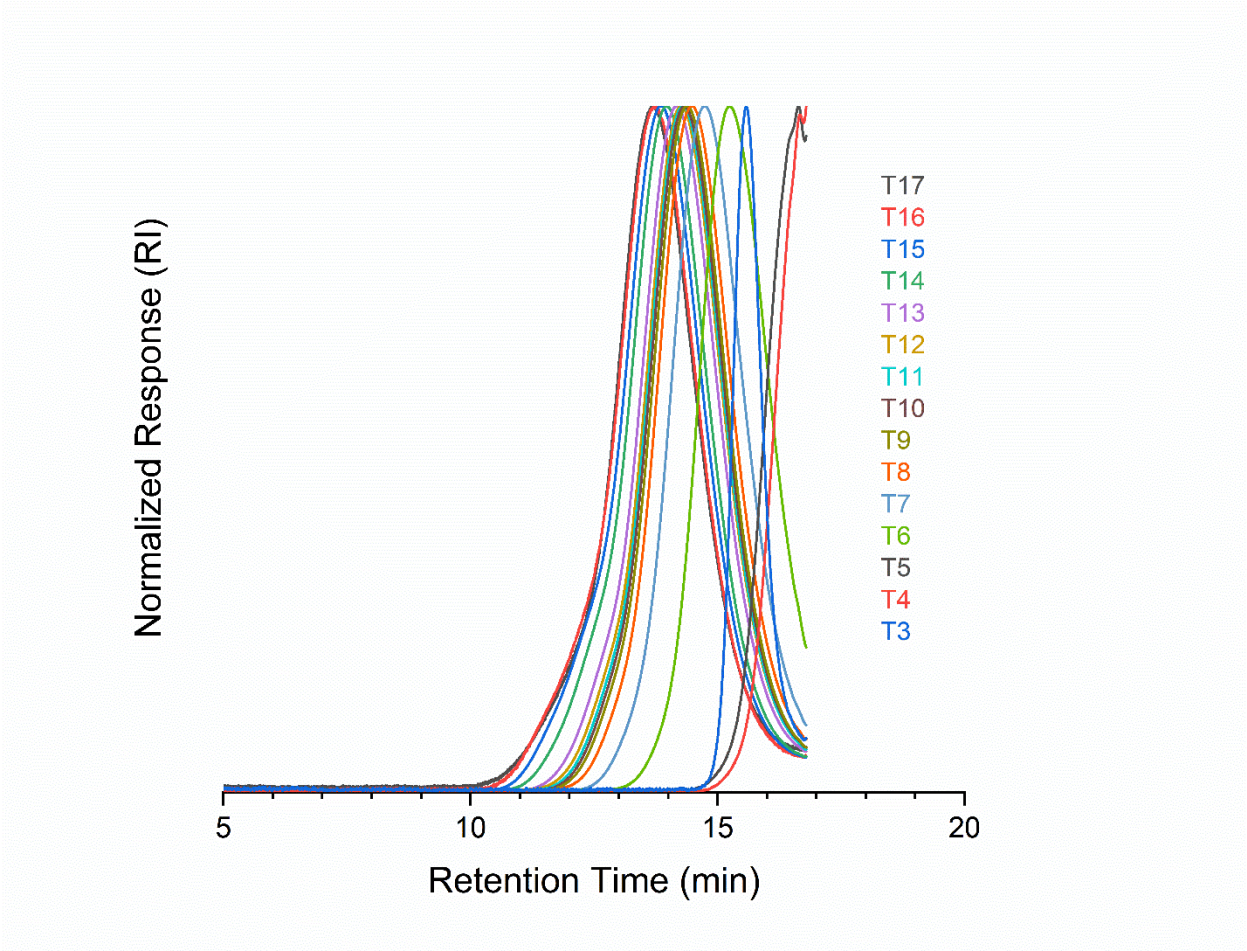


Figure S21. SEC results monitoring the polymerization of MB and MS as detected by RI Table S1).

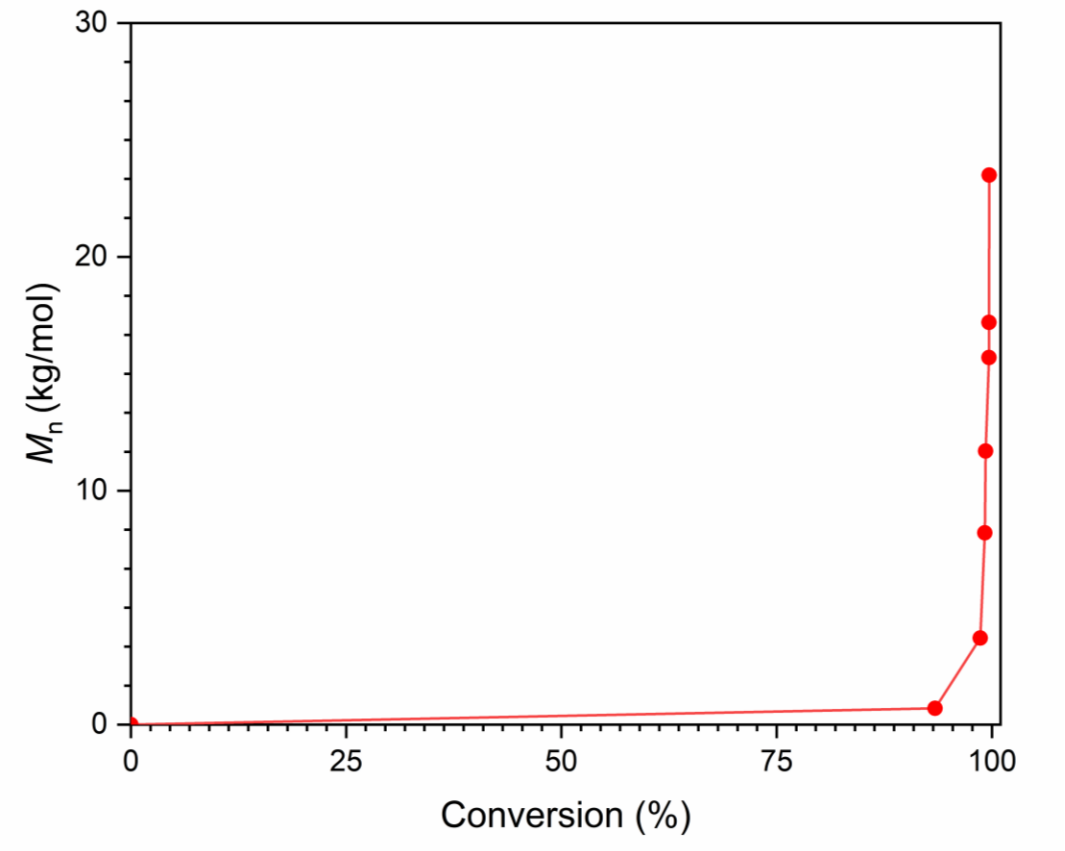


Figure S22. Plot of M_n vs conversion throughout the polymerization of PMBMS.

Table S1. Conversion (p), degree of polymerization (1/(1-p)), M_n, and $Đ$ as a function of time for PMBMS synthesis.

				RI		LS	
Condition	Timepoint	Time (min)	p	M_n (kg/mol)	$Đ$	M_n (kg/mol)	$Đ$
T = 180 °C, P = 760 Torr	T0	0	2.5	0	-	0	-
	T1	30	33.9	0	-	0	-
	T2	60	59.1	0	-	0	-
	T3	90	72.2	1.3	1.16	0	-
	T4	150	80.2	2.6	1.30	0	-
	T5	215	84.2	1.5	1.28	0	-
T = 200 °C, P = 0.05 Torr	T6	231	96.5	3.8	1.81	0	-
	T7	241	97.9	6.2	2.09	5.4	2.02
	T8	248	98.4	7.7	2.28	7.3	2.06
	T9	253	98.6	8.6	2.38	8.8	2.09
	T10	258	98.6	9.0	2.43	8.7	2.25
	T11	264	98.7	9.3	2.48	9.2	2.24
	T12	269	98.8	9.5	2.61	9.4	2.35
	T13	279	98.9	10.3	2.68	10.9	2.39
	T14	293	99.1	12.5	3.01	13.6	2.75
	T15	309	99.2	14.4	3.22	16.0	2.98
	T16	337	99.3	15.8	3.43	13.3	4.01
	T17	362	99.3	15.3	3.72	14.8	3.29

Swell tests of cross-linked poly((MB-*alt*-CS)$_x$-*stat*-(MB-*alt*-MS)$_{1-x}$) (PMBCS$_x$-PMBMS$_{1-x}$)

Typically, small pieces of the prepared thermosets were weighed (ca. 10 – 50 mg) and placed in 20 mL scintillation vials. 10.0 mL of DCM was then added to the vial, which was capped. The sample was equilibrated for 48 h. After 48 h, the samples were removed, patted down with a Kimwipe®, and quickly weighed while swollen. Then the samples were dried under vacuum (0.05 Torr) for 48 h and weighed again. Swell tests were performed in triplicate and the results were averaged. Gel fractions were calculated with the following equation:

$$Sol\ fraction = \left[\frac{W_o - W_i}{W_o}\right] \textbf{ Equation S1}$$

$$Gel\ fraction = 1 - Sol\ fraction \textbf{ Equation S2}$$

Where W_o is the initial weight of the dried thermoset and W_i is the mass of the dried thermoset following the DCM extraction during the swell test.[8] Time points taken during a test swelling experiment indicated constant values of mass for the swollen thermoset between 24 and 114 h, demonstrating that equilibrium for these systems is achieved rapidly and within 48 h.

Estimation of Cross-linking Density Using the Flory-Rehner Equation

Molar mass between cross-links (M_x) were estimated using the Flory-Rehner Equation[8] shown below

$$M_x = -\frac{d_p V_s \left(V_f^{\frac{1}{3}} - \frac{V_f}{2}\right)}{\ln(1 - V_f) + V_f + \chi V_f^2} \textbf{ Equation S3}$$

where d_p is the experimentally determined density of the thermosets (1.16 g/mL for all thermosets), V_s is the molar volume of the swelling solvent (64 mL/mol for DCM), V_f is the

volume fraction of the polymer, and χ is the solvent interaction parameter. V_f is further defined as

$$V_f = \left[1 + \frac{d_p}{d_s}\left(\frac{M_a}{M_b} - 1\right)\right]^{-1} \textbf{ Equation S4}$$

where d_s is the swelling solvent density (1.327 g/cm^3 for DCM), M_a is the mass of the swollen thermoset and M_b is the mass of the dried thermoset prior to swelling, both values having been obtained during the swell tests described above, with a V_f calculated for each swell test run. Furthermore, χ can be estimated by the equation below[9]

$$\chi = 0.34 + \frac{V_s}{RT}(\delta_1 - \delta_2)^2 \textbf{ Equation S5}$$

where R is the ideal gas constant in units of J mol^{-1} K^{-1}, T is temperature in K, V_s is the molar volume of the solvent as defined previously, and δ_1 and δ_2, the solubility parameter of the thermoset and solvent, respectively, both with units of (J/cm^3)$^{1/2}$. Solubility parameters of common solvents such as DCM ((20.2 J/cm^3)$^{1/2}$) have been tabulated,[10] while the solubility parameter for both PMBMS and PMBCS were calculated using the Small's cohesive energies equation[11,12]

$$\delta = d_p \frac{\sum F_1}{M_0} \textbf{ Equation S6}$$

where $\sum F_1$ is the sum of the group molar attraction constants and M_0 is the molar mass of the repeat unit. δ_{PMBMS} and δ_{PMBCS} were calculated to be 19.4 (J/cm^3)$^{1/2}$ and 18.2 (J/cm^3)$^{1/2}$, respectively, and were similar to that calculated for the structurally similar poly(butylene succinate).[13] Solvent parameters for each thermoset were then calculated as a weighted average of the PMBMS and PMBCS solvent parameters, with

$$\delta_1 = \delta_{thermoset} = (1 - F_{MBCS})\delta_{PMBMS} + F_{MBCS}\delta_{PMBCS}$$ **Equation S7**

The values of M_a, M_b, V_f, δ_1, χ, and M_x are tabulated in Table S2.

M_x values determined using the Flory-Rehner equation (equation S3) are approximately half the values of M_x determined by DMTA results. Despite these differences, $M_{x,swell}$ values decrease with increasing $F_{MBCS,}$ as observed for $M_{x,DMTA}$ values (Table S3). Disparities in M_x values determined from swelling and DMTA experiments have been previously reported and are likely due to the limitations of the Flory-Rehner equation for this system resulting from the lower limit for M_x of just a few hundred grams per mole.[14–16]

Table S2. Tabulated values for the Flory-Rehner equation estimation of molar mass between cross-links (M_x).

F_{MBCS}	M_a (mg)	M_b (mg)	V_f	δ_1 $(J/cm^3)^{1/2}$	χ	M_x (kg/mol)	Average M_x (kg/mol)
0.40, Trial 1	71.9	17.5	0.269	18.9	0.385	1.0	0.8 ± 0.2 (± 20%)
0.40, Trial 2	38.8	11.9	0.336			0.6	
0.40, Trial 3	49.7	14.0	0.310			0.7	
0.29, Trial 1	170.6	34.1	0.222	19.0	0.377	1.42	1.48 ± 0.05 (± 3%)
0.29, Trial 2	202.3	38.9	0.214			1.53	
0.29, Trial 3	195.1	38.1	0.217			1.49	
0.19, Trial 1	323.1	42.9	0.149	19.1	0.370	3.1	3.0 ± 0.1 (± 5%)
0.19, Trial 2	321.4	42.3	0.148			3.2	
0.19, Trial 3	359.0	49.9	0.156			2.9	

Table S3. Gel fractions and M_x values determined for the thermosets from DMTA and swell test results.

Entry	F_{MBCS}	Gel Fraction	$M_{x,DMTA}$ (kg /mol)	$M_{x,swell}$ (kg /mol)
1	0.40	0.95 ± 0.07	1.4	0.8 ± 0.2
2	0.29	0.92 ± 0.01	3.2	1.5 ± 0.1
3	0.19	0.89 ± 0.01	6.3	3.0 ± 0.1

Degradation experiments of cross-linked poly((MB-*co*-CS)$_x$-*stat*-(MB-*co*-MS)$_{1-x}$) (PMBCS$_x$-*stat*-PMBMS$_{1-x}$)

The stability of PMBCS$_x$-*stat*-PMBMS$_{1-x}$ thermosets suspended in 3 M solutions of HCl and NaOH in DI water, as well as in DI water, all under ambient conditions. For a given F_{MBCS} thermoset composition, three square specimens were cut out of a previously set sheet of crosslinked material. For F_{MBCS} = 0.20, specimen samples were typically 6 x 6 x 1 mm in dimensions and typically weighed ~40 mg. For F_{MBCS} = 0.40, specimen samples were typically 6 x 6 x 0.5 mm and typically weighed ~20 mg. Each F_{MBCS} mole fraction thermoset (performed in triplicate) were immersed in in the above three solutions (typically 10 mL) in 20 mL scintillation vials. The samples were capped and left to sit undisturbed under ambient conditions. At each time point the samples were removed from their respective media, washed in DI water, and dried under vacuum at room temperature for 24 h. The samples were the weighed and immersed back in their original vial with the aqueous solution. This processed was repeated at each time point. Results are compiled in Table S4 and shown graphically in Figure S23.

Table S4. Degradation (as percentages of initial mass) data for thermoset (F_{MBCS} = 0.2) degradation experiments.

Day	F_{MBCS} = 0.20 (Mass, %)		
	3 M HCl	DI water	3 M NaOH
0	100	100	100
7	98.5 ± 0.2	100.0 ± 0.2	93 ± 5
14	98.2 ± 0.2	100.1 ± 0.6	90 ± 5
20	96.9 ± 0.9	99.7 ± 0.9	88 ± 5
29	97.3 ± 0.2	98.9 ± 0.7	82 ± 4

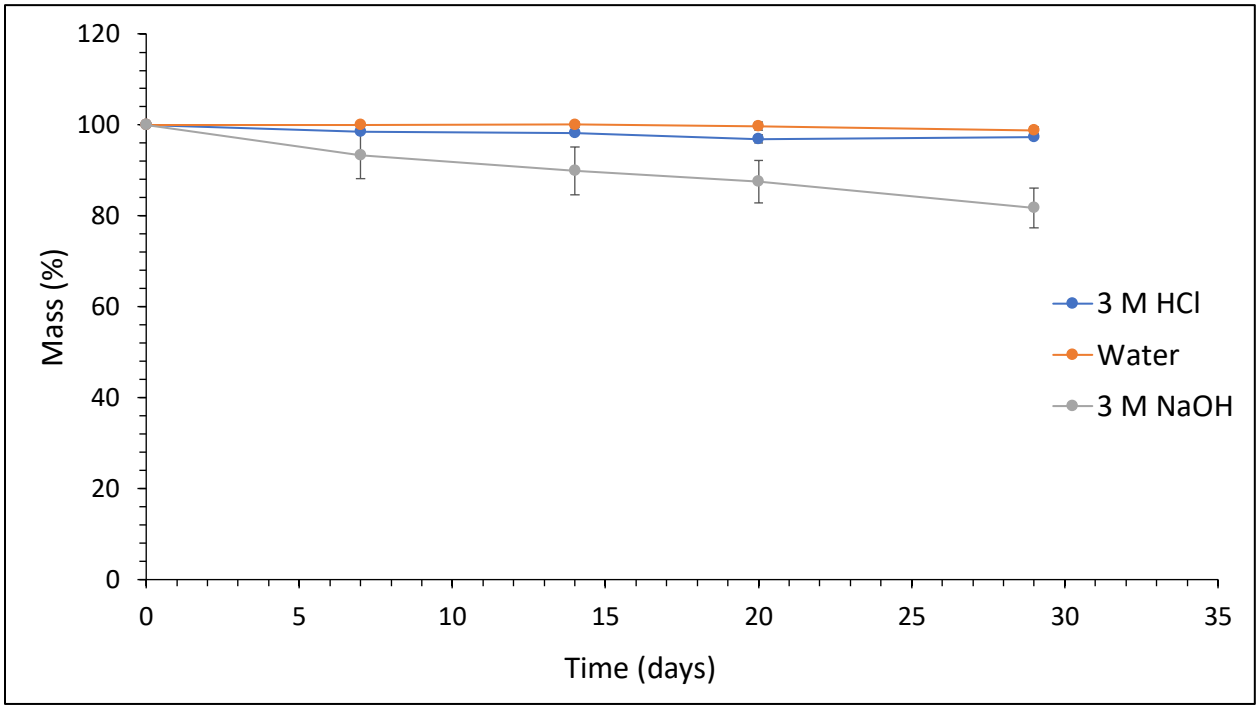


Figure S23. Graphical representation of data in Table S4.

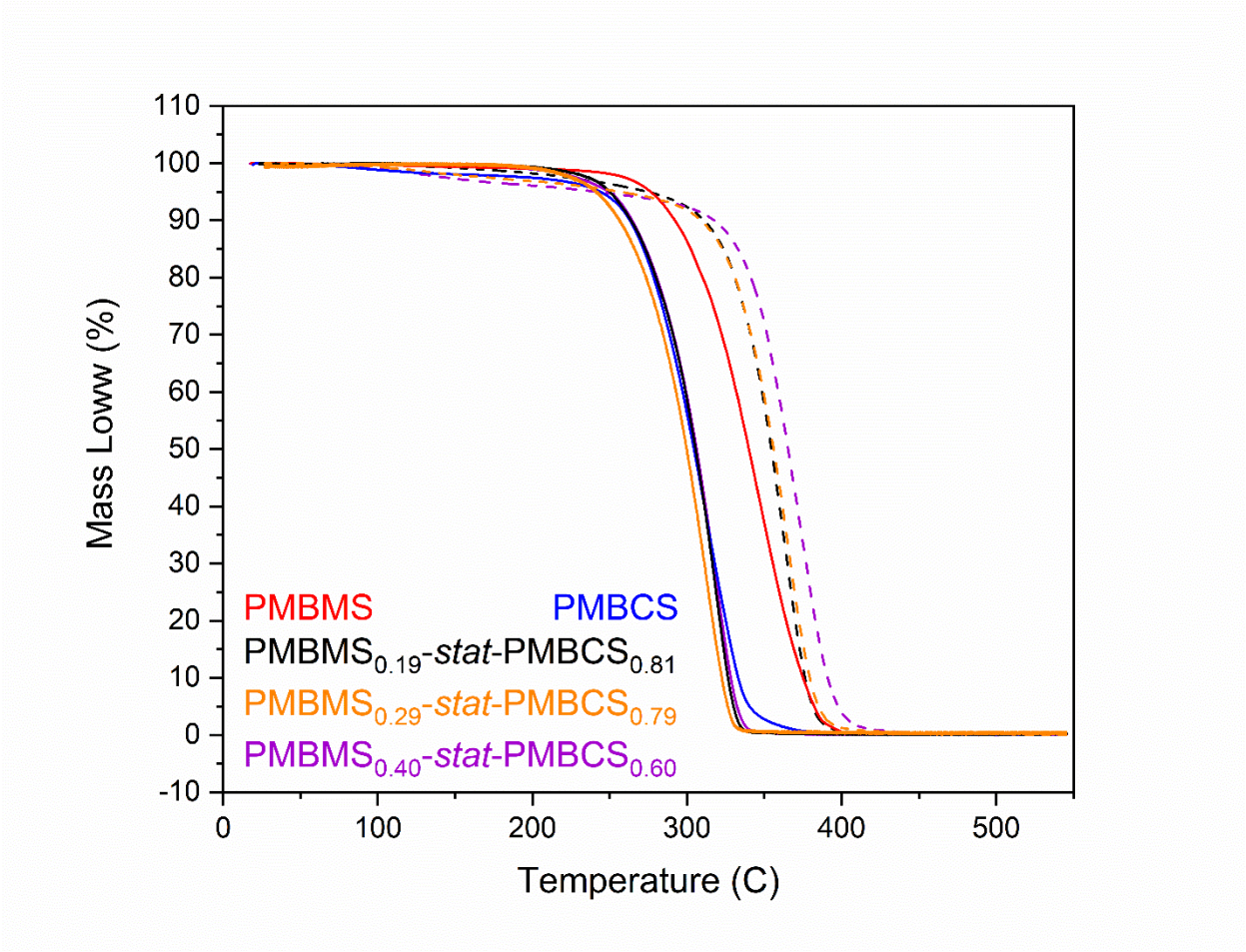


Figure S24. (a) Thermal gravimetric analysis mass loss (%) vs. temperature (10 °C/min) traces of various prepolymers (solid lines) or crosslinked thermosets (dashed lines)

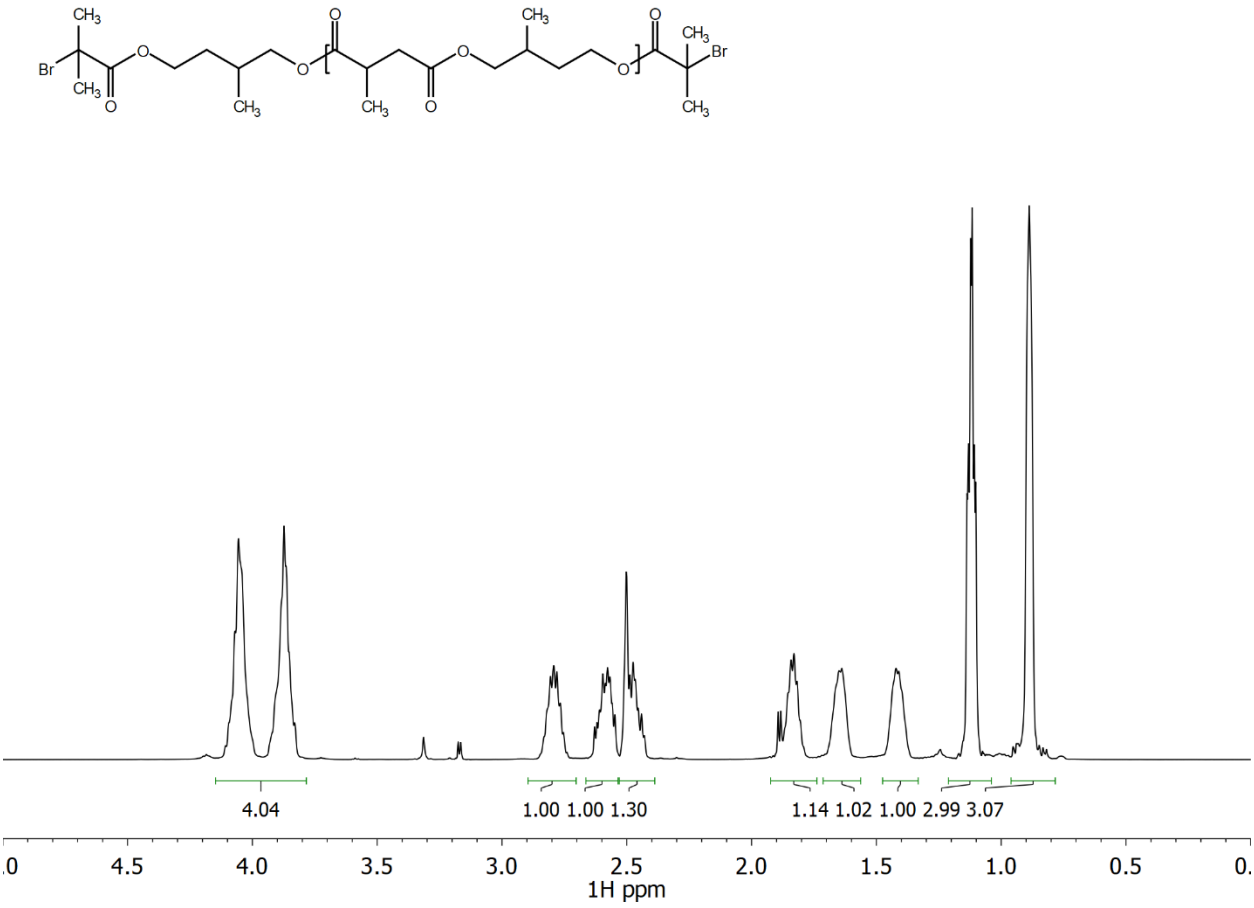


Figure S25. ^{1}H NMR spectra of Br-PMBMS-Br in DMSO-d_6.

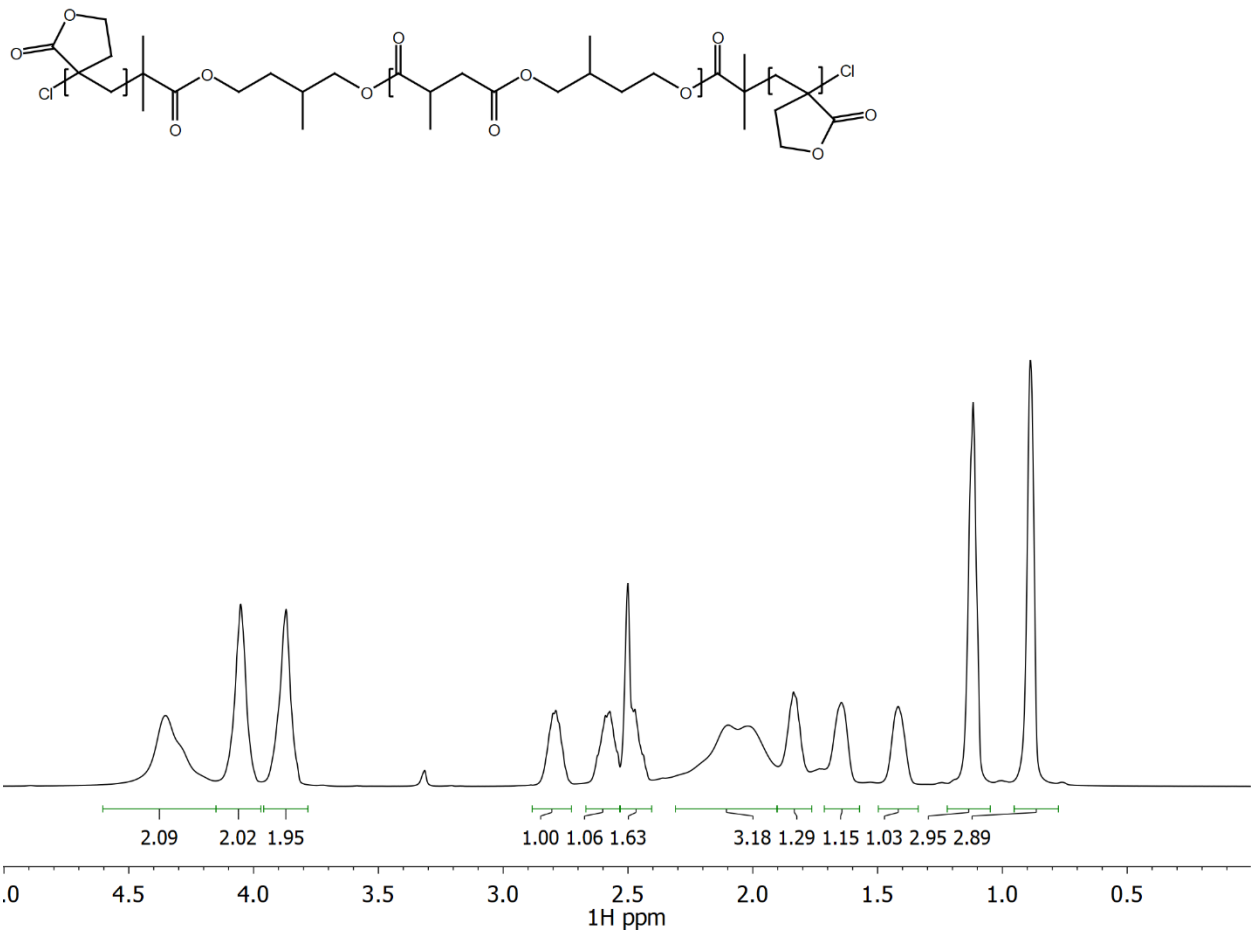


Figure S26. ^{1}H NMR spectra of PMBL-PMBMS-PMBL in DMSO-d_6.

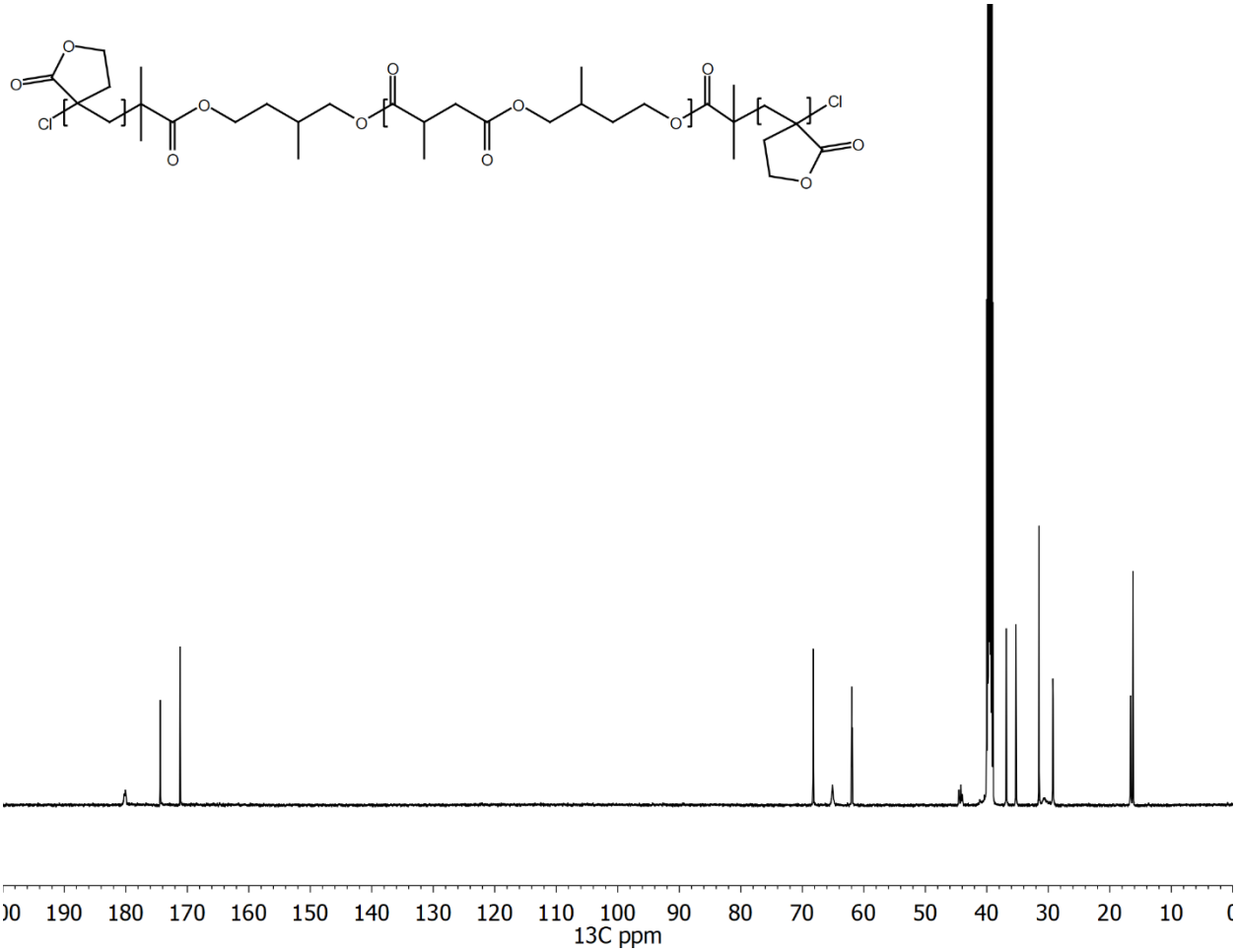


Figure S27. ^{13}C NMR spectra of PMBL-PMBMS-PMBL in DMSO-d_6.

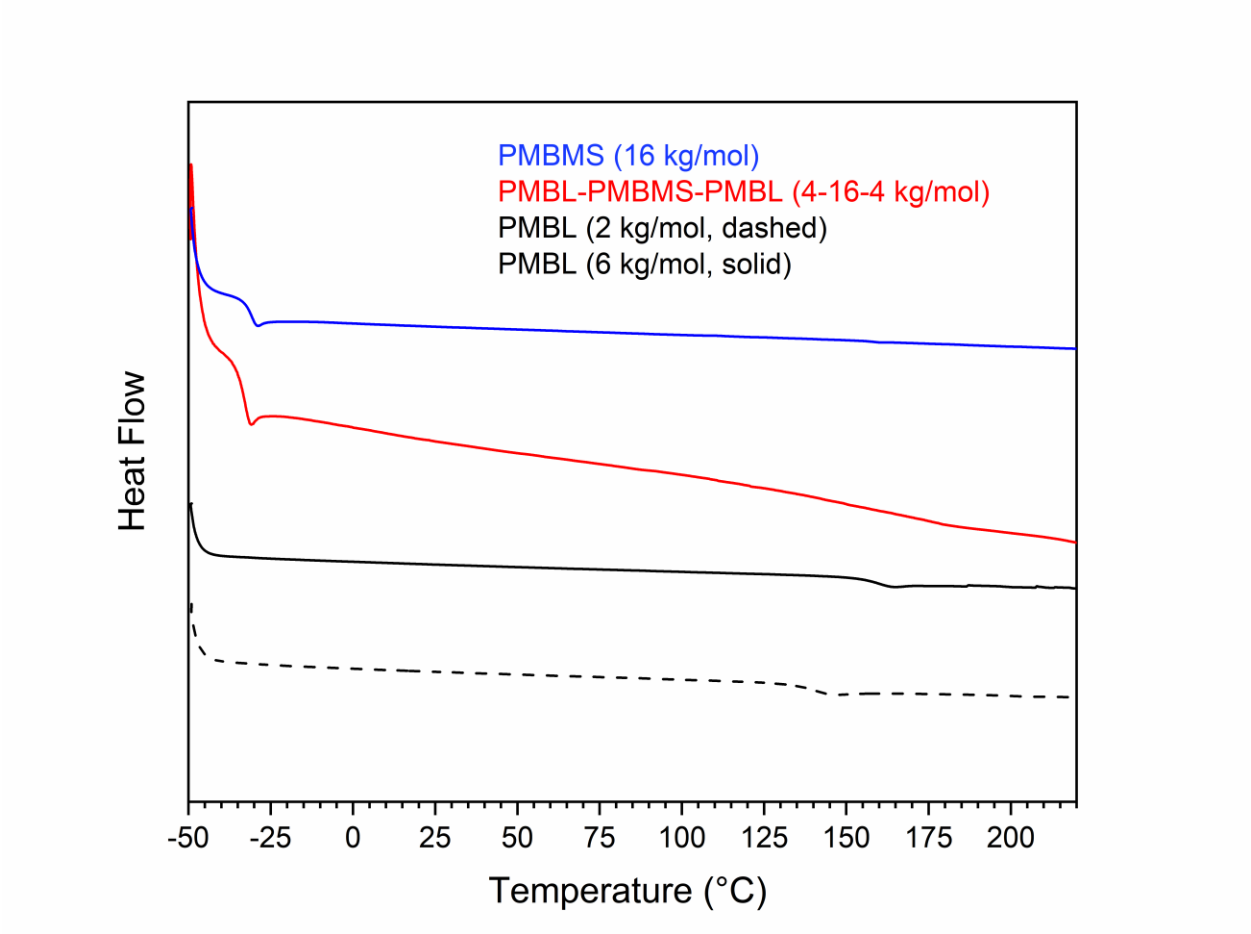


Figure S28. Differential scanning calorimetry heat flow vs. temperature (30 °C/min, second heat) traces of homo- or triblock polymers of PMBMS and PMBL, exo up.

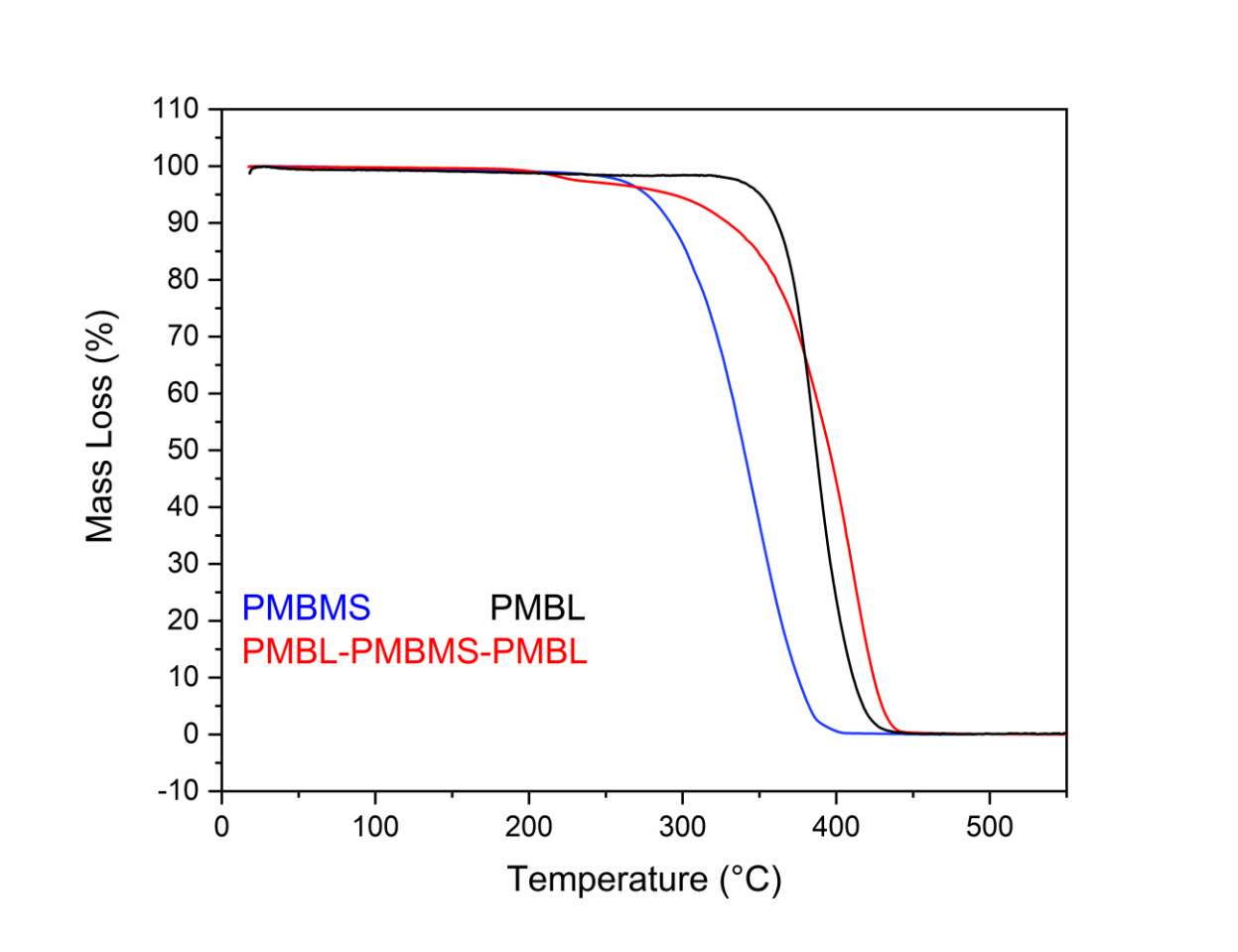


Figure S29. Thermal gravimetric analysis mass loss (%) vs. temperature (10 °C/min for PMBMS, 30 °C/min for PMBL-PMBMS-PMBL or PMBL) traces of homo- or triblock polymers of PMBMS and PMBL.

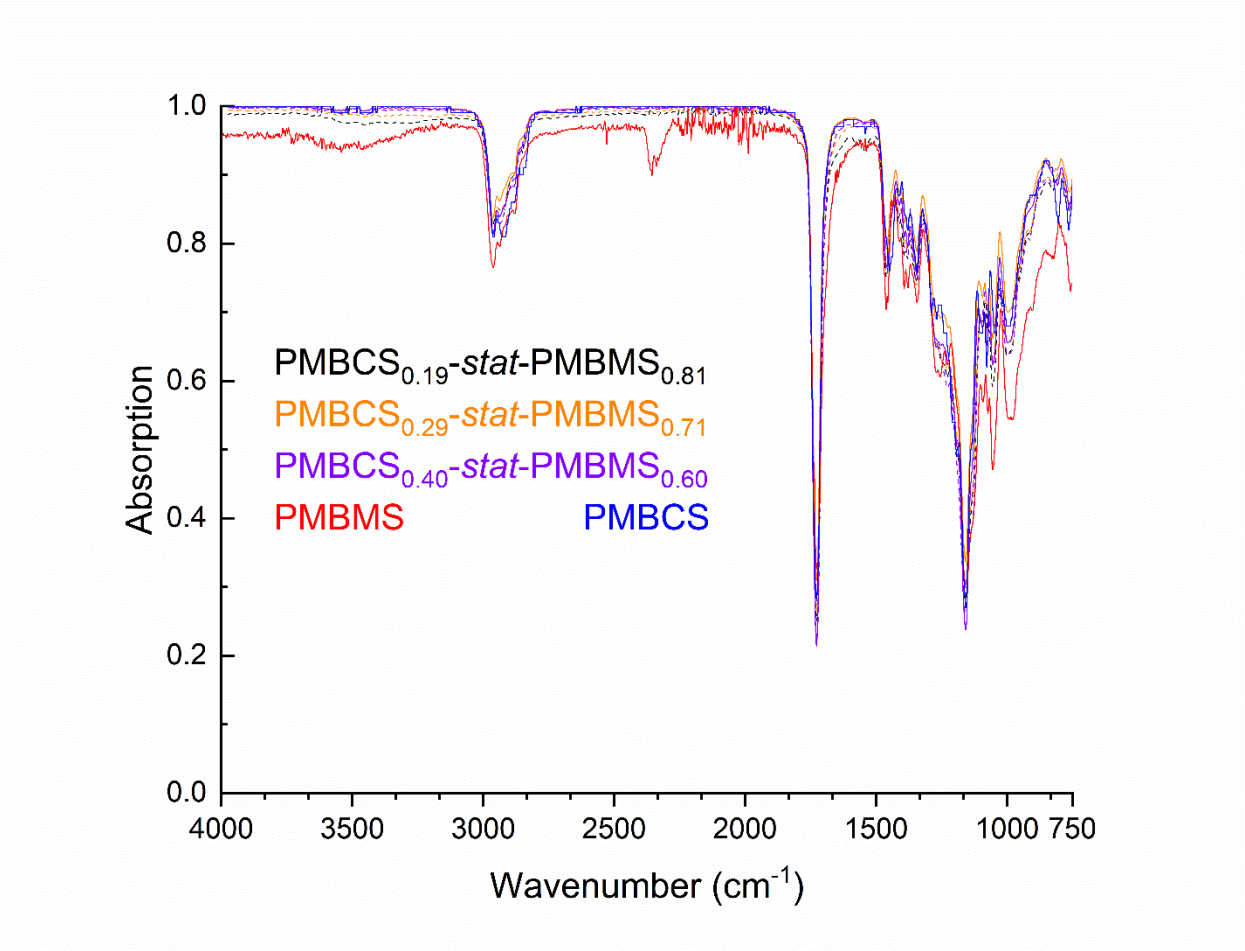


Figure S30. Superimposed infrared (IR) spectra of the PMBMS, PMBCS, and prepolymers (solid lines) or crosslinked thermosets (dashed lines).

Dynamic mechanical analysis for M_e

Dynamic analysis of PMBMS and PMBL were performed at various temperatures within the linear viscoelastic remine. For this analysis, an oscillatory stress is applied to the material and the sinusoidal stress response is measured; this affords a complex modulus that is decoupled into the in-phase (G') and out-of-phase (G") components. The loss tangent (tan(δ)), or the ratio of the viscous modulus G" to the elastic modulus G', was also calculated. For PMBL, data were collected at 250 and 260 °C (Figure S31) – above this temperature, PMBL began to degrade on the rheometer. For PMBMS, horizontal shift factors (a_T) were determined by aligning the loss

tangent curves and subsequently applied to each frequency sweep to generate a master curve via time-temperature superposition.

Using data from the master curve, the entanglement molar mass (M_e) was estimated using the following equation[9]

$$M_e = \frac{\rho RT}{G_N} \quad \textbf{Equation S8}$$

where ρ is the density, R is the universal gas constant, T is the temperature, and G_N is the plateau modulus. The plateau modulus was defined as the point during the rubbery plateau where the loss tangent (tan(δ)) is at a minimum, as this corresponds to the point at which the elastic modulus is most dominant.

Using a temperature of 20 °C, densities of 1.12 g/mL for PMBMS or 1.38 g/mL for PMBL, and G_N of 358820 Pa for PMBMS or 435430 Pa for PMBL, the entanglement molar masses were roughly estimated as 6.3 kg/mol for PMBMS and 10.6 kg/mol for PMBL.

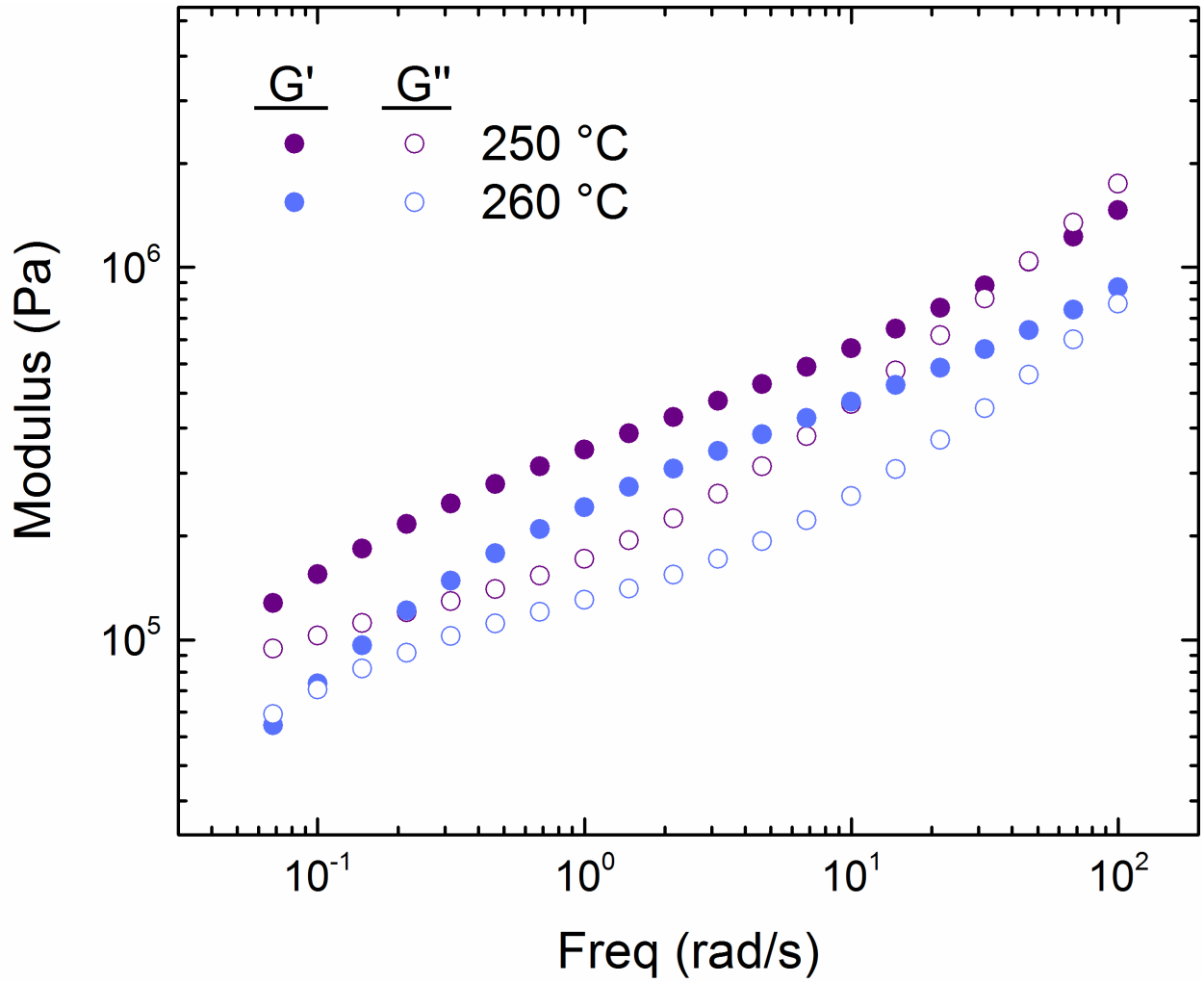


Figure S31. Dynamic frequency sweeps of PMBL, measuring the modulus as a function of frequency at 250 and 260 °C. PMBL degraded on the rheometer above 260 °C, and moduli vs frequency data was not acquired at higher temperatures. The plateau modulus, G_N, was roughly estimated to be 358820 Pa at the minimum tan(δ) value (M_e = 10.5 kg/mol). The strain used in these experiments was 0.05%.

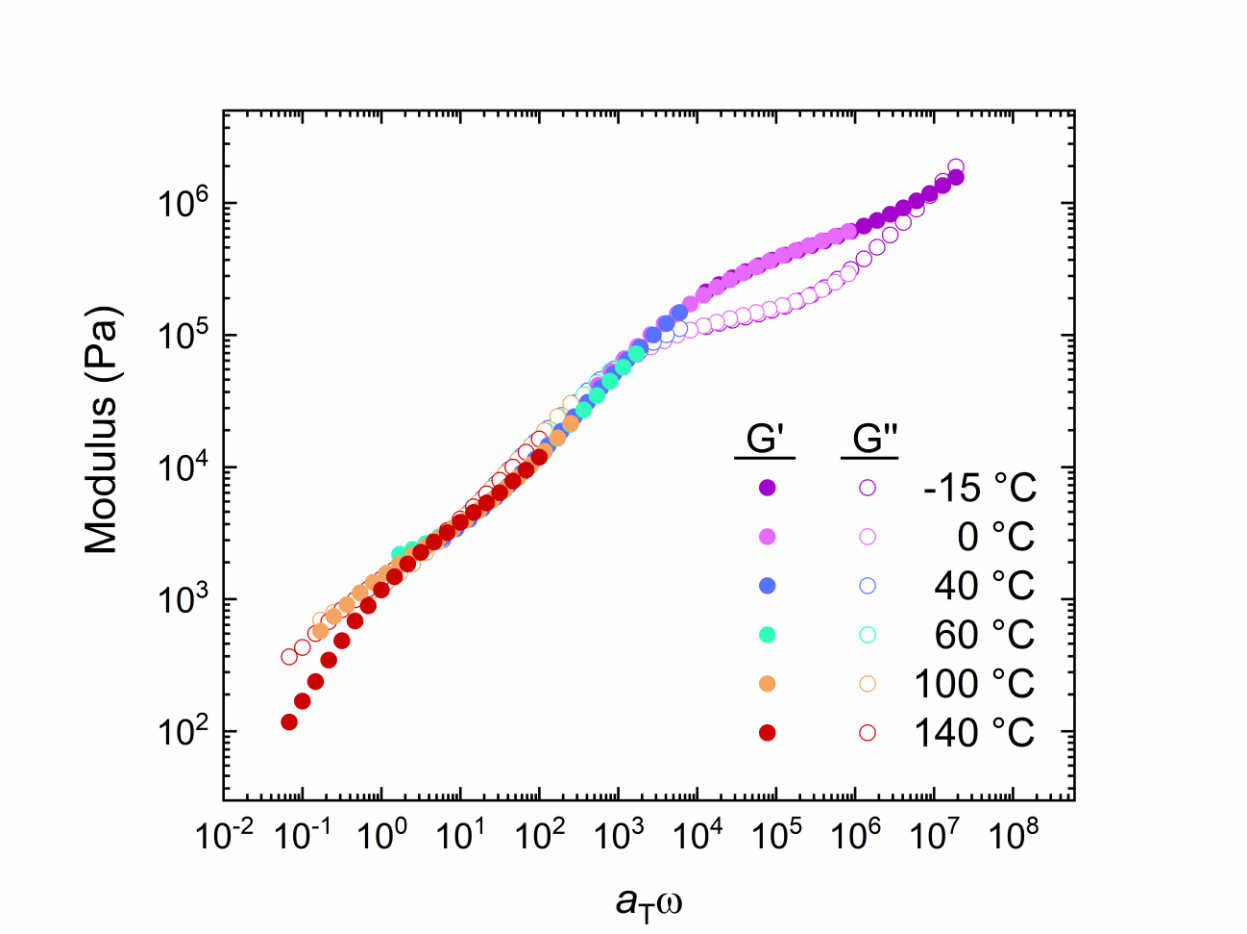


Figure S32.A master curve of PMBMS generated from applying shift factors (a_T) to dynamic frequency sweep data obtained at various temperatures. The plateau modulus, G_N, was roughly estimated to be 435000 Pa at the minimum tan(δ) value (M_e = 6.3 kg/mol). The strain used in these experiments was 0.05%.

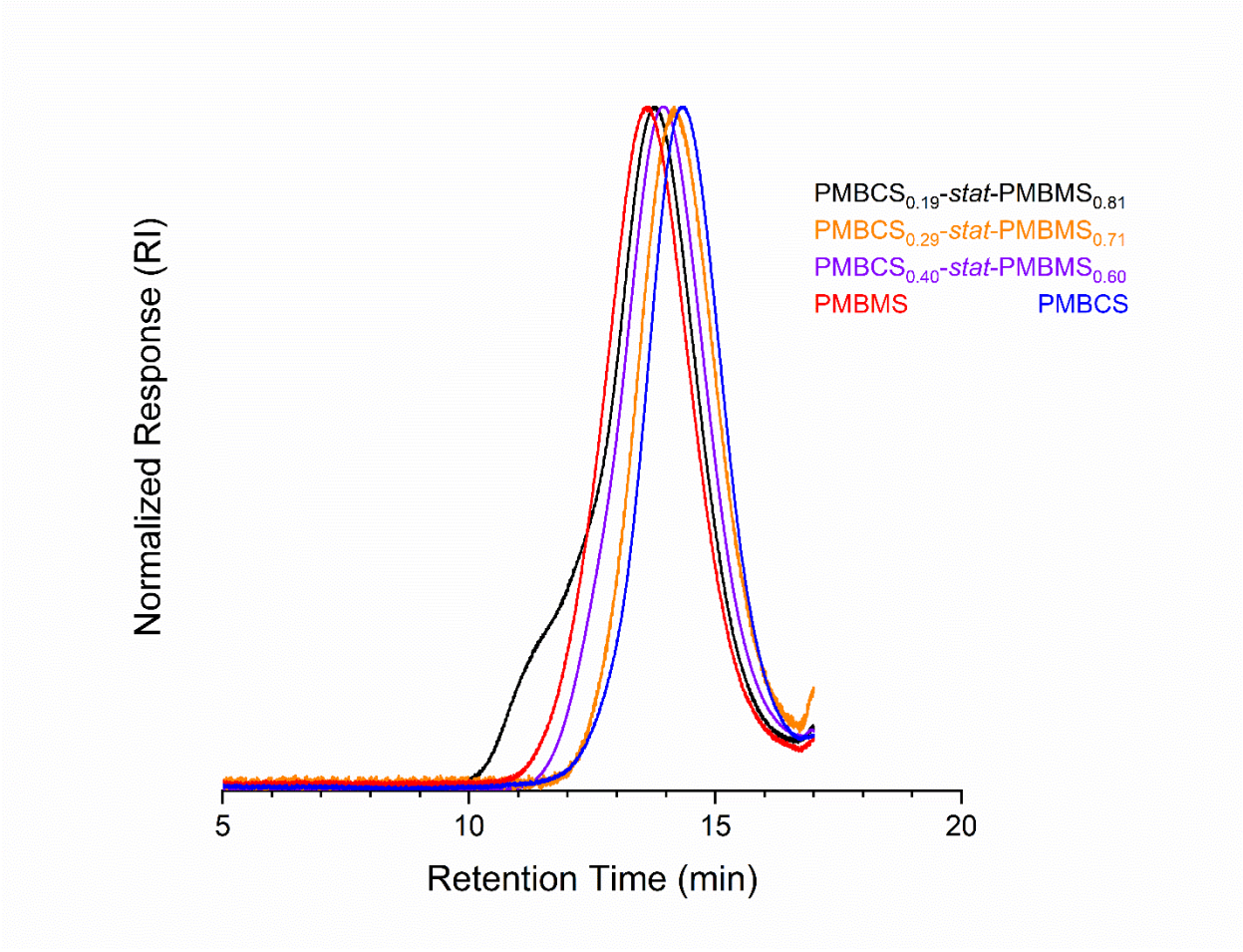


Figure S33. Size exclusion chromatography (SEC) traces for PMBMS, PMBCS, and PMBCS$_x$-*stat*-PMBMS$_{1-x}$ statistical terpolymers that served as thermoset prepolymers.

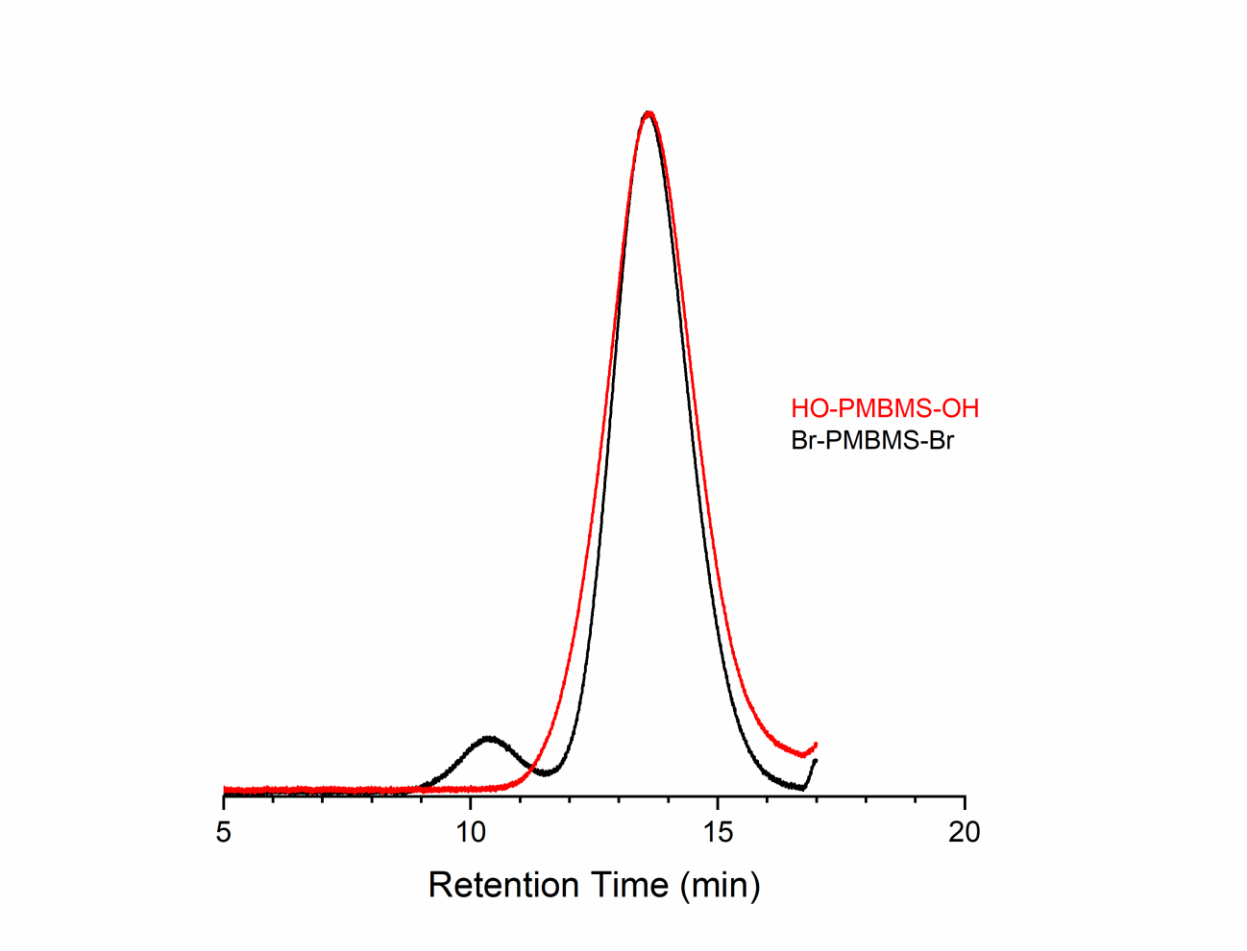


Figure S34. Size exclusion chromatography (SEC) for HO-PMBMS-OH (red) and Br-PMBMS-Br (black), indicating a high molecular weight tail in Br-PMBMS-Br after HO-PMBMS-OH functionalization.

Green Metrics

Green metrics[17] were evaluated for various small molecule transformations and polymerizations reported in the main text (see Table 5). Isolated yields were calculated in the usual way, as the ratio of the moles of product isolated from the moles of the limiting reagent starting material multiplied by one hundred. Atom economy (AE)[18] was calculated with the equation below.

$$AE\ (\%) = \frac{molecular\ weight\ of\ the\ desired\ product}{molecular\ weight\ of\ all\ the\ reactants}\ x\ 100 \quad \textbf{Equation S9}$$

Additionally, process mass intensity (PMI)[19] was estimated with the equation below.

$$PMI = \frac{total\ mass\ of\ materials\ used\ in\ a\ process\ (kg)}{mass\ of\ isolated\ product\ (kg)} \quad \textbf{Equation S10}$$

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