Supporting Information

Precision Ethylene-Styrene Copolymers through the Ring Opening Metathesis Polymerization of 3-Phenyl Cyclododecenes

Sebla Onbulak and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431

*Corresponding author (e-mail: hillmyer@umn.edu)

Table of Contents

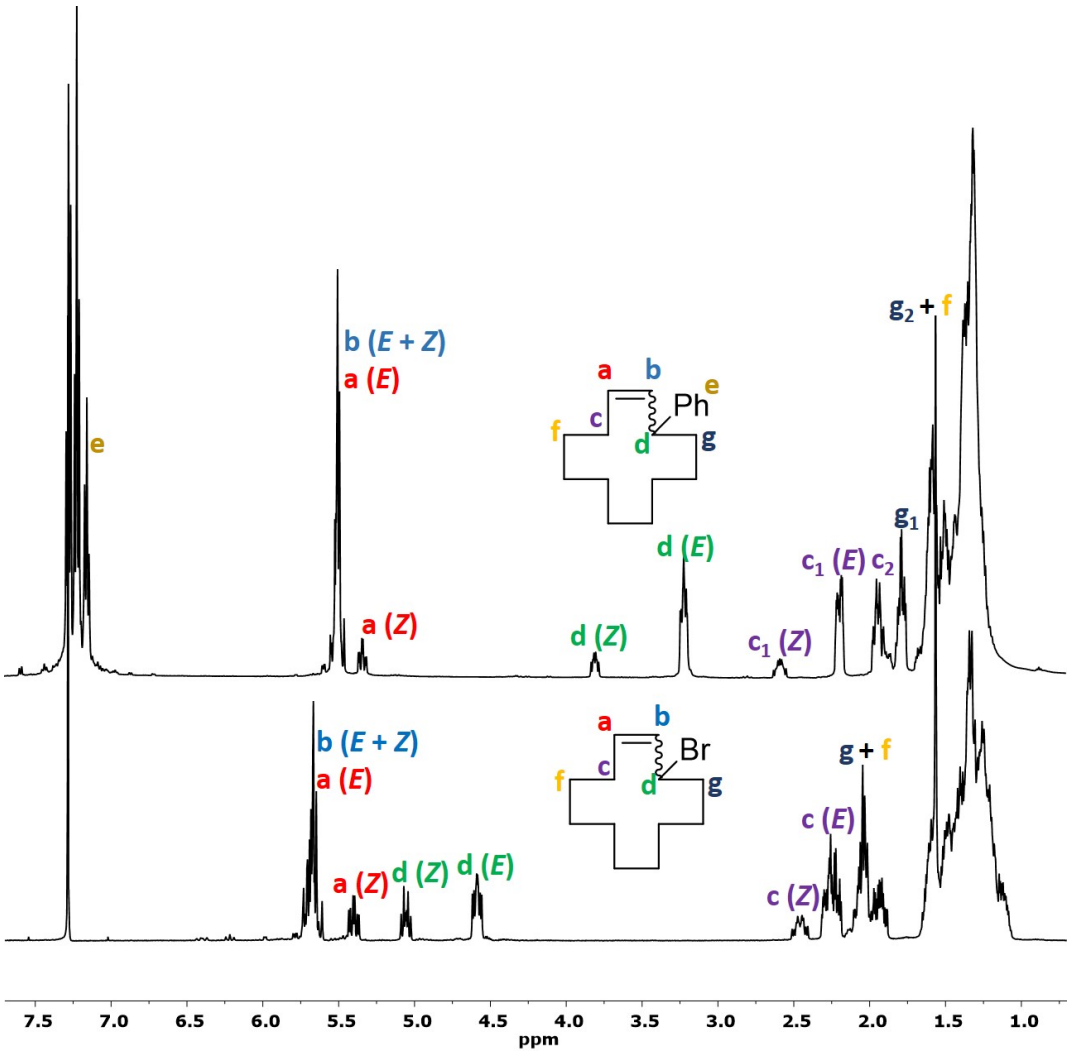


Figure S1. ^{1}H NMR spectra of *E*,*Z*-3-phenyl-1-cyclododecene (top) and *E*,*Z*-3-bromo-1-cyclododecene in $CDCl_3$.

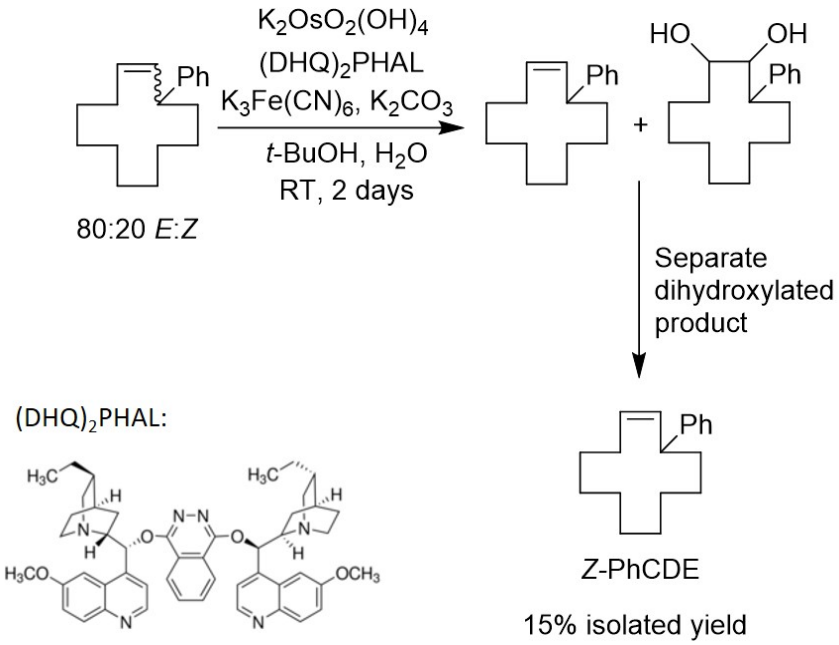


Figure S2. Synthesis of *Z*-3-Phenyl-1-cyclododecene.

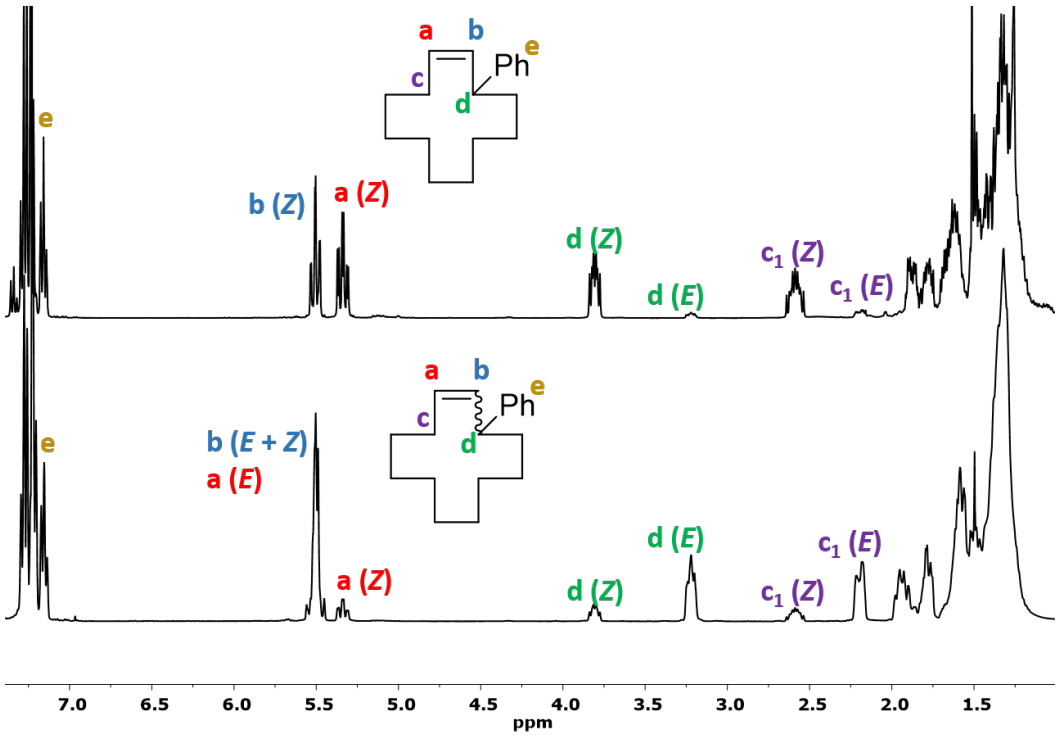


Figure S3. ^{1}H NMR spectra of *E*,*Z*-3-phenyl-1-cyclododecene (top) and *Z*-3-phenyl-1-cyclododecene (bottom) in $CDCl_3$.

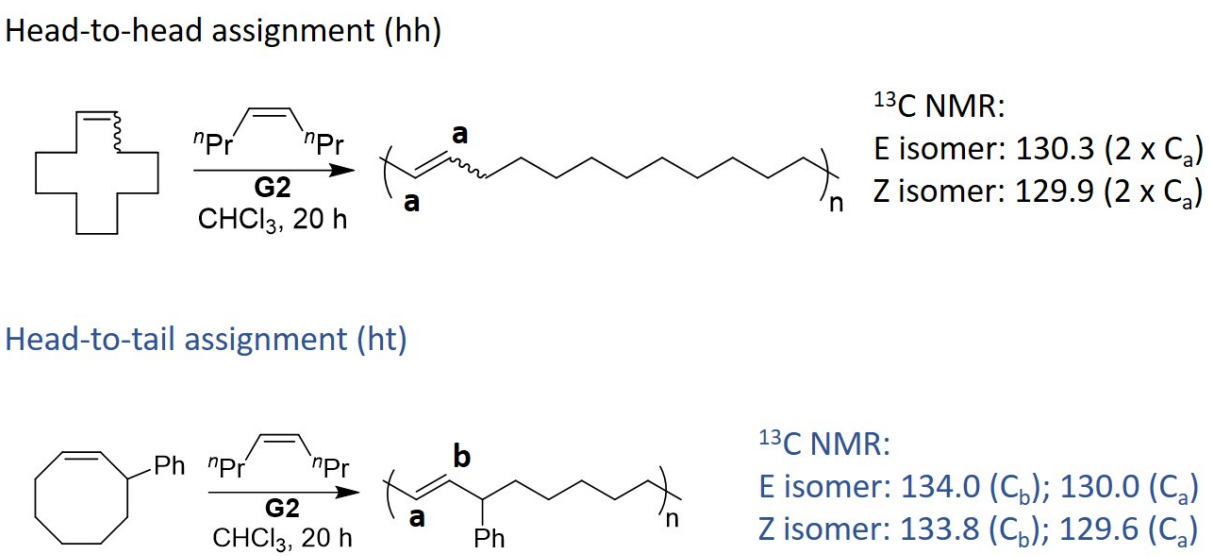


Figure S4. Synthesis of poly(CDE) and poly(3PhCOE) polymers by ROMP for hh and ht regioisomer assignments by ^{13}C NMR spectroscopy.

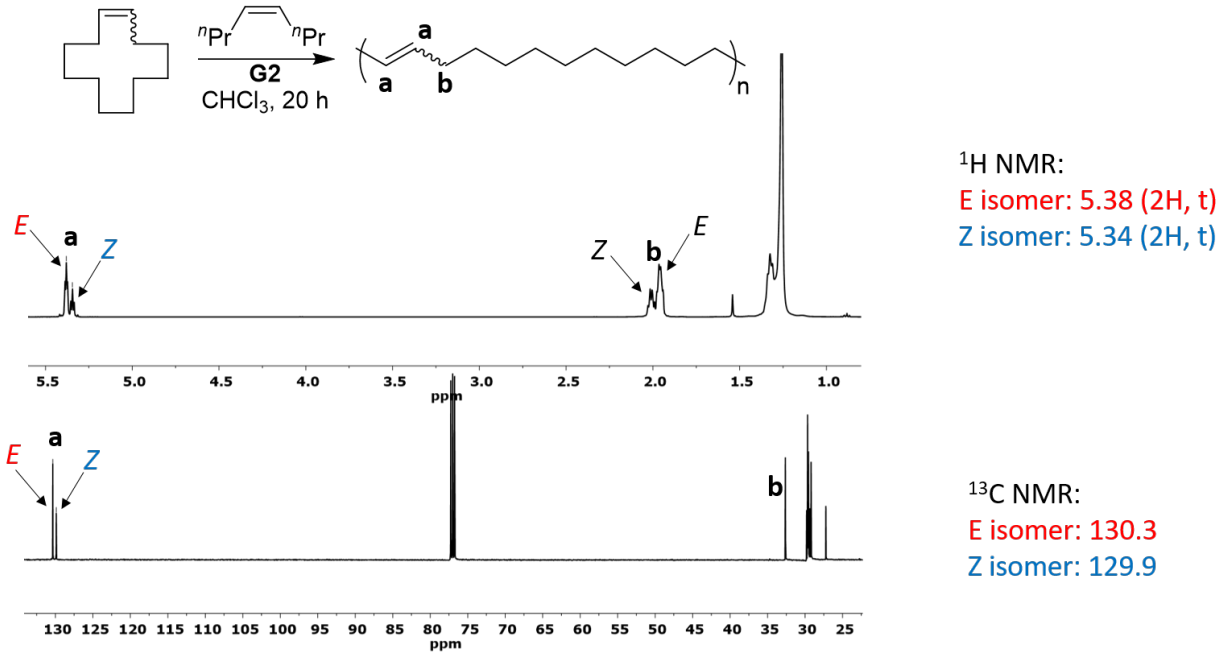


Figure S5. ^{1}H NMR and ^{13}C NMR spectrum of poly(CDE) polymer in $CDCl_3$

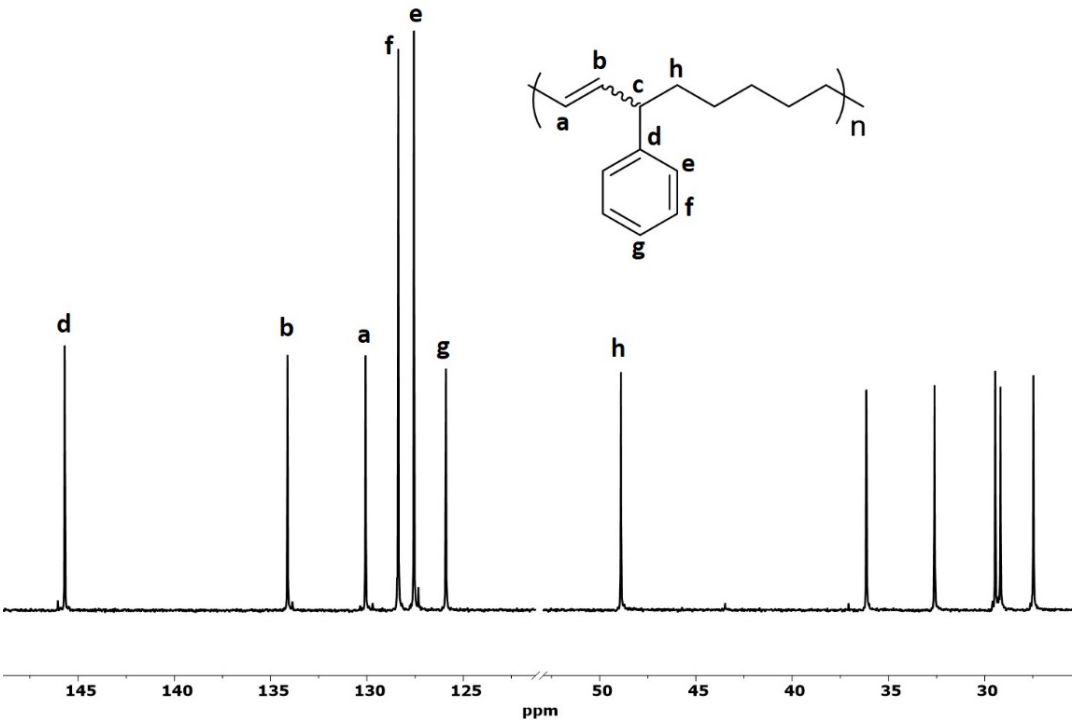


Figure S6. ^{13}C NMR spectrum of poly(3PhCOE) polymer in $CDCl_3$.

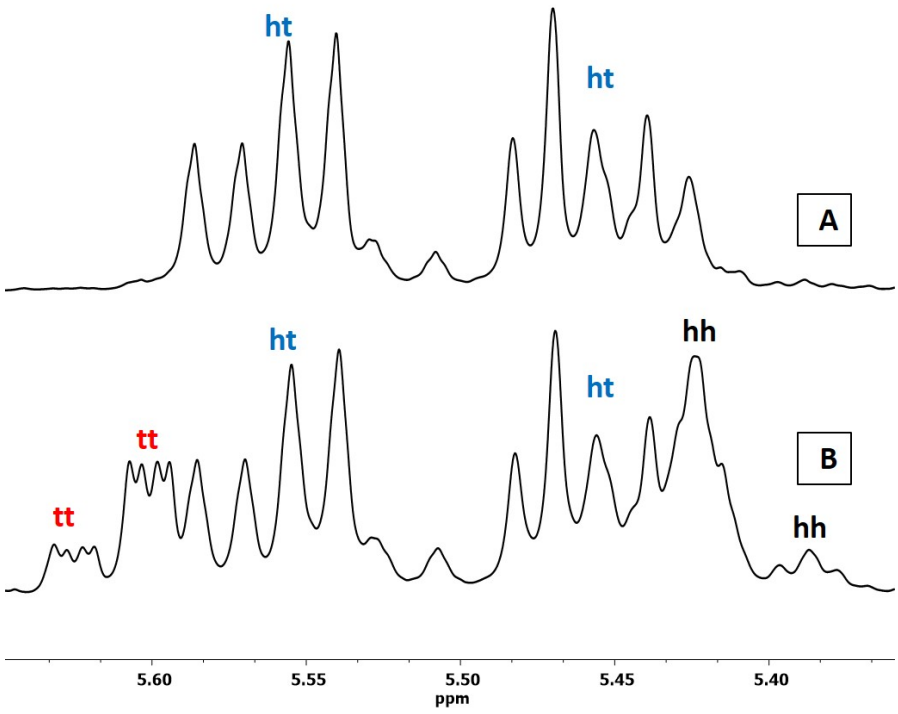


Figure S7. Partial ^{1}H NMR spectra of the (A) polymer **P1** with the CTA present, and (B) polymer **P13** without the CTA in $CDCl_3$.

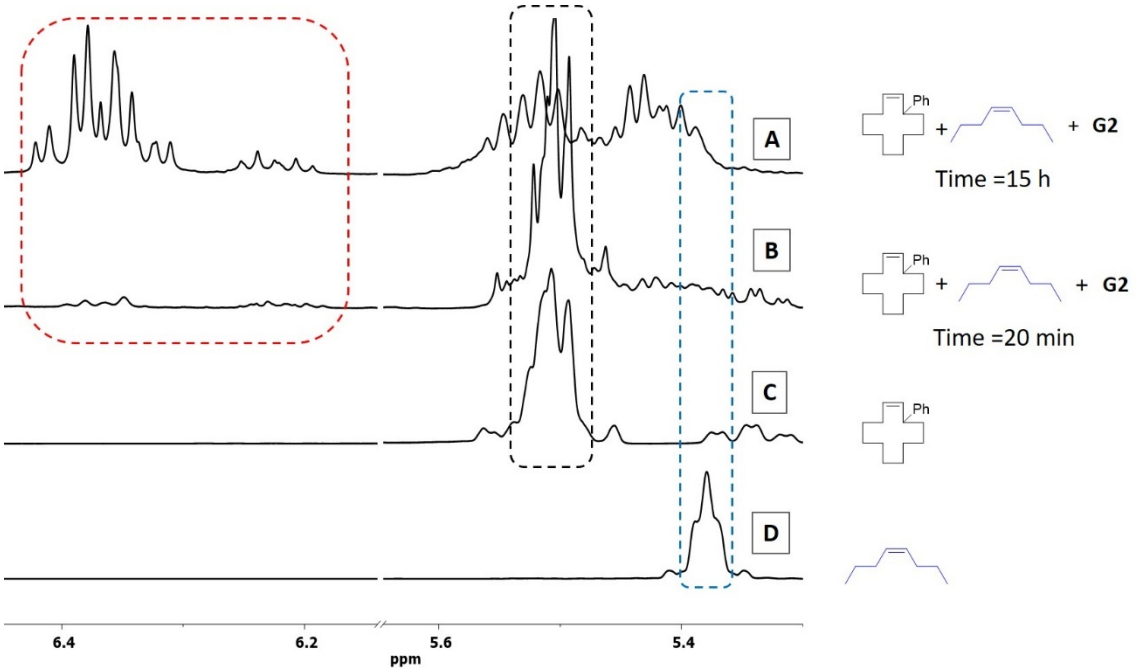


Figure S8. Partial ^{1}H NMR spectra of (A) ROMP reaction after 15 h, (B) ROMP reaction after 20 min, (C) PhCDE monomer and (D) *cis*-4-octene CTA in $CDCl_3$. The equivalences that were used for the ROMP reaction of monomer:CTA:G2 was 1:1:1.

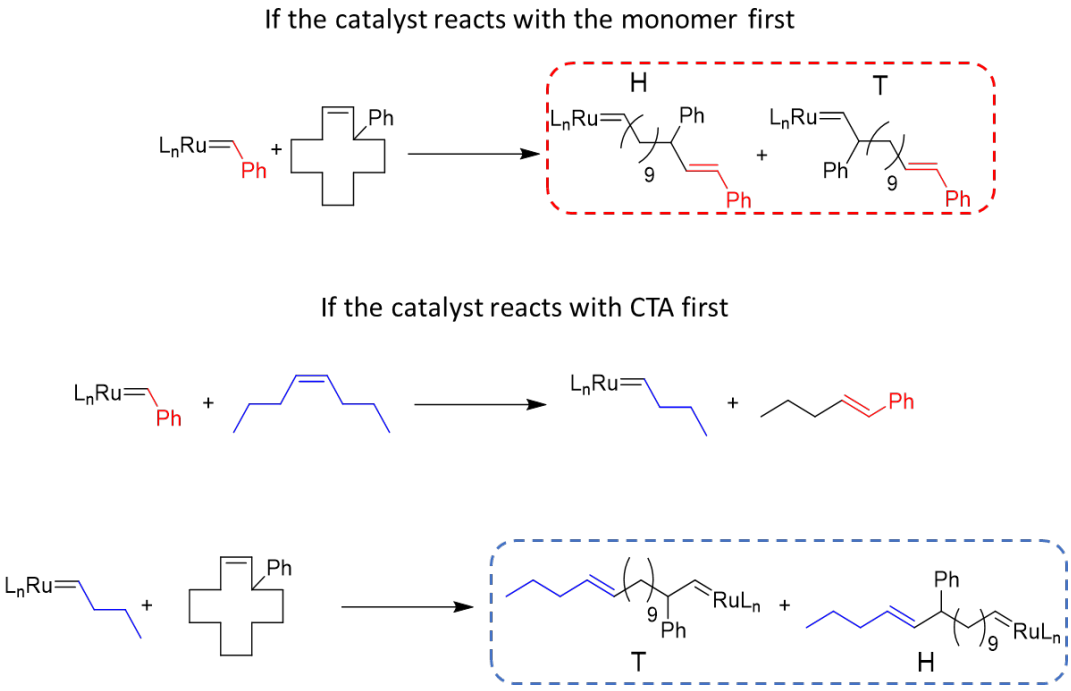


Figure S9. The first initiating species that are formed with and without the CTA present in the ROMP reaction mixture. The equivalences that were used for the ROMP reaction of monomer:CTA:G2 was 1:1:1.

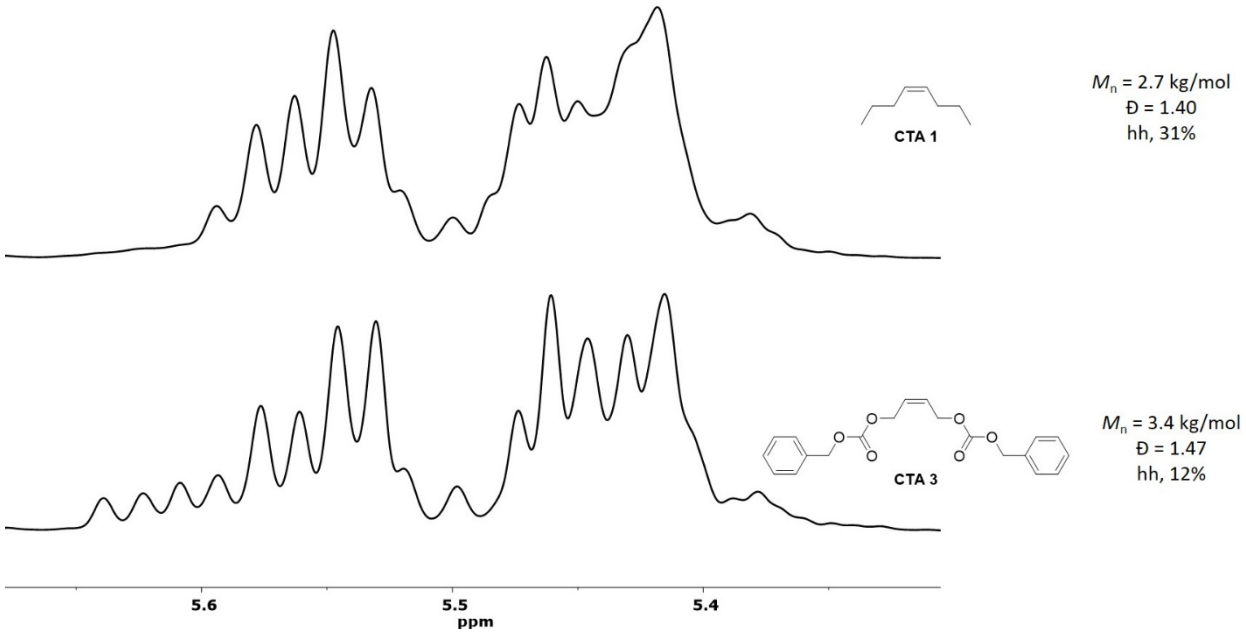


Figure S10. Partial ^{1}H NMR spectra of low molar mass polymer synthesized with cis-4-octene CTA (top) and with carboxybenzyl CTA (bottom) in $CDCl_3$. The hh error dropped from 31% to 12% with the change in the CTA.

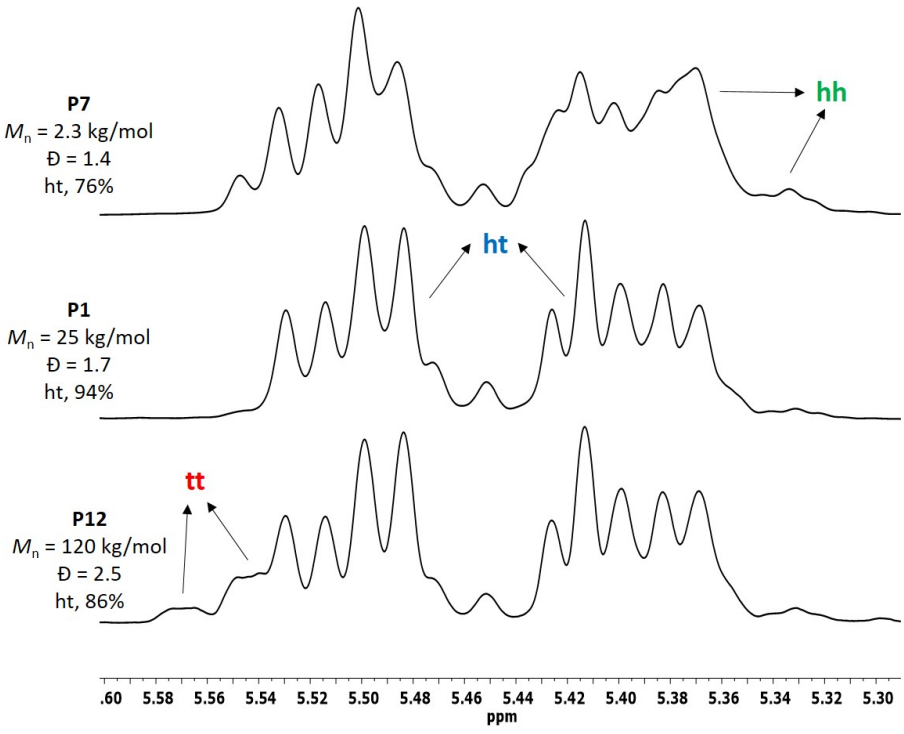


Figure S11. The change in the error with the change in the molar mass of the polymer. Partial ^{1}H NMR spectra of **P12**, **P1** and **P7** polymers synthesized with cis-4-octene CTA in $CDCl_3$.

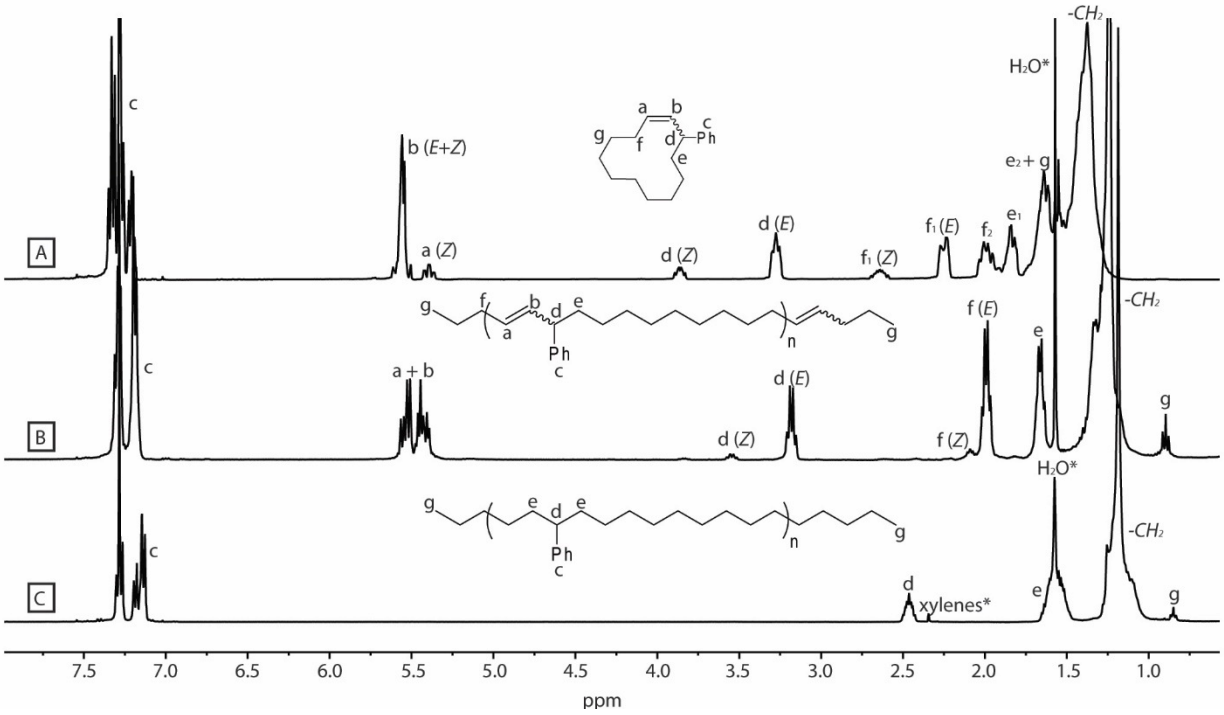


Figure S12 ^{1}H NMR spectra of (A) 3PhCDE monomer, (B) poly(3PhCDE) polymer, and (C) hydrogenated poly(3PhCDE) polymer in $CDCl_3$.

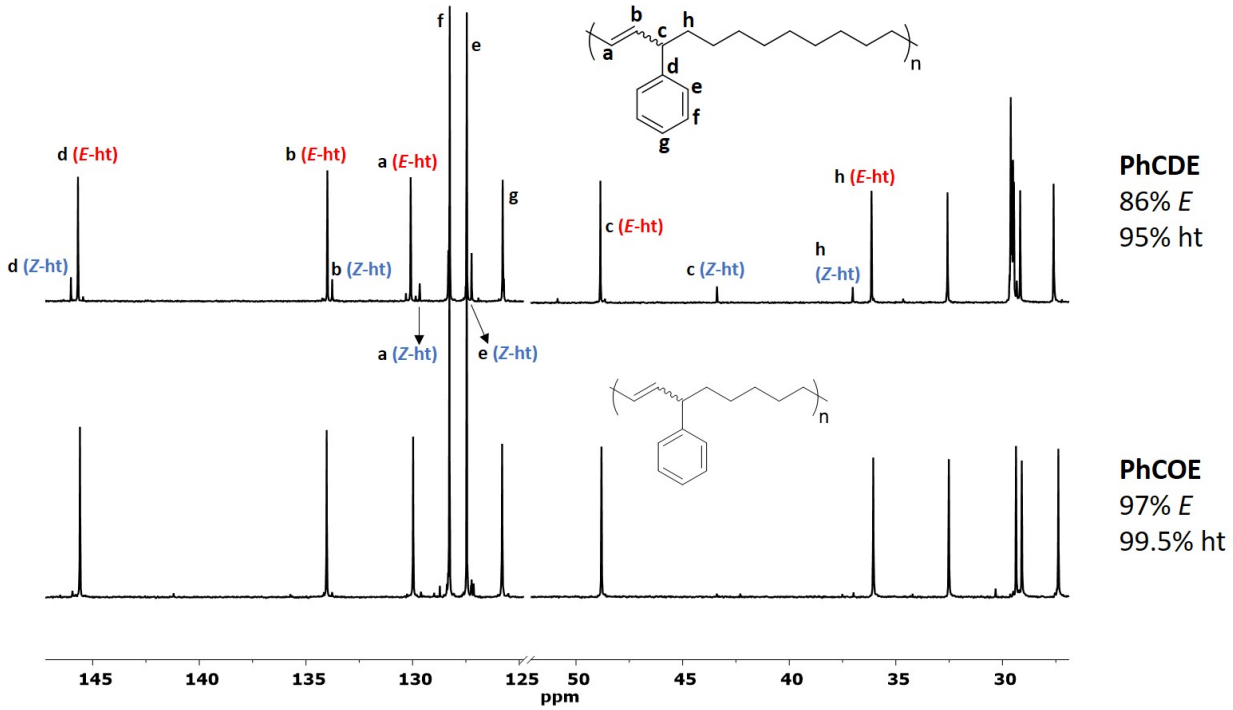


Figure S13. Difference in the ^{13}C NMR spectra of unsaturated poly(3PhCOE) model compound (bottom) vs poly(3PhCDE) (top).

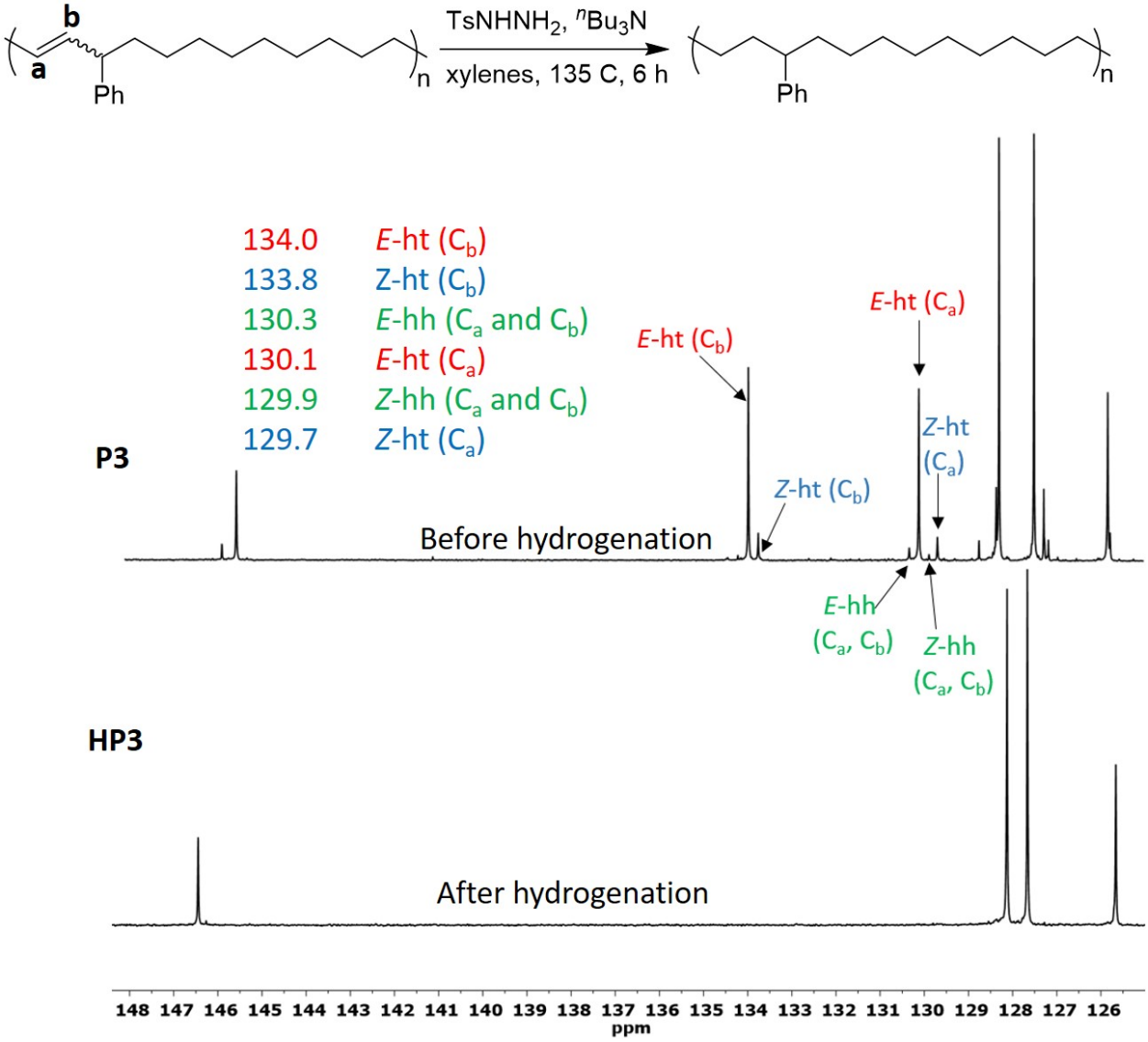


Figure S14. Partial ^{13}C NMR spectra and isomer assignment of **P3** before (top) and after hydrogenation (bottom).

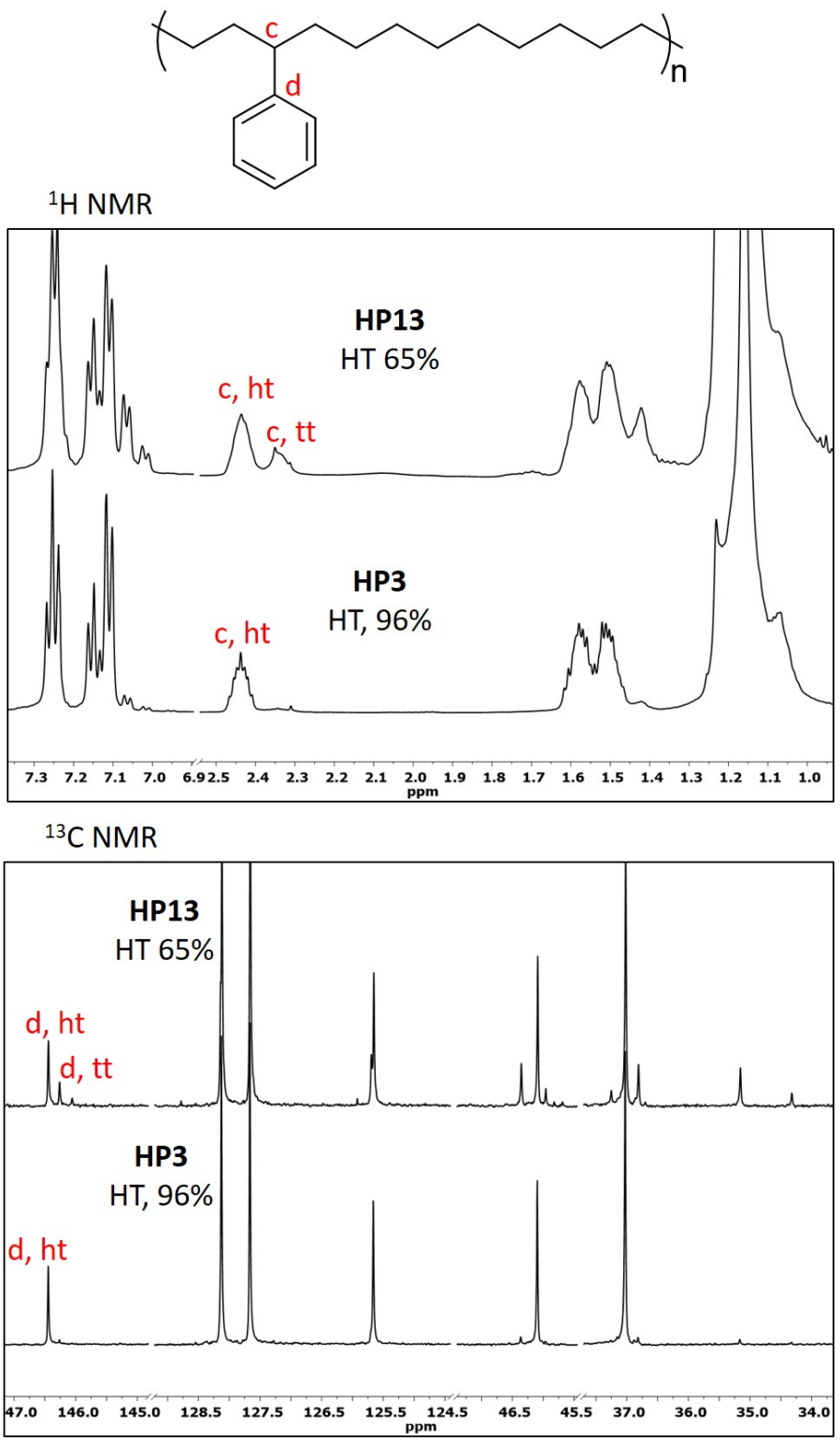


Figure S15. Partial ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of the (A) polymer **HP13** with low regioregularity, and (B) polymer **HP3** with high regioregularity in $CDCl_3$.

The nonlinearity of the pseudo first-order kinetic plot may be due to slow initiation at early times where an increase in the rate of conversion was observed.

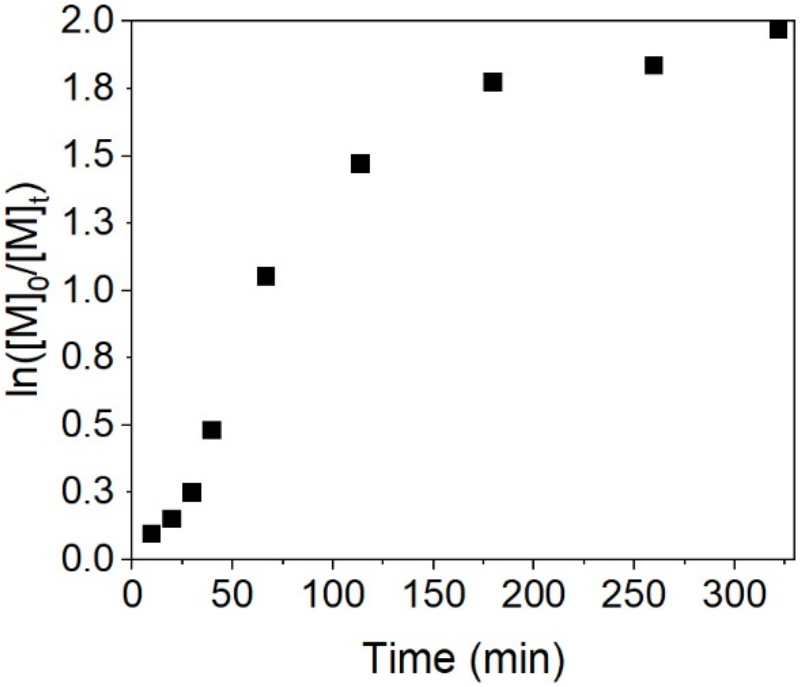
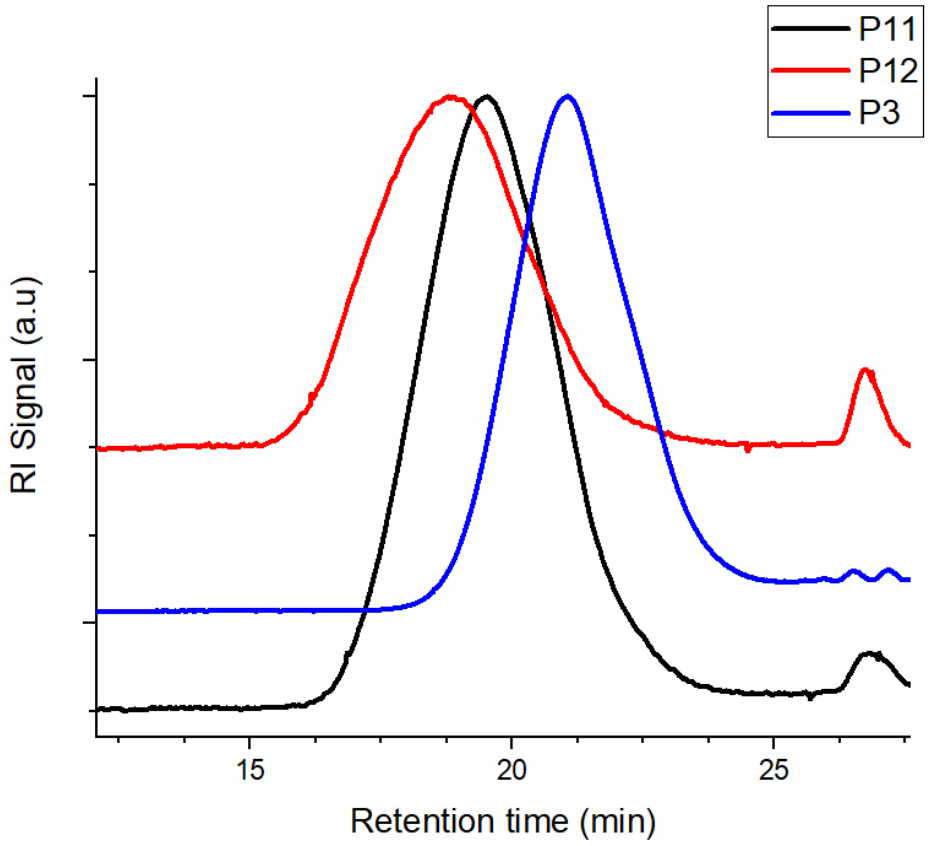


Figure S16. Pseudo first-order kinetic plot of the ROMP of 3PhCDE. The data was taken from the solution polymerization of 3PhCDE with G2 catalyst at 40 ˚C for 15 h. Initial monomer concentration was 4M, whereas the catalyst concentration was 0.05 mol%.



Polymer[a]	M_w (kg mol^{-1})	M_n (kg mol^{-1})	Đ (M_w/M_n)
	SEC	SEC	SEC
P3	50	28	1.8
P11	170	84	2.0
P12	310	120	2.5

Figure S17. SEC characterization curves and data for selected poly(3PhCDE) polymers. All polymerizations were carried using 0.05 mol% G2 catalyst and *cis*-4-octene as a chain transfer agent (CTA). SEC characterization data was determined based on chloroform SEC, PS standards.