Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

Oligomerization and polymerization of 5-ethylidene-2-norbornene by cationic palladium and nickel catalysts

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I. General Considerations

All reactions were performed under an inert nitrogen atmosphere utilizing standard vacuum line and glovebox techniques unless otherwise noted. All NMR-scale reactions were prepared in a glovebox and monitored in Teflon-sealed NMR tubes. Solvents were dried and degassed with argon using a Pure Process Technology solvent system and stored over 3 Å molecular sieves.

Gel permeation chromatography (GPC) was performed on a Waters 2695 separations module liquid chromatograph equipped with either four Waters Styragel HR columns (WAT044225, WAT044231, WAT044237, and WAT054460) arranged in series or two Agilent Resipore columns (PL1113-6300) maintained at 35 °C. Tetrahydrofuran was used as the mobile phase at a flow rate of 1.0 mL/min. Molecular weight and dispersity data are reported relative to polystyrene standards. All molecular weight and dispersity data are reported with a normalized RI signal. Glass transition temperatures (T_g) of dried polymer samples were measured using differential scanning calorimetry (DSC) on a TA Instruments Discovery DSC. All T_g values were obtained from a second heating scan after the thermal history was removed. All heating and cooling rates were 10 °C/min. Decomposition onset temperatures (T_d) of dried polymer samples were measured by thermal gravimetric analysis (TGA) on a TA Instruments Q5000 Thermogravimetric Analyzer. Polymer samples were heated from ambient temperatures to 500 °C at a heating rate of 10 °C/min. Values of T_d (temperature at 5% weight loss) were obtained from wt % vs. temperature (°C) plots.

High resolution mass spectra were collected on a ThermoScientific Q Exactive HF-X with a mass range of 50 to 4,000 Da with an atmospheric-pressure chemical-ionization probe, and resolution up to 100,000 at *m/z* 400 at 1 Hz, >750,000 at *m/z* 400 at slower scan repetition rates. Oligomer samples were analyzed by atmospheric pressure chemical ionization mass spectrometry (APCI-MS) in CH_2Cl_2/CH_3OH mixtures. Samples with M_n exceeding 1,000 as determined by GPC could not be successfully ionized and analyzed using this mass spectrometry technique.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on 400, 500, or 600 MHz spectrometers. NMR characterization data are reported at 25 °C, unless specified otherwise. All of the NMR solvents were purchased from Cambridge Isotopes Laboratories. Dichloromethane-d_2 (CD_2Cl_2) was degassed by three freeze−pump−thaw cycles, dried by passage through a small column of activated alumina, and stored over 3 Å molecular sieves. ^1H chemical shifts are reported in parts per million relative to residual protio solvent resonances. Metal complexes $[(\eta^6\text{-mesitylene})Ni(\eta^3\text{-2-Me-allyl})][BAr^F_4]$,[1] $[(\eta^6\text{-mesitylene})Pd(\eta^3\text{-allyl})][PF_6]$,[1] $(P^tBu_3)PdMeCl$,[2] and $NaBAr^F_4$,[3] were prepared according to literature procedures. 5-Ethylidene-2-norbornene (ENB) was purchased from Sigma Aldrich, degassed by three freeze−pump−thaw cycles and stored at −35 °C under nitrogen. All of the other reagents were commercially available and used without further purification.

II. Catalytic Procedures

General procedure for determining conversion of ENB.

Conversion of ENB, defined as the percent ENB consumed during the reaction, was determined by ^{1}H NMR spectroscopy. After the given reaction time, a 100 μL aliquot was removed from the reaction mixture immediately prior to quenching. The aliquot was then diluted with 400 μL $CDCl_3$ and 10 μL mesitylene internal standard and 10 μL methanol quencher were added. Conversion was determined by relative integration of the aromatic resonance on the mesitylene standard (6.82 ppm) against the cyclic olefinic resonances of ENB (ca. 6.1 ppm overlapping for both *E* and *Z* isomers), as seen in Figure 1.

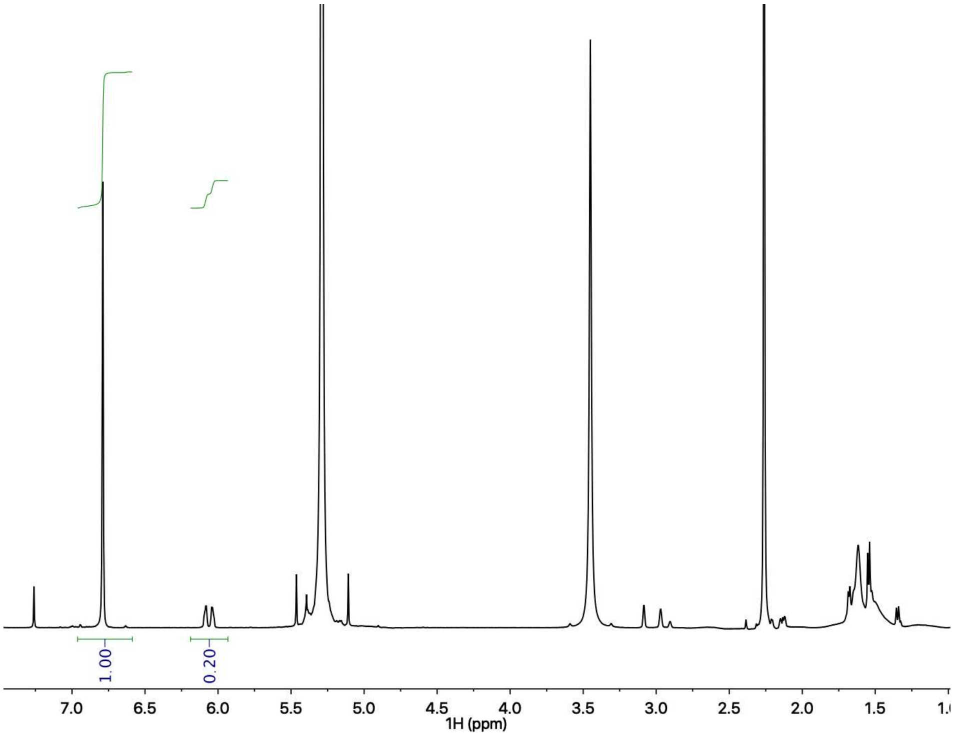

Figure S1. Representative ^{1}H NMR spectrum to determine the conversion of ENB.

Procedure for determining concentration of ethylene in dichloromethane at 25 °C.

In a nitrogen-filled glovebox, a screw-cap NMR tube was charged with 1 mL CD_2Cl_2 and 14.8 mg (0.0912 mmol) hexamethylbenzene internal standard. Due to the marginal solubility of hexamethylbenzene in dichloromethane at that concentration, $Fe(C_5H_5)_2$ (11.9 mg, 0.0733 mmol) was also added as an internal standard and was fully soluble. Ethylene was then purged through the solution in the tube for approximately two minutes, and a ^1H NMR spectrum was acquired. The final volume of the solution was approximately 800 µL after sparging with ethylene, making the final concentration of $Fe(C_5H_5)_2$ approximately 90 mM. The concentration of ethylene in solution, at 25 °C, was measured to be 220 mM.

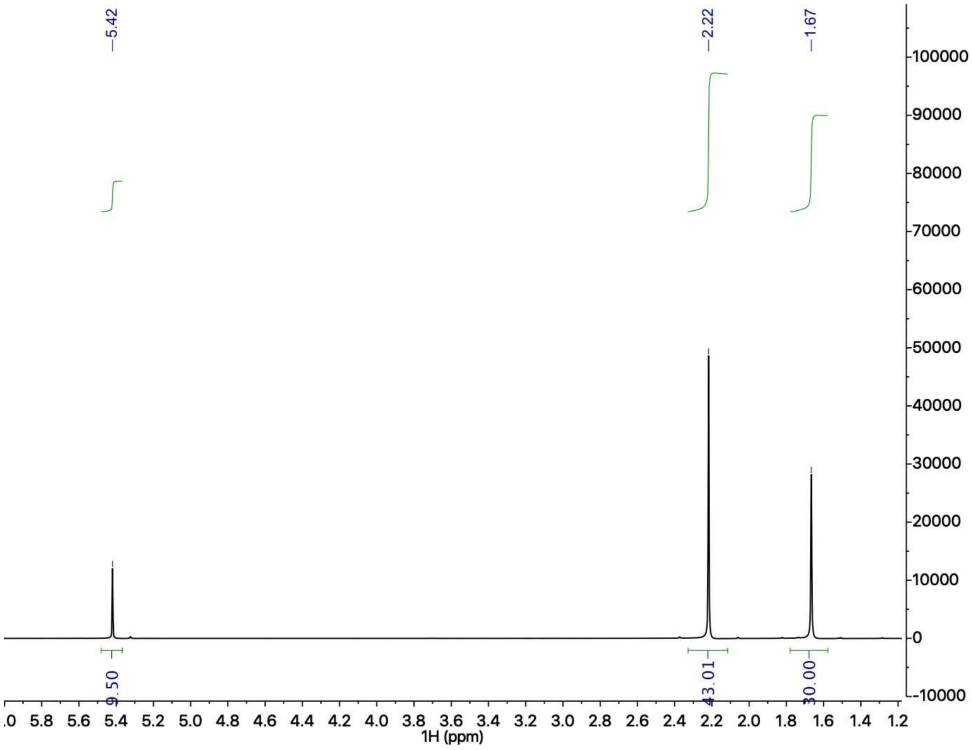

Figure S2. ^1H NMR spectrum used to determine concentration of ethylene in CD_2Cl_2 at 25 °C.

Procedure for ENB homopolymerization by [(mes)Pd(allyl)][PF_6]

In a nitrogen-filled glovebox, a septum-capped reaction tube was charged with ENB (151 μL, 1.1 mmol) and 4.25 mL dichloromethane, giving a total volume of 4.4 mL to afford a 250 mM solution of ENB. To a separate vial was added [(mes)Pd(allyl)][PF_6] (4.1 mg, 0.0099 mmol) and dichloromethane (800 μL). To the reaction tube containing the ENB solution was then added 400 μL of the [(mes)Pd(allyl)][PF_6] solution (0.0049 mmol). The tube was capped and allowed to stir outside of the glovebox at room temperature for two hours. Conversion of ENB was determined as described above. The tubes were subsequently quenched with methanol and the product dried *in vacuo* and analyzed by GPC. An exactly analogous procedure was employed for the homopolymerization of ENB by [(mes)Pd(allyl)][PF_6] with a longer reaction time of 24 hours.

Procedure for ENB homopolymerization by [(mes)Pd(allyl)][PF_6] and PR_3 (R = ^{t}Bu, Ph)

A detailed procedure for the case of R = P^tBu_3 is given here. In a nitrogen-filled glovebox, a septum-capped reaction tube was charged with ENB (151 μL, 1.1 mmol) and 4.25 mL dichloromethane, giving a total volume of 4.4 mL to afford a 250 mM solution of ENB. To a separate vial was added [(mes)Pd(allyl)][PF_6] (4.1 mg, 0.0099 mmol) and dichloromethane (800 μL). In another vial, a solution of P^tBu_3 in dichloromethane (10 mg, 0.049 mmol in 2 mL) was prepared. To the ENB-containing reaction tube was added 178 μL of the P^tBu_3 solution (0.0049 mmol), followed by 400 μL of the [(mes)Pd(allyl)][PF_6] solution (0.0049 mmol). The tube was capped and allowed to stir outside of the glovebox at room temperature for two hours. Conversion of ENB was determined as described above. The tubes were subsequently quenched with methanol and the product dried *in vacuo* and analyzed by GPC. Exactly analogous reactions were also carried out with PPh_3 in place of P^tBu_3.

Table S1. GPC characterization of polymer obtained via of homopolymerizations of ENB by $[(mes)Pd(allyl)]^+$ alone and with phosphine ligands.

Ligand	**Time (h)**	**Conversion**	***M*** M_n (Da)	M_w (Da)	*Đ*
No additive	2	23%	1100	3000	2.6
No additive	24	51%	1400	4600	3.4
1 eq P^tBu_3	2	100%	42,000	55,000	1.3
2 eq P^tBu_3	2	100%	42,000	52,000	1.2
1 eq PPh_3	2	100%	22,000	59,000	2.7
2 eq PPh_3	2	0%	-	-	-

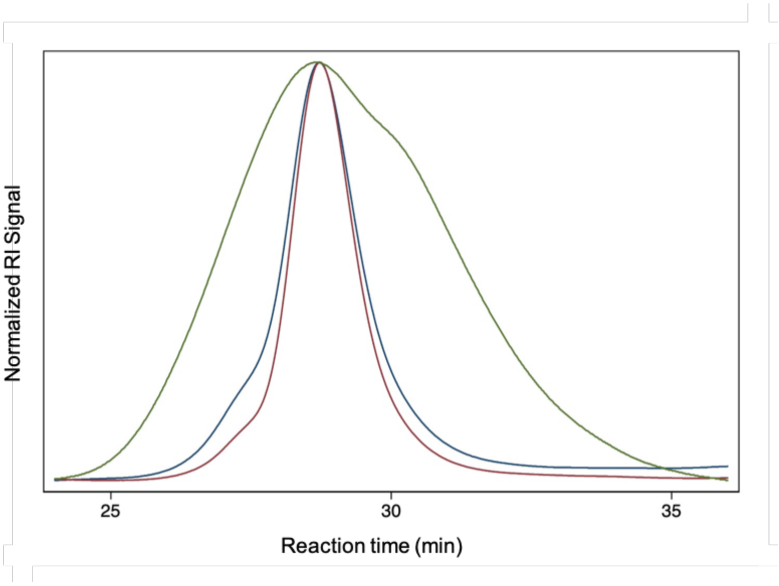

Figure S3. GPC overlay of ENB homopolymers obtained using [(mes)Pd(allyl)]$^+$ and 1 equiv. PPh_3 (green), 1 equiv. P^tBu_3 (blue), and 2 equiv. P^tBu_3 (red) after 2 hour reactions.

General procedure for homopolymerization of ENB with $(P^tBu_3)PdMeCl/NaBAr^F_4$

In a nitrogen-filled glovebox, a septum-capped reaction tube was charged with the desired amount of ENB and 4 mL dichloromethane. Separately, a scintillation vial was charged with $NaBAr^F_4$ (0.018 mmol) and a dichloromethane solution of $(P^tBu_3)PdMeCl$ (0.018 mmol Pd). An aliquot of the catalyst solution was injected into the septum-capped reaction tube by syringe to initiate the reaction. At initiation, the 4.4 mL reaction mixture contained 1 mM of the $(P^tBu_3)PdMeCl/NaBAr^F_4$ catalyst system and ENB varying between 250 mM and 1000 mM. The mixtures were allowed to stir at 25 ºC for two hours outside of the glovebox, at which point an aliquot (100.0 µL) was removed. The aliquot was diluted with $CDCl_3$, and methanol (10.0 µL) and mesitylene (10.0 µL) were added to the aliquot. The monomer conversion was determined by integration of remaining ENB resonances relative to a mesitylene internal standard in ^{1}H NMR spectra. Methanol (10 mL) was added to the bulk reaction solution to quench and precipitate any oligomeric or polymeric materials and the resulting powders were isolated by filtration and dried *in vacuo*.

Table S2. GPC characterization of ENB homopolymers obtained using $(P^tBu_3)PdMeCl/NaBAr^F{}_4$ at varying initial ENB concentration in dichloromethane over 2 hours.

ENB Concentration (mM)	[Catalyst]	Conversion	M_n (Da)	M_w (Da)	Đ
250	1 mM	100%	23,000	26,000	1.1
500	1 mM	100%	46,000	50,000	1.1
750	1 mM	100%	73,000	77,000	1.1
1000	1 mM	100%	100,000	108,000	1.1

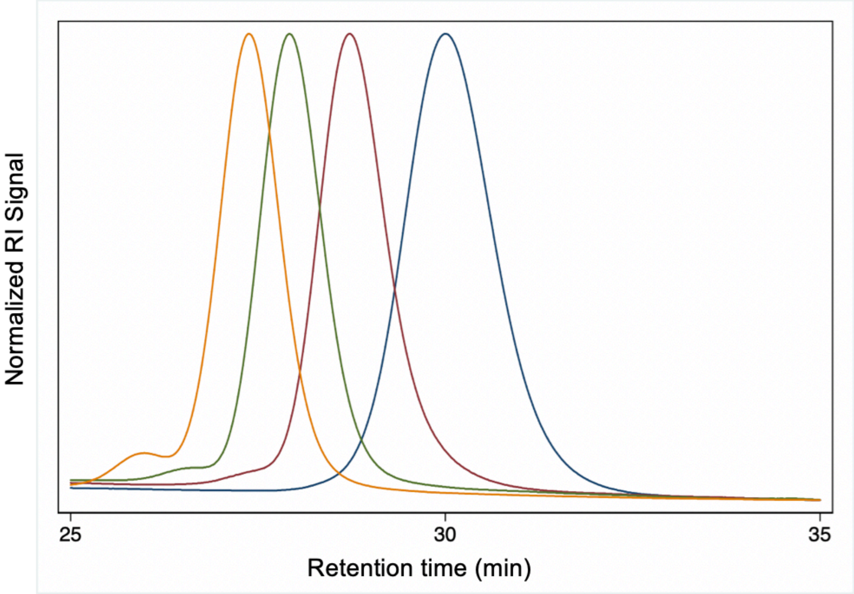

Figure S4. GPC overlay of ENB homopolymers produced from different initial ENB concentrations: 1000 mM (yellow), 750 mM (green), 500 mM (red), and 250 mM (blue).

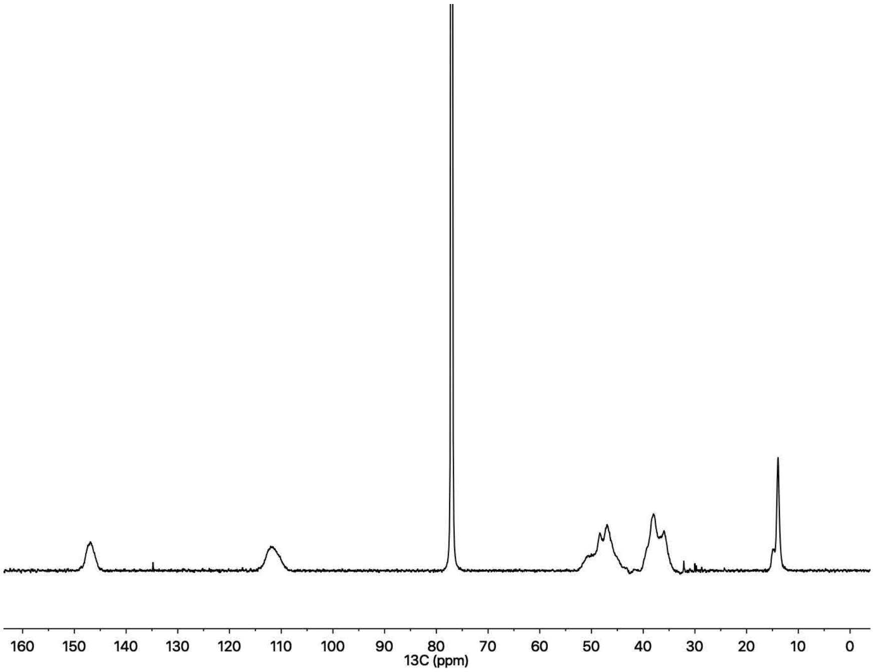

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of ENB homopolymer (M_n 23,000) from (P^tBu_3)PdMeCl/NaBAr$^F_4$ system in $CDCl_3$.

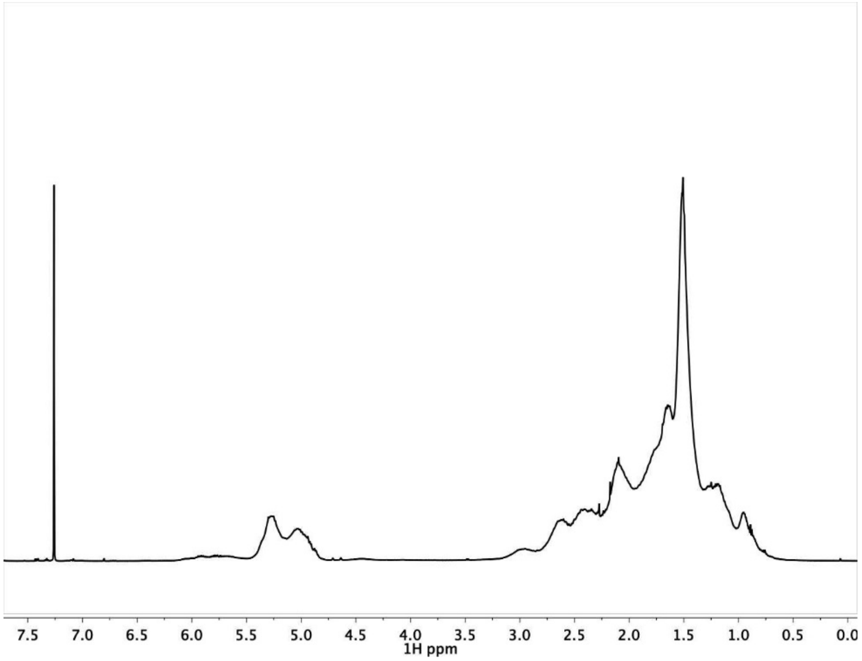

Figure S6. ^{1}H NMR spectrum of ENB homopolymer (M_n 23,000) from (P^tBu_3)PdMeCl/NaBAr$^F_4$ system in $CDCl_3$.

Time course of ENB homopolymerization by $(P^tBu_3)PdMeCl/NaBAr^F_4$

In a nitrogen-filled glovebox, four septum-capped reaction tubes were charged with ENB (151 µL, 1.1 mmol) and 4 mL dichloromethane. Separately, a scintillation vial was charged with $NaBAr^F_4$ (16.0 mg, 0.018 mmol) and a dichloromethane solution of $(P^tBu_3)PdMeCl$ (1.6 mL, 11.3 mM, 0.018 mmol Pd). To each septum-capped reaction tube, 400 µL of the catalyst solution was added by syringe, leading to a final concentration of 1 mM $(P^tBu_3)PdMeCl/NaBAr^F_4$ and 250 mM ENB in 4.4 mL dichloromethane. The reactions were allowed to stir at 25±1 ºC for 30 seconds, 1 minute, 5 minutes, and 10 minutes, respectively, before being quenched with methanol (1 mL). The monomer conversion was determined by integration of remaining ENB resonances relative to a mesitylene internal standard in ^1H NMR spectra. The samples were precipitated out of methanol and then dried *in vacuo*.

Table S3. GPC characterization of ENB homopolymers obtained at different reaction times.

Time (min)	**Conversion**	M_n	M_w	*Đ*
0.5	19%	6,400	7,600	1.2
1	46%	15,000	20,000	1.3
5	86%	25,000	28,000	1.1
10	100%	27,000	30,000	1.1

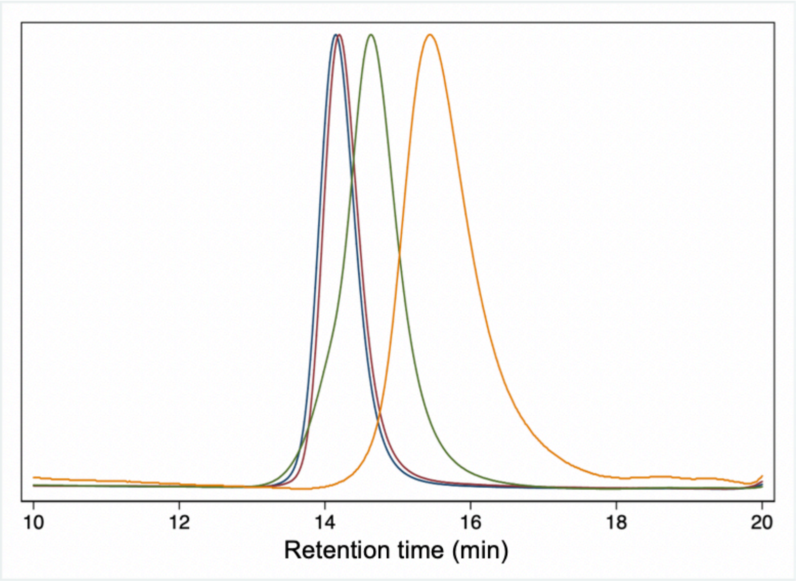

Figure S7. GPC overlay of ENB homopolymers obtained from by (P^tBu_3)PdMeCl/NaBAr$^F{}_4$ at varying reaction times: 0.5 min (yellow), 1 min (green), 5 min (red), 10 min (blue).

Homopolymerization by (P^{t}Bu$_3$)PdMeCl/NaBAr^F$_4$ with second ENB charge

In a nitrogen-filled glovebox, two vials were charged with ENB (151 µL, 1.1 mmol) and 4 mL dichloromethane. Separately, a scintillation vial was charged with NaBAr^F$_4$ (8.0 mg, 0.009 mmol) and a dichloromethane solution of (P^{t}Bu$_3$)PdMeCl (0.8 mL, 0.009 mmol Pd). To each reaction vial, 400 µL of the catalyst solution was added by syringe, leading to a final concentration of 1 mM (P^{t}Bu$_3$)PdMeCl/NaBAr^F$_4$ and 250 mM ENB in 4.4 mL dichloromethane. The reactions were allowed to stir at 25±1 ºC. After 20 minutes, one of the vials was charged with more ENB (300 µL, 2.2 mmol) and allowed to stir at 25±1 ºC for an additional 30 minutes. Both vials were quenched precipitated out of methanol (2 mL) and then dried *in vacuo*.

Table S4. GPC characterization of ENB homopolymers

Number of ENB charges	**Total ENB added**	M_n	M_w	*Đ*
1	1.1 mmol	22,000	27,000	1.2
2	3.3 mmol	56,000	75,000	1.3

Table S5. GPC characterization of ENB homopolymers obtained using [(mes)Pd(allyl)]$^+$ and (P^{t}Bu$_3$)PdMeCl.

PR_3	Catalyst	Conversion	M_n (Da)	M_w (Da)	*Đ*
-	[(mes)Pd(allyl)]$^+$	23%	1,100	3,000	2.6
P^{t}Bu$_3$	[(mes)Pd(allyl)]$^+$	100%	39,000	49,000	1.3
-	(P^{t}Bu$_3$)PdMeCl /NaBAr$^F{}_4$	100%	23,000	26,000	1.1

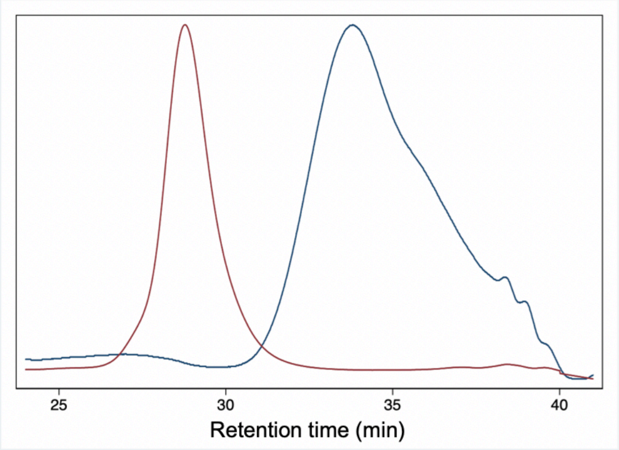

Figure S8. GPC trace overlay of ENB homopolymerizations by [(mes)Pd(allyl)][PF$_6$] alone (blue trace) and with P^{t}Bu$_3$ (red trace).

Procedure for norbornene polymerization by [(mes)Pd(allyl)][PF_6]

In a nitrogen-filled glovebox, a septum-capped reaction tube was charged with norbornene (103 mg, 1.1 mmol) and 4 mL dichloromethane. To a separate vial was added [(mes)Pd(allyl)][PF_6] (4.1 mg, 0.0099 mmol) and dichloromethane (800 μL) . To the reaction tube containing norbornene was then added 400 μL of the [(mes)Pd(allyl)][PF_6] solution (0.0049 mmol). The tube was capped and the reaction stirred outside of the box at room temperature for two hours. Precipitation of polymer was observed less than five minutes after addition of the [(mes)Pd(allyl)][PF_6] solution. Conversion of monomer was determined by removing an aliquot from the reaction prior to quenching and analyzing by ^{1}H NMR spectroscopy using a mesitylene internal standard. By ^{1}H NMR analysis, the reaction went to full conversion. The tube was subsequently quenched with methanol and the product dried *in vacuo.* The isolated white powder product (95 mg, 92% yield) was insoluble in toluene, pentane, THF, and chlorinated solvents which precluded solution characterization.

General procedure for the polymerization of ENB by (P^tBu_3)PdMeCl/NaBAr$^F{}_4$ in the presence of 1-hexene

In a nitrogen glovebox, four septum-capped reaction tubes were charged with ENB (151 μL, 1.1 mmol), the desired amount of 1-hexene, and 4 mL dichloromethane. Separately, a vial was charged with NaBAr$^F{}_4$ (16.0 mg, 0.018 mmol) and a solution of (P^tBu_3)PdMeCl (1.6 mL, 11.3 mM, 0.018 mmol Pd). To each septum-capped reaction tube was added 400 μL of the catalyst solution by syringe, leading to a final concentration of 1 mM (P^tBu_3)PdMeCl/NaBAr$^F{}_4$, 250 mM ENB, and between 30 and 250 mM 1-hexene. The reactions were allowed to stir at room-temperature for two-hours outside of the glovebox, and were subsequently quenched with methanol. Full conversion of monomer was determined by ^{1}H NMR spectroscopy relative to a mesitylene internal standard. Quantitative yields of polymer powder were precipitated out of methanol and dried *in vacuo*.

Table S6. GPC characterization of hexene-terminated ENB polymers produced by (P^{t}Bu$_3$)PdMeCl/NaBAr^F$_4$ in the presence of 1-hexene.

[hexene] (mM)	**[Catalyst]**	**Conversion**	***M$_n$*** (Da)	***M$_w$*** (Da)	***Đ***
250	1 mM	100%	10,500	15,000	1.4
~80	1 mM	100%	17,000	21,000	1.3
50	1 mM	100%	18,100	23,000	1.3
~30	1 mM	100%	21,000	23,000	1.1

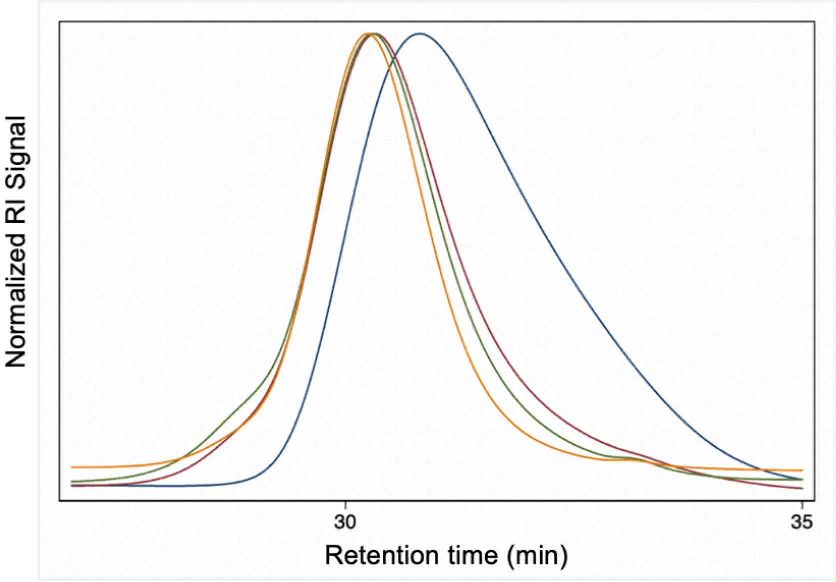

Figure S9. GPC overlay of hexene-terminated ENB polymers produced produced by (P^{t}Bu$_3$)PdMeCl/NaBAr^F$_4$ in the presence of 250 mM (blue), 80 mM (red), 50 mM (green), 30 mM (yellow) 1-hexene.

Reaction of ENB with (P^tBu_3)PdMeCl/NaBAr$^F_4$ in the presence of 1 atm C_2H_4

In a nitrogen-filled glovebox, a Schlenk flask was charged with ENB (605 μL, 4.5 mmol) and dichloromethane (16.6 mL). Ethylene was then purged through the solution for approximately two minutes. The flask was allowed to stir at room temperature under 1 atm ethylene for approximately fifteen minutes. Meanwhile, in the glovebox, a septum-capped glass vial was charged with NaBAr$^F_4$ (17.3 mg, 0.021 mmol) and a solution of (P^tBu_3)PdMeCl (6.5 mg, 0.018 mmol) in dichloromethane (400 μL). All 400 μL of the catalyst solution was added via syringe to the stirring ENB solution under a positive pressure of ethylene. The reaction mixture quickly changed color from yellow to dark grey. After stirring for two hours at 25 ºC under 1 atm ethylene, a 100 μL aliquot of the reaction was withdrawn to determine conversion of monomer via ^{1}H NMR spectroscopy using mesitylene as an internal standard. Conversion of monomer was determined to be 28%. The reaction solution was immediately quenched with methanol (10 mL) after removing the aliquot to determine conversion. White polymer was precipitated and dried *in vacuo* (160 mg, 30% yield). The polymer, analyzed by GPC, exhibited M_n 900, M_w 1,200, and $Đ$ 1.4.

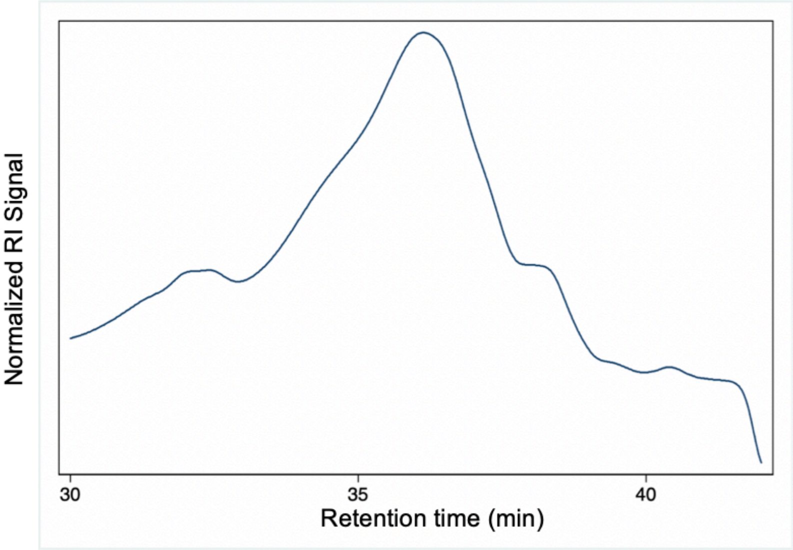

Figure S10. GPC trace of ENB polymer obtained via chain transfer with C_2H_4 in $(P^tBu_3)PdMeCl/NaBAr^F{}_4$ system.

The addition of C_2H_4 to (P^tBu_3)PdMeCl/NaBAr$^F_4$ in CD_2Cl_2

A Teflon-sealed NMR tube was charged with (P^tBu_3)PdMeCl (4.1 mg, 0.011 mmol) and NaBAr$^F_4$ (10.8 mg, 0.012 mmol) in approximately 500 µL CD_2Cl_2. The tube was quickly attached to a Schlenk-line via its Teflon cap, and was rapidly charged with ethylene after evacuating the headspace of the cap to remove oxygen. The yellow solution immediately turned dark brown upon the addition of ethylene. A ^1H NMR spectrum was taken approximately 15 minutes after charging the tube with ethylene, and only free P^tBu_3 was visible by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

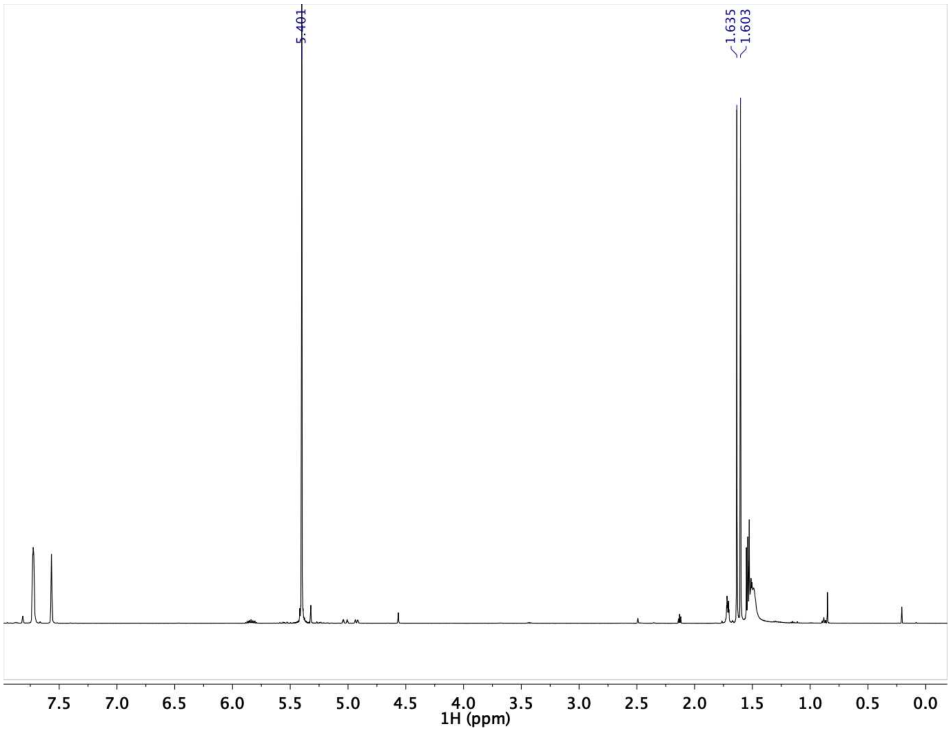

Figure S11. ^1H NMR spectrum of the solution obtained by addition of C_2H_4 to (P^tBu_3)PdMeCl and NaBAr$^F_4$ in CD_2Cl_2.

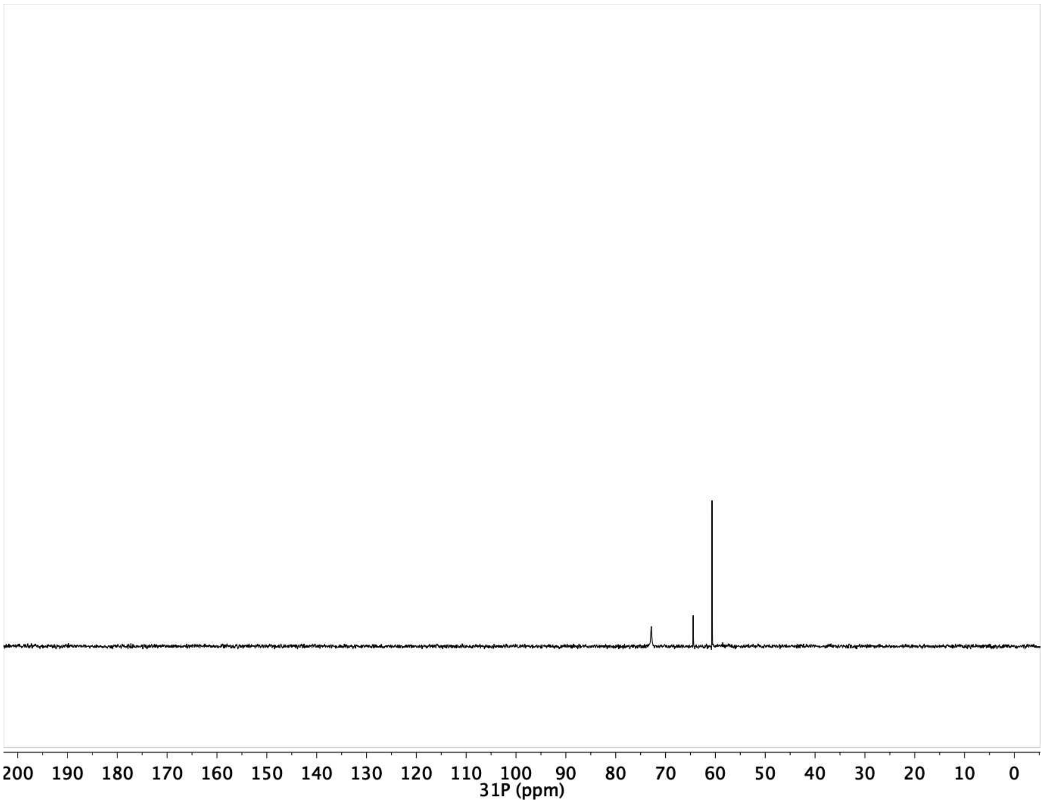

Figure S12. $^{31}P\{^1H\}$ NMR spectrum of the solution obtained by addition of C_2H_4 to $(P^tBu_3)PdMeCl$ and $NaBAr^F{}_4$ in CD_2Cl_2.

General procedure for ENB homopolymerization catalyzed by [(mes)Ni(Me-Allyl)][BAr$^F{}_4$]

In a nitrogen-filled glovebox, four septum-capped reaction tubes were charged with the desired amount of ENB and 4 mL dichloromethane. A separate vial was charged with [(mes)Ni(Me-allyl)][BAr$^F{}_4$] (20.9 mg, 0.019 mmol, in 1.6 mL CH_2Cl_2) was added. The vial was quickly swirled, and 400 μL of the corresponding solution was added to each septum-capped reaction tube such that they each contained 1 mM of the [(mes)Ni(Me-allyl)][BAr$^F{}_4$] catalyst solution and ENB concentrations ranging 250 mM and 1000 mM. The solutions were allowed to stir at room-temperature for two-hours outside of the glovebox, and were subsequently quenched with methanol. The monomer conversion was determined by ^{1}H NMR spectroscopy using a mesitylene internal standard.

The homopolymerization of ENB by [(mes)Ni(Me-allyl)][BAr$^F{}_4$] was repeated as described above with 250 mM ENB, but allowed to stir at room-temperature for 24 hours. The reaction was quenched and worked up as described above.

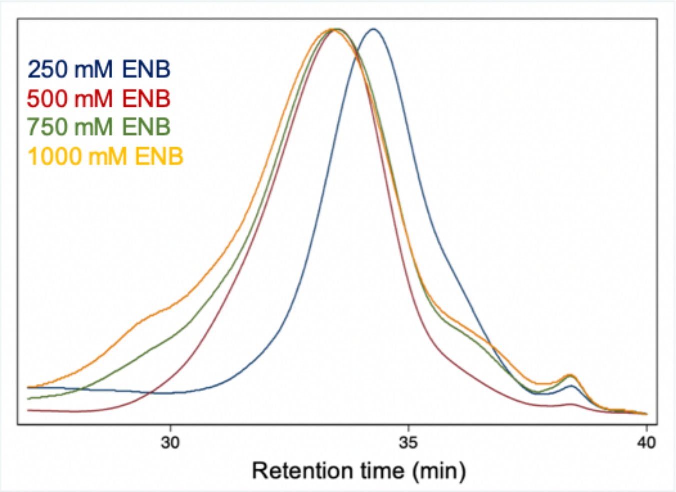

Figure S13. GPC overlay of ENB homopolymers obtained using [(mes)Ni(Me-allyl)]$^+$ (2 hour reaction times).

Table S7. GPC characterization of ENB homopolymers obtained using [(mes)Ni(Me-allyl)]$^+$.

[ENB] (mM)	**Reaction time (h)**	**Conversion**	M_n (Da)	M_w (Da)	**Đ**
250	2	10%	2,200	3,200	1.4
250	24	60%	2,000	4,300	2.2
500	2	15%	3,700	6,300	1.7
750	2	19%	2,900	7,200	2.5
1000	2	25%	3,900	8,300	2.1

Procedure for norbornene polymerization by [(mes)Ni(Me-allyl)][BAr^F$_4$]

In a nitrogen-filled glovebox, a septum-capped reaction tube was charged with norbornene (108 mg, 1.1 mmol) and 4 mL dichloromethane. To a separate vial was added [(mes)Ni(allyl)][BAr^F$_4$] (10.0 mg, 0.0099 mmol) and dichloromethane (800 μL). To the reaction tube containing norbornene was then added 400 μL of the [(mes)Ni(Me-allyl)][BAr^F$_4$] solution (0.0049 mmol). The tube was capped, and allowed to stir outside of the box at room-temperature for two hours. Precipitation of polymer was observed less than five minutes after addition of the [(mes)Ni(Me-allyl)][BAr^F$_4$] solution. Full conversion of monomer was confimed by removing an aliquot from the reaction and analyzing by ^{1}H NMR spectroscopy using a mesitylene internal standard. The tube was subsequently quenched with methanol and the product dried *in vacuo.* The isolated white powder (98 mg, 90% yield) was insoluble in toluene, pentane, THF, and chlorinated solvents thus precluding solution characterization.

General procedure for the polymerization of ENB by [(mes)Ni(Me-allyl)][BAr$^F{}_4$] and PR$_3$

In a nitrogen-filled glovebox, four septum-capped reaction tubes were charged with ENB (151 μL, 1.1 mmol) and 4 mL dichloromethane. To the tubes was added a solution of phosphine (P^{t}Bu$_3$ or PPh$_3$) in dichloromethane such that the final concentration of phosphine in each tube would be either 1 mM or 2 mM, respectively. A separate vial was charged with [(mes)Ni(Me-allyl)][BAr$^F{}_4$] (28.8 mg, 0.026 mmol) and dichloromethane (2.4 mL). To each tube was added 400 μL of the Ni solution such that the concentration of Ni in each tube was 1 mM and the ENB concentration was 250 mM. The mixtures were allowed to stir at room temperature for two-hours outside of the glovebox. Aliquots were taken to determine monomer conversion by ^{1}H NMR spectroscopy against a mesitylene internal standard. The reactions were quenched with methanol, product dried *in vacuo* and analyzed by GPC.

Table S8. GPC characterization of ENB homopolymers obtained using $[(\text{mes})\text{Ni}(\text{Me-allyl})]^+$ and PR_3.

Additive	**Conversion**	**M_n** (Da)	**M_w** (Da)	***Đ***
-	10%	2,200	3,200	1.4
1 eq P^tBu_3	61%	1,100	2,000	1.7
2 eq P^tBu_3	52%	1,200	2,100	1.9
1 eq PPh_3	55%	7,400	11,000	1.5
2 eq PPh_3	30%	< 500	< 500	n/a

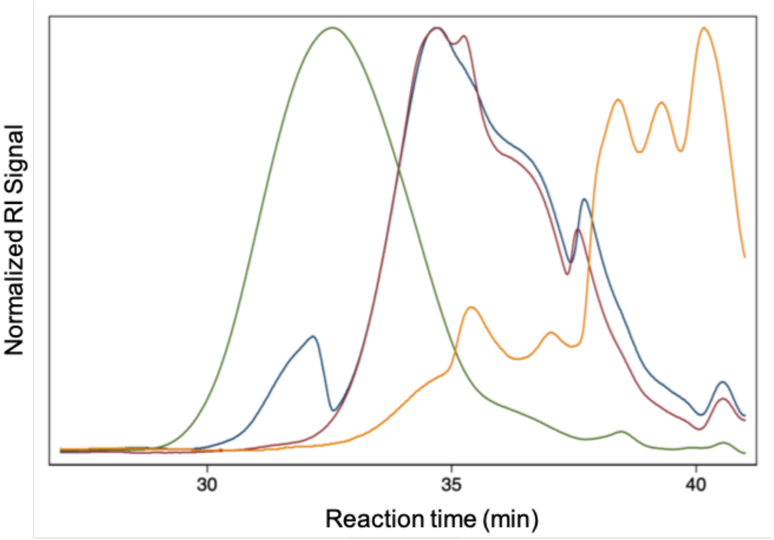

Figure S14. GPC overlay of ENB homopolymers obtained using $[(\text{mes})\text{Ni}(\text{Me-Allyl})]^+$ and 1 equiv. P^tBu_3 (blue), 2 equiv. P^tBu_3 (red), 1 equiv. PPh_3 (green), 2 equiv. PPh_3 (yellow).

Procedure for the reaction of ENB with [(mes)Ni(Me-allyl)][BAr$^F{}_4$] in the presence of 1-hexene

In a nitrogen-filled glovebox, four septum capped reaction tubes were charged with ENB (151 µL, 1.1 mmol) and 4 mL dichloromethane. To each tube was added the desired amount of 1-hexene to reach 250 mM, 80 mM, 50 mM, and 30 mM 1-hexene, respectively. A separate vial was charged with [(mes)Ni(Me-allyl)][BAr$^F{}_4$] (20.8 mg, 0.019 mmol) and dichloromethane (2.4 mL). To each tube was added 400 µL of the Ni solution such that the concentration of Ni in each tube was 1 mM and the concentration of ENB was 250 mM. The reactions were allowed to stir at room temperature for two hours outside of the glovebox. Aliquots of the tubes were taken to determine monomer conversion by ^{1}H NMR spectroscopy against a mesitylene internal standard. The reactions were quenched with methanol, product dried *in vacuo* and analyzed by GPC. Exactly analogous reactions were also carried out for 24 hours in the presence of 30 mM and 80 mM 1-hexene.

Table S9. GPC Characterization of hexene-terminated ENB oligomers using [(mes)Ni(Me-allyl)][BAr$^F{}_4$] as catalyst (M_n 870 – 2,300 Da).

[1-hexene] **mM**	**Time**	**Conversion**	M_n (Da)	M_w (Da)	**Đ**
250	2 hrs	50%	870	1800	2.1
~80	2 hrs	55%	1515	2300	1.5
~80	24 hrs	82%	1900	4600	2.4
50	2 hrs	50%	1900	2600	1.3
~30	2 hrs	41%	2300	3200	1.4
~30	24 hrs	80%	2500	6800	2.7

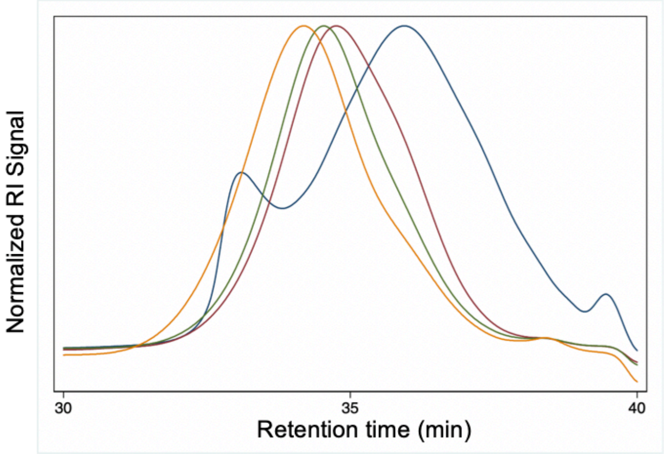

Figure S15. GPC overlay of hexene-terminated ENB oligomers obtained using [(mes)Ni(Me-allyl)][BAr$^F{}_4$] as catalyst in the presence of blue (250 mM), red (80 mM), green (50 mM), yellow (30 mM) 1-hexene (2 hour reaction times).

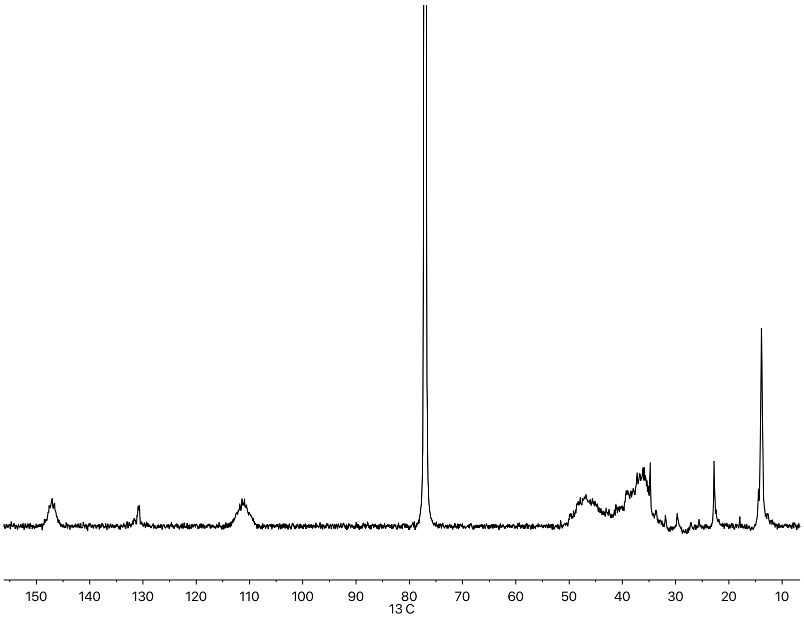

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of polymer obtained via chain transfer with 1-hexene using [(mes)Ni(Me-allyl)][BAr^{F}_4] as catalyst.

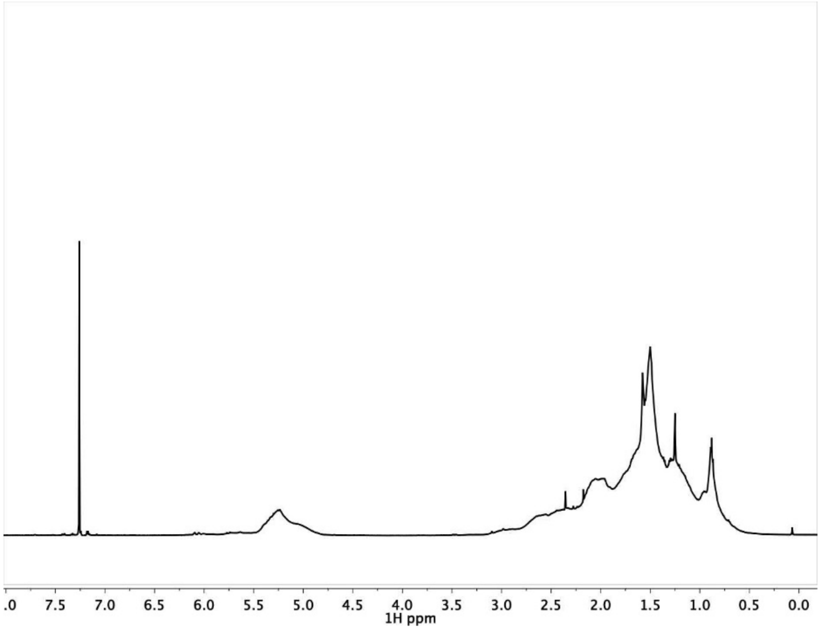

Figure S17. ^{1}H NMR spectrum in $CDCl_3$ of polymer obtained via chain transfer with 1-hexene using [(mes)Ni(Me-allyl)][BAr^{F}_4] as catalyst.

Procedure for the polymerization of ENB by [(mes)Ni(Me-allyl)][BAr$^F{}_4$] and PPh$_3$ in the presence of 1-hexene

In a nitrogen-filled glovebox, four septum-capped reaction tubes were charged with ENB (151 µL, 1.1 mmol) and 4 mL dichloromethane. To the tubes was added 1-hexene, such that the tubes were of increasing concentration of 1-hexene (250 mM, 80 mM, 50 mM, and 30 mM, respectively). A separate vial was charged with PPh$_3$ (13.0 mg, 0.050 mmol) in dichloromethane (2.6 mL). To each reaction tube was added 234 µL of the PPh$_3$ solution. A separate vial was charged with [(mes)Ni(Me-allyl)][BAr$^F{}_4$] (19.6 mg, 0.018 mmol) and dichloromethane (2.4 mL). To each tube was added 400 µL of the Ni solution such that the concentration of Ni and PPh$_3$ in each tube was 1 mM and the concentration of ENB was 250 mM. The reactions were allowed to stir at room-temperature for two-hours outside of the glovebox. Aliquots of the tubes were taken to determine monomer conversion by ^{1}H NMR spectroscopy using a mesitylene internal standard. The reactions were quenched with methanol, product dried *in vacuo* and analyzed by GPC and MS-APCI. ENB polymerizations (250 mM) in the presence of 1-hexene (30 mM and 80 mM) were repeated as described above, except that the reactions were allowed to stir for twenty-four hours. The reactions were quenched and worked up as described above.

Table S10. GPC characterization of hexene-terminated ENB oligomers produced using [(mes)Ni(Me-allyl)][BAr$^F{}_4$] and PPh$_3$ in the presence of 1-hexene.

Concentration of 1-hexene (mM)	**Time (h)**	**Conversion**	***M*$_n$**	***M*$_w$**	***Đ***
250	2	73%	< 500	< 500	n/a
~80	2	68%	460	670	1.5
~80	24	91%	600	770	1.3
50	2	60%	660	990	1.5
~30	2	78%	750	1200	1.6
~30	24	95%	1070	1800	1.7

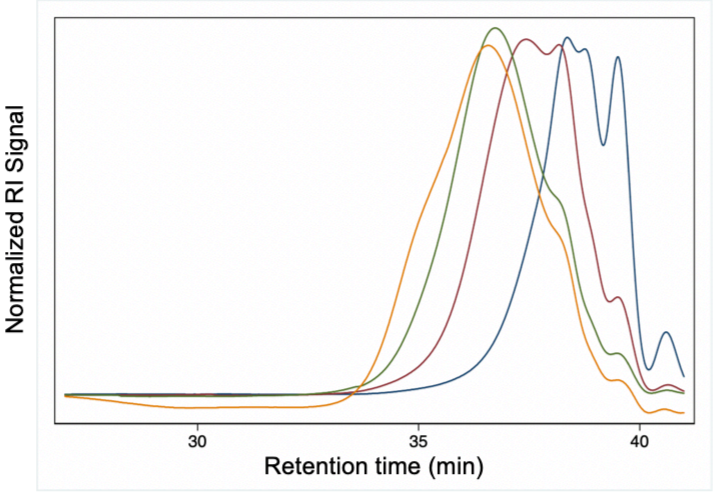

Figure S18. GPC overlay of ENB oligomers produced using [(mes)Ni(Me-allyl)][BAr$^F{}_4$] and PPh$_3$ in the presence of 250 mM (blue), 80 mM (red), 50 mM (green), 30 mM (yellow) 1-hexene (2 hour reaction times).

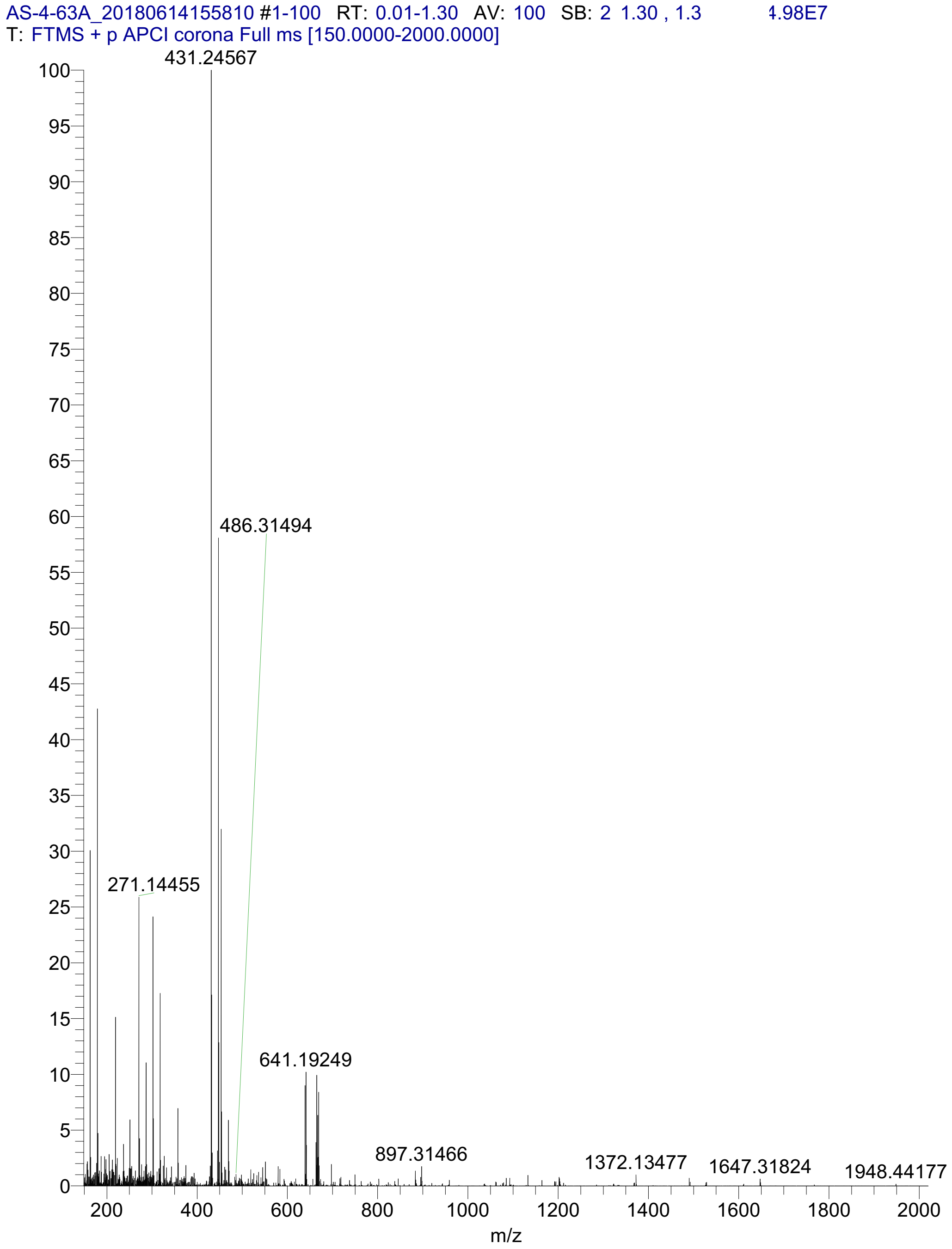

Figure S19. Mass spectrum of 1-hexene terminated ENB oligomer (M_n 270 Da by GPC)**.**

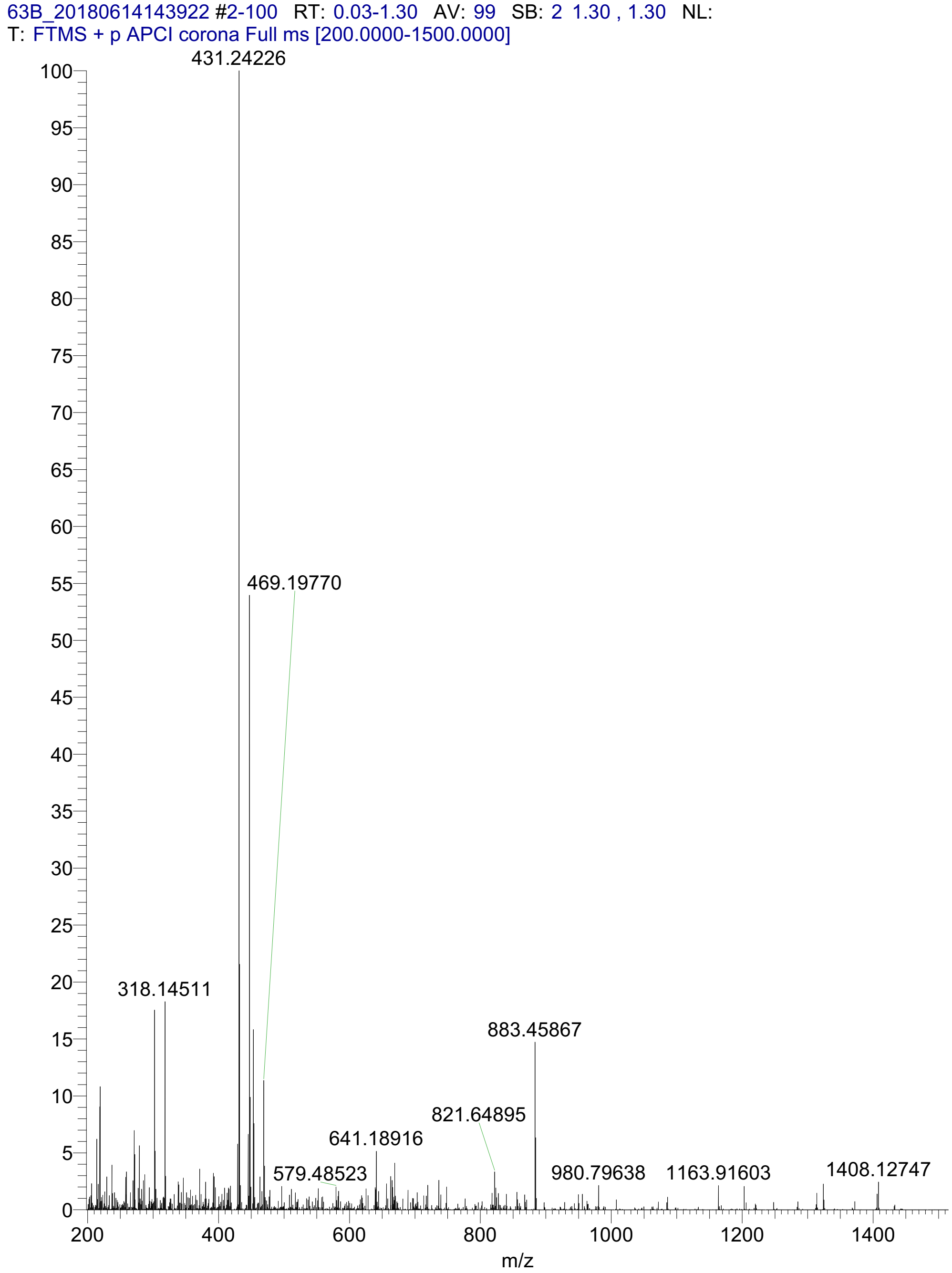

Figure S20. Mass spectrum of 1-hexene terminated ENB oligomer (M_n 460 Da by GPC).

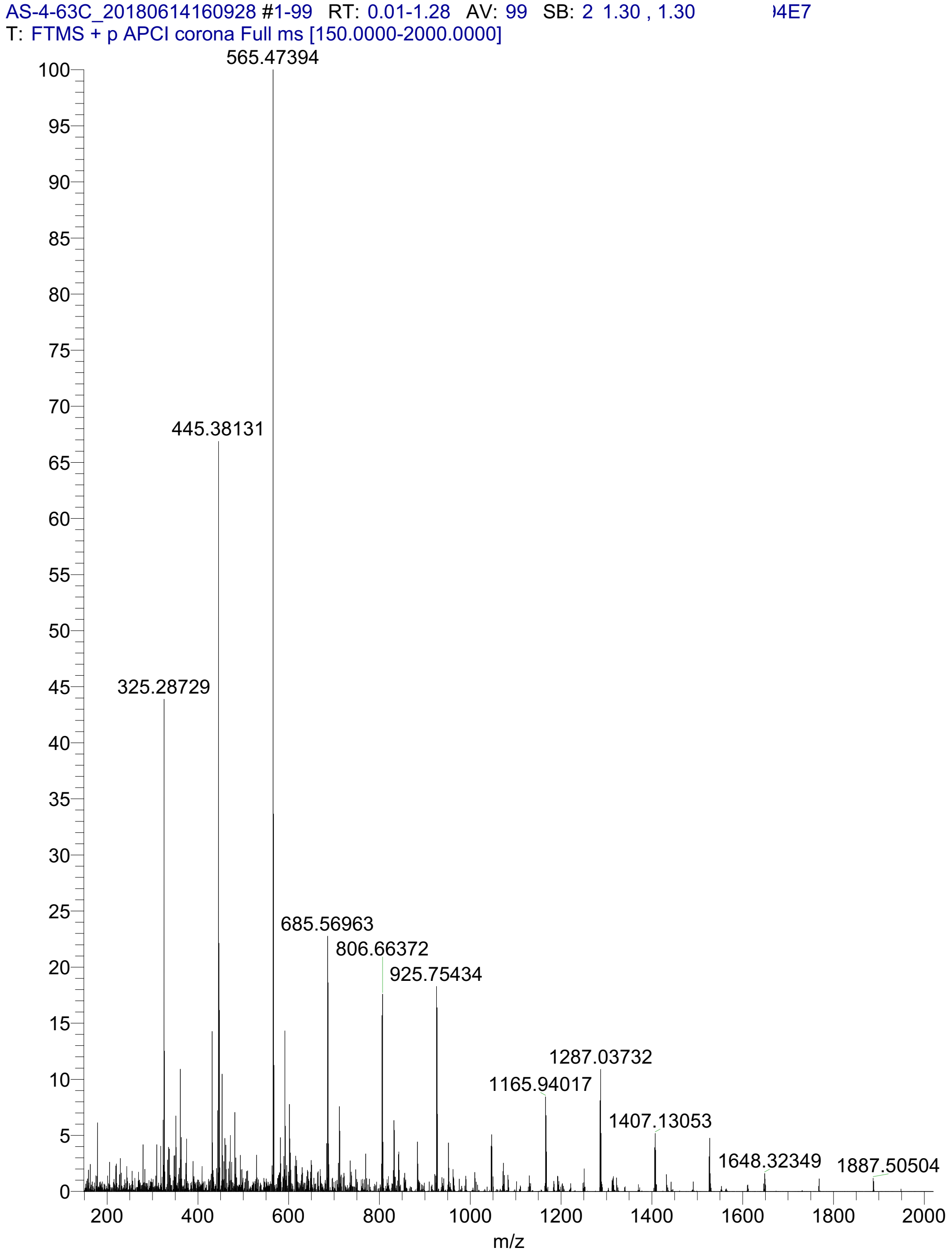

Figure S21. Mass spectrum of 1-hexene terminated ENB oligomer (M_n 660 Da by GPC).

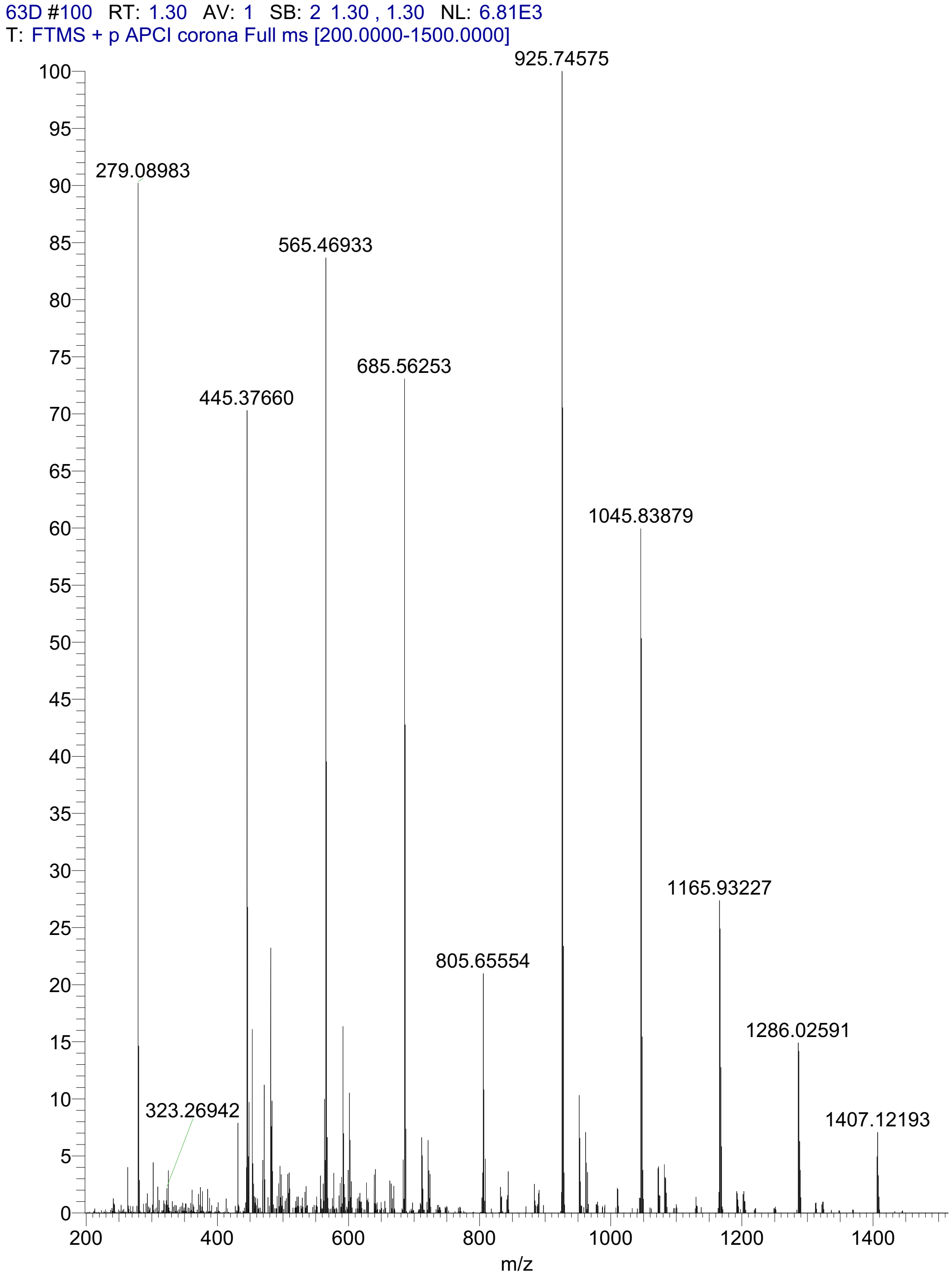

Figure S22. Mass spectrum of 1-hexene terminated ENB oligomer (M_n 750 Da by GPC).

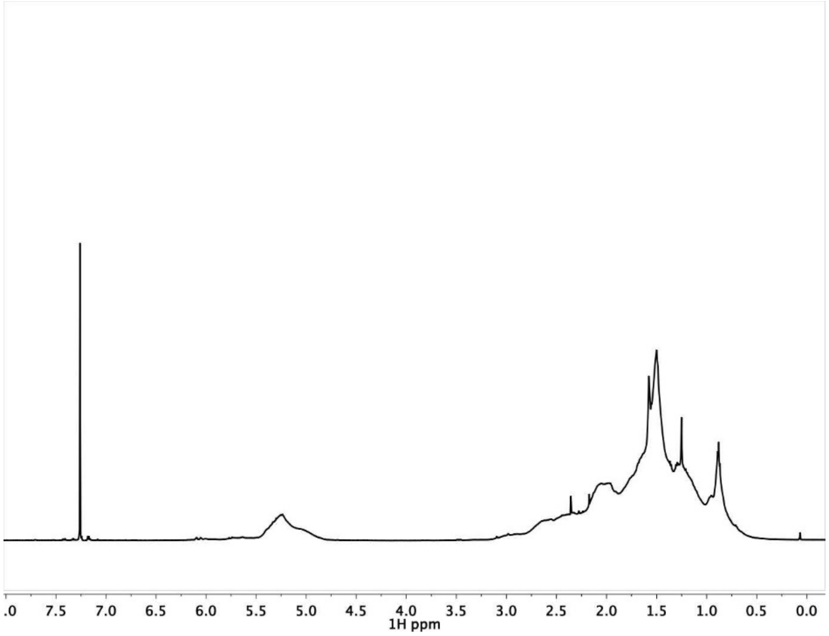

Figure S23. ^{1}H NMR spectrum in CDCl$_3$ of 1-hexene terminated ENB oligomer with an M_n of 660 Da.

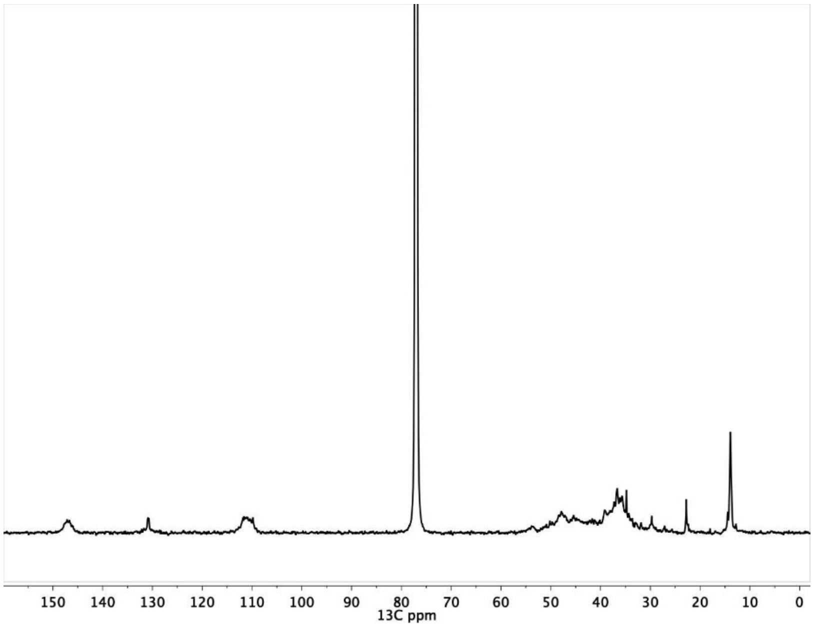

Figure S24. ^{13}C{^{1}H} NMR spectrum in CDCl$_3$ of 1-hexene terminated ENB oligomer with an M_n of 660 Da.

General procedure for the reaction of ENB with [(mes)Ni(Me-allyl)][BAr^F$_4$] in the presence of 1 atm C_2H_4

In a nitrogen-filled glovebox, a Schlenk flask was charged with ENB dichloromethane. In a separate septum-capped vial, a solution of [(mes)Ni(Me-allyl)][BAr^F$_4$] in dichloromethane was prepared. The Schlenk flask was purged with ethylene on a Schlenk line for approximately two minutes and was allowed to stir under ethylene flow for approximately ten minutes at room temperature. The Schlenk flask was then charged with the Ni catalyst solution via syringe under a positive pressure of ethylene. The reaction was allowed to stir at room temperature under ethylene for two hours at which point an aliquot from the reaction was removed to determine the monomer conversion via ^{1}H NMR spectroscopy using an internal mesitylene standard. The reaction was then quenched with methanol, product pumped to dryness *in vacuo* and analyzed by NMR spectroscopy, GPC, and APCI–MS.

Table S11. GPC characterization of ethylene-terminated ENB oligomers using [(mes)Ni(Me-allyl)][$BAr^F{}_4$] as catalyst.

Additive	**Catalyst loading**	**Concentration of ENB (mM)**	**Conversion**	M_n (Da)	M_w (Da)	**Đ**
-	1 mM	250	10%	2200	3200	1.4
1 atm C_2H_4	1 mM	250	100%	890	1600	1.8
1 atm C_2H_4	1 mM	250	100%	930	1500	1.7
1 atm C_2H_4	1 mM	125	100%	740	1200	1.6
1 atm C_2H_4	0.5 mM	125	100%	750	1300	1.7

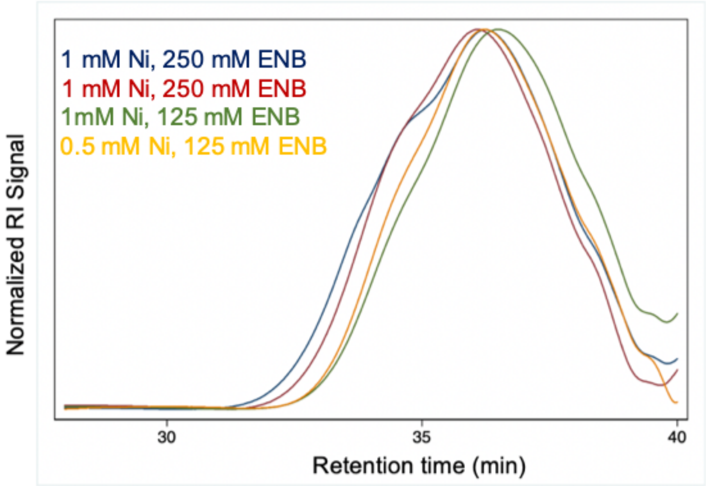

Figure S25. GPC trace overlay of ENB oligomers (Table S11) obtained via chain transfer by C_2H_4 using [(mes)Ni(Me-allyl)]$^+$.

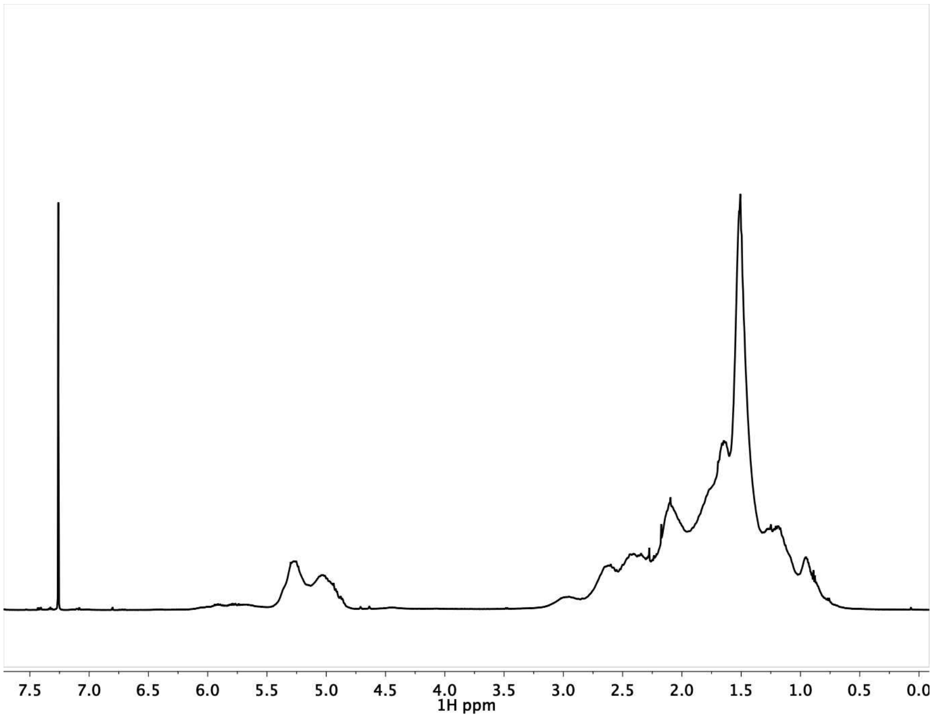

Figure S26. ^{1}H NMR spectrum in $CDCl_3$ of ethylene-terminated ENB oligomer (M_n 890 Da).

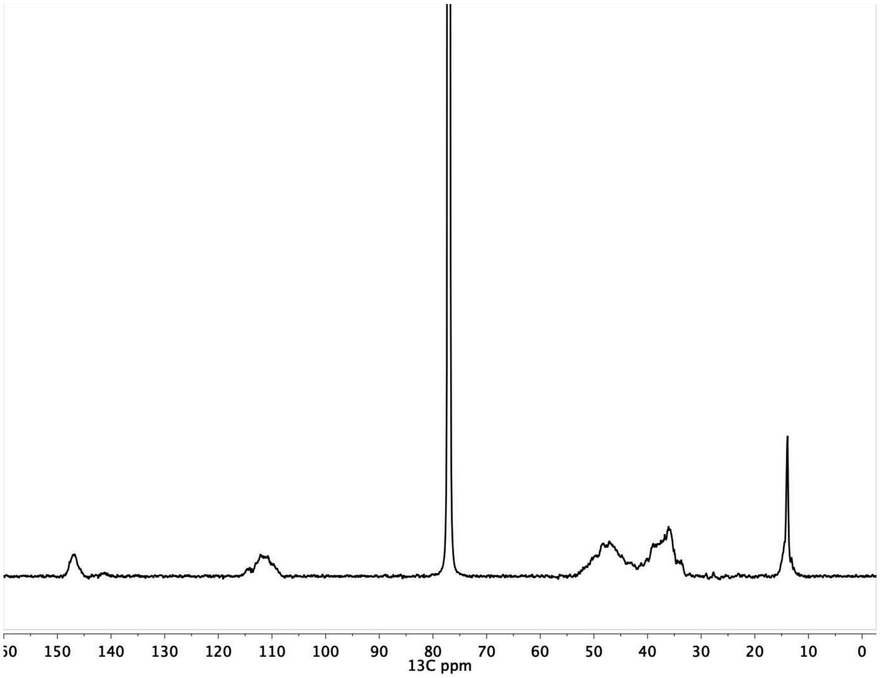

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of ethylene-terminated ENB oligomer (M_n 890 Da).

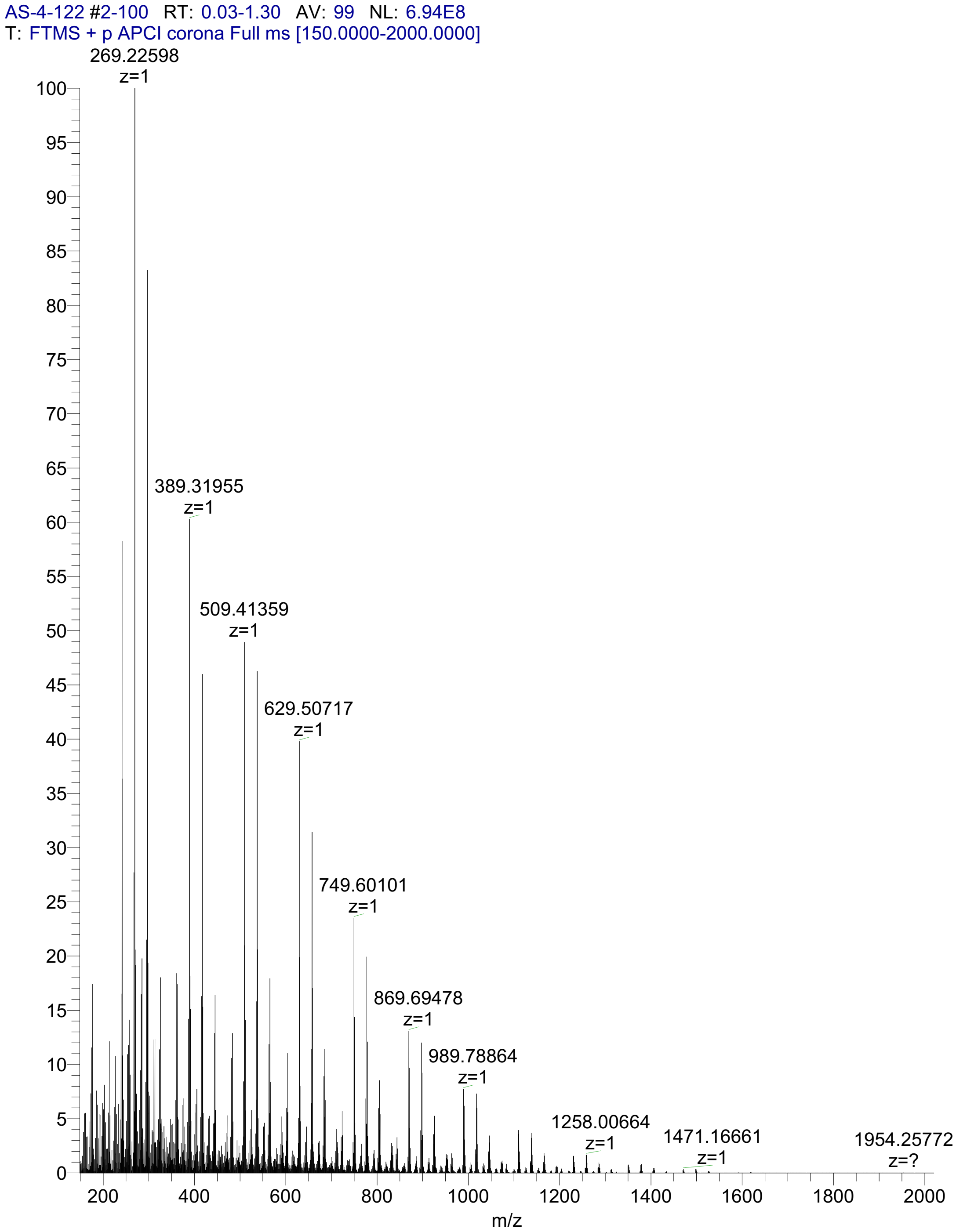

Figure S28. Mass spectrum of ethylene-terminated ENB oligomer (M_n 890 Da).

Procedure for the polymerization of norbornene by [(mes)Ni(Me-allyl)][BAr$^F{}_4$] under 1 atm C_2H_4

In a nitrogen-filled glovebox, a Schlenk flask was charged with norbornene (105 mg, 1.1 mmol) in dichloromethane. In a separate septum-capped vial, a solution of [(mes)Ni(Me-allyl)][BAr$^F{}_4$] (10.0 mg, 0.0099 mmol) in dichloromethane (800 μL) was prepared. The Schlenk flask was purged with ethylene on a Schlenk line for approximately two minutes and was allowed to stir under ethylene flow for approximately ten minutes at room temperature. The Schlenk flask was then charged with the Ni catalyst solution (400 μL) via syringe under a positive pressure of ethylene. The reaction was allowed to stir at room temperature under ethylene for two hours, at which point an aliquot from the reaction was removed to determine the monomer conversion via ^{1}H NMR spectroscopy using an internal mesitylene standard. The reaction was then quenched with methanol and pumped to dryness *in vacuo*. The monomer was determined to have been fully consumed in the reaction by ^{1}H NMR spectroscopy. The polymer product was analyzed by GPC (M_n 2,040 Da, M_w 5,000 Da, *Đ* 2.4).

General procedure for the polymerization of ENB by [(mes)Ni(Me-allyl)][BAr$^F{}_4$] and PR$_3$ under 1 atm C$_2$H$_4$

In a nitrogen-filled glovebox, a Schlenk flask was charged with ENB in dichloromethane and the PR$_3$ (PPh$_3$, PMePh$_2$, or PEt$_3$), such that the total concentration of PR$_3$ in solution was 1 mM. In a separate septum-capped vial, a solution of [(mes)Ni(Me-allyl)][BAr$^F{}_4$] in dichloromethane was prepared. The Schlenk flask was purged with ethylene on a Schlenk line for approximately two minutes and the solution allowed to stir under ethylene flow for approximately ten minutes at room temperature. The Schlenk flask was then charged with the Ni catalyst solution via syringe under a positive pressure of ethylene. The reaction was stirred at room temperature under ethylene for two hours at which point an aliquot was removed to determine the monomer conversion via ^{1}H NMR spectroscopy using an internal mesitylene standard. The reaction was then quenched with methanol and pumped to dryness *in vacuo* and products from the phosphines analyzed by NMR spectroscopy, GPC and MS-APCI.

Table S12. GPC characterization of ethylene-terminated ENB oligomers using [(mes)Ni(Me-allyl)][BAr^F$_4$] as catalyst and various ligands.

Ligand	**Conversion**	**M_n (Da)** **GPC**	**M_w (Da)** **GPC**	***m/z*** **MS-APCI**
1 mM PPh_3 (145°)	100%	<500	<500	269.22507
1 mM $PMePh_2$ (136°)	100%	<500	<500	389.31867
1 mM PEt_3 (132°)	77%	<500	<500	389.31867

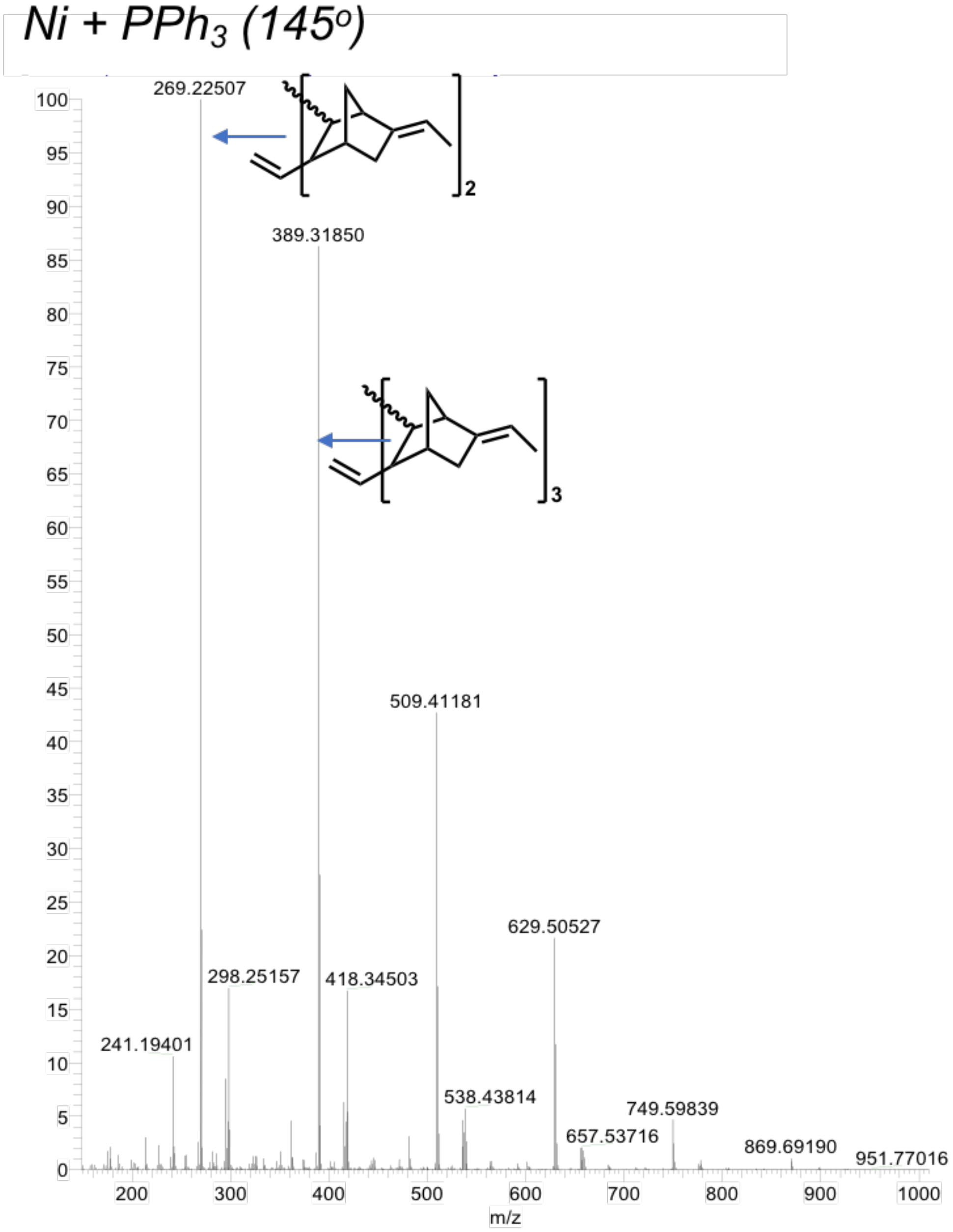

Figure S29. Mass spectrum of ethylene-terminated ENB oligomer using $[(mes)Ni(Me\text{-}allyl)]^+$ and PPh_3.

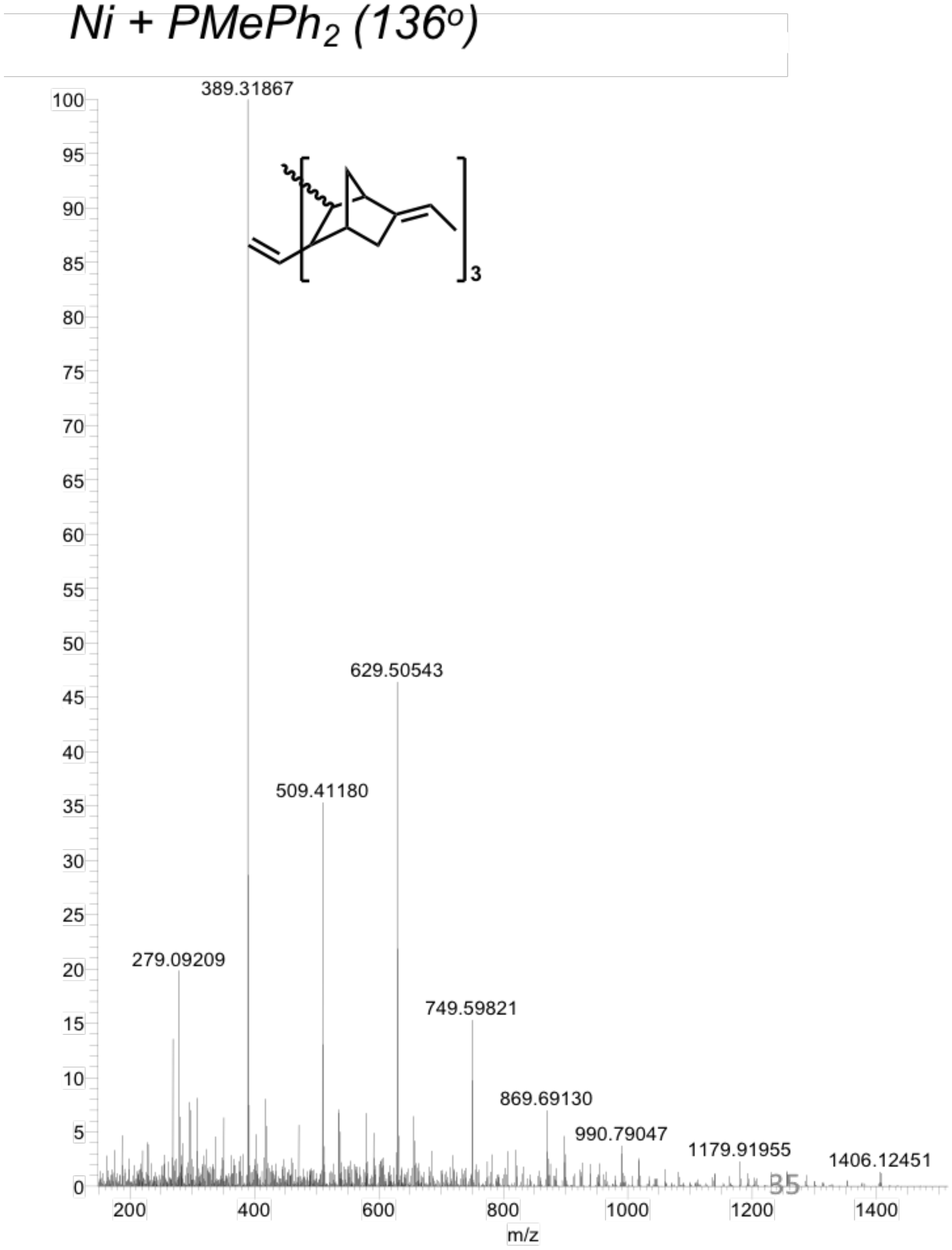

Figure S30. Mass spectrum of ethylene-terminated ENB oligomer using [(mes)Ni(Me-allyl)]$^+$ and PMePh$_2$.

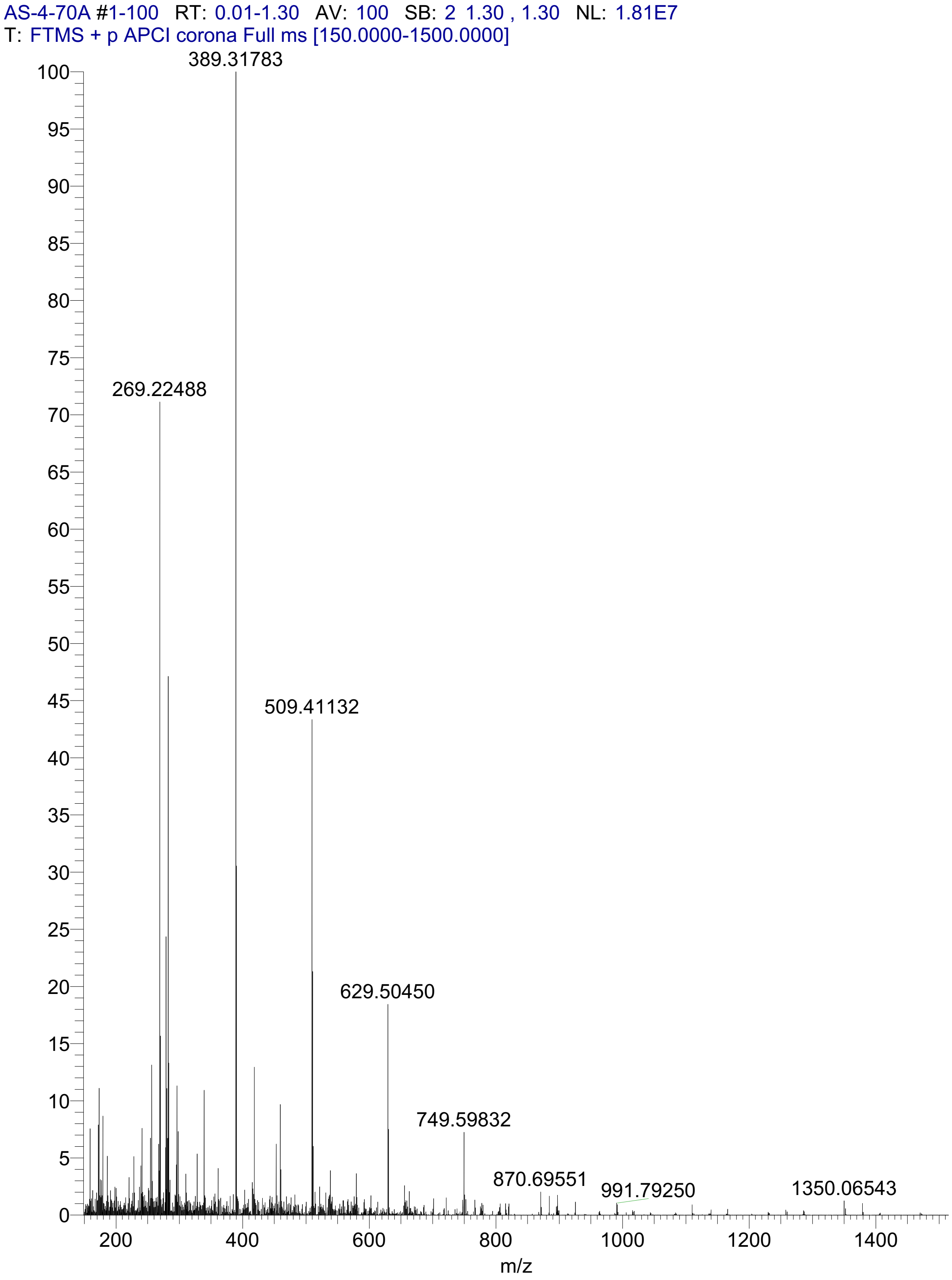

Figure S31. Mass spectrum of ethylene-terminated ENB oligomer using [(mes)Ni(Me-allyl)]$^+$ and PEt$_3$.

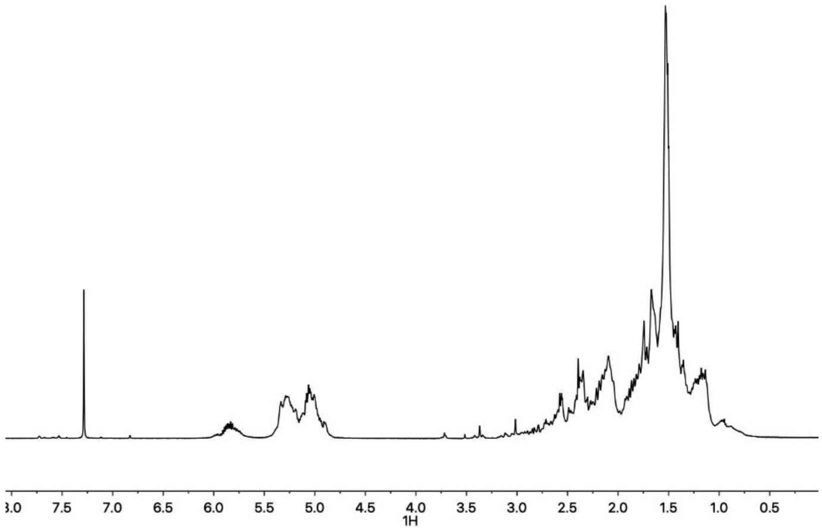

Figure S32. ^{1}H NMR spectrum in CDCl$_3$ of ethylene-terminated ENB oligomer (M_n < 500 Da).

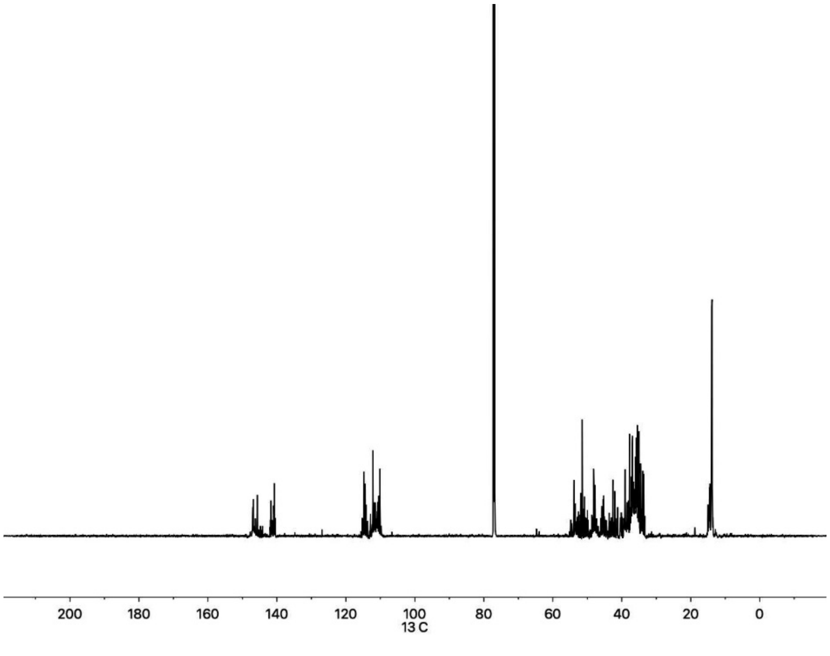

Figure S33. ^{13}C{^{1}H} NMR spectrum in CDCl$_3$ of ethylene-terminated ENB oligomer (M_n < 500 Da).

Polymerization of ENB by [(mes)Ni(Me-allyl)][BAr$^F{}_4$] under 200 psi C_2H_4

In a nitrogen-filled glovebox, a 300 mL Parr reactor was charged with a solution of ENB in dichloromethane (250 mM, 28.5 mL). The reactor was removed from the glovebox, and charged with ethylene (200 psi) and vented twice. A solution of [(mes)Ni(Me-allyl)][BAr$^F{}_4$] in dichloromethane, (35.0 mg, 0.032 mmol) was quickly added to the Parr reactor at atmospheric pressure through an addition port, such that the total concentration of Ni would be 1 mM, and the port was quickly closed. The reactor was rapidly charged with 200 psi ethylene, vented, and charged again with 200 psi ethylene (total time from addition of catalyst did not exceed five minutes). The reaction equilibrated to 200 psi, and was allowed to stir at room temperature for two hours. The reactor was vented and an aliquot was removed and analyzed by ^{1}H NMR spectroscopy to determine monomer conversion using and internal mesitylene standard. The remaining solution was quenched with methanol and product was dried *in vacuo*. The dried, viscous product was analyzed by NMR spectroscopy and MS-APCI.

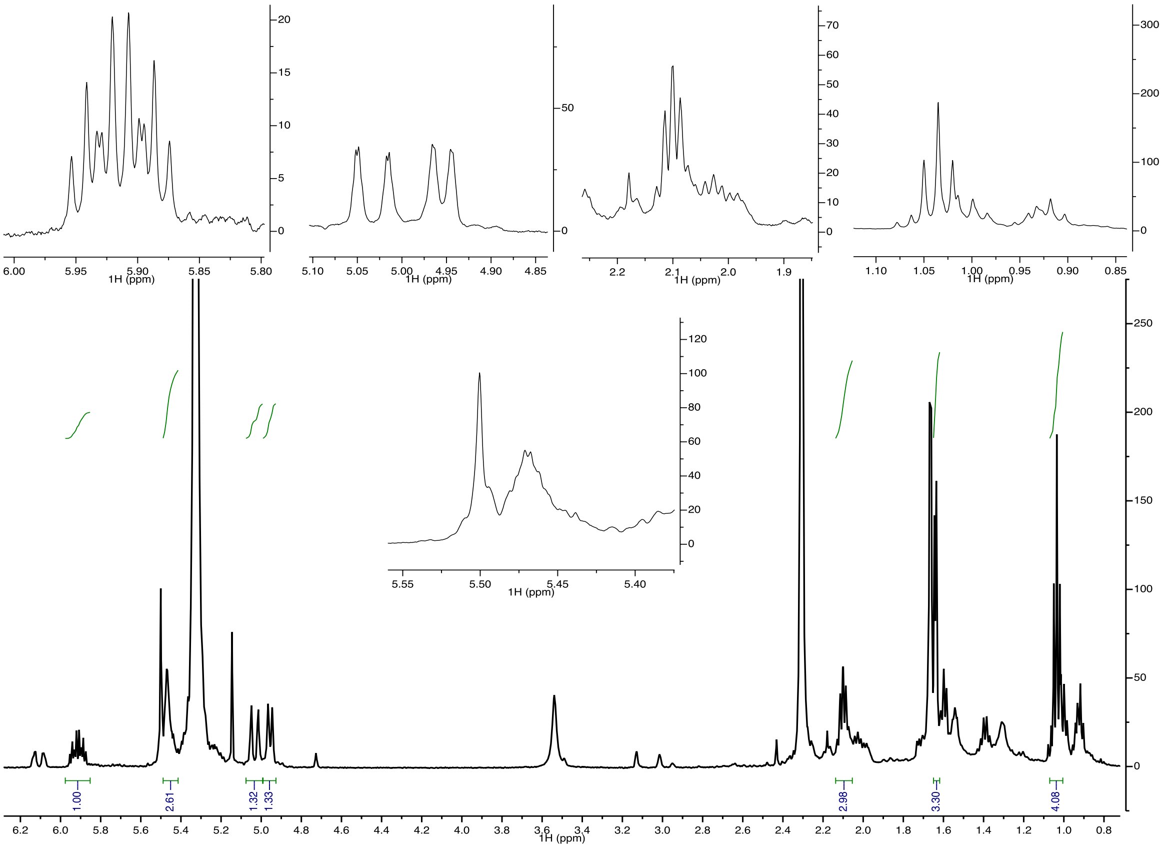

Figure S34. ^{1}H NMR spectrum in $CDCl_3$ before workup showing presence of 1-butene and 2-butene.

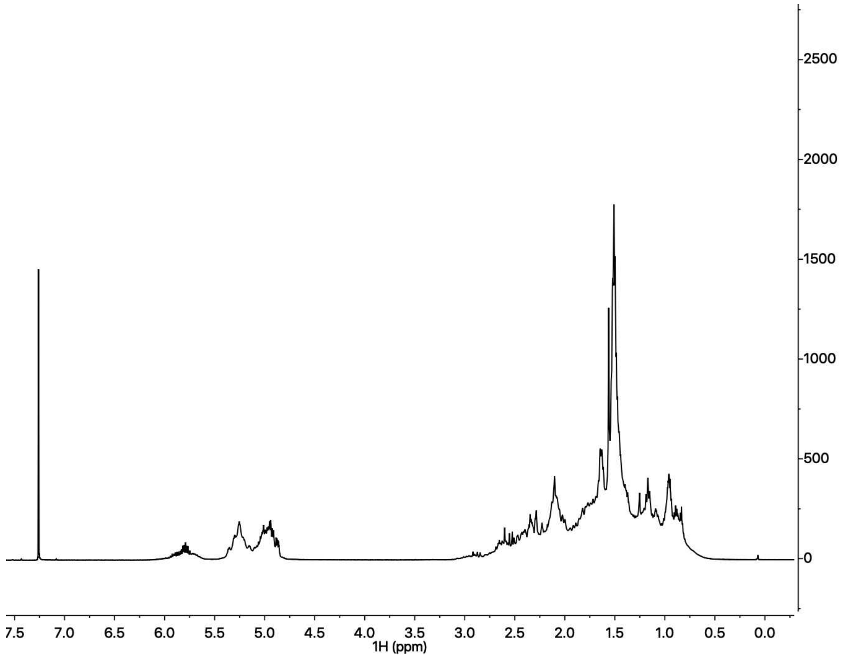

Figure S35. ^{1}H NMR spectrum in $CDCl_3$ of ENB oligomer obtained using [(mes)Ni(Me-Allyl)]$^+$ at 200 psi C_2H_4.

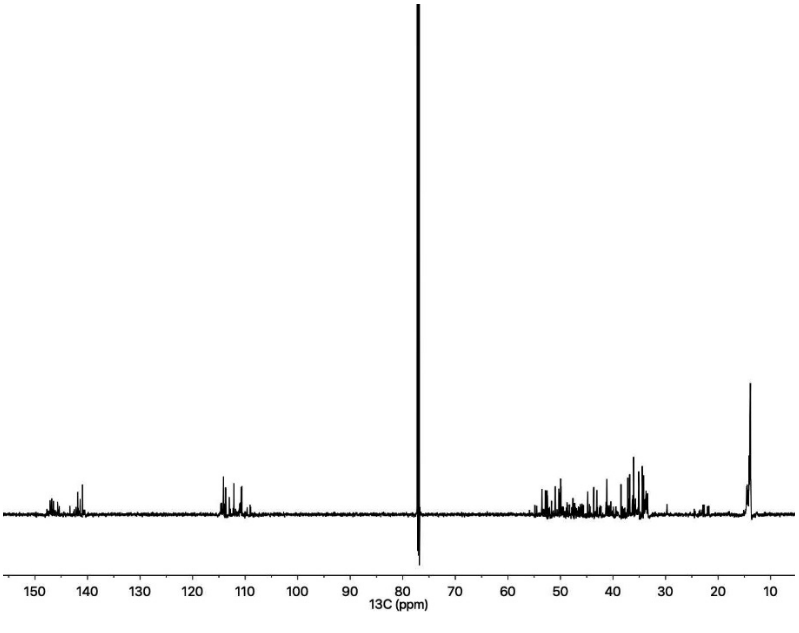

Figure S36. $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$ of ENB oligomer obtained using [(mes)Ni(Me-Allyl)]$^+$ at 200 psi C_2H_4.

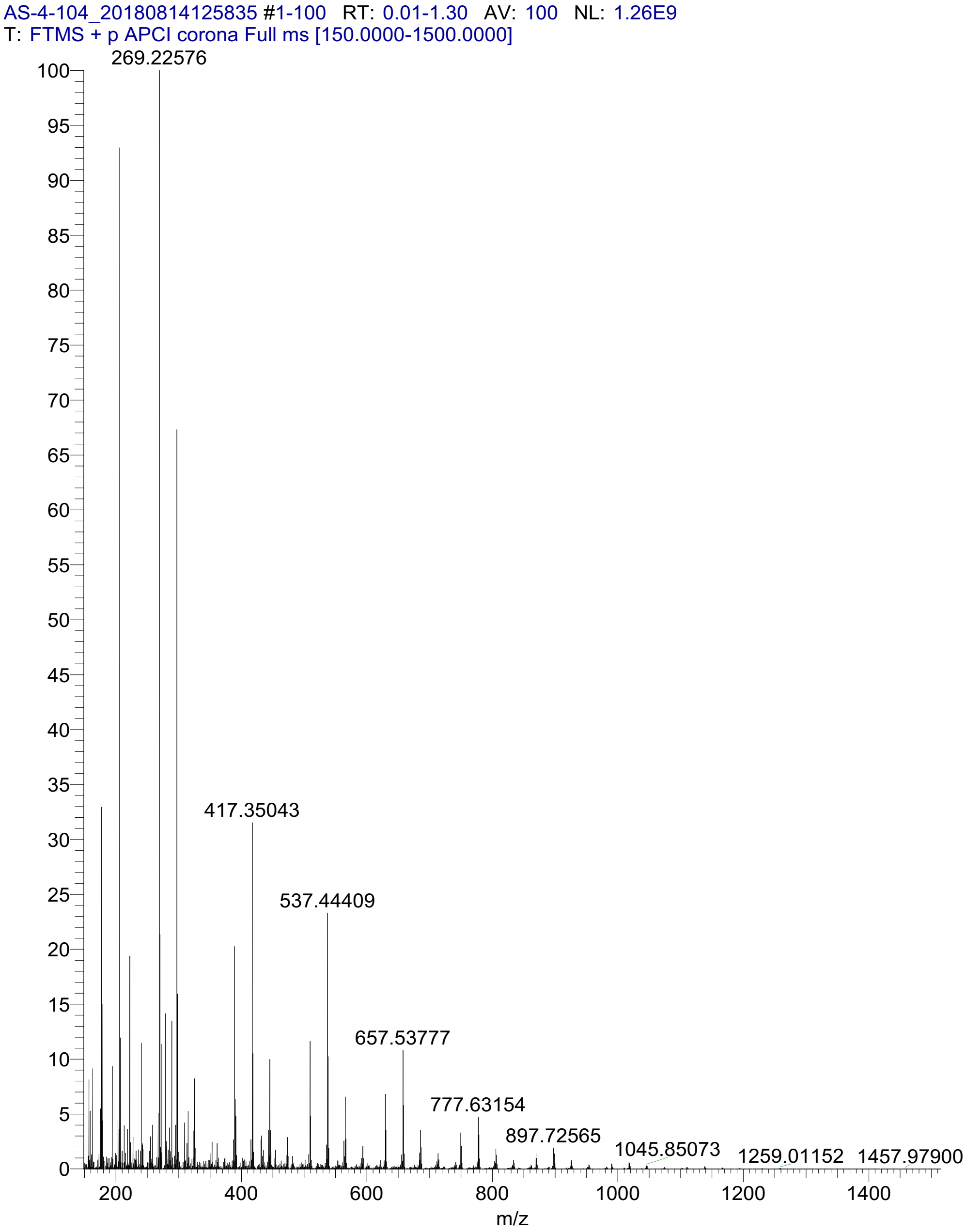

Figure S37. Mass spectrum of ENB oligomer obtained using [(mes)Ni(Me-Allyl)]$^+$ at 200 psi C_2H_4.

General procedure for the hydrogenation of ENB polymers and oligomers

The procedure was adapted from a protocol for the hydrogenation of bulky olefins.[4] In a nitrogen-filled glovebox, a Schlenk flask was charged with ENB-derived material and anhydrous dichloromethane (resulting oligomer or polymer concentration of 500 mM) and the solution was purged with hydrogen at 0 °C for approximately two minutes. After allowing the mixture to stir under hydrogen for approximately ten minutes at 0 °C, a solution of [(1,5-cyclooctadiene)Ir(PCy_3)(pyridine)][PF_6] (1 mol% relative to monomer unit of the polymer) was added in five equal portions over one hour at 0 °C, such that the final concentration of Ir in solution was 5 mM. After the final catalyst addition, the reaction was allowed to warm up slowly to room temperature over one hour at which point the reaction was quenched with methanol (2 mL). The product was dried *in vacuo* and analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, as well as GPC.

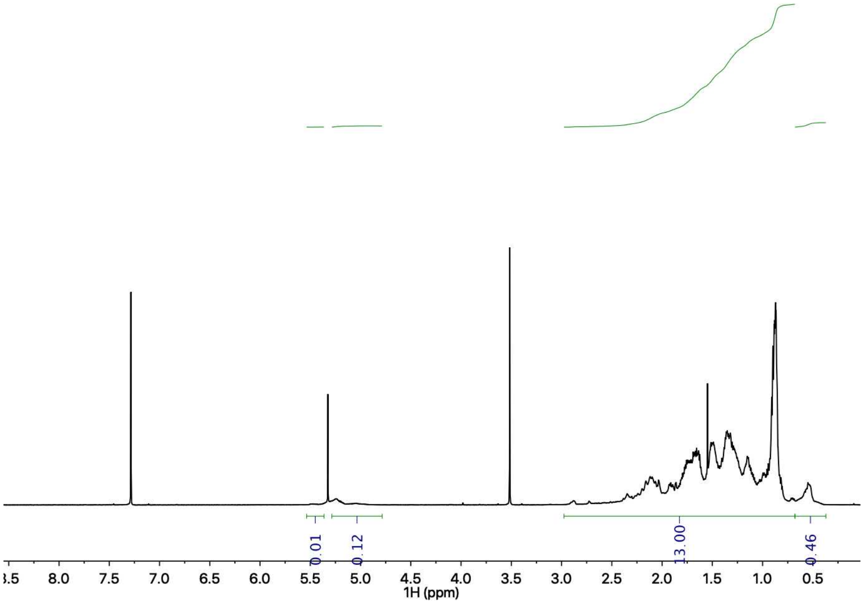

Figure S38. ^{1}H NMR spectrum in CDCl$_3$ of hydrogenated ENB oligomer.

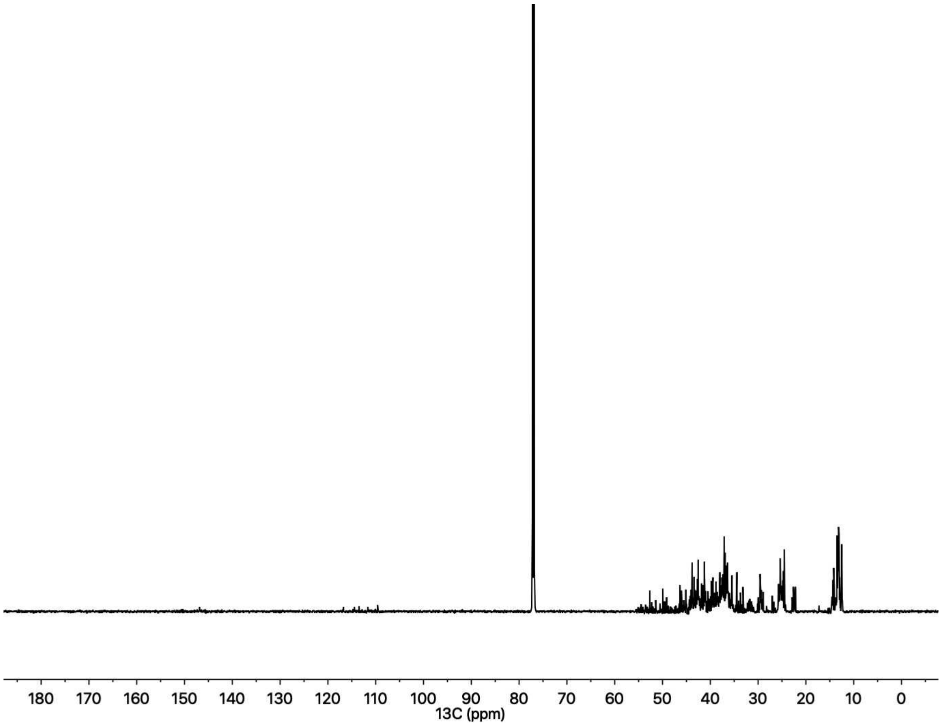

Figure S39. ^{13}C{^{1}H} NMR spectrum in CDCl$_3$ of hydrogenated ENB oligomer.

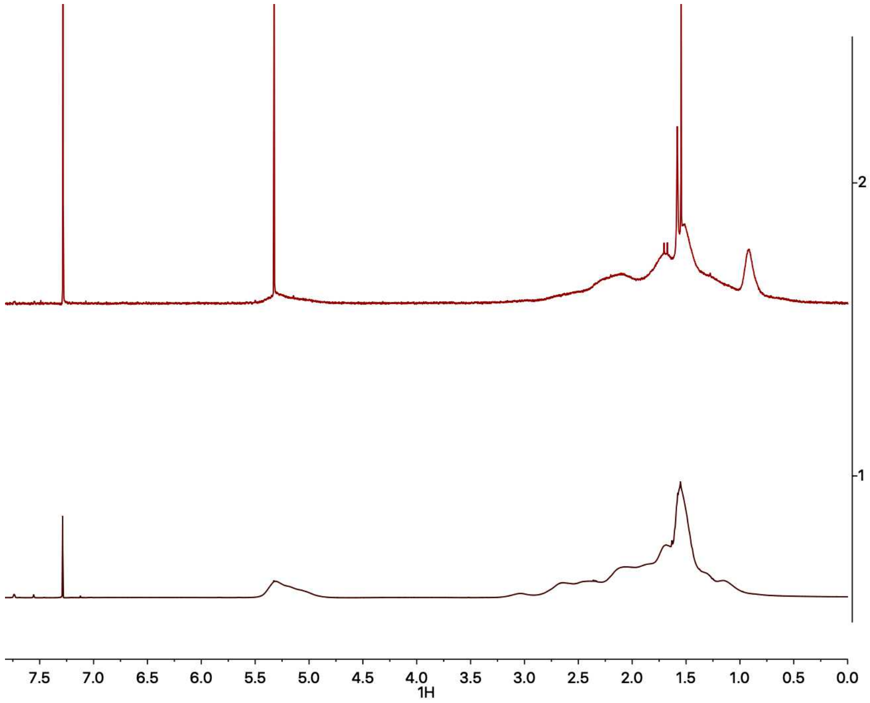

Figure S40. ENB homopolymer before (bottom) and after (top) hydrogenation.

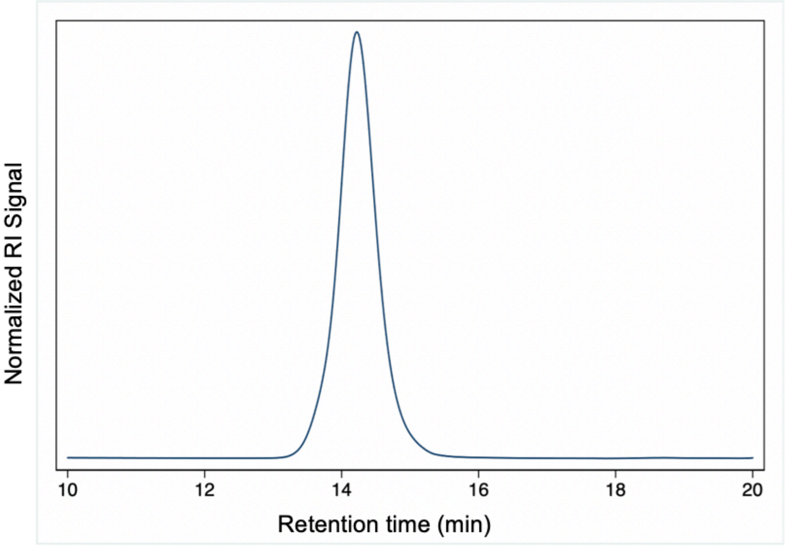

Figure S41. GPC trace of ENB homopolymer after hydrogenation.

III. Characterization of Material Properties

Modified work-up for DSC measurements

Once the reaction was quenched with methanol, it was immediately filtered through a silica plug to remove catalyst and dried *in vacuo*. The product was then dissolved in pentane, filtered again through a short silica plug to remove any residual catalyst and dried *in vacuo.* All DSC measurements were taken after determining T_D by TGA. First heat traces are reported in blue, second heat traces in red, and the cooling cycle in green.

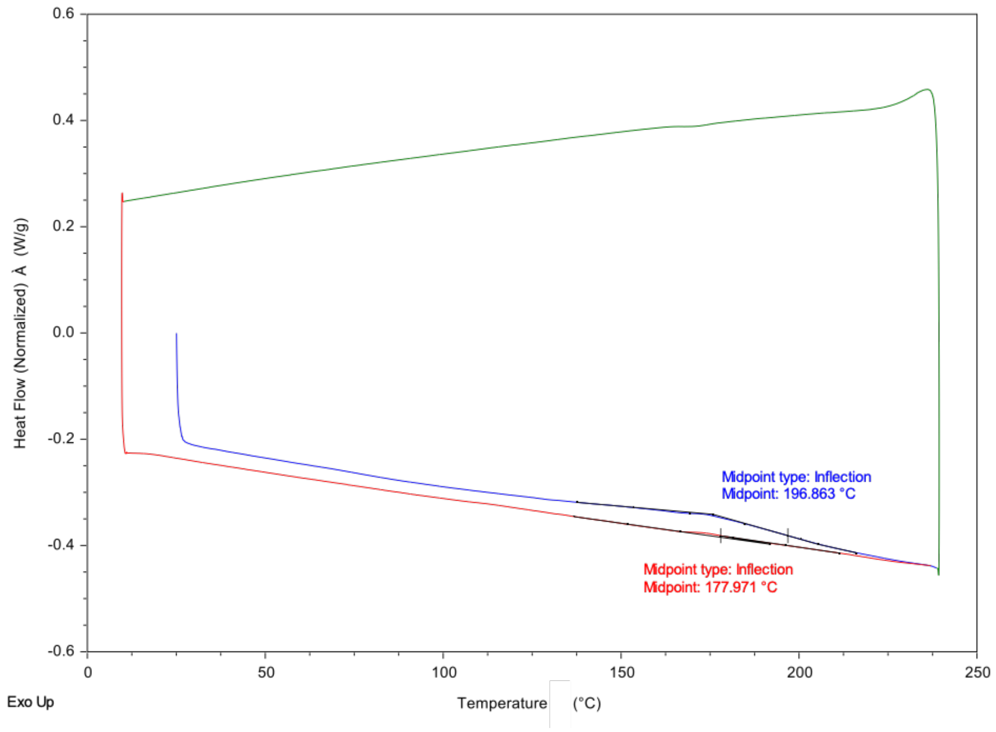

Figure S42. DSC trace to determine T_g of ENB homopolymer (M_n 25,000 Da).

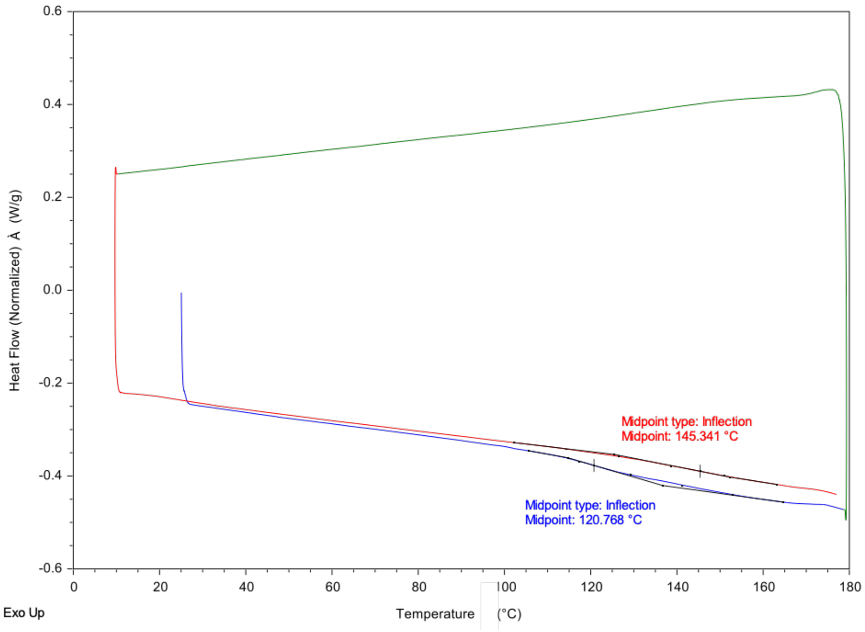

Figure S43. DSC trace to determine T_g of ethylene-terminated ENB oligomer (M_n 1,700 Da).

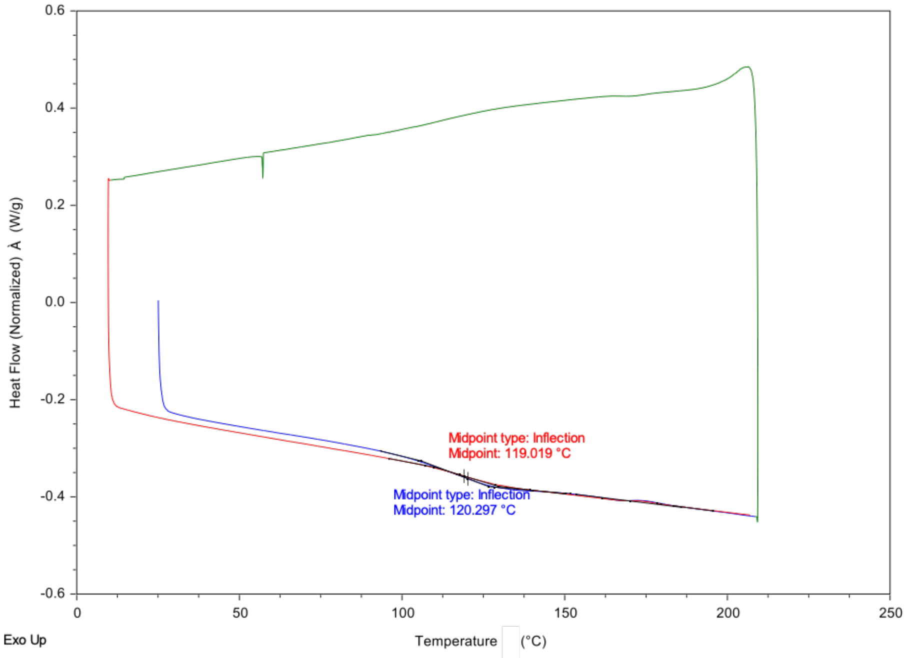

Figure S44. DSC trace to determine T_g of ethylene-terminated ENB oligomer (M_n 1,000 Da).

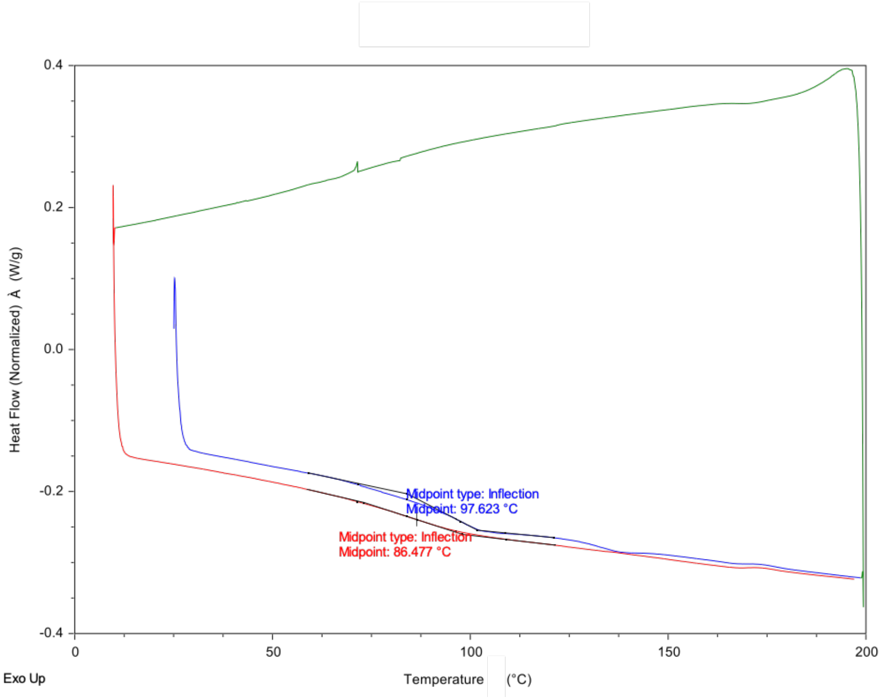

Figure S45. DSC trace to determine T_g of ethylene-terminated ENB oligomer (M_n 800 Da).

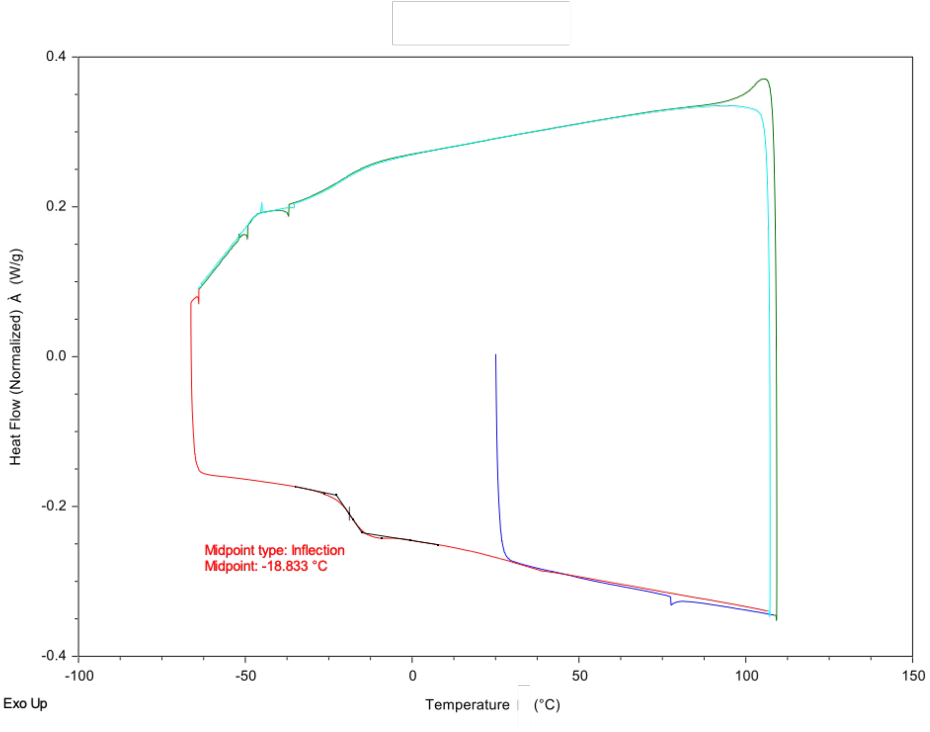

Figure S46. DSC trace to determine T_g of ethylene-terminated ENB oligomer (M_n 400 Da).

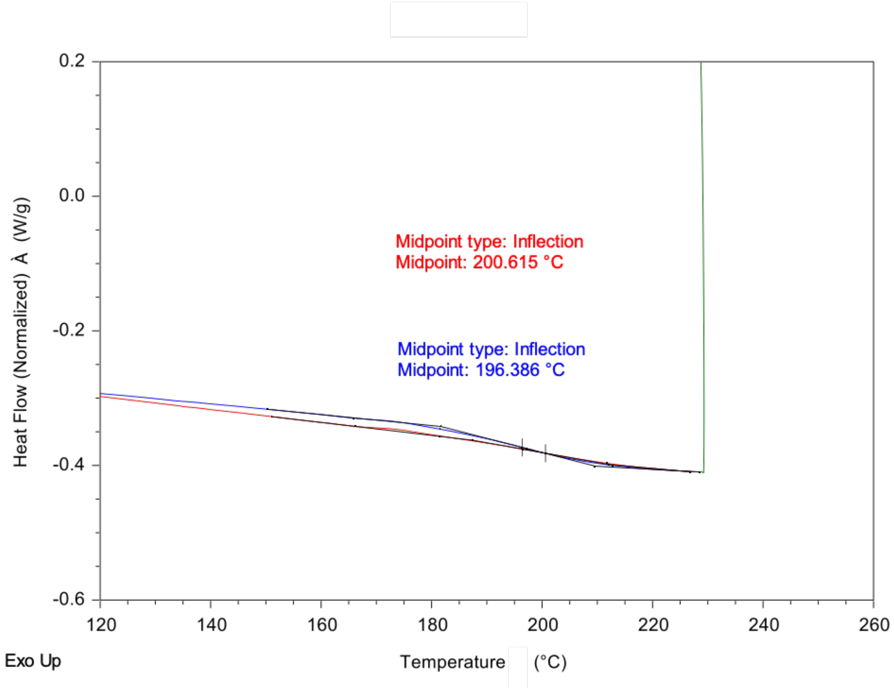

Figure S47. DSC trace to determine T_g of hexene-terminated ENB oligomer (M_n 2,500 Da).

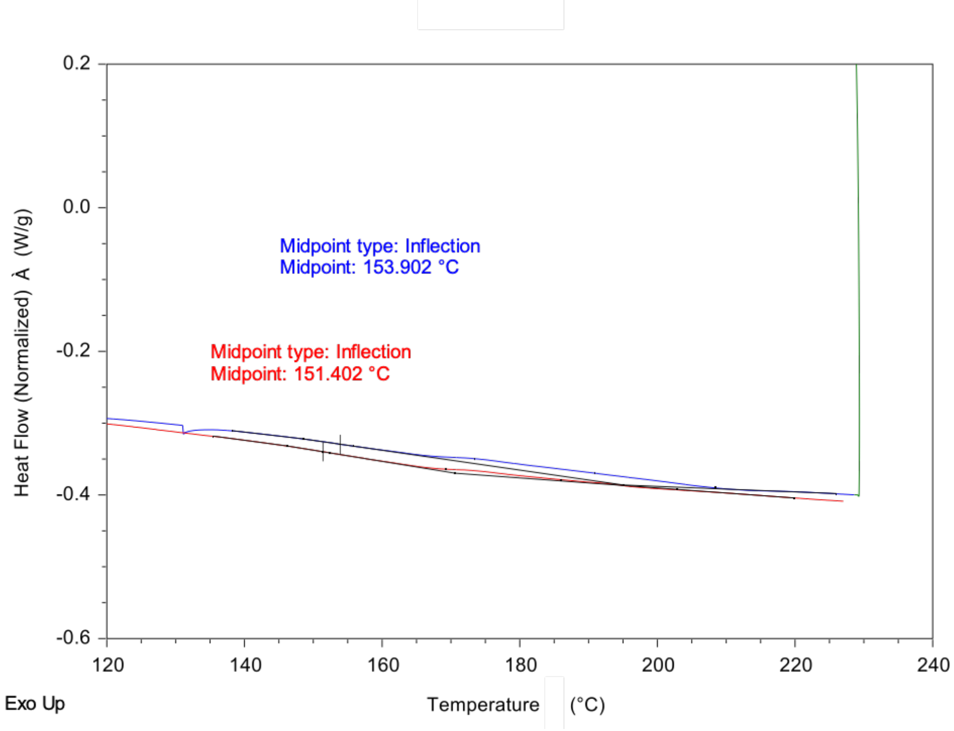

Figure S48. DSC trace to determine T_g of hexene-terminated ENB oligomer (M_n 1,900 Da).

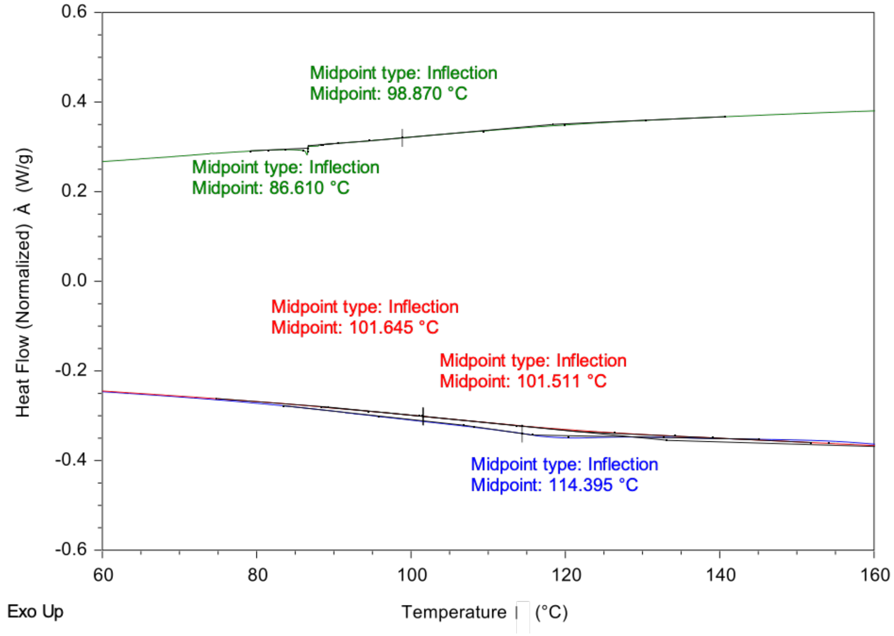

Figure S49. DSC trace to determine T_g of hexene-terminated ENB oligomer (M_n 1,070 Da).

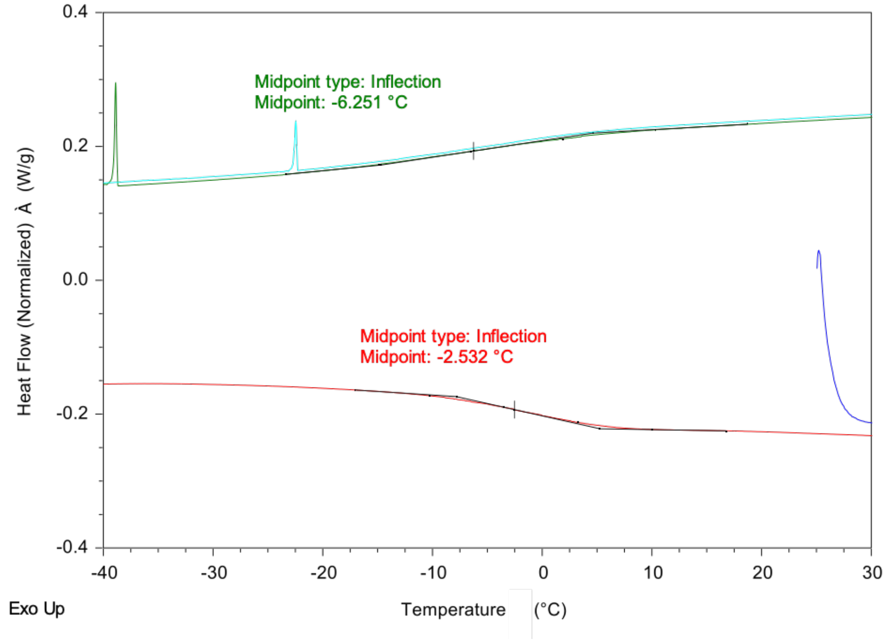

Figure S50. DSC trace to determine T_g of hexene-terminated ENB oligomer (M_n 600 Da).

IV. REFERENCES

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