

Supplementary Information for:

Sequential ROMP of cyclooctenes as a route to linear polyethylene block copolymers

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Experimental Details.

Materials.

Bulk solvents (chloroform, tetrahydrofuran, methanol, toluene) were obtained from Avantor. Chloroform and tetrahydrofuran were dried using a home-built solvent column packed with activated alumina. Magnesium, benzyl bromide, *cis*-cyclooctene (COE), acetyl chloride, carbon tetrachloride, *N*-bromosuccinimide, *p*-toluenesulfonyl hydrazide and triethylamine were all purchased from Sigma-Aldrich chemical company. COE was dried over CaH₂ before distilling under vacuum. All other reagents were used as received.

Characterization.

¹H nuclear magnetic resonance (NMR) spectroscopy was performed on a Varian Inova 500 instrument operating at 500 MHz. Solutions were prepared in either deuterated chloroform (CDCl₃) for unsaturated polymers (and certain saturated statistical copolymers – see Results and Discussion) or in deuterated 1,1,2,2-tetrachloroethane (TCE-*d*₂) (Cambridge Isotope Laboratories) at elevated temperature (100 °C) for saturated block copolymers at approximately 15 mg/mL. All spectra were after 64 transients using a relaxation delay of 5 s with chemical

shifts reported as δ (ppm) relative to the ^1H signals from hydrogenous solvent (7.26 ppm for CHCl_3 ; 6.00 ppm for TCE).

Size-exclusion chromatography (SEC) was used to evaluate the molecular weight evolution and polydispersity index in the unsaturated. Samples were prepared at concentrations near 1 mg/mL in CHCl_3 . The instrument operates at 35 °C using three Plgel 5 μm Mixed-C columns in series with molecular weight range 400–400 000 g mol $^{-1}$. The columns are housed in a Hewlett-Packard (Agilent Technologies) 1100 series liquid chromatograph equipped with a Hewlett-Packard 1047A refractive index detector. PDIs are reported with respect to polystyrene standards obtained from Polymer Laboratories.

Differential scanning calorimetric (DSC) analysis was performed on a Q1000 instrument from TA Instruments calibrated with an Indium standard. Samples were initially heated to above the highest transition temperature and held isothermally for 5 min to remove discrepancies originating from variable thermal history. The samples were subsequently cooled to –120 °C at a rate of 10 °C min $^{-1}$ followed by heating to 120 °C again at a rate of 10 °C min $^{-1}$; data from the second heating cycle is presented. Data analysis (T_m ; $T_{g,L}$; $\Delta H_{m,C}$) was performed using Universal Analysis software from TA Instruments.

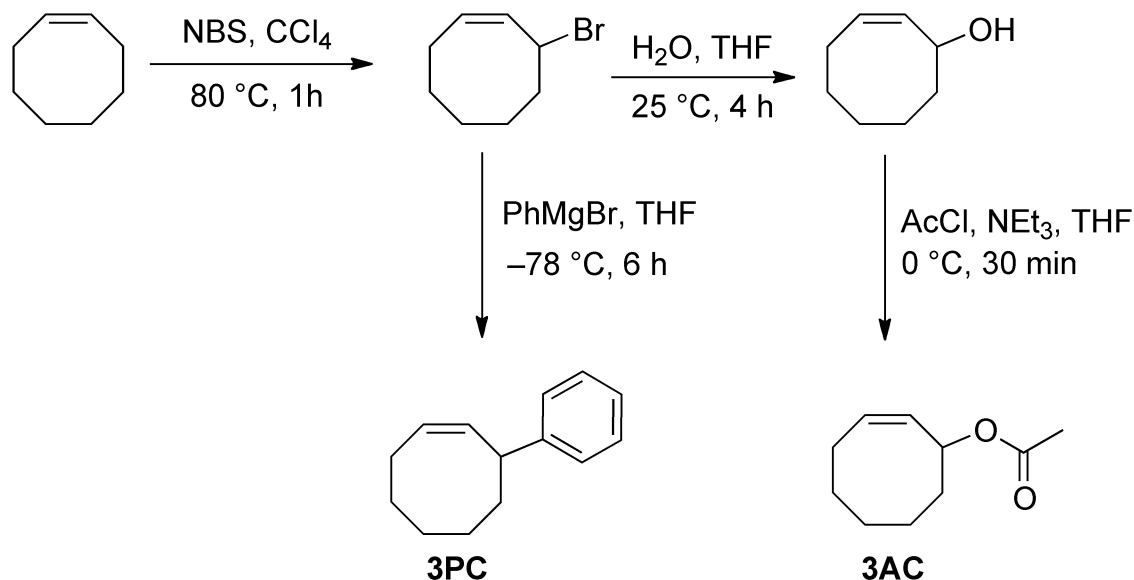
Small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) was measured at the Advanced Photon Source (APS) at Argonne National Laboratories at beamline 5-ID-D. The beamline is maintained by the Dow-Northwestern-Dupont Collaborative Access Team (DND-CAT). The source produces X-rays with a wavelength of 0.84 Å. The sample to detector distance was 5.65 m and the detector radius is 81 mm. Scattering intensity was monitored by a Mar 165 mm diameter CCD detector with a resolution of 2048 \times 2048. The two-dimensional scattering patterns were azimuthally integrated to afford one-dimensional profiles presented as spatial frequency (q) versus scattered intensity.

Synthetic Details.

The synthesis of functional monomers used in this work are summarized schematically in Scheme S1. The monomer 3PC was synthesized according to the procedure previously reported, as was the monomer 5AC.ⁱ The synthesis of 3AC has been previously reported, although an alternative route was performed to those in the literature. 3AC preparation was described as early as 1954 by silver acetate reaction with 3-bromocyclooctene in acetic acid.ⁱⁱ Other similar

strategies were attempted by employing different metal acetates for direct acetoxylation of cyclooctene, for example.ⁱⁱⁱ

Scheme S1. Synthesis of monomers 3PC, 3AC, and 5AC



3-phenyl cyclooctene (3PC).

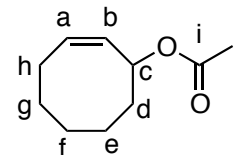
The synthetic procedure was identical to that previously reported.^{iv}

3-acetoxy cyclooctene (3AC).

Cyclooct-2-ene-1ol (3OHCOE) was prepared similarly to a previous report.^v Briefly, 50 mL of deionized water and 30 mL of THF was added to a round-bottom flask containing 15.0 g of 3-bromocyclooctene (79.3 mmol). The mixture was stirred for 15 h at ambient temperature. The aqueous phase becomes acidic, indicating that HBr is generated. The mixture was diluted with ~100 mL of diethyl ether (Et₂O) and washed with ~200 mL of saturated NaHCO₃, ~100 mL of water, ~100 mL of saturated NaCl. The organic layer was separated and dried over MgSO₄ and the solvent was removed to afford cyclooct-2-en-1-ol (3OHCOE). The product was fractionally distilled to afford 7.7 g (77 %) of clear, colorless liquid. ¹H NMR (CDCl₃): δ (ppm) = 5.61 [**a**, dddd, 1H, *J* = 10.7, 9.0, 7.3, 1.7 Hz]; 5.52 [**b**, ddd, 1H, *J* = 10.8, 6.7, 1.2 Hz]; 4.66 [**c**, bm, 1H]; 2.05–2.22 [**h**, m, 2H]; 1.91 [**d**, m, 1H]; 1.65 [**g**, m, 2H]; 1.55 [**f**, m, 2H]; 1.50 [**d**, m, 1H]; 1.40 [**e**,

m, 2H]. ^{13}C NMR (CDCl_3); δ (ppm) = 135.20 [b]; 128.17 [a]; 69.14 [c]; 38.49 [d]; 29.10 [g]; 26.25 [h]; 25.90 [f]; 23.69 [e].

The 3OHCOE (1.5 g; 11.9 mmol) was dissolved in 25 mL of dry THF in a sealed round bottom flask under argon. Triethylamine (1.5 mL; ~ 1.1 g; 10.7 mmol) was added via syringe and the entire solution was cooled with an ice-bath. Acetyl chloride (1.5 mL; 1.65 g; 21 mmol; 1.8 equiv. was added dropwise via syringe over 30 minutes, whereby the solution turns pink and white precipitate forms. The homogeneous solution was stirred while warming to ambient temperature over approximately 3 hours, during which the pink color disappeared. The reaction solution was quenched with 5 mL of water. The product was extracted with ca. 20 mL of methylene chloride (CH_2Cl_2). The aqueous phase was removed, and the organic phase was washed with water, saturated NaCl and dried over MgSO_4 . Solvent removal yielded the desired product as a clear, colorless liquid, which could be fractionally distilled under high vacuum. ^1H NMR (CDCl_3): δ (ppm) = 5.64 [a, m, 1H], 5.62 [c, m, 1H]; 5.45 [b ddd, 1H, $J = 10.8, 7.1, 1.3$ Hz]; 2.02 [j, s, 3H]; 1.3–2.3 [d–h, m, 10H]. ^{13}C NMR (CDCl_3); δ (ppm) = 170.5 [i]; 130.7 [b]; 129.7 [a]; 72.3 [c]; 35.1 [e]; 28.8 [g]; 26.3 [d]; 25.8 [h]; 23.3 [f]; 21.42 [j].



Block copolymers 3RC-*b*-COE.

The synthetic preparation of the different block copolymers was nearly identical. The only variation made is the monomer feed ratios; the molar ratios of monomers was adjusted to target different compositions in the final copolymers. Briefly, the synthesis of poly(3PC₂₅-*b*-COE₇₅) was carried out as follows: Freshly distilled 3PC monomer (1.07 g; 5.75 mmol) was dissolved in 10 mL of dry THF under an argon atmosphere in a two-neck round bottom flask. The catalyst was added as a solution (30 mg; 3.4×10^{-5} mol in 0.5 mL THF) through a rubber septum. The solution turned from light green to orange color within 10 s, indicating initiation of the polymerization. The reaction mixture was stirred at ambient temperature for 60 minutes, at which point COE monomer was added via syringe (2.9 g; 26 mmol). The reaction mixture immediately solidified and stirring ceased. The reaction mixture was diluted with approximately 20 mL of THF after 1 minute and subsequently quenched by addition of a ~ 100 mg of ethyl vinyl ether. The solution changed to a dark brown color, suggesting termination and was further

dilution with 120 mL THF to facilitate precipitation. The polymer was isolated by precipitation into ~ 1 L of methanol, followed by drying at ambient temperature under vacuum for 1 day to afford 3.8 g of block copolymer.

Synthesis of statistical copolymers poly(3RC-*s*-COE).

The synthesis of all statistical copolymers was identical except for changes in the monomer feed ratios to target various different compositions in the final copolymers and changes in the chain-transfer agent concentration to target various average degrees of polymerization. The synthesis of poly(3PC₂₅-*s*-COE₇₅) was conducted as follows: The freshly distilled monomers 3PC (1.0 g; 5.4 mmol) and COE (3.4 mL; 2.9 g; 26 mmol) were dissolved in 25 mL of dry THF under an argon atmosphere. The chain transfer agent 1,4-diacetoxy-2-butene (10 μ L; 6×10^{-5} mol) was added to the solution followed by the catalyst G2 as a solution (2.5 mg; 3×10^{-6} mol in 0.2 mL THF). The polymerization was heated to 40 °C and stirred for 6 h. The reaction was quenched by adding several drops of ethyl vinyl ether after diluting with 25 mL THF and stirring for an additional 5 min. The polymer was isolated by precipitation into ~ 500 mL of methanol. The polymer was dried under vacuum at ambient temperature for at least 1 day to afford 3.7 g of copolymer.

Hydrogenation of copolymers.

The hydrogenation of both block copolymers and statistical copolymers were conducted nearly identically except for small variations in reaction time. The hydrogenation of poly(3PC₂₅-*b*-COE₇₅) was conducted as follows, based on a previously described protocol^{vi}: 2.0 g of the unsaturated block copolymers was dissolved in 100 mL of xylenes with a trace amount of butylated hydroxytoluene (BHT) in a thick-walled glass reactor with a Teflon screw cap and a side-arm with a Teflon stop-cock. 6.0 g of *p*-toluene sulfonyl hydrazide was added to the mixture before sealing the screw-cap and connecting the side arm to a Schlenk line. Three consecutive freeze-pump-thaw cycles were performed before finally refilling with argon. The reaction mixture was heated at 130 °C for between 3 and 8 h, after which the solution was cooled to ambient temperature and precipitated into a 10-fold excess of slightly acidic methanol (acidified with ~30 mL of 1 M HCl_{aq}).

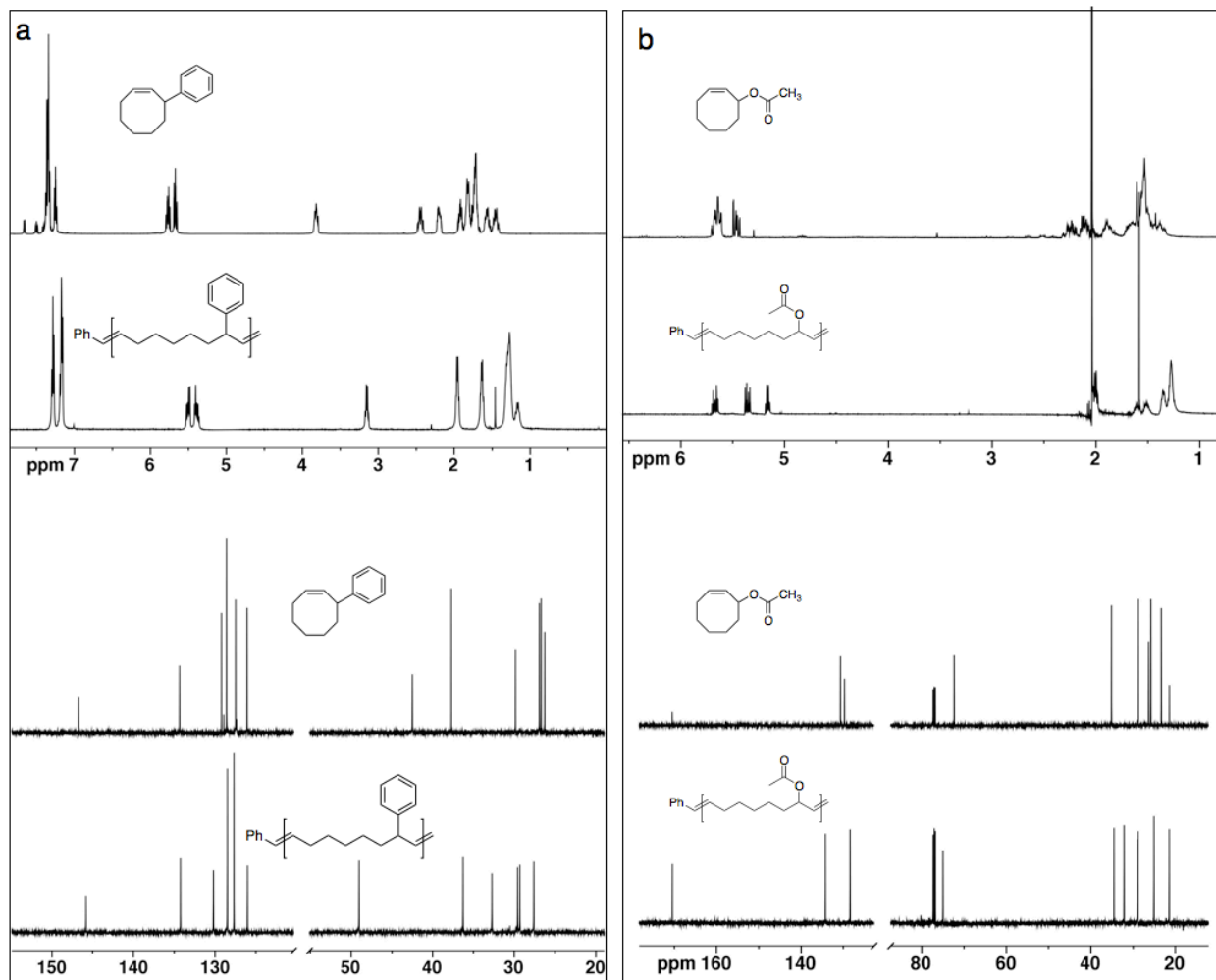


Figure S1. ^1H and ^{13}C NMR spectra of (a) 3PC monomer and the corresponding homopolymer after ROMP and (b) 3AC monomer and the corresponding homopolymer.

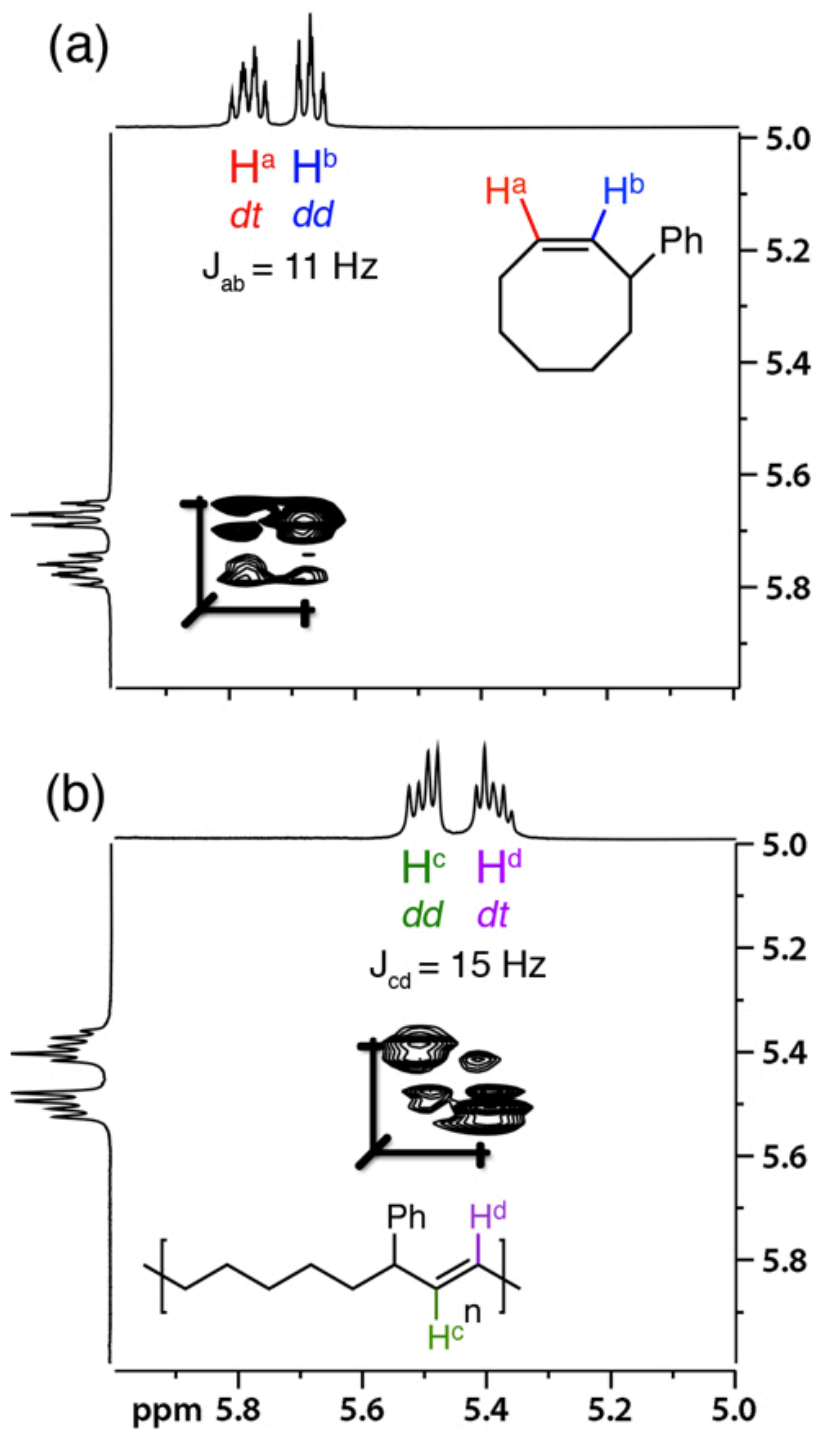


Figure S2. H–H COSY spectra of (a) 3PC monomer and (b) poly(3PC) homopolymer.

The monomer 3PC gives two olefinic signals, inherent to the asymmetric structure. The proton H^b shows doublet of doublet of doublet of doublet (dddd) multiplicity with the largest

coupling constant $J_{ab} = 10.4$ Hz consistent with the *Z* configuration about the double bond as observed in the commercially available *cis*-cyclooctene starting material for the substituted monomer synthesis. This configuration is consistent with the product retaining the configuration of the starting unsubstituted COE. The one-dimensional ^1H NMR spectrum of the polymer shows only two signals with 1:1 integration in the olefinic region corresponding to the alkenyl protons adjacent to the phenyl-substituted carbon and the unsubstituted carbon. The ^{13}C NMR spectrum of the monomer shows twelve discrete signals associated with the twelve distinct carbons (4 aromatic signals, 8 cyclooctene signals) in the asymmetric monomer. The polymer from ROMP with **G3** also contains merely 12 discrete signals. This alone suggests a highly regular polymerization with stereo- and regio-specificity during each metathesis reaction. There are two possible scenarios that would provide this regularity. The polymer either exhibits pure *cis* (*i.e.*, *Z*) or pure *trans* (*i.e.*, *E*) configuration, as suggested by the sole two olefinic signals at 146 and 134 ppm. With respect to regiospecificity, the two possible scenarios include perfectly head-to-tail (HT) or perfectly alternating head-to-head and tail-to-tail isomers (HH-*alt*-TT). Accurately elucidating the resulting microstructure requires further investigation by H–H COSY and IR spectroscopy. The olefin signals for the polymer, H^c and H^d , show doublet of doublet (dd) and doublet of triplet (dt) multiplicity at chemical shifts of 5.50 and 5.39 ppm, respectively. The olefinic coupling constant of these signals is $J_{cd} = 15.2$ Hz, which is consistent with *E* configuration about the double bond. This configuration purportedly agrees with the preferred orientation of catalyst residue relative to monomer during ring-opening metathesis, which was ultimately illuminated by the stoichiometric metathesis reaction between **G2** and 3PC. The H–H COSY spectrum for poly3PC provides conclusive evidence for the scenario in which perfect HT regiospecificity predominates. The proton signals H^c and H^d are strongly coupled, which strongly suggests adjacency; the two signals that would hypothetically result from HH-*alt*-TT would presumably not be correlated due to the relatively large spatial separation. Extensive characterization is provided in a previous publication.^{iv}

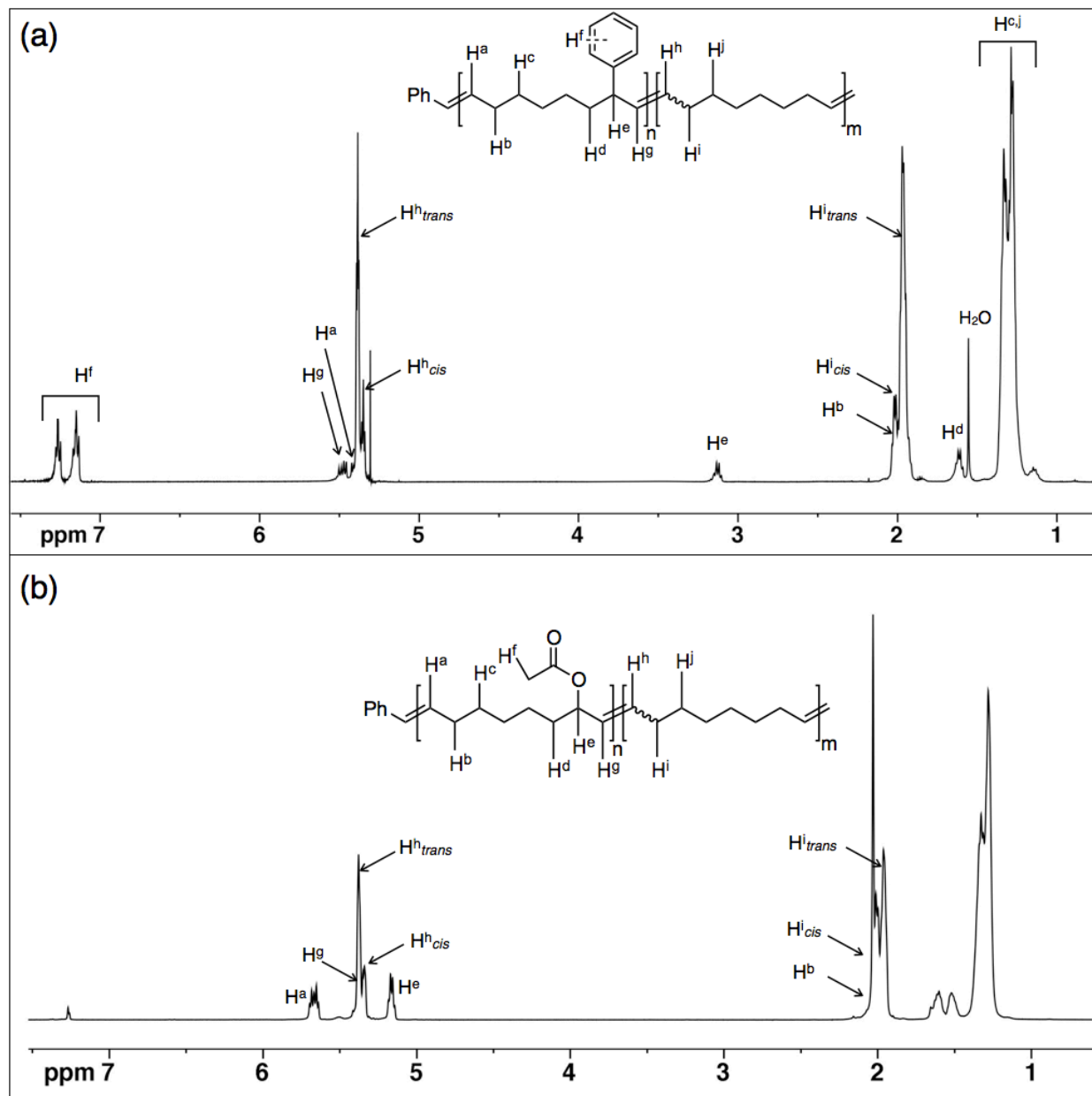


Figure S3. ^1H NMR spectrum for (a) sample poly(3PC₄₀-b-COE₆₀) and (b) sample poly(3AC₅₀-b-COE₅₀) in CDCl₃ at 20 °C with detailed signal designations.

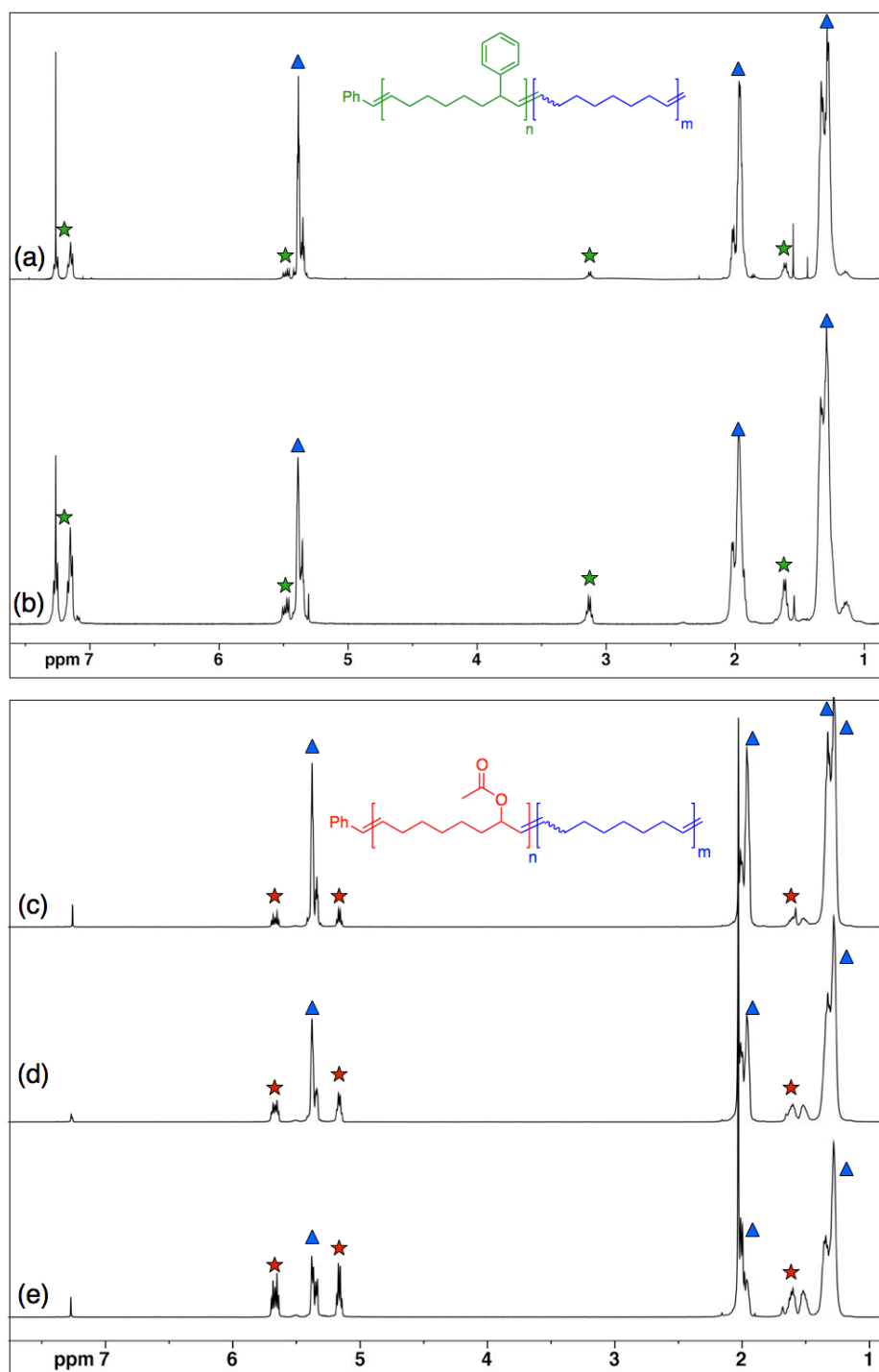


Figure S4. Block copolymer composition comparison with ^1H NMR spectroscopy for two poly(3PC-*b*-COE) copolymers with (a) 76 wt % PCOE and (b) 62 wt % PCOE and three poly(3AC-*b*-COE) copolymers with (c) 75 wt % PCOE, (d) 50 wt % PCOE and (e) 25 wt % PCOE. The respective signals associated with the different components are designated: PCOE block (blue triangles) poly(3PC) block (green stars); poly(3AC) block (red stars).

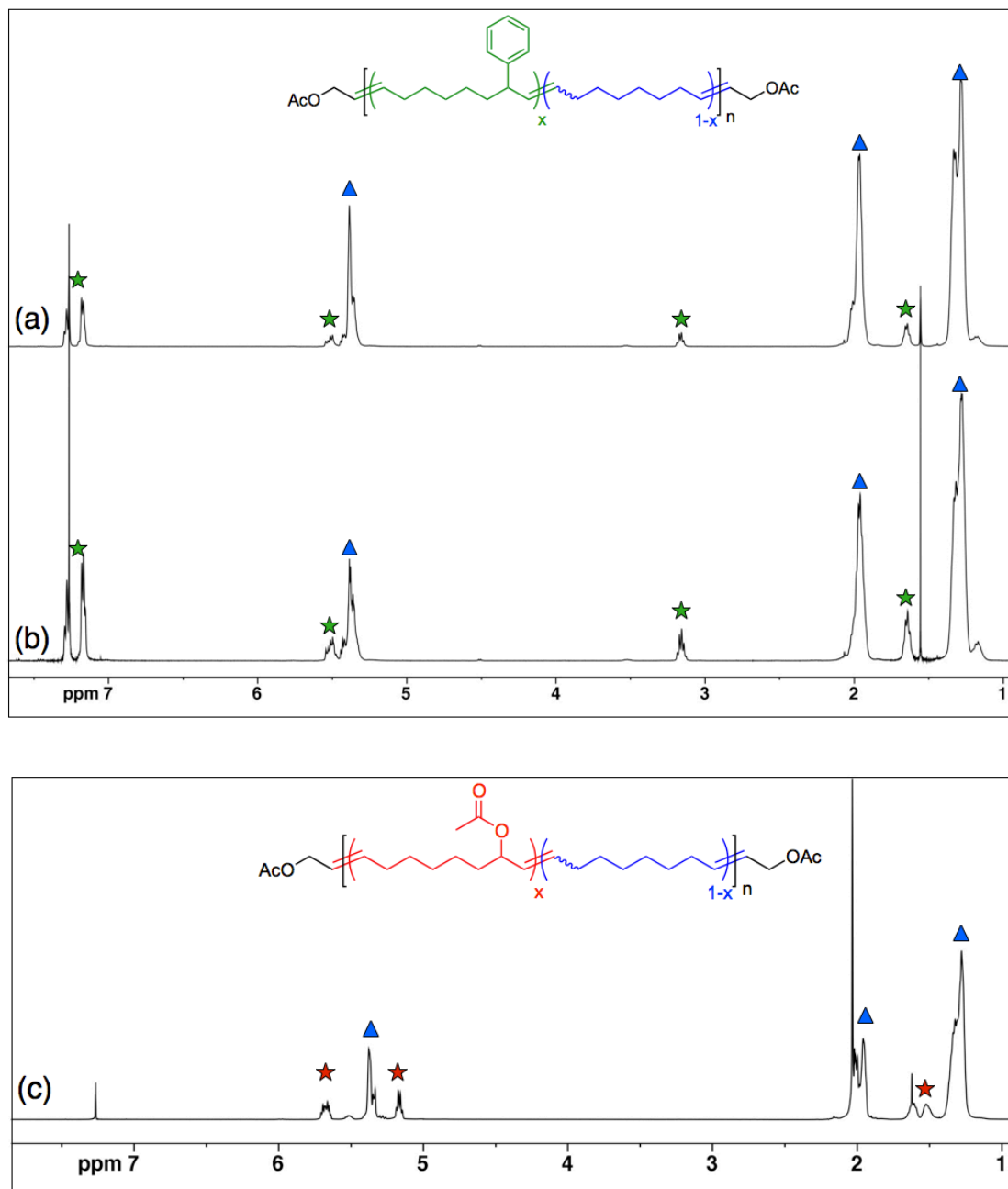


Figure S5. Statistical copolymer composition comparison with ^1H NMR spectroscopy for two poly(3PC-*s*-COE) copolymers with (a) ~75 wt % PCOE and (b) ~60 wt % PCOE and (c) poly(3AC-*s*-COE) with ~40 wt % PCOE. The integration of the characteristic signals for PCOE (blue triangles) the poly(3PC) block (green stars) and poly(3AC) (red stars) are indicated.

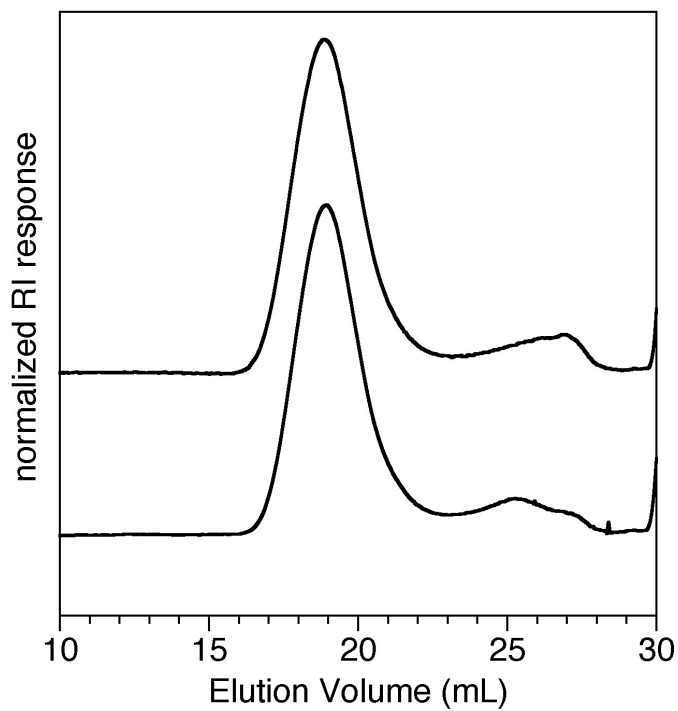


Figure S6. Comparison of SEC chromatograms for simultaneous polymerization of 3PC and COE to give statistical copolymers poly(3PC_{25-s}-COE₇₅) (top) and poly(3PC_{40-s}-COE₆₀) (bottom).

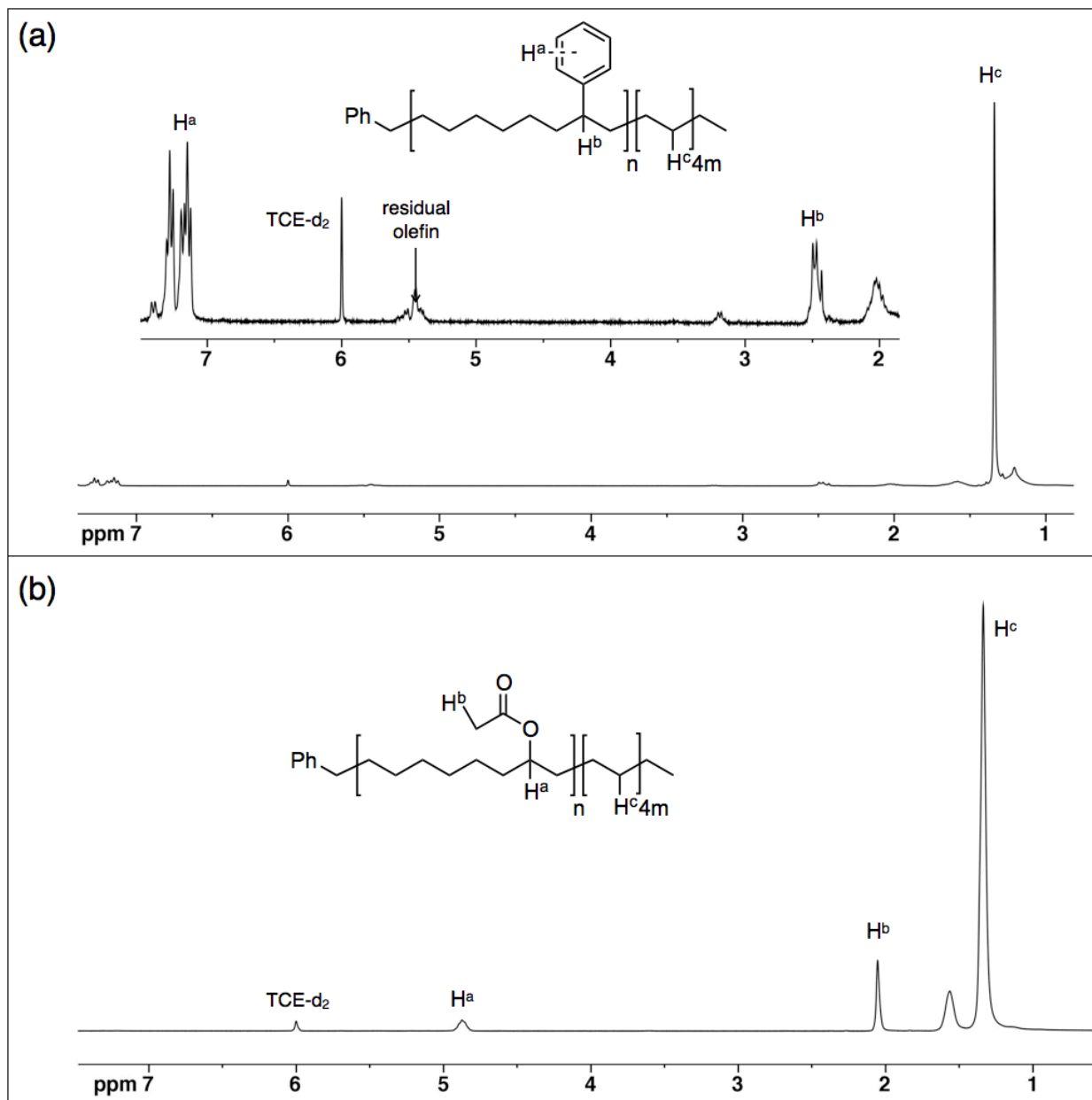


Figure S7. ¹H NMR spectrum for (a) *h*-poly(3PC₄₀-*b*-COE₆₀) showing the saturated backbone – CH₂– signals (H^c; 1.3 ppm), the unsaturated aryl proton signals (H^a; 7.3–7.1 ppm) and some residual unsaturated olefin protons (5.5 ppm; >95% saturation) and (b) *h*-poly(3AC₅₀-*b*-COE₅₀). Measured at 100 °C in 1,1,2,2-tetrachloroethane-*d*₂ (TCE-*d*₂).

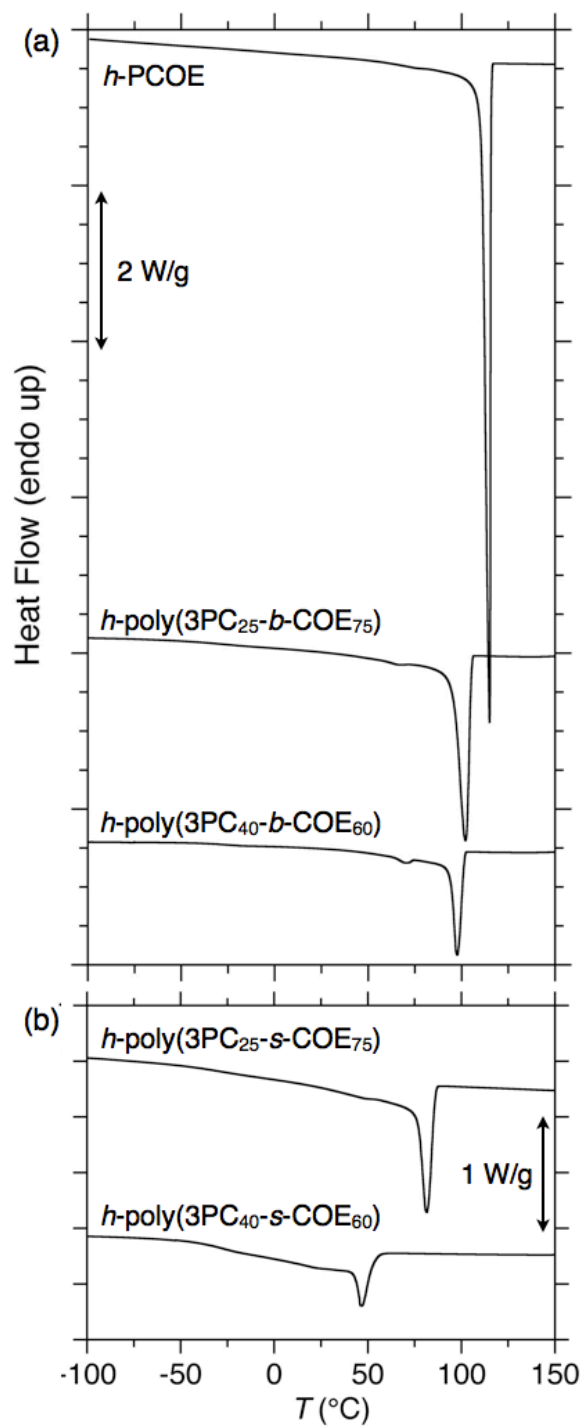


Figure S8. DSC cooling curves for (a) LPE homopolymer and block copolymers h -poly(3PC₂₅- b -COE₇₅) and h -poly(3PC₄₀- b -COE₆₀) and (b) statistical copolymer h -poly(3PC₂₅- s -COE₇₅) and h -poly(3PC₄₀- s -COE₆₀).

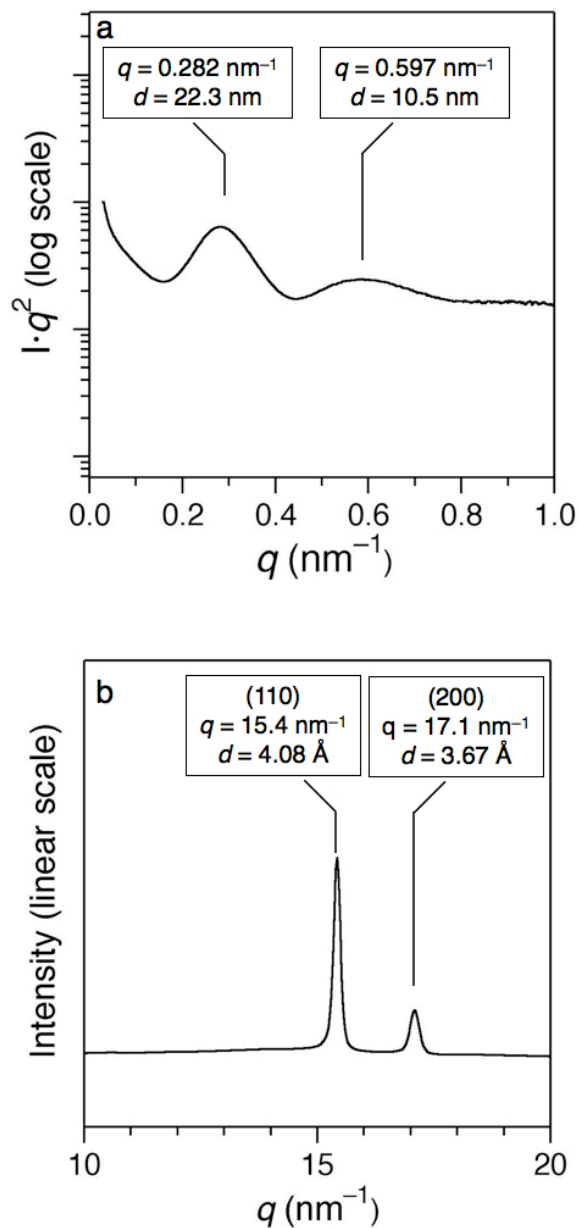


Figure S9. One-dimensional profiles from (a) SAXS and (b) WAXS of a linear polyethylene sample ($M_n = 20 \text{ kg mol}^{-1}$) at ambient temperature after cooling at $10 \text{ }^\circ\text{C min}^{-1}$ from homogeneous melt.

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