SUPPORTING INFORMATION

Multiblock Copolymers by Thiol Addition Across Norbornene

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Experimental

Materials and Instruments

Dihydroxyl-terminated poly(ethylene oxide) (PEO) (M_n = 4.6 kDa, Đ = 1.03), dihydroxyl-terminated polydimethylsiloxane (PDMS) (M_n = 4.5 kDa, Đ = 1.72), dihydroxyl-terminated polystyrnene (PS) (M_n = 4.8 kDa, Đ = 1.14), dithiol-terminated PEO (M_n = 4.5 kDa, Đ = 1.04), 5-norbornene-2-carboxylic acid (99% *exo*) (NB), triphenyl phosphine (PPh$_3$), diisopropyl azodicarboxylate (DIAD), 1,8-octanedithiol (ODT), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (PI), tetrahydrofuran (THF), dichloromethane (DCM), and methanol (MeOH) were purchased from Alfa Aesar, Sigma Aldrich, Acros Organics, Gelest, Polymer Source or Laysan Bio and used without further purification unless otherwise stated.

^{1}H NMR spectra were recorded at 300 MHz, using a Bruker DPX-300 NMR spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Gel permeation chromatography (GPC) was performed using Agilent 1260 series system with a PL gel 5 μm guard column, two 5 μm analytical Mixed C columns and a 5 μm analytical Mixed D column (Agilent), incubated to 40 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration and toluene was used for the flow marker. Thermogravemetric analysis (TGA) measurements were taken using a TA Instruments TGA Q500 with a heating rate of 10 °C/min up to 600 °C under nitrogen. Differential Scanning Calorimetry (DSC) measurements were taken using a TA Instruments DSC Q200 (two cycles). Samples were analyzed using a heating rate of 10 °C/min under a flow of nitrogen (50 mL/min). Atomic force microscope (AFM) images were obtained with a Veeco Dimension 3100 Scanning Probe Microscope in the tapping mode with silicon tips. SAXS samples were mounted between two Kapton® films. SAXS patterns were obtained from an Osmic MaxFlux Cu Kα X-ray source

with a wavelength of 1.54 Angstroms and a two-dimensional gas-filled wire array detector (both

Molecular Metrology, Inc.) at a distance of 1.476 m from the sample. The raw data were

calibrated against the peak position of a silver behenate standard, which has a scattering vector of

$q = 1.076$ 1/nm. Two-dimensional images were reduced to the one-dimensional form using

angular integration. Domain spacings were calculated from the principal scattering maxima (q*)

with $d = 2\pi/q*$.

Functionalization of Precursor Polymers

PEO and PDMS precursors were prepared by previously described methods.[1] To prepare

the polystyrene precursor, α,ω-dihydroxy terminated PS(4.0 g, 0.833 mmol), NBCOOH (0.345

g, 2.5 mmol) and PPh$_3$ (0.656 g, 2.5 mmol) were dissolved in THF (35 mL), which had been pre-

dried over calcium hydride, distilled from sodium and benzophenone, equilibrated in an ice bath

and purged with N$_2$. DIAD (0.506 g, 2.5 mmol) was dissolved in dry THF (5 mL) and

equilibrated in an ice bath, and purged with N$_2$. The DIAD solution was added drop wise to the

stirring polymer solution under N$_2$ flow. After the addition, the N$_2$ line was removed and the

solution was allowed to slowly warm up to room temperature as it stirred overnight. The product

was precipitated three times into MeOH and collected by filtration at 87% yield. Figure S1

represents the NMR of the resulting product in CDCl$_3$. The reaction gave 91% conversion by

comparing the alkene peaks at 6.09 ppm to the methylene groups next to the ether linkage at 3.74

ppm.
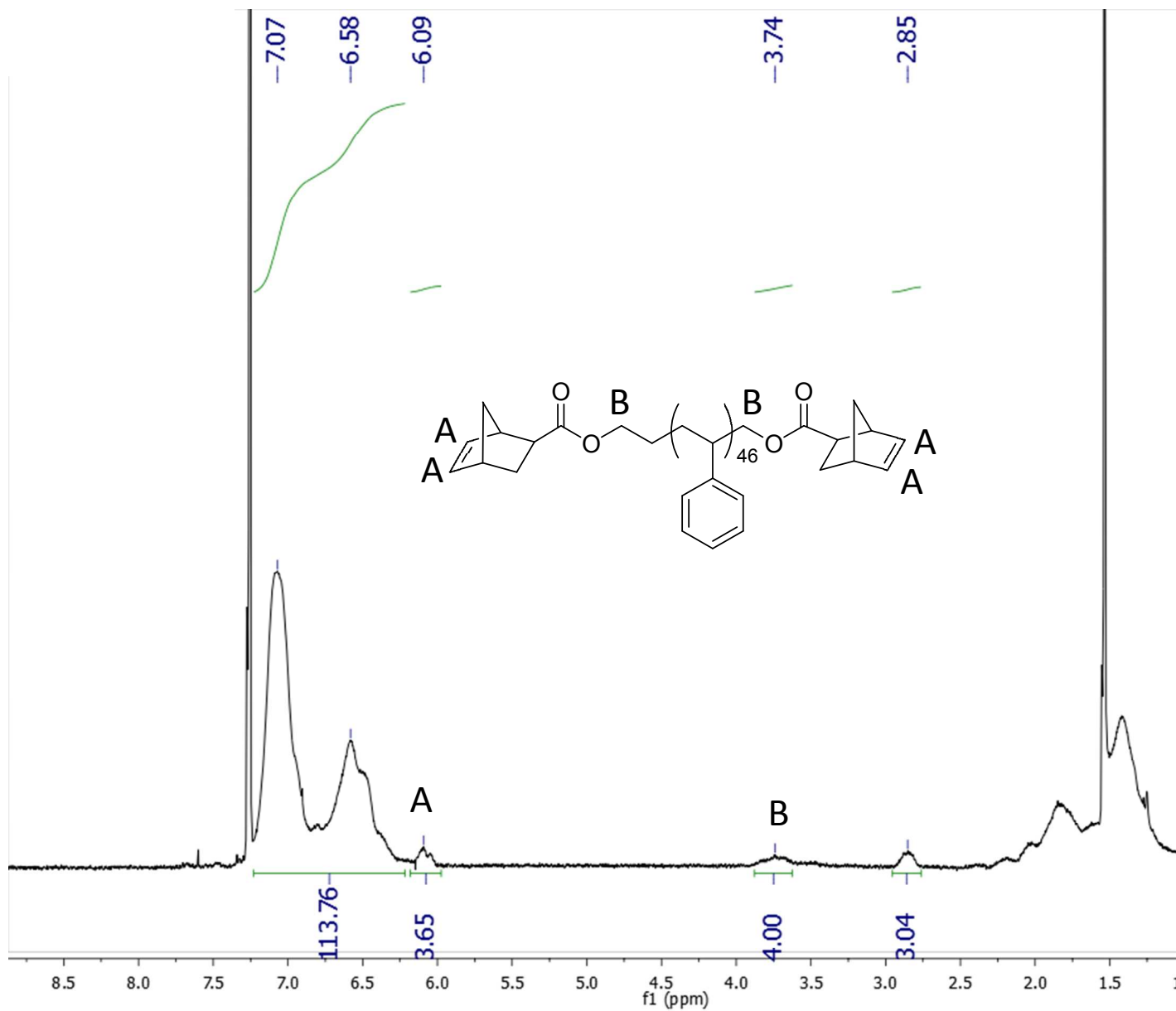
Figure S1. ^{1}H-NMR characterization of norbornene end-functionalized PS.

## Random Multiblock Synthesis (R2 and R3)

Norbornene-functionalized PEO (50.0 mg, 10.3 μmol), PS (50.0 mg, 9.92 μmol), and 1-8 octanedithiol (ODT) (3.77 μL, 20.5 μmol) were dissolved in PI solution (0.372 mL, concentration of 5.37 mg/mL in THF) and THF (0.628 mL). An equimolar ratio between the

norbornene end groups on the polymer and the thiol functional groups was used. The concentration of the polymer in solution was 100 mg/mL. The amount of PI used was 2 weight % of the polymer starting material. The solid polymer was dissolved in the solution using a heat gun for several seconds. Nitrogen gas was bubbled through solution for 30 seconds. The solution was cured under UV light (wavelength=365 nm) for 1.5 hours. The solution was then precipitated in cyclohexane (10 mL) because did not dissolve the PEO and dissolved the PS slowly. Once stirred for several minutes, the solution was cooled in the -20 °C freezer for 30 minutes. The precipitated polymer was separated from the solvent using gravity filtration. The filter paper was left to dry in the hood and vacuum chamber overnight.

PDMS (31.1 µL, 6.67 µmol), PS (33.6 mg, 6.67 µmol), norbornene-functionalized PEO (32.3 mg, 6.67 µmol), and ODT (3.68 µL, 20.0 µmol) were dissolved in PI solution (0.357 mL, concentration of 5.37 mg/mL in THF), and THF (0.245 mL). The initial concentration of the polymer in solution was 100 mg/mL. The amount of PI used was 2 weight % of the polymer starting material. Nitrogen gas was bubbled through the solution for 30 seconds. The solution was cured under UV light (wavelength=365 nm) for 1.5 hours. The solution was then precipitated in methanol (10 mL) and stirred. The vial was placed on a rotary evaporator to remove excess solvent and left in the vacuum chamber to dry overnight at 80 °C.
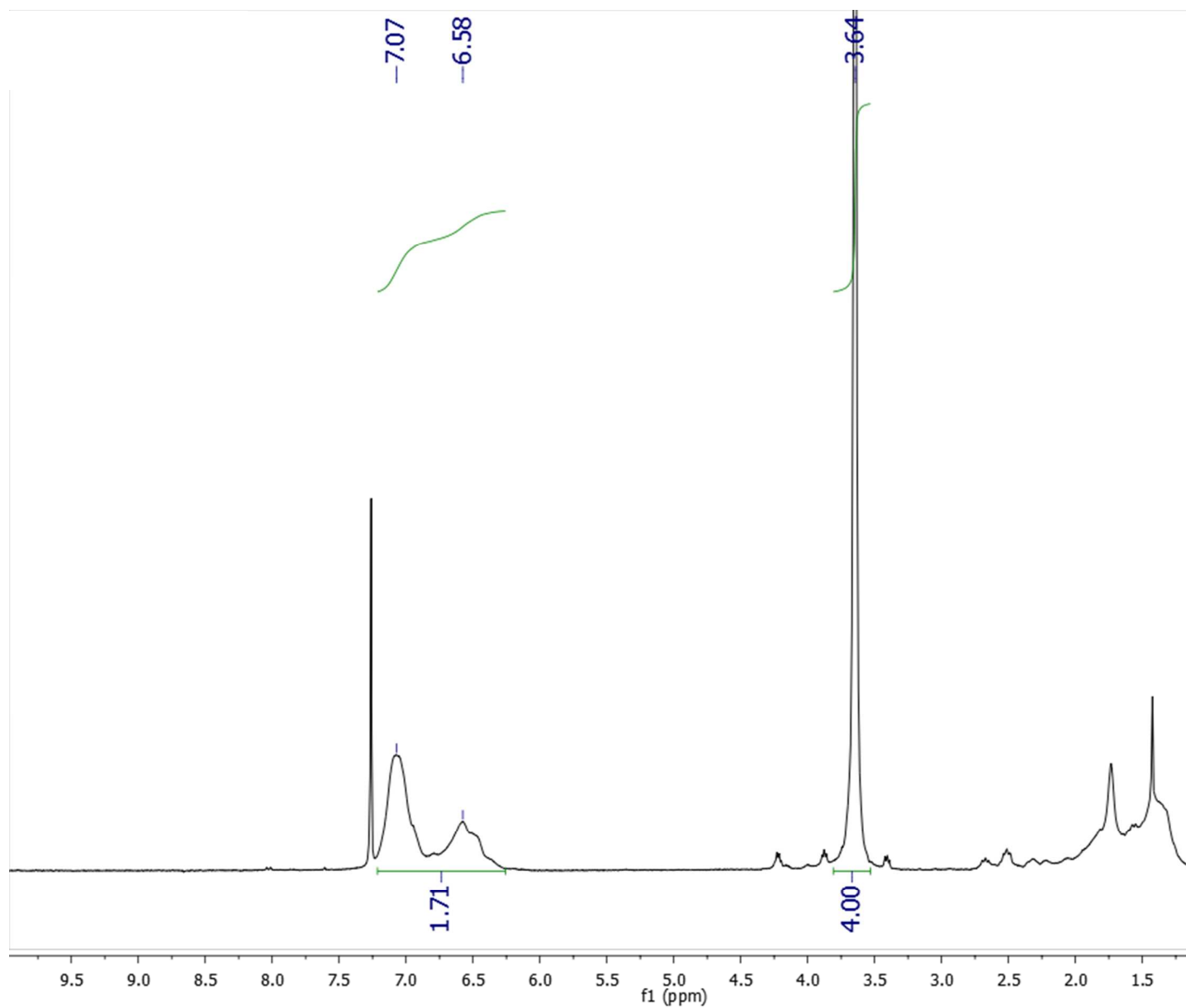
Figure S2. ^{1}H NMR of multiblock copolymer R2 showing approximately equal incorporation of both homopolymers (55 wt% PEO, 45 wt % PS) and full conversion of norbornene end groups by the absence of the peak at 5.98 ppm.
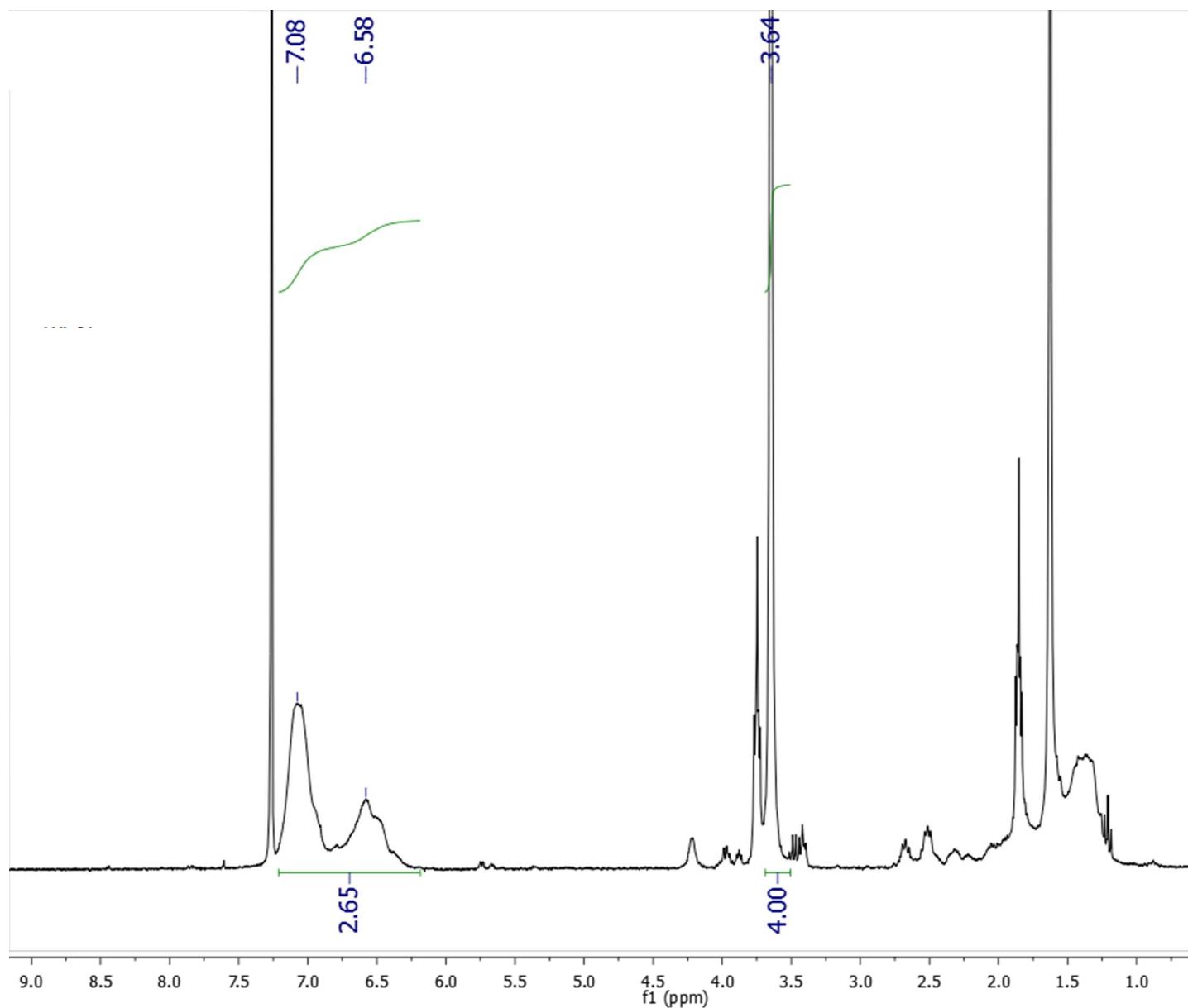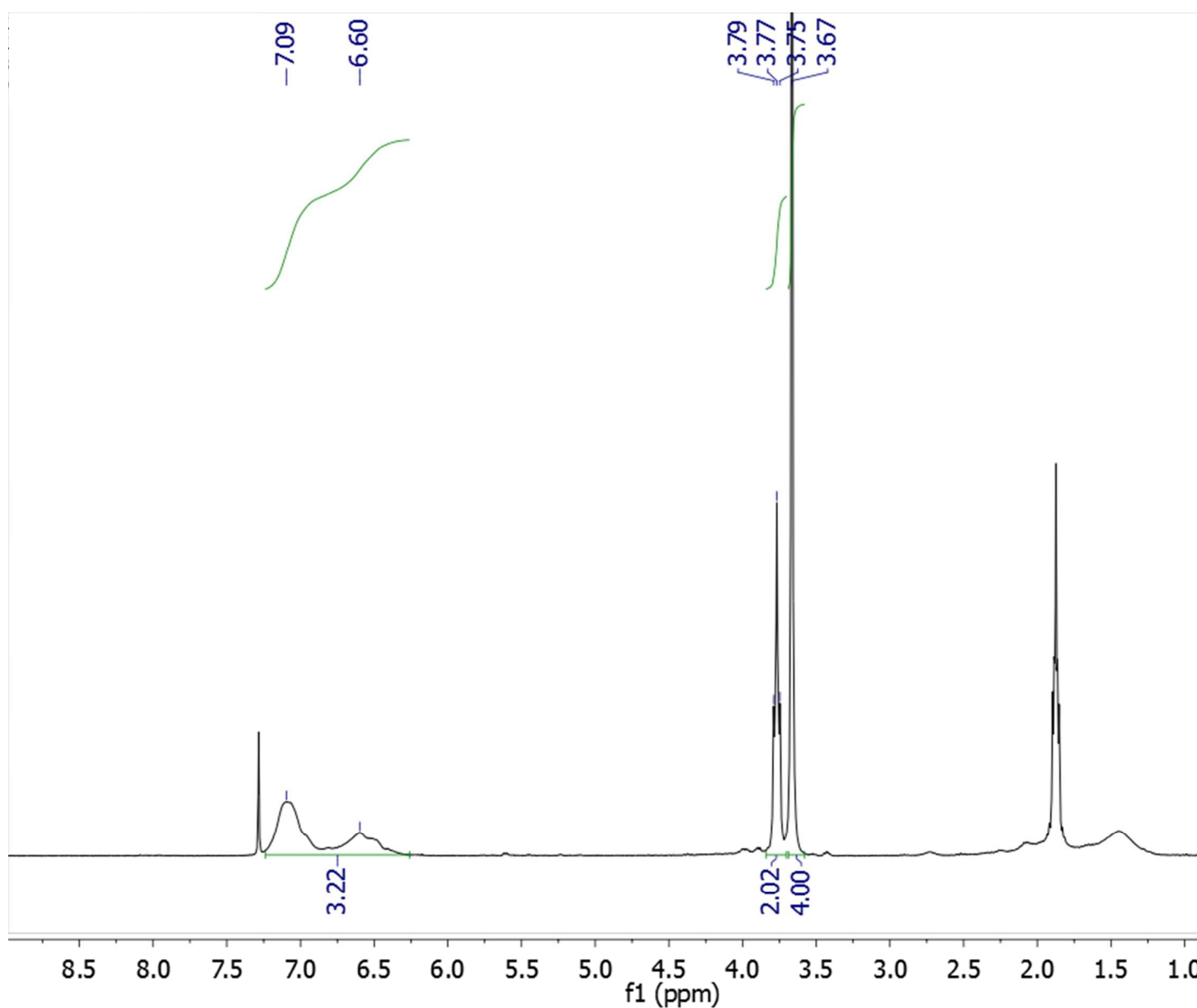
Figure S3. ^{1}H-NMR of multiblock copolymer R3 showing incorporation of all homopolymer blocks (24 wt% PEO, 29 wt% PS and 47 wt% PDMS) and full conversion of norbornene end groups by the absence of a peak at 5.98 ppm.

Alternating Multiblock Synthesis (A2)

PS (100 mg, 19.8 μmol) and di-thiol PEO (67.5 mg, 19.9 μmol) were dissolved in PI solution (0.624 mL, concentration 5.37 mg/mL) and THF (1.05 mL) for a polymer concentration

of 100 mg/mL. The solution was degassed and stirred overnight under 365 nm UV exposure. The newly formed multiblock copolymer was then precipitated in diethyl ether, filtered and dried overnight under vacuum at 80 °C. Samples for ^{1}H NMR and GPC were prepared in CDCl$_3$ and THF, respectively. Thin films for AFM were prepared by spin coating a solution of 12 mg/mL multiblock copolymer in toluene at 2500 r.p.m. for one minute, followed by thermal annealing at 130 °C for 72 hours.

Figure S4. ^{1}H NMR of multiblock copolymer A2 showing incorporation of both homopolymer

blocks (40 wt% PEO and 60 wt% PS) and full conversion of norbornene end groups by the
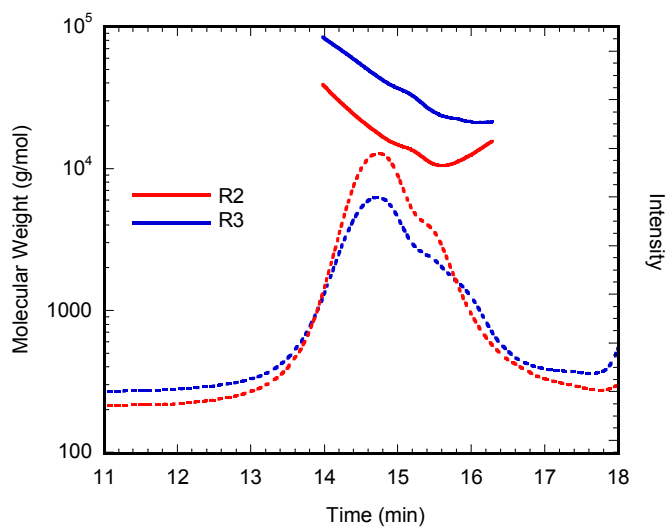
absence of a peak at 5.98 ppm.

GPC

Table S1. Precursor Polymers. Values are taken from PS standards in THF.

Homopolymer	M_n (g/mol)	Đ
PEO	6800	1.03
PS	8600	1.14
PDMS	8900	1.24
PEO-thiol	4500	1.04

Table S2. Multiblock Copolymers. Values are taken from PS standards in THF.

| Sample	M_n (g/mol)	Đ	n (avg number of blocks)
R2	29,700	1.7	3.7
R3	31,800	1.4	3.9
A2	29,300	1.6	4.5

Figure S5. MALLS GPC of **R2** (red) and **R3** (blue). The dashed lines give the intensity of the

refractive index detector while the solid lines give absolute molecular weight based on dn/dc

calculated for each sample. **R2** has an M_n 16,000 g/mol and an M_w of 18,000 g/mol while **R3**

has an M_n of 35,000 g/mol and an M_w of 41,000 g/mol.

Table S3. Volume Fractions of Multiblock Copolymers. PEO density was assumed to be 1.13

g/mL, based on standard PEO crystallinity.

| Sample	%PS	%PEO	%PDMS
R2	52%	48%	N/A
R3	35%	31%	34%
A2	61%	39%	N/a

Thermal Analysis
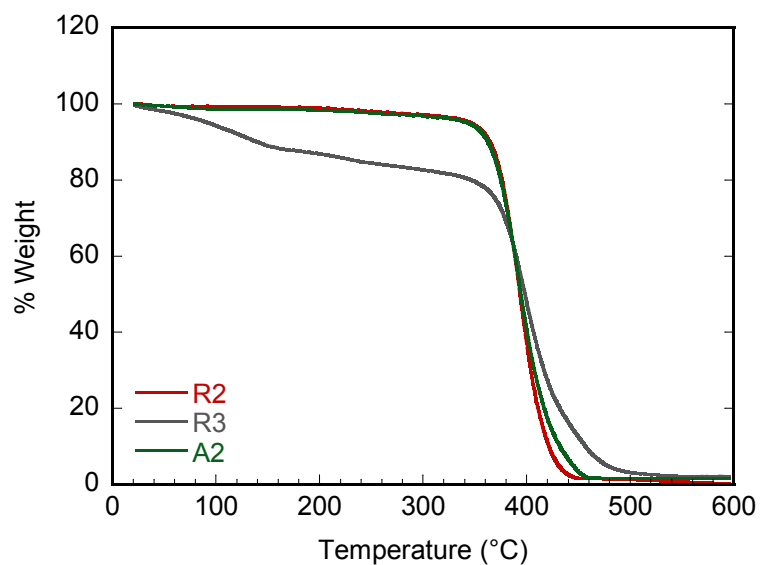
Figure S6. TGA of multiblock copolymers. **R2** and **A2** have high thermal stability which would

allow for thermal annealing in the future.
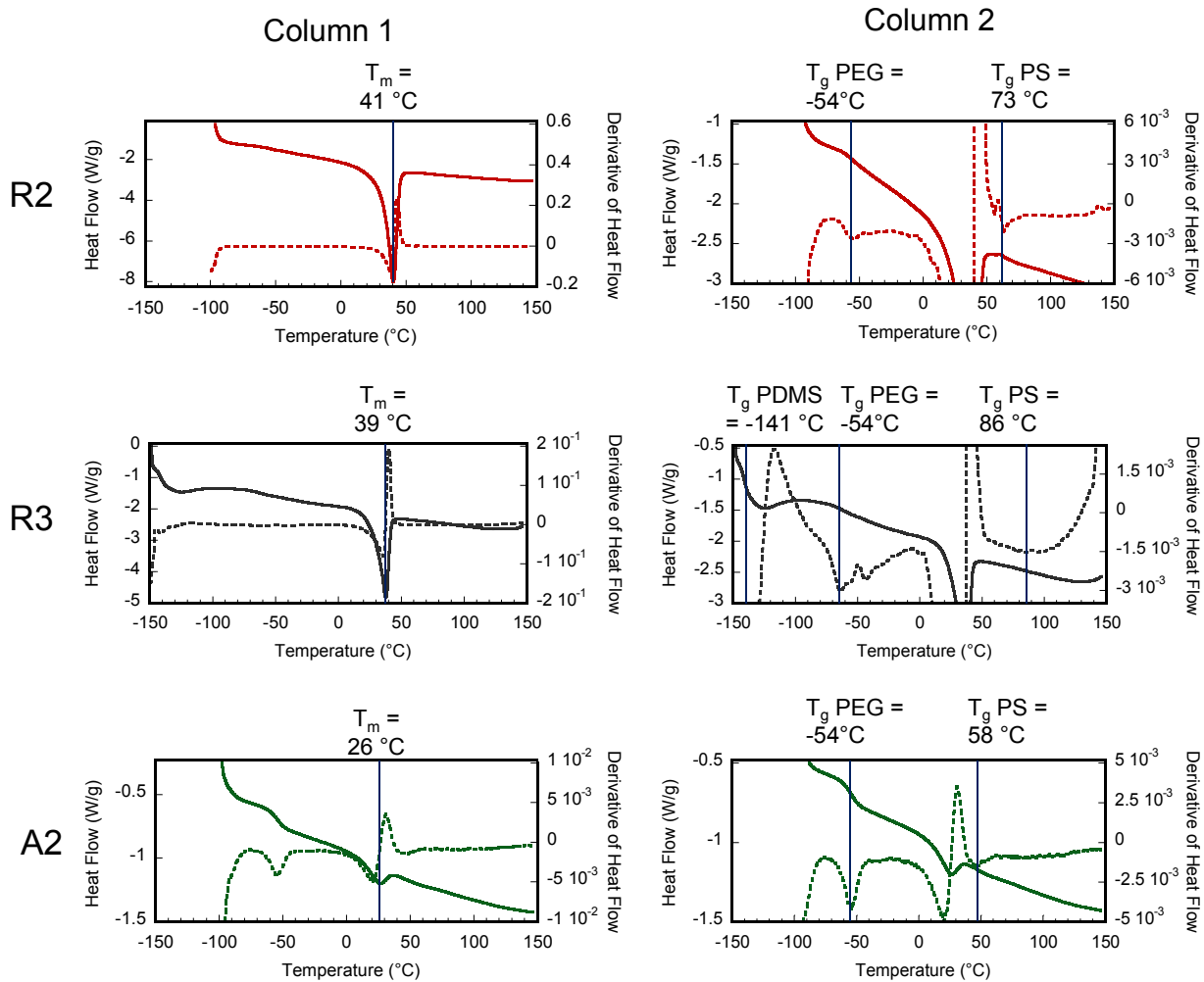
Figure S7. DSC traces for each of the multiblock copolymers. Column 1 shows heat flow vs temperature and the derivative of heat flow vs. temperature full scale while Column 2 expands the Y-axis for clarity.

SAXS
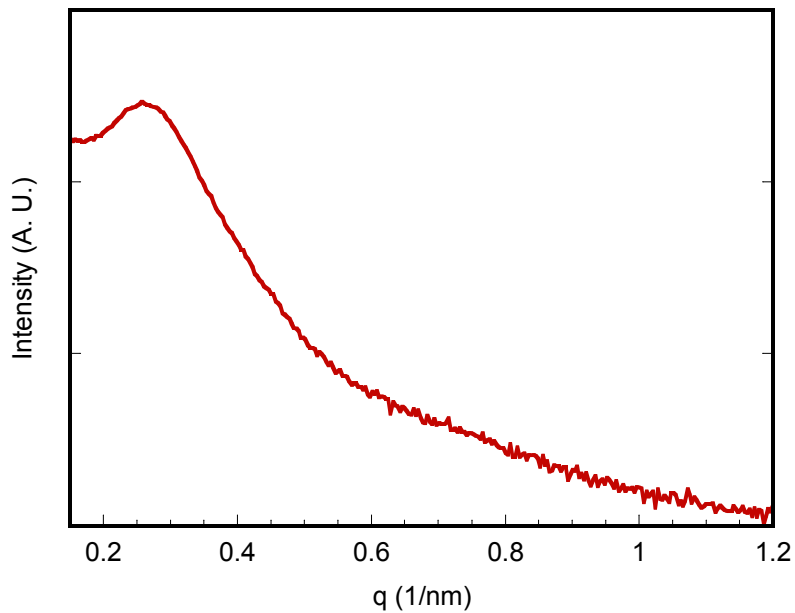
Figure S8. Small angle x-ray scattering from multiblock **R2**. The broad peak and absence of

higher order peaks show that this sample is disordered. The domain spacing of 24 nm was found

using d = 2π/q*.