

Supporting Information for:
**Polyolefin Graft Copolymers Through a Ring-Opening
Metathesis Grafting Through Approach**

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EXPERIMENTAL DETAILS

Materials. All solvents used for purification were purchased from Fisher Scientific and used as received. Anhydrous tetrahydrofuran (THF) used for hydroboration reaction and toluene used for macromonomer synthesis were obtained from a solvent purification system. Anhydrous chloroform (CHCl_3) used for ring opening metathesis polymerization (ROMP) was purified according to the method reported in literature.¹ All commercial chemicals were purchased from Sigma-Aldrich and used as received unless further noted. Cyclooctene (COE) and chain transfer agent (CTA) *cis*-4-octene were distilled over calcium hydride before use. Allyl terminated atactic polypropylenes (aPP-Allyl) were kindly provided by the ExxonMobil Corporation. $^1\text{H-NMR}$ (500 MHz, *d*- CHCl_3 , 25 °C): δ = 5.81 (dd, 1H), 5.00 (m, 2H), 4.75 (m, 0.02H), 4.68 (m, 0.02H) 2.07 (m, 1H), 1.89 (m, 1H), 0.40-1.80 (m, 512H or 1189H). $^1\text{H-NMR}$ spectroscopy experiments indicate 98% allyl functionality and 2% vinylidene. $M_{n,\text{NMR}}$ = 3.6 kg/mol and 8.3 kg/mol, respectively, for two allyl terminated aPP (aPP-Allyl) polymers. IR (ν , cm^{-1}): 2760-3000 and 1775-1900 (alkyl), 1150 (C=C). IR (ν , cm^{-1}): 2957, 2912, 2867, 2836, 1461, 1378, 1155, 968; 910 (C=C). The characterization of the other end group R is presented in Figure S15. The $^{13}\text{C-DEPTH-135}$ results indicate R is predominantly a n-propyl group.

Representative Synthesis of aPP-OH. aPP-OH was prepared using allyl terminated aPP (aPP-Allyl) by hydroboration/oxidation reaction (Scheme 1). The procedure is modified based on a report by Dasin *et al.*² In a 500mL three-neck round-bottom flask, aPP-Allyl (11.6 g, 4.0 kg/mol, 2.2 mmol) was dissolved in dry THF (100mL). Then the mixture was purged with argon for 30min. After cooling the reaction to 0 °C, 9-borabicyclo[3.3.1]nonane (9-BBN) (35ml, 0.5M in THF, 17.5 mmol) was introduced dropwise by a syringe. The mixture was stirred at room temperature for 18 h. The reaction was chilled to 0 °C before slow addition of methanol (MeOH) (7.5 mL, 185 mmol) at 0 °C and aq. NaOH (6 N, 15 mL, 90 mmol) and H_2O_2 (30 %, 29 mL, 161 mmol). The mixture was heated gradually to 40 °C and stirred for 10 h before it was cooled down to room temperature. After removing the solvent using a rotavapor, the solid was dissolved in minimal chloroform and precipitated into a large excess of cold methanol with 40 vol% HCl (pH = 5) in triplicate. The recovered polymer was dried *in vacuo* at 50 °C for 24 h. $^1\text{H-NMR}$ analysis indicated about 99% conversion. Yield: 9.86 g (85 %). $^1\text{H-NMR}$ (500 MHz, *d*- CHCl_3 , 25 °C): δ = 3.63 (t, 2H), 0.4-1.8

(m, 680H or 1442H). $M_{n,NMR} = 4.8$ kg/mol and 11.0 kg/mol, respectively for two aPP-OH polymers. IR (ν , cm^{-1}): C-O at 1060. Details are provided in Figure S1 and Figure S3.

Representative Synthesis of aPP_MM. The macromonomer was prepared via alkoxycarbonylation reaction using a similar procedure from the synthesis of a 4-substituted cyclooctene derivative reported by Onbulak *et al.*³ In a 1L Parr reactor, aPP-OH (11.5 g, 2.0 mmol) was dissolved in 50 mL dry toluene, and added with 1,5-cyclooctadiene (4.4 mL, 36 mmol), PdCl₂ (64 mg, 0.36 mmol), and PPh₃ (379 mg, 1.4 mmol). The reactor was then sealed and thoroughly purged with CO. The final pressure was increased to 600 psig by charging CO and the reactor was heated to 90 °C. The reaction was stirred for 48 h. The resultant mixture was filtered through Celite and the solvent was removed using a rotavapor. The polymer was purified by dissolving into CHCl₃ and precipitated into MeOH three times, followed by drying *in vacuo* at 60 °C for 2 days. The conversion was 97% for aPP_MM_5k and 98% for aPP_MM_11k. ¹H-NMR (500 MHz, *d*-CHCl₃, 25 °C): $\delta = 5.66$ (m, 2H), 4.02 (t, 2H), 2.45 (m, 1H), 2.06-2.26 (m, 3H), 2.01 (m, 1H), 1.85 (m, 1H), 0.60-1.80 (m, 512H or 1189H). $M_{n,NMR} = 5.2$ kg/mol and 11.0 kg/mol for the two aPP_MM. ¹³C-NMR (500 MHz, *d*-CHCl₃, 25 °C): $\delta = 130.27, 65.28, 46.31, 45.64, 43.45, 27.36, 25.95, 24.22, 24.20, 20.42$. IR (ν , cm^{-1}): C=O at 1598. Details are given in Figure S1-S4 and Table 1.

Representative Synthesis of PE-g-aPP Copolymers. The polyolefin copolymers PE-g-aPP were prepared through two steps: ROMP and hydrogenation (Scheme 2).

Step 1. ROMP. Macromonomer aPP_MM_5k (0.375 g, 0.07 mmol, 1 eq.), and cyclooctene (1 mL, 99 eq.) was dissolved in CHCl₃ (anhydrous) (9.5 mL) in a single-neck round-bottom flask inside a glove box. The copolymerization was initiated by addition of 0.5mL of third generation Grubbs catalyst (G3 catalyst) stock solution (0.02 eq.). The flask was then sealed with a rubber septum and stirred at 50 °C for 20 h. Finally, the reaction was quenched with 0.5 mL ethyl vinyl ether and stirred at room temperature for an additional 20 min. The copolymers were recovered by precipitation into a large excess of MeOH. The polymer was redissolved in CHCl₃ and precipitated into MeOH a second time. The products were dried *in vacuo* overnight at room temperature, affording white opaque solid polymers. Yield: ~90%. ¹H-NMR (500 MHz, *d*-CHCl₃, 25 °C): $\delta = 5.20$ -5.46 (m), 1.91-2.07 (m), 0.60-1.80 (m). NMR spectra and LS-SEC information are available in Figure S5-S6 and Table S1.

Step 2. Hydrogenation.^{1,3} Into a round-bottom flask with a stir bar, unsaturated copolymers, p-toluenesulfonyl hydrazide (TsNH-NH₂) (3.5 eq. to the double bonds), tributylamine (*n*-Bu₃N) (3.2 eq. to the double bonds), butylated hydroxytoluene (BHT) (0.025 eq. to the double bonds) were charged followed by *o*-xylene (50 g/mL). The flask was then equipped with a condenser and refluxed for 18 h in air. The hot solution was then precipitated into a large excess of cold MeOH. Then the white polymer solid was separated by filtration and dissolved into *o*-xylene by heating at 130 °C, followed by precipitation into cold hexane. This procedure was repeated another two times to remove all the unattached aPP. 0.5 wt.% BHT was added to the hexane before last precipitation. The resulting copolymers were dried at 80 °C *in vacuo* overnight. The NMR spectra showed a quantitative hydrogenation of double bonds (>99% conversion). Yield: 50~70%. ¹H-NMR (500 MHz, *d*-toluene, 90 °C): δ = 2.03-2.13 (m), 0.8-1.50 (m). Details are available in Figure 1, Table 2, Figure S7 and Table S2.

Synthesis of Linear Polyethylene (PE).⁴ Cyclooctene (COE) (6 mL, 46 mmol), chain transfer agent (CTA) *cis*-4-octene (6.6 μ L, 0.042 mol), and THF (22.5 mL) were added into a 100mL two-neck round-bottom flask. The mixture was purged with argon for 20min and then heated to 35 °C. Next, the reaction was initiated by addition of second generation Grubbs catalyst (G2 catalyst) from a stock solution in CHCl₃ (anhydrous) (0.36 mg, 0.00042 mmol). The reaction was stirred at the set temperature for 3h before it was cooled down and quenched with 1 mL of ethyl vinyl ether. After stirring at room temperature for an additional 20 min, the solution was precipitated into a large excess of MeOH twice. The product was dried at room temperature *in vacuo* overnight. Hydrogenation and purification processes were similar to that described for graft copolymers. High temperature NMR spectroscopy confirms the polymer was fully hydrogenated (conversion >99%) with absence of unsaturated bonds. ¹H-NMR (500 MHz, *d*-toluene, 90 °C): δ = 0.8-1.50 (m). Details are available in Figure 1, Table 2, Figure S7 and Table S2.

Copolymerization Kinetics Study. The kinetics of COE and MM copolymerization were evaluated by monitoring the conversion of the two monomers by NMR spectroscopy *in situ* at room temperature. COE (1.5 μ L, 0.012 mmol), aPP_MM_5k (42 mg, 0.016 mmol), and *d*-chloroform (anhydrous) (0.5 mL) were mixed in a NMR tube in a glove box and sealed with a rubber septum. A stock solution of G3 catalyst was prepared in the glove box and 2 μ L of the

solution was injected into the NMR tube using an air-tight microsyringe right before insertion of the NMR tube into the instrument. Data was collected continuously with $d1 = 5s$ and $nt = 4$ for each experiment. The reaction progress monitored by NMR spectroscopy is shown in Figure S8. The conversion of MM and COE was estimated by the integrations of peaks at 2.28-2.44 ppm ($I_1 = 2HM+1HPM$), 3.99-4.17 ppm ($I_2 = 2HPM+2HM$), 5.28-5.61 ppm ($I_3 = 2HPM+2HPm$), and 5.63-5.77 ppm ($I_4 = 2HM+2Hm$) in the 1H -NMR spectrum (Figure S8). The conversion of MM = $(I_3-I_1)/I_2 \times 2$, and the conversion of COE = $(I_4+I_2-2I_1)/(I_3+I_4-I_2)$.

Molecular Characterization. Nuclear magnetic resonance (NMR) spectra at 25 °C (1H -NMR, ^{13}C -NMR, HSQC) were collected on a Bruker HD-500, Ax-400 or AV-500 for aPP macromonomers, and unsaturated polymers including PCOE and PCOE-g-aPP in d -CHCl₃. Hydrogenated products were characterized in d -toluene on a Bruker AV-500 at 90 °C. The kinetic experiment data was recorded on a Bruker AV-500 d -CHCl₃ at 25 °C. Residual solvent peaks were used as references: 7.26 ppm for d -CHCl₃ and 2.08 ppm for d -toluene.

The molar mass and dispersity of aPP_MMs, unsaturated PCOE-g-aPPs and linear PCOE were measured by size exclusion chromatography (SEC) analysis using an Agilent 1260 series instrument with three successive Styragel columns with THF as the mobile phase (1 mL/min at 25 °C). The detectors employed were a Wyatt Technology DAWN Heleos II 18-angle laser light scattering (MALLS) detector and a Wyatt OPTILAB T-rEX refractive index detector. Absolute molar mass (M_w) was determined by LS signals assuming 100% mass recovery method. After hydrogenation, the molar mass was measured by high-temperature SEC (HT-SEC) PL-GPC 220 equipped with three PLGel 10 μm Mixed-B columns and trichlorobenzene at 135 °C. The refractometer signal was collected and the molar mass was estimated using the universal calibration by PS standards ($K = 15.2 \times 10^{-5}$ dL/g, $\alpha = 0.76$) and Mark-Houwink constants of PE ($K = 30.1 \times 10^{-5}$ dL/g, $\alpha = 0.75$). The Fourier transform infrared (FTIR) spectra were obtained on a Bruker Alpha Platinum ATR-FTIR spectrometer with a diamond crystal operated in the attenuated total reflection (ATR) mode. The resolution was set to 4 cm^{-1} and 32 scans for each experiment.

Thermal Characterization. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q500. Samples were heated under nitrogen to 500 °C at a ramping rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were conducted on a TA Instruments Discovery DSC with N₂ purging at 10 °C/min. The samples were sealed in hermetic aluminum T-Zero pans. A heating cycle was programmed to erase thermal and processing history of the samples. The second heating cycles were used to determine the thermal transition temperatures.

X-ray Scattering Characterizations. Samples were prepared by hot pressing at 150 °C into films with a thickness of 0.5-0.6 mm, followed by rapid quenching on a cold water-jacket press. The X-ray scattering experiments were conducted using beamline 5-ID-D at Argonne National Laboratory (ANL). The data was collected on a CCD area detector using an energy of 17 keV and a wavelength of 0.76 Å. The sample-to-detector distances were calibrated using silver behenate. Plots of intensity (I) vs. scattering wave vector (q) were obtained by azimuthal integration of two-dimensional X-ray scattering data, where $q = 4\pi\lambda^{-1}\sin(\theta/2)$ (θ is the scattering angle and λ is the wavelength). For wide-angle X-ray scattering (WAXS), hot-pressed free standing samples were mounted onto a washer and characterized at room temperature. For small-angle X-ray scattering (SAXS) experiments, the samples were loaded and hermetically sealed in DSC pans in a glove box.

Rheological Properties Characterizations. Small-amplitude oscillatory shear rheology experiments were conducted on a TA Instruments Rheometric Series ARES 1 or ARES 2 using 8 mm diameter parallel plates under nitrogen atmosphere. A strain sweep was performed before each shear experiment to insure the shear strain was within the linear viscoelastic region. Dynamic frequency shear experiments were conducted for PE and each PE-g-aPP copolymer at 130 °C, 150 °C, 170 °C, 190 °C, and 210 °C in the frequency range of 0.01-100 rad/s. Dynamic master curves were generated by time-temperature superposition (TTS) with a reference temperature T_0 of 150 °C.

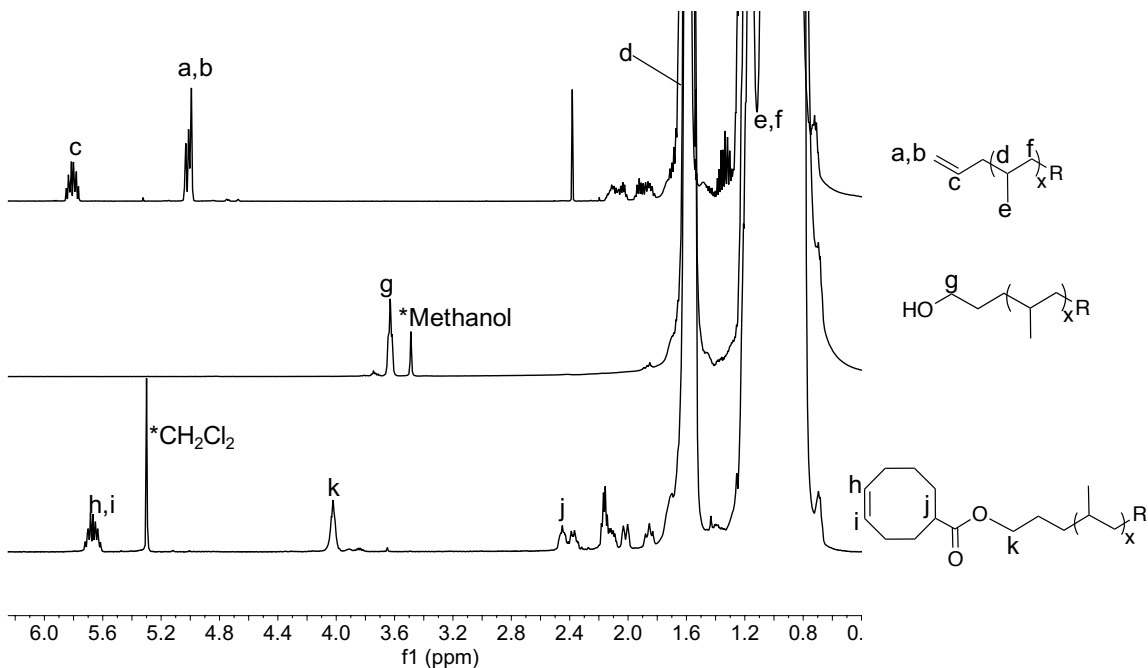


Figure S1 $^1\text{H-NMR}$ spectra of aPP-Allyl, aPP-OH and aPP_MM (aPP_MM_5k, 500 Hz, $d\text{-CHCl}_3$).

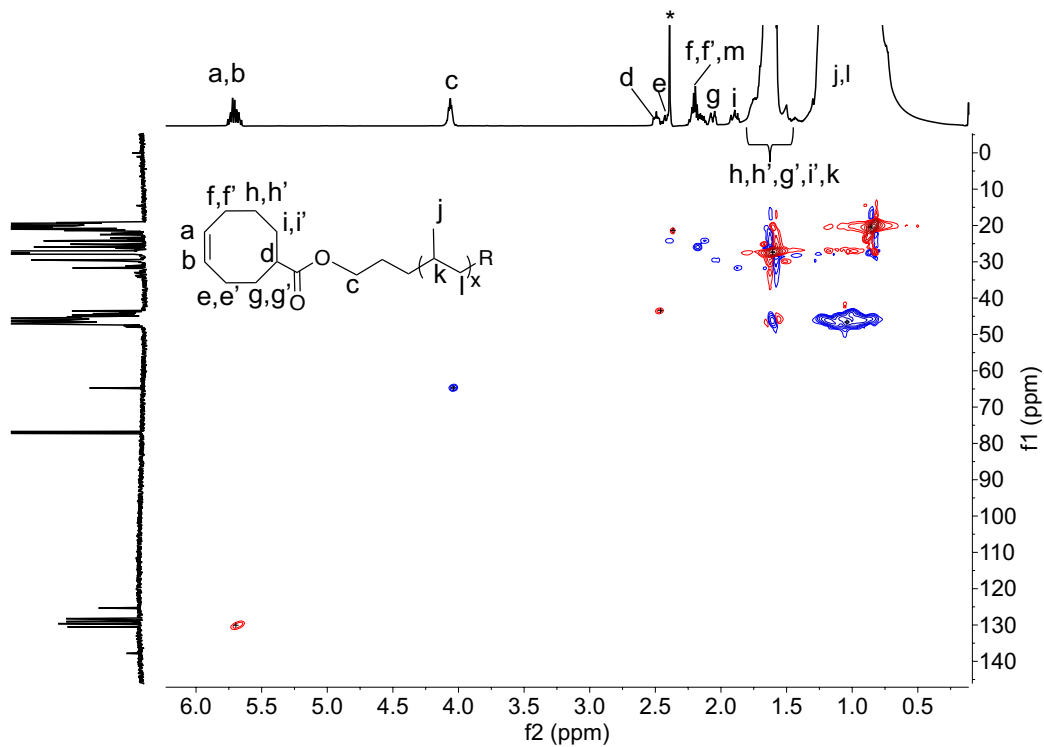


Figure S2 HSQC 2D-NMR of aPP_MM_5k (500 Hz, $d\text{-CHCl}_3$. CH_2 in blue, CH and CH_3 in red.

* refers to incidental toluene).

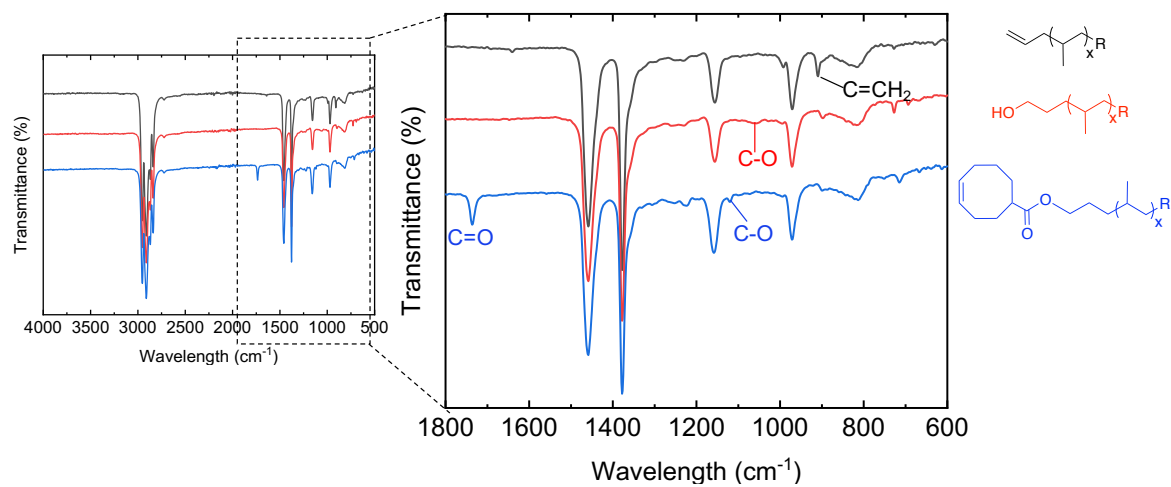


Figure S3 ATR-FTIR spectrum for MM synthesis.

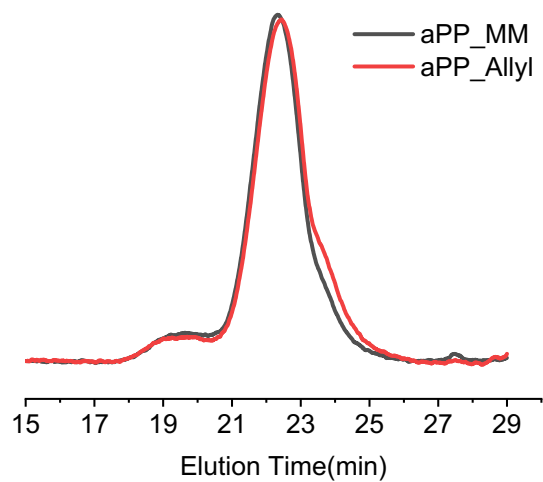


Figure S4 LS-SEC traces (refractometer signal) of aPP-MM_{11k} and the corresponding aPP-Allyl.

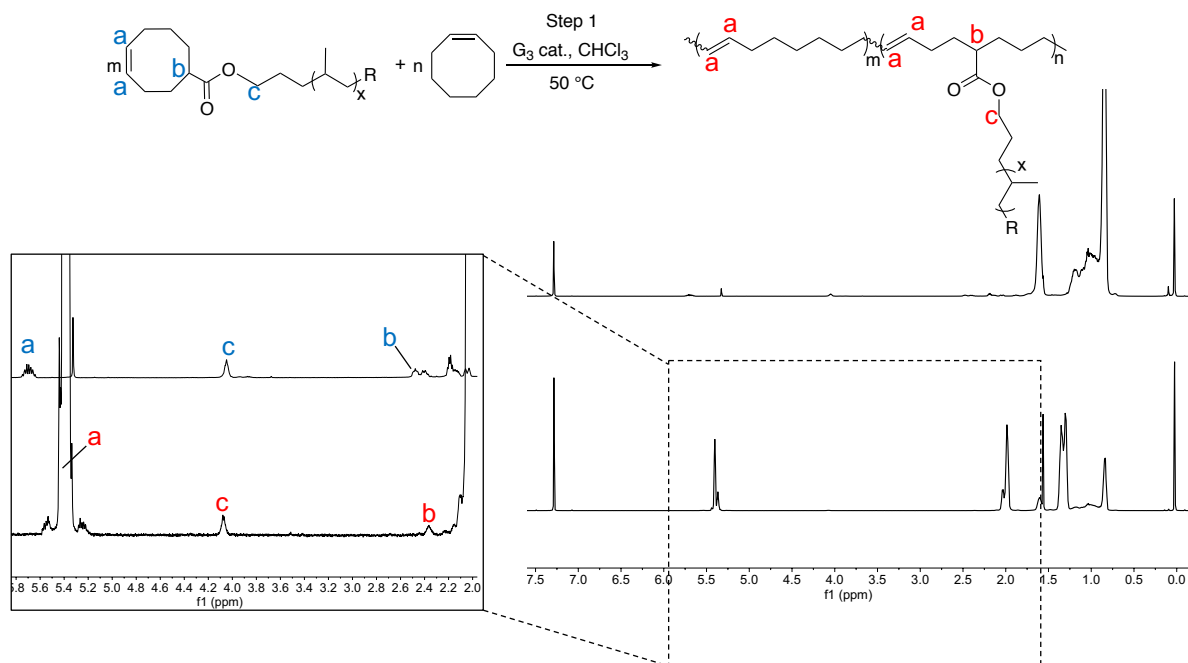


Figure S5 Representative $^1\text{H-NMR}$ spectra for synthesis of PCOE-g-aPP copolymer (PCOE-g-aPP-1) and aPP_MM_5k.

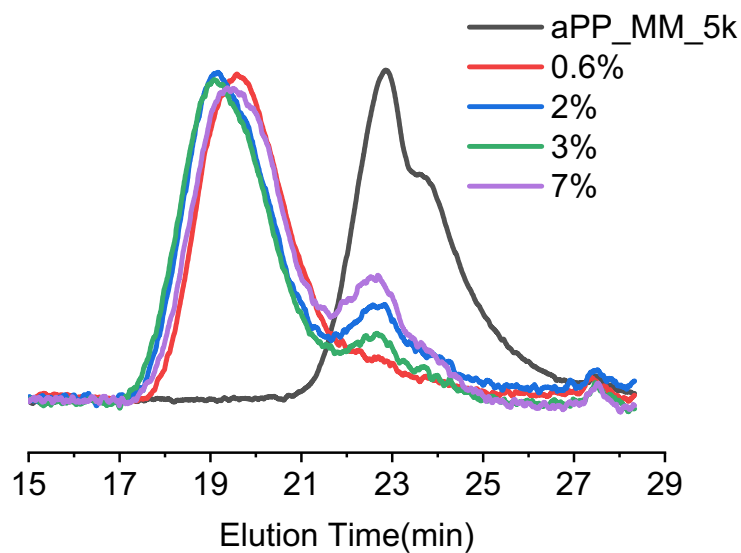


Figure S6 LS-SEC (refractometer signal) of PCOE-g-aPPs with different macromonomer feed molar percentage.

Table S1 Effect of feed molar percentage of MM on COE and aPP_MM copolymerization.

Name	F_{MM}^a (%)	m^b	$M_{n,LS}^c$ (kg/mol)	$M_{w,LS}^c$ (kg/mol)	D_{LS}^c
PP-MM_5k			5.7	7.5	1.3
PCOE-g-aPP_1	0.6	0.6	115	173	1.5
PCOE-g-aPP_2	2	2	241	362	1.5
PCOE-g-aPP_3	3	2	214	364	1.7
PCOE-g-aPP_4	7	-	252	403	1.6

^aFeed molar percentage of MM. ^bThe number of grafts per 100 COE units is calculated by using molar ratio of PE and aPP by high temperature ¹H-NMR spectroscopy in toluene and molar mass of the aPP determined by ¹H-NMR spectroscopy in CDCl₃ at room temperature. ^cDetermined by LS-SEC in THF at 25°C.

Table S2 HT-SEC results and thermal degradation temperature (T_d).

Polymers	$M_{n,HT}^a$ (kg/mol)	D_{HT}^a	ΔH_m^b (J/g)	$T_{d,1\%}^c$ (°C)
PE	65	2.2	187	321
PE-g-aPP_5k_4	104	2.1	112	350
PE-g-aPP_5k_18	87	2.1	77	289
PE-g-aPP_5k_20	160	2.2	61	356
PE-g-aPP_11k_18	86	3.5	53	376

^aMolar masses measured in TCB at 135°C and calculated using universal calibration and Mark-Houwink constants of PE. ^bDSC experiments conducted at a ramping rate of 10°C/min. Data from the 2nd heating cycle. ^c T_d at 1% weight loss.

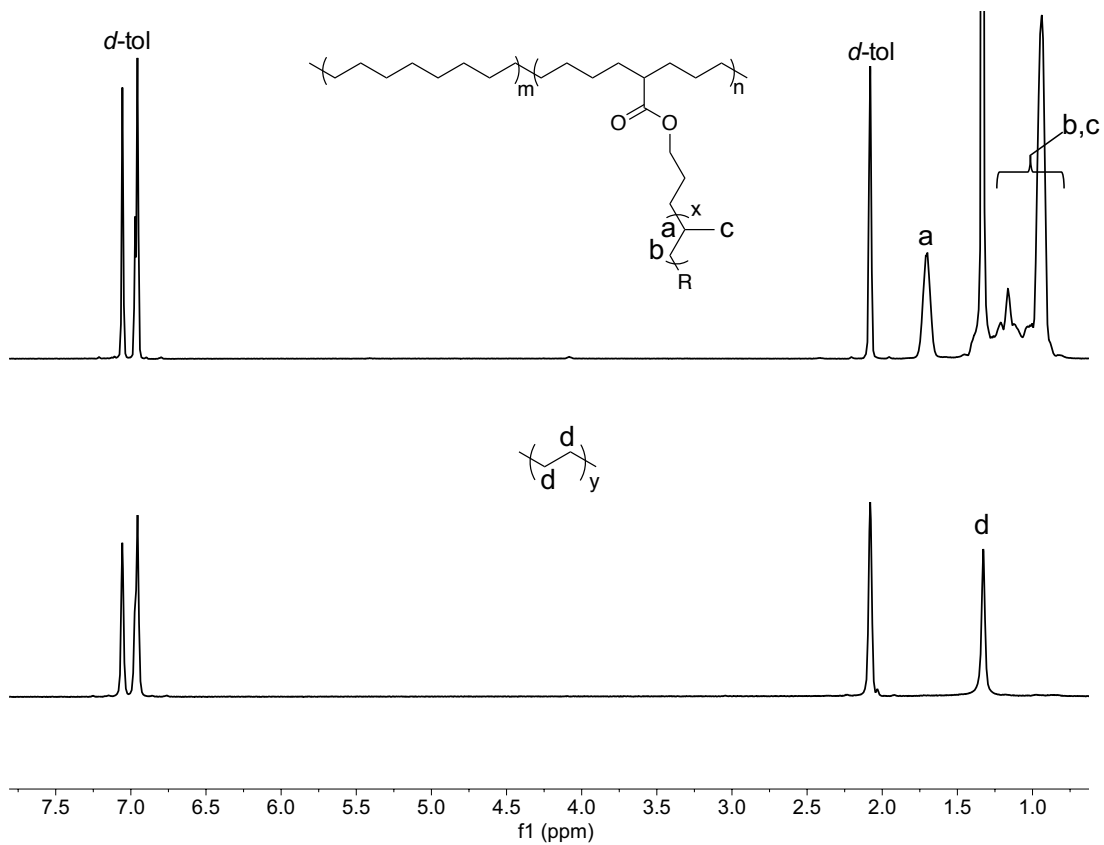


Figure S7 $^1\text{H-NMR}$ spectra of representative PE-g-aPP (PE-g-aPP_11k_18) and linear PE.

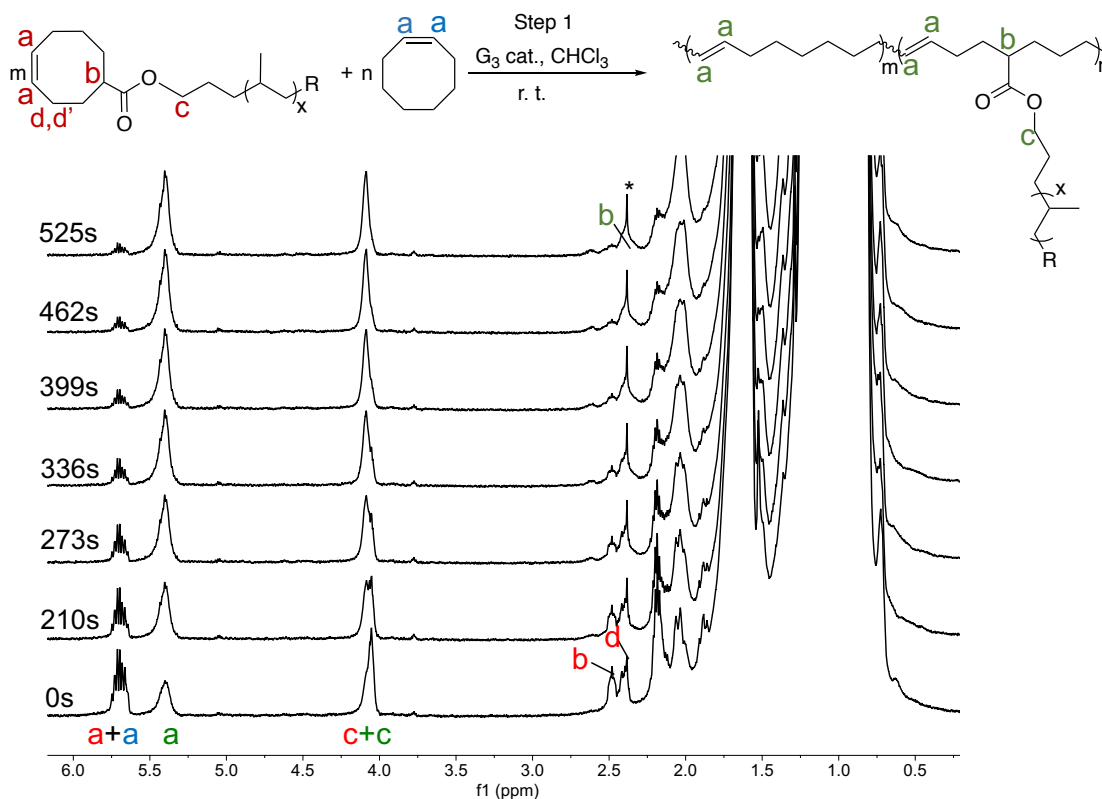


Figure S8 Kinetic study of ROMP grafting-through reaction by in situ $^1\text{H-NMR}$ spectroscopy. (500 Hz in $d\text{-CHCl}_3$. $[\text{MM}]:[\text{COE}] = 68:32$, $[\text{COE}] = 0.0317\text{mM}$. * represents proton signal from incidental toluene, the integration of which was considered when calculating the conversions.)

Fitting of r_{COE} and r_{MM} for Ring Opening Copolymerization of COE and MM.⁵

According to BSL method, the curves were fitted using the following equations:

$$p_{\text{AB}}(p_{\text{A}}) = 1 - n_{\text{A}}(1 - p_{\text{A}}) - (1 - n_{\text{A}})(1 - p_{\text{A}})^{r_{\text{B}}}$$

$$p_{\text{AB}}(p_{\text{B}}) = 1 - n_{\text{A}}(1 - p_{\text{B}})^{r_{\text{A}}} - (1 - n_{\text{A}})(1 - p_{\text{B}})$$

where p_{AB} is total conversion, n_{A} and n_{B} are molar percentages of A and B monomers, p_{B} and p_{A} are monomer conversions, r_{A} and r_{B} are reactivity ratios.

Total conversion vs. monomer conversion is plotted for both MM and COE. The blue dot line is the simulation for random copolymerization where $r_{\text{A}} = r_{\text{B}} = 1$. In this study, $r_{\text{A}} = r_{\text{COE}} = 0.75 \pm 0.02$, $r_{\text{B}} = r_{\text{MM}} = 1.42 \pm 0.05$, and $r_{\text{COE}} \times r_{\text{MM}} = 1.06 \pm 0.01$, indicating a near random copolymerization.

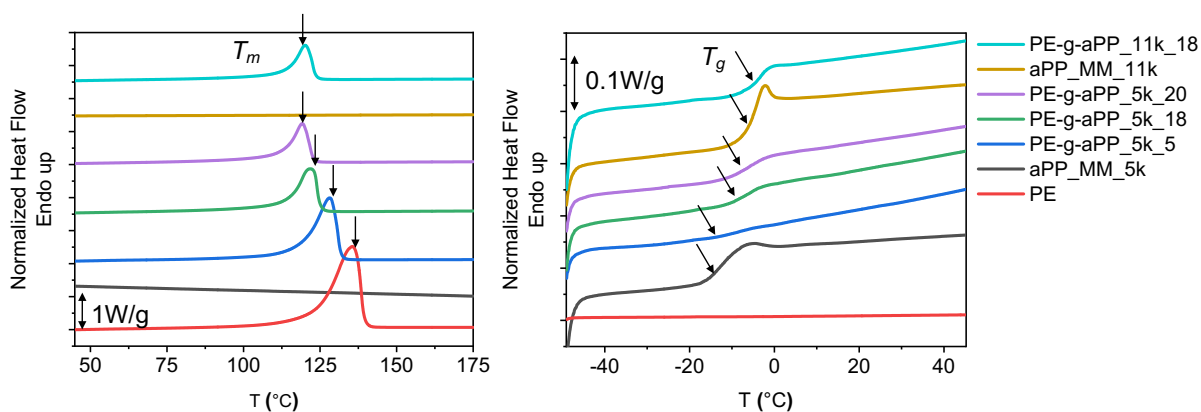


Figure S9 DSC analyses conducted at 10 min/°C (2nd heating cycle). The curves are shifted with Y offsets for clarity.

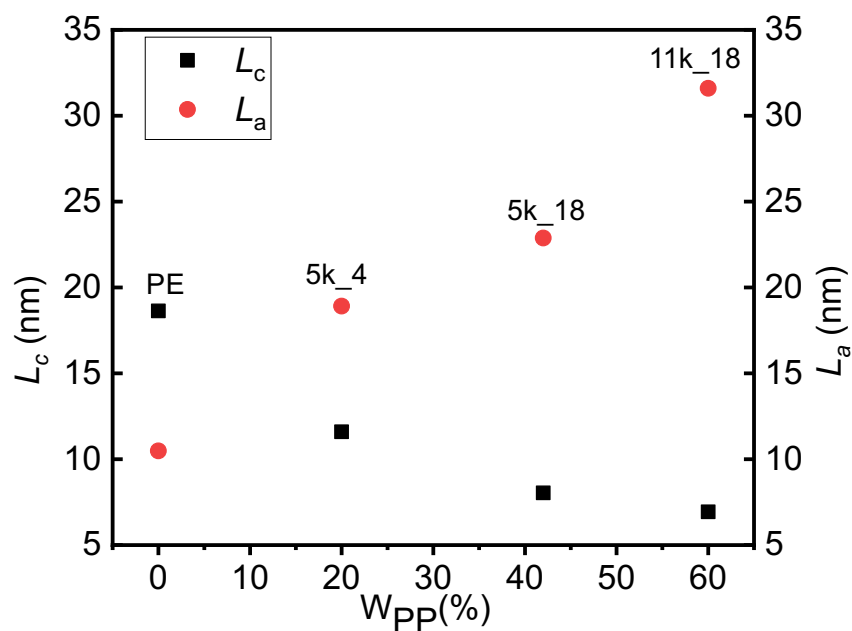


Figure S10 Thickness of crystalline (c) and amorphous (a) domains. $L_c = d \times X_c$, $L_a = d \times (1 - X_c)$.

Table S3 Rheological WLF parameters for the linear PE and the selected PE-g-aPPs.

Name	C_1	C_2 (°C)
PE	1.7	219
PE-g-app_5k_4	5.0	300
PE-g-app_5k_18	8.5	483
PE-g-app_11k_18	3.4	170

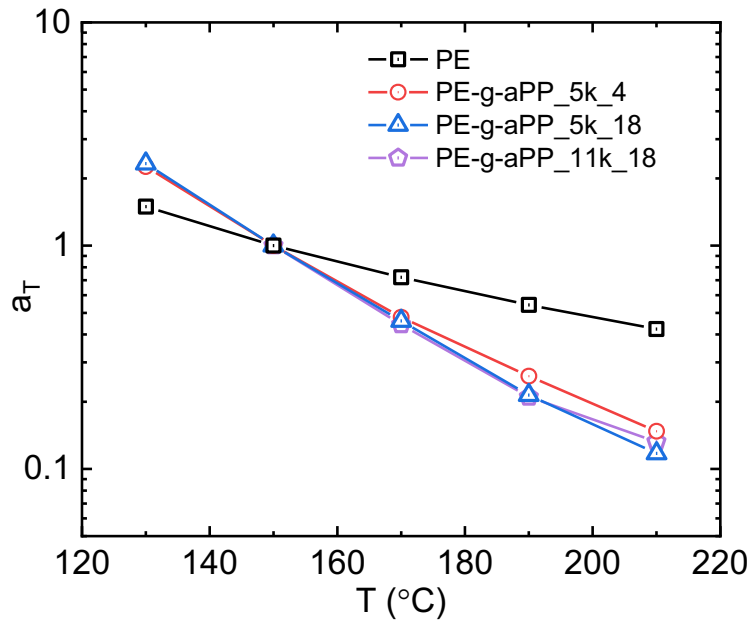


Figure S11 Shift factor a_T as a function of temperature for the selected samples. $T_0 = 150$ °C.

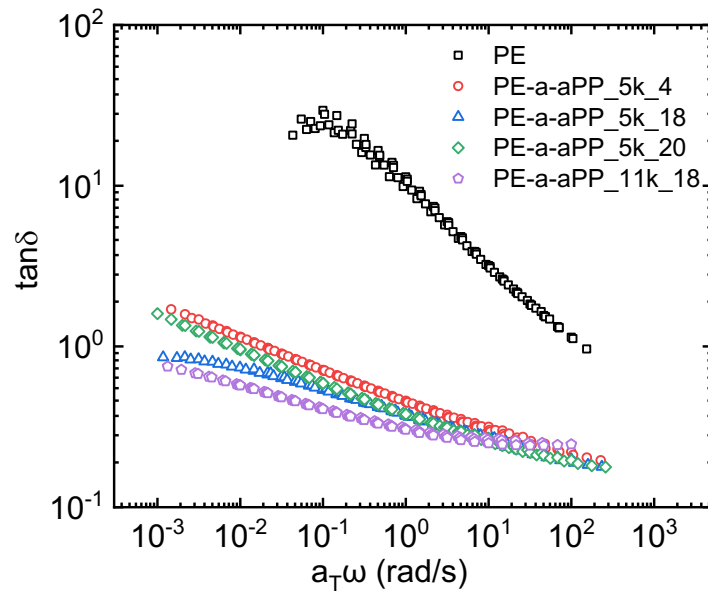


Figure S12 Tan δ vs. $a_T\omega$.

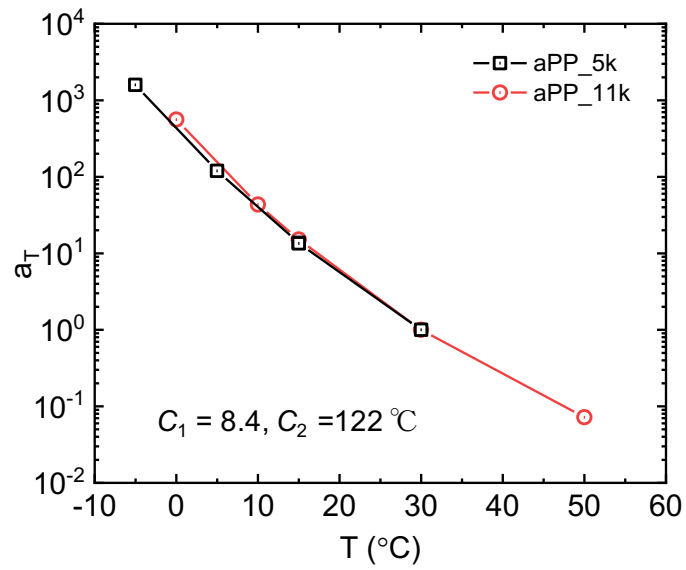


Figure S13 Shift factor a_T as a function of temperature for aPP_MMs. $T_0 = 30$ °C.

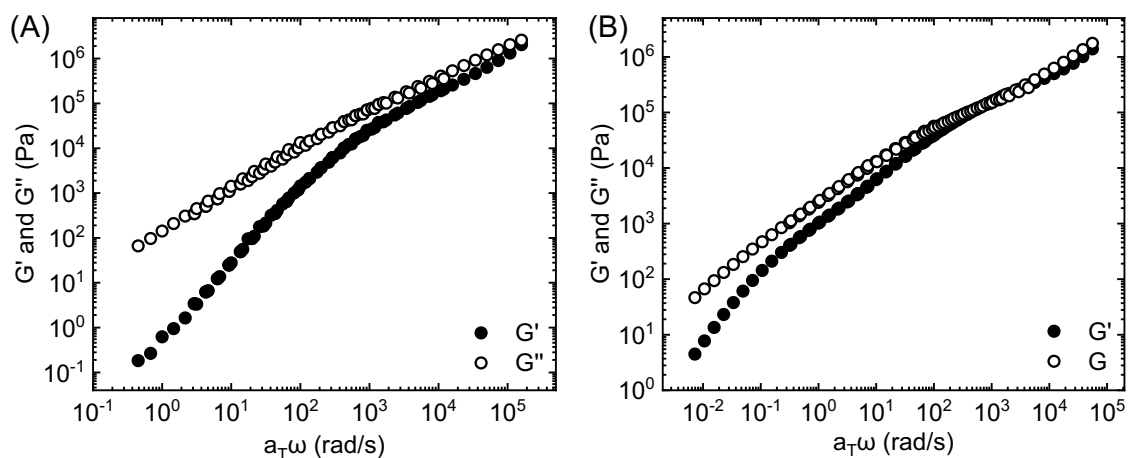


Figure S14 Master curves for aPP_MM_5k (A) and aPP_MM_11k (B), with closed dots for G' and open dots for G'' . $T_0 = 30\text{ }^\circ\text{C}$.

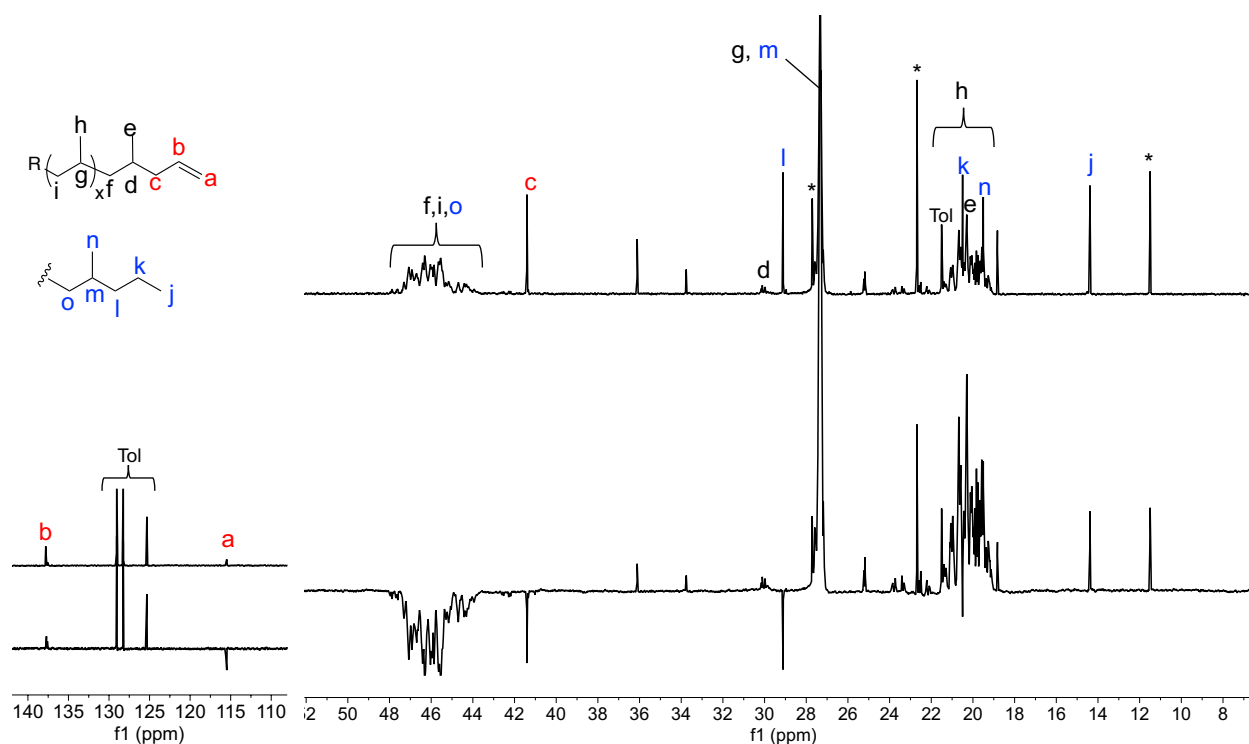


Figure S15 ^{13}C -DEPTH-135 NMR spectra of allyl-aPP_3k in $d\text{-CHCl}_3$. Tol represents incidental toluene. * peaks are from iso-butyl group from the catalyst.

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