Electronic Supporting Information

Expanding the poly(2-oxazoline) block copolymer possibilities through nitroxide mediated polymerisation

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Experimental

Materials. 2-Ethyl-2-oxazoline 99+% (Acros Organics, EtOx) was dried over calcium hydride and distilled under reduced pressure prior to use and stored under N_2. Methyl p-toluenesulfonate 98% (Aldrich, MeTos) was distilled under reduced pressure and stored under nitrogen. Dry dichloromethane 99+% (DCM) was purchased from Acros Organics. Tetrahydrofuran (THF), N,N-diisopropylethyl amine (DIPEA) Styrene (S), pentafluorostyrene (PFS), 4-vinyl pyridine (4VP), 4-vinyl benzyl chloride (4VBC), isobornyl acrylate (IBOA), tert-butyl acrylate (*t*BA), poly(ethylene glycol) methyl ether acrylate (PEGMEA), 4-hydroxybutyl acrylate (4HBA), isoprene (I), myrcene (M), farnesene (F), ocimene (O), N-isopropyl acrylamide (NIPAAm), N-diacetone acrylamide (DAAm), N,N-diethyl acrylamide (DEAAm) and N-(2-hydroxyethyl acrylamide) (HEAAm) were all purchased from Sigma Aldrich and used as received.

Synthesis of PEtOx$_{19}$-SG1 macroinitiator. EtOx (5.00 g, 50.44 mmol, 20 eqv), MeTos (381 µL, 2.52 mmol, 1 eqv) and DCM (12.50 mL) were added to a sealed microwave vial with stirrer

bar and degassed with N_2 for 15 minutes. A small aliquot was taken to calculate [M]:[I] via ^{1}H NMR. The vial was then placed in an oil bath and the reaction proceeded for 90 minutes at 100 ˚C stirring at 600 rpm. After 90 minutes, the vial was removed from the oil bath, allowed to cool to room temperature and placed under a positive pressure of N_2 whilst a small aliquot was taken for monomer conversion and molecular weight analysis. Next, SG1-MAMA (3.84 g, 10.08 mmol, 4 eqv), DIPEA (1.30g, 10.08, 4 eqv) and DCM (7.00 mL) were added to the microwave vial with stirring. The nitrogen line was removed, and the microwave vial was placed back into the oil bath for 18 hours set at 40 ˚C. After the reaction was completed, the microwave vial was cooled to room temperature and a relief needle was inserted into the seal to release the pressure from the vial. The reaction mixture was concentrated under vacuum and precipitated twice into cold ether. The product was redissolved in minimum DCM and washed with 2 x 20mL deionised water and 1 x 20 mL brine. The organic layer was dried with $MgSO_4$, filtered and dried under reduced pressure to yield the product P(EtOx)$_{19}$-SG1 (2.92 g, off-white powder).

Typical synthesis of PEtOx-poly(styrenic/acrylate/diene/acrylamide). PEtOx$_{19}$-SG1 (100 mg, 0.044 mmol, 1 eqv), monomer (~100 eqv) and THF (pre-calculated volume to form a 1.0, 1.5, 2.0 or 2.5M solution with respect to the monomer, see **Table 1**) were all added to a sealed microwave vial with stirrer bar and degassed with N_2 for 15 minutes. A small aliquot was taken to calculate [M]:[I] via ^{1}H NMR. The vial was then placed in an oil bath set at 110 ˚C for 24 hours stirring at 600 rpm. After 24 hours the vial was removed from the oil bath and cooled to room temperature. A small aliquot was taken for ^{1}H NMR and GPC analysis. Apart from **PI**, **PF**, and **PO**, each diblock copolymer was isolated from non-endcapped homopolymer via one of the following methods in accordance with **Table S1**.

***Purification via precipitation*.** The crude reaction mixture was precipitated twice into the chosen solvent (**Table S1**) that is selective for the homopolymer and THF but not the diblock copolymer. The copolymer was then dried under reduced pressure to yield the purified diblock copolymer.

Purification via liquid-liquid extraction. The crude reaction mixture was dissolved in DCM (10 mL) and washed with deionised water (6 x 10 mL) The organic layer was dried with $MgSO_4$, filtered and dried under reduced pressure to yield the purified diblock copolymer.

Purification via dialysis. The crude reaction mixture was placed in a SpectraPor® 1-5 RC dialysis tubing with a molecular weight cut-off of 3.5 kD and dialysed against deionised water

for 5 days. The dialysis water was changed after the first 6 hours and then once every 24 hours. The polymer solution was then freeze dried to yield the purified diblock copolymer.

^{1}H Nuclear Magnetic Resonance (NMR). All spectra were recorded on a Bruker Advance III HD 400 MHz. $CDCl_3$ was used as the solvent for all pre-polymerization samples. $CDCl_3$ was used as the solvent for all pure samples except for P4HBA and PHEAAm as DMSO-D_6 was used for these samples. The residual $CHCl_3$ or DMSO served as a reference peak for the chemical shift, δ. Data analysis was performed using TopSpin 3.2 software.

Gel Permeation Chromatography (GPC). For all samples except P4VP, P4HBA, PHEAAm, measurements were performed using THF (2% TEA and 0.01% BHT) as the eluent. The Agilent Technologies 1260 Infinity instrument was equipped with a refractive index (RI) and 308 nm UV detectors, a PLgel 5 μm guard column, and a PLgel 5 μm mixed D column (300 × 7.5 mm). Samples were run at 1 mL min^{-1} at 40 °C. Poly(methyl methacrylate) standards (Agilent PMMA calibration kits, M-M-10 and M-L-10 MW range 500-120,000) were used for the calibration. Before injection (100 μL), the samples were filtered through a PTFE membrane with 0.2 μm pore size. For P4VP, P4HBA and PHEAAm, measurements were performed using DMF (5 mM NH_4BF_4) as the eluent. The Agilent 1260 Infinity II-MDS instrument was equipped with a refractive index (RI), viscometer, light scattering (LS), variable wavelength detectors and two PLgel Mixed-D columns. The instrument was calibrated with linear PMMA standards (500–1,500,000 g mol−1). The flow rate was 1 mL min−1 and temperature was set to 50 ˚C. All samples were passed through 0.2 micron nylon filters prior to GPC measurements. The data was determined by conventional calibration using Agilent GPC/SEC software and plotted in OriginPro 2023b.

Table S1. List of the purification technique for each PEtOx-based diblock copolymer synthesised via NMP.

Polymer	Purification Method
PS	Precipitation (MeOH)
P4VP	Precipitation (MeCN)
PPFS	Precipitation (MeCN)
P4VBC	Precipitation (MeCN)
P*t*BA	Liquid-liquid extraction (DCM/H_2O)
PIBOA	Precipitation (MeCN)
PMePEGA	Dialysis

P4HBA	Precipitation (DCM)
PI	Rotary evaporation
PM	Precipitation (MeCN)
PO	Low O conversion – unable to isolate
PF	Low F conversion – unable to isolate
PNIPAAm	Dialysis
PDAAm	Liquid-liquid extraction (DCM/H_2O)
PDEAAm	Dialysis
PHEAAm	Dialysis

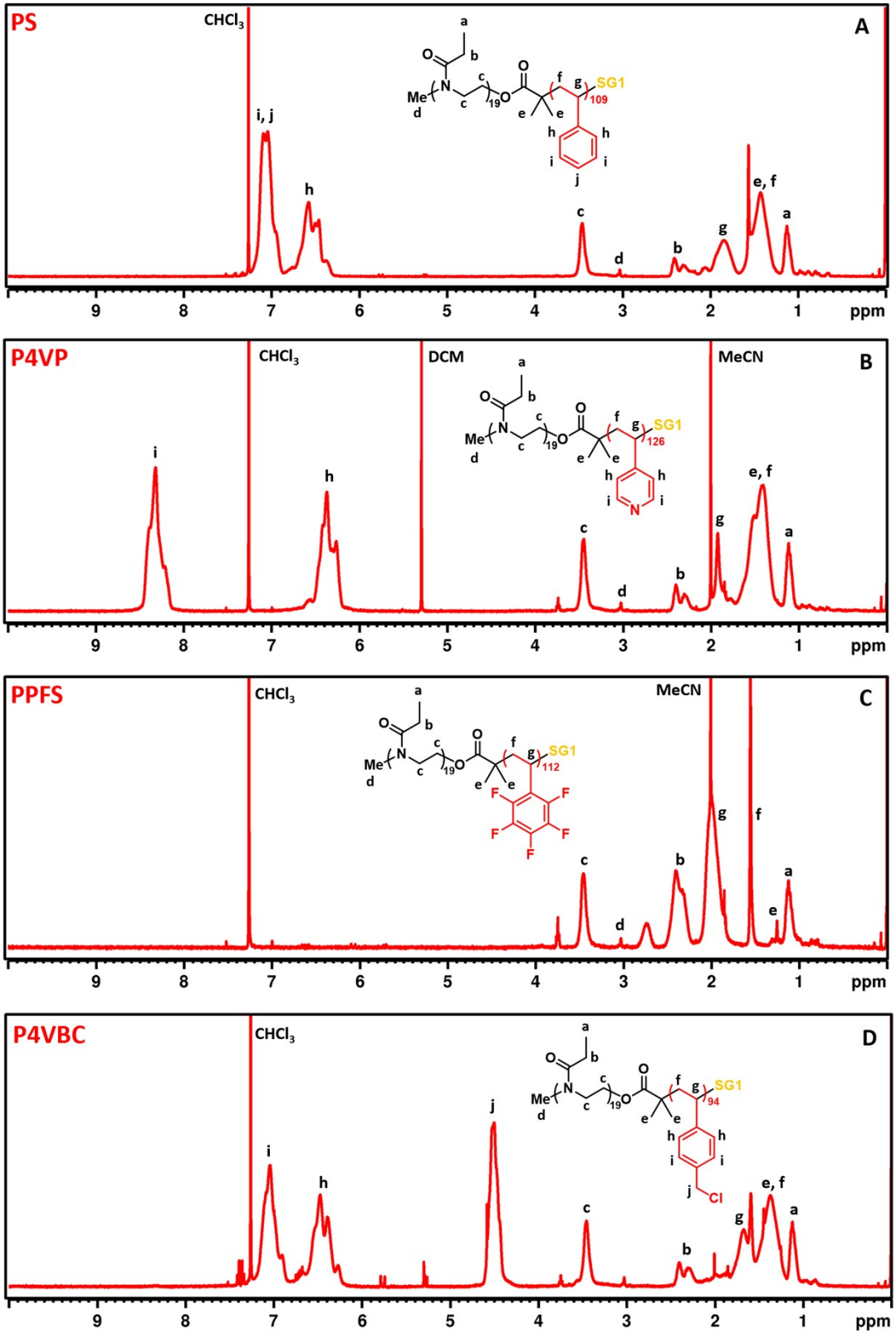

Figure S1. ^{1}H NMR spectra of the purified PEtOx-*b*-vinyl diblock copolymers **A**) PS **B**) P4VP **C**) PPFS and **D**) P4VBC. 400 MHz, 298K, $CDCl_3$.

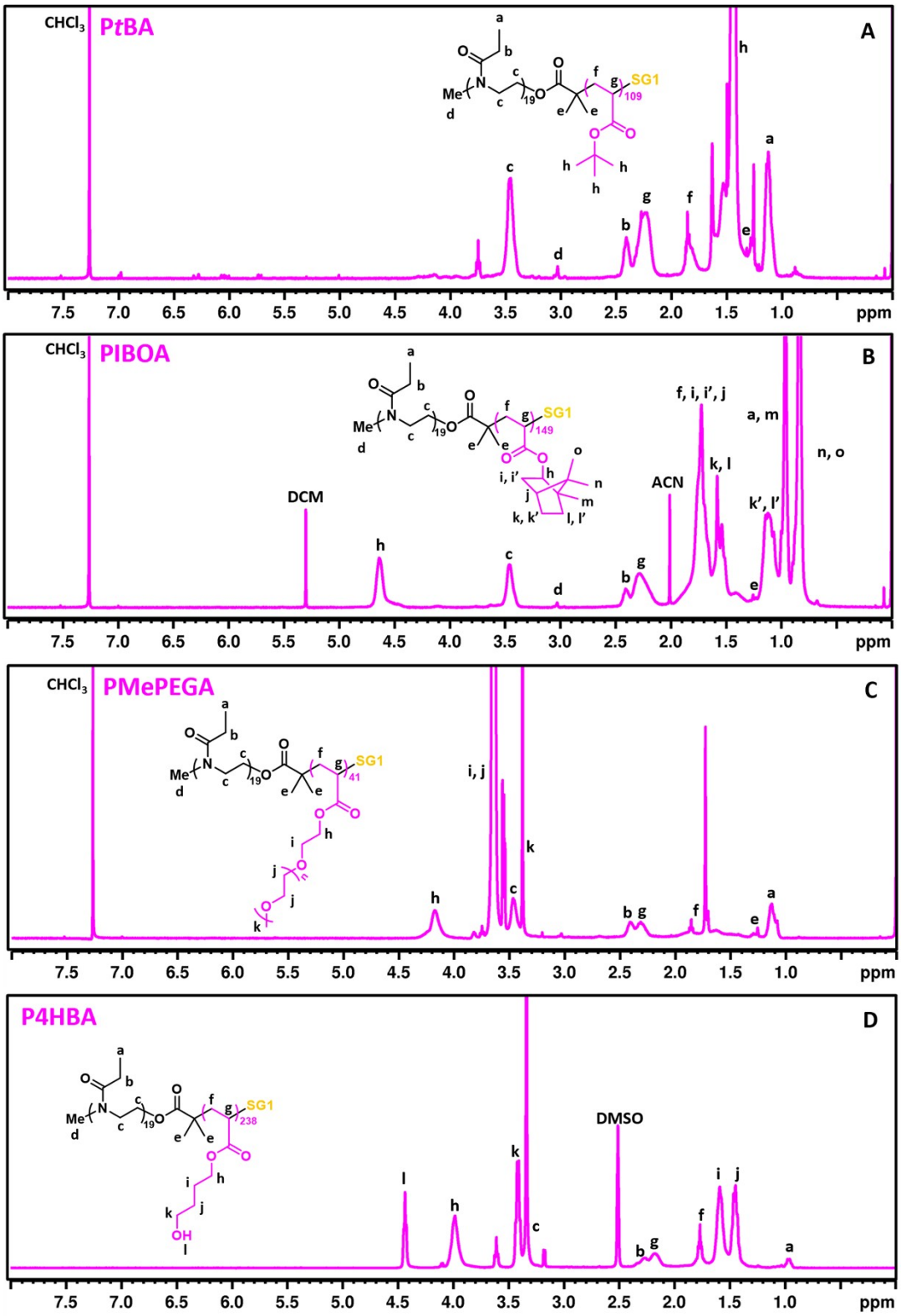

Figure S2. ^{1}H NMR spectra of the purified PEtOx-*b*-vinyl diblock copolymers **A**) P*t*BA **B**) PIBOA **C**) MePEGA and **D**) P4HBA. 400 MHz, 298K, $CDCl_3$ (P*t*BA, PIBOA, PMePEGA) and DMSO-d6 (P4HBA).

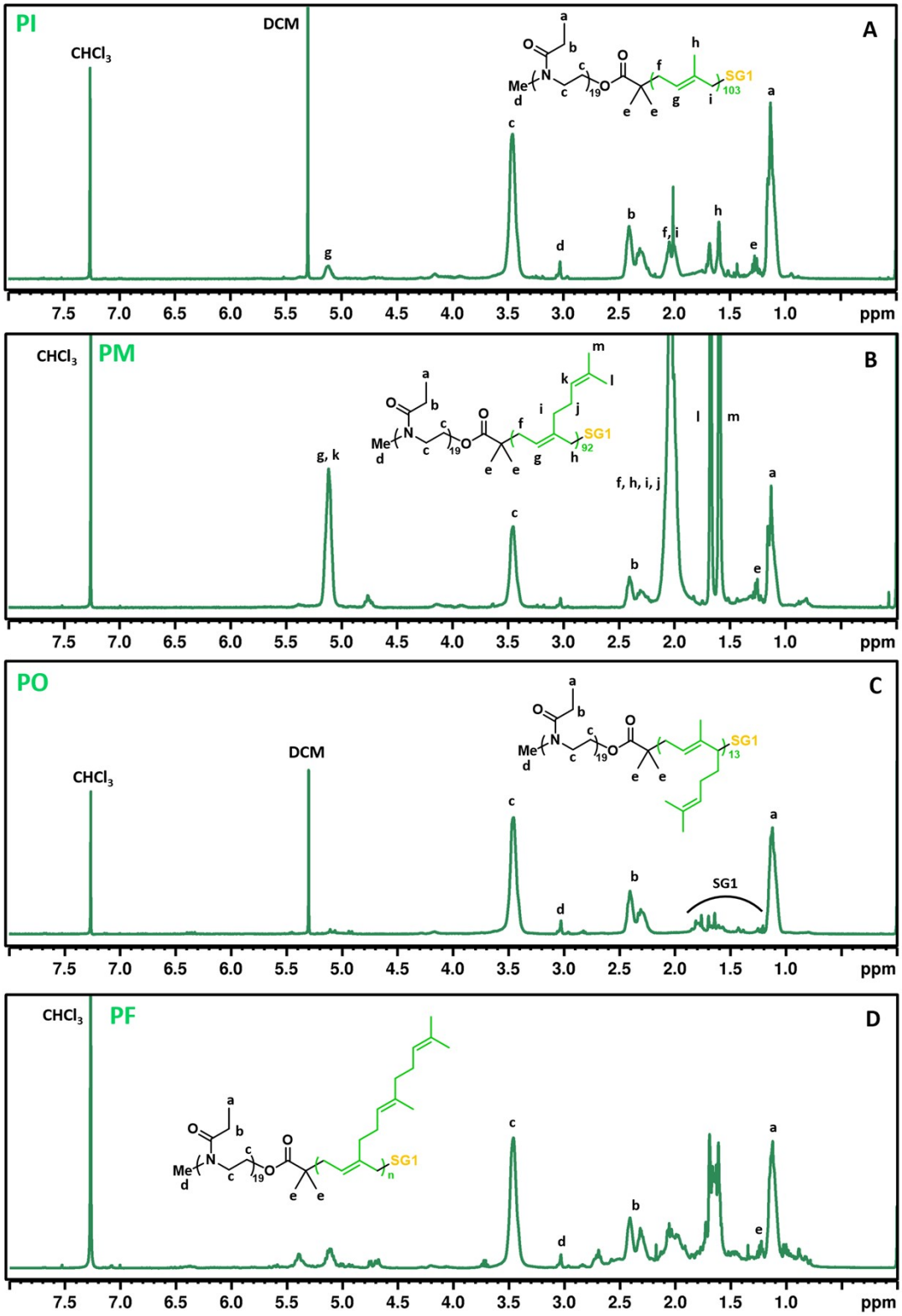

Figure S3. ^{1}H NMR spectra of the purified PEtOx-*b*-vinyl diblock copolymers **A**) PI **B**) PM **C**) PO and **D**) PF. 400 MHz, 298K, $CDCl_3$.

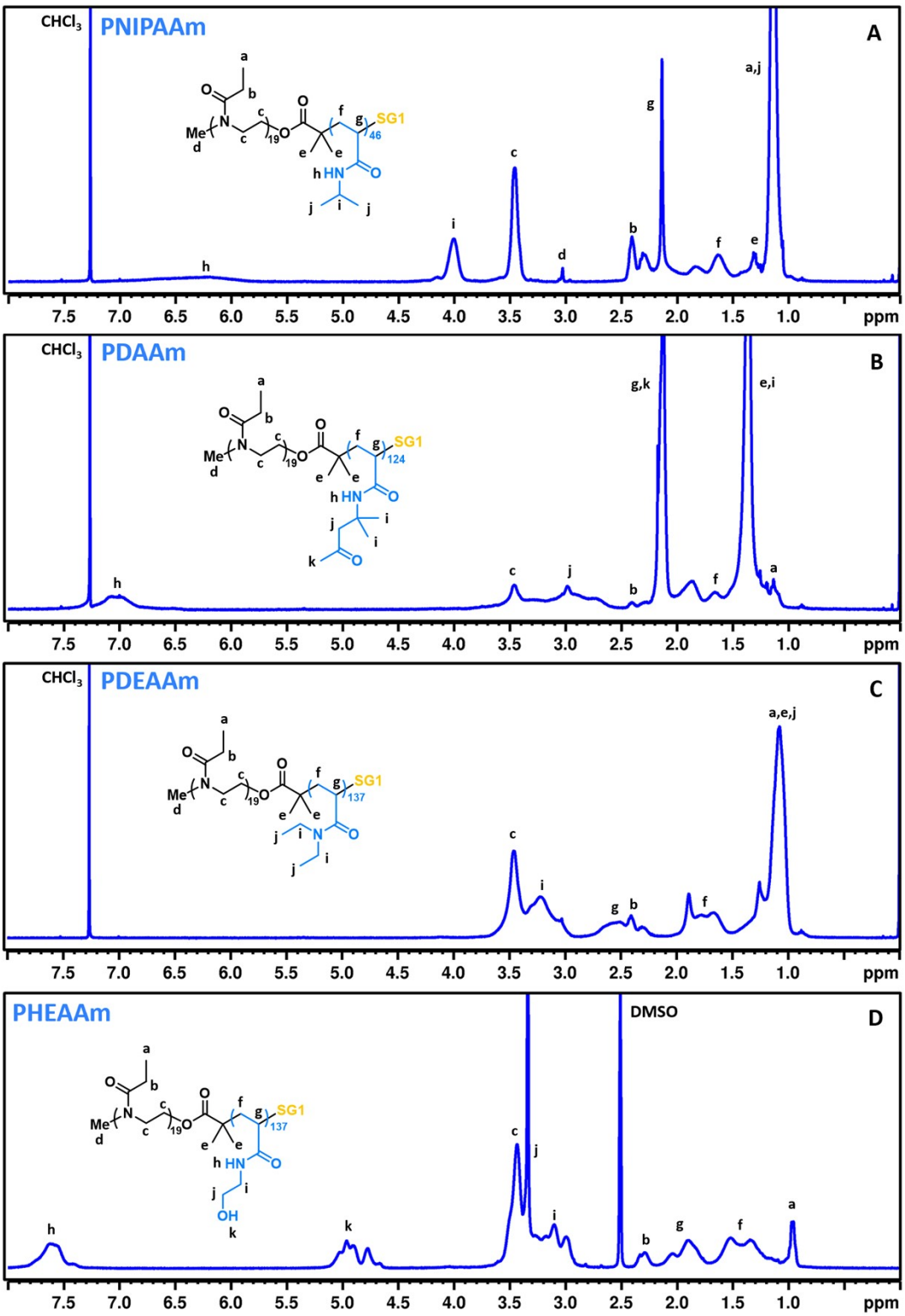

Figure S4. ^{1}H NMR spectra of the purified PEtOx-*b*-vinyl diblock copolymers **A**) PNIPAAm **B**) PDAAm **C**) PDEAAm and **D**) PHEAAm. 400 MHz, 298K, $CDCl_3$ (PNIPAAm, PDAAm, PDEAAm) and DMSO-d6 (PHEAAm).

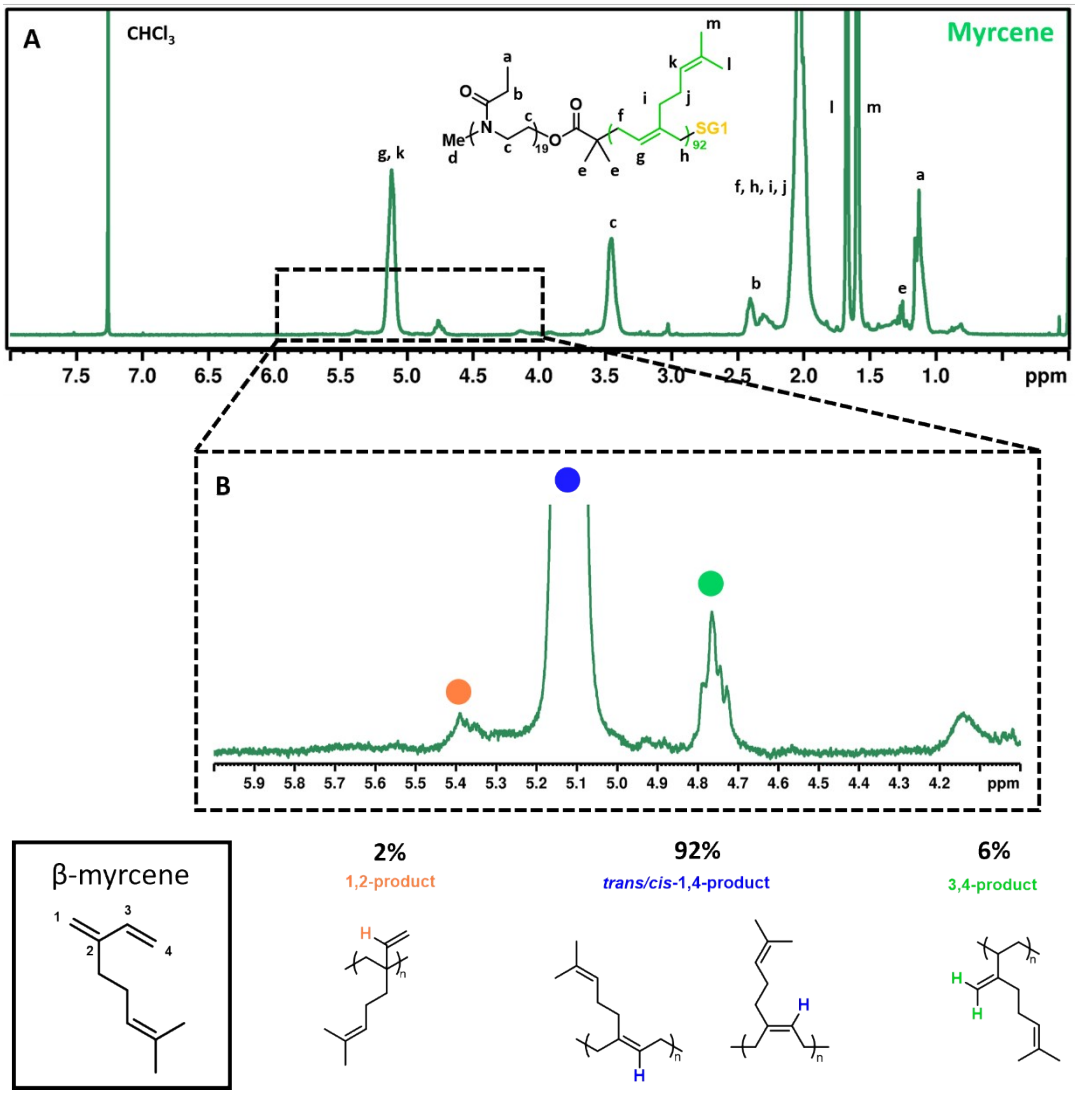

Figure S5. **A**) ^{1}H NMR spectra of the purified PEtOx-*b*-PM diblock copolymer. **B**) Zoom-in of the ^{1}H spectra showing the proton environments corresponding to the different stereochemistry products of poly(myrcene). 400 MHz, 298K, $CDCl_3$.

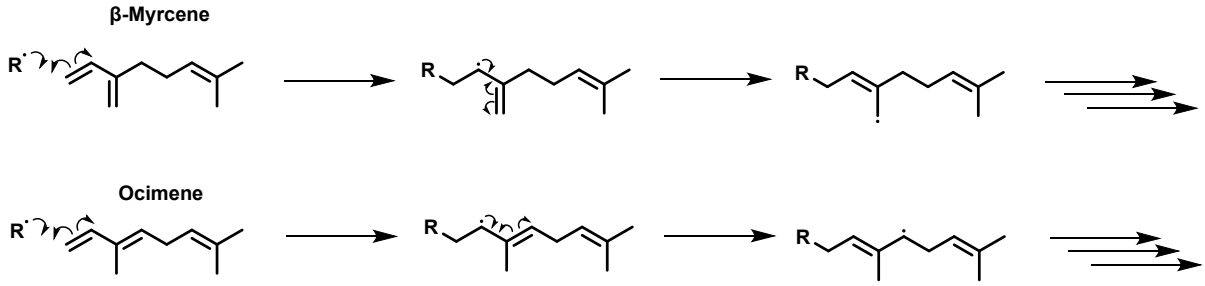

Figure S6. Mechanisms showing the formation of a primary propagating radical for myrcene and a secondary propagating radical for ocimene.