Homogeneous Polyhedral Oligomeric Silsesquioxane (POSS)-Supported Pd-Diimine Complex and Synthesis of Polyethylenes End-Tethered with a POSS Nanoparticle via Ethylene "Living" Polymerization

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Supporting Information

Experimental Section

Materials

All manipulations involving air- and/or moisture-sensitive compounds were performed in a N_2 filled glove box or using Schlenk techniques. The cationic Pd-diimine complexes, including $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6–(iPr)$_2$C$_6$H$_3$) (**1**), and $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_2)_3C(O)OCH_3]^+SbF_6^-$ (**2**), were synthesized according to the literature procedure.[1] Chlorobenzene (99%, Aldrich) was refluxed over CaH_2 under N_2 and distilled before use. Acryloisobutyl-POSS was purchased from Hybrid Plastics Inc. and was used as received. Ultra-high purity N_2 and polymerization grade ethylene (both from Praxair) were purified by passing through 3A/5A molecular sieve and Oxiclear columns to remove moisture and oxygen, respectively, before use. Other chemicals, including anhydrous dichloromethane, anhydrous pentane, anhydrous diethyl ether, tetrahydrofuran (THF) and methanol were obtained from Aldrich and were all used as received.

Characterizations and Measurements

^1H nuclear magnetic resonance (NMR) spectra of the Pd-diimine complexes (**1** and **3**), acryloisobutyl-POSS, and the polymers synthesized were obtained on a Varian Gemini 2000

200 MHz spectrometer at ambient temperature. ^{13}C NMR spectrum of **3** was obtained on a Bruker AV500 spectrometer at ambient temperature. CD_2Cl_2 and $CDCl_3$ were used, respectively, as the solvent for the Pd-diimine complexes and polymers in NMR measurements. Elemental analyses of complex **3** were performed on a Thermo FLASHEA 1112 Elemental Analyzer. Fourier transform infrared (FTIR) spectrum of **3** was obtained on a Spectrum GX spectrometer (Perkin-Elmer). Electrospray Ionisation Mass Spectrometry (ESI MS) measurement of complex **3** was performed on a Waters/Micromass Quattro Ultima triple quadrupole. Solutions of complex **3** were made up in dichloromethane/methanol.

Gel permeation chromatography (GPC) measurements of the polymer samples were measured on a Waters Alliance 2965 Separation Module equipped with a Waters 2410 differential refractive index (dRI) detector and three Polymer Laboratory 30 cm mixed columns (PLgel 10μm MIXED-B 300×7.5mm). The system operated at 30 °C and THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards (PL EasiVials) covering molecular weights from 580 to 6,035,000 g/mol were used for column calibration.

GPC with on-line multi-angle laser light scattering measurements of the polymer samples were conducted on a Polymer Laboratory PL-GPC220 system equipped with a differential refractive index detector and an on-line miniDAWN (Wyatt Technology) three-angle (45°, 90°, and 135°) laser light scattering system. One guard column (PL 1110-1120), and three Polymer Laboratory 30 cm mixed columns (PLgel 10μm MIXED-B 300×7.5mm, linear range of molecular weight: 500-10,000,000 g/mol) were used. The mobile phase was THF and the flow rate was 1.0 mL/min. The system operated at 30°C. 200 μL of a 3-7 mg/mL polymer solution was injected. ASTRA software (v. 5.3.2) from Wyatt Technology was used to acquire data from the three angles (detectors) and the differential refractometer. A dn/dc value of 0.078 determined in the literature [2] for highly branched polyethylenes by chain walking polymerization was used for the polymers in THF at 30°C. The calculated polymer mass obtained by integrating the polymer elution peak using this dn/dc value matches very well with the known injected polymer mass.

Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments Q100 DSC equipped with a refrigerated cooling system (RCS) under a N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. A N_2 purging flow of 50 mL/min was used. Samples (~ 10 mg) were heated from room temperature up to 100°C at 10°C /min and cooled to –90°C at 10°C /min, and the data were then collected on the second heating ramp from –90°C to 100°C at 10°C/min.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 thermogravimetric analyzer. Measurements were carried out in N_2 with a continuous N_2 flow of 60 mL/min. A N_2 flow at 40 mL/min was used as the balance purging gas. In a typical run, the sample (~ 10 mg) was heated from 100 ^{o}C to 700 ^{o}C at a heating rate of 20 ^{o}C/min.

Wide-angle X-ray diffraction (WAXRD) analyses on the polymer samples were carried out on a Philips PW 1710 diffractometer with Co Kα radiation (40 kV and 30 mA, λ = 1.79 Å) at ambient temperature. The diffraction data were obtained with 2θ from 3° to 60° and with a step size of 0.02° and a counting time of 6 seconds.

Synthesis of POSS-supported Pd-diimine complex (3)

Complex **1** (1.30 g, 1.62 mmol) and acryloisobutyl-POSS (1.81 g, 1.94 mol, 1.2 equiv.) were added into a Schlenk flask containing 40 ml of dichloromethane/diethyl ether mixture (1/1 volume ratio). The orange solution was stirred under nitrogen protection for two days at room temperature. The solvent of the resulting solution was removed *in-vacuo*. The resulting solid was then redissolved in 5 mL of CH_2Cl_2. Pentane (5 mL) was added slowly to yield a small amount of solid (unreacted complex **1**). The solution was filtered through a 0.2 μm syringe filter to remove the solid. The solvent in the filtered solution was removed *in-vacuo*. The resulting solid was redissolved in 5 mL of CH_2Cl_2. Pentane (15 mL) was added slowly to yield an orange precipitate and the supernatant was decanted. This dissolution/precipitation procedure was repeated twice. Finally, the precipitated solid was washed three times with diethyl ether (10 mL) and dried *in-vacuo* overnight at room temperature, yielding the product as an orange powder of **3** (~ 1.1 g, 40% yield). Anal. Calcd for ($C_{63}H_{115}O_{14}N_2Si_8SbF_6Pd$): C, 44.89; H, 6.88; N, 1.66. Found: C, 43.34; H, 6.86; N, 1.83. IR measurment: 1638 cm^{-1} [ν(C(O))], 1118 cm^{-1} [Si-O-Si], 483 cm^{-1} [Si-O], 1231 and 739 cm^{-1} [Si-CH_2].

^{1}H NMR (500 MHz, CD_2Cl_2, rt.) δ 7.40-7.20 (m, 6H, H_{aryl}), 3.21 (t, 2H, $OCH_2CH_2CH_2Si$), 2.96 (septet, 2H, *CH*Me_2), 2.94 (septet, 2H, C″*H*Me_2), 2.41 (t, 2H, $PdCH_2CH_2CH_2C(O)$), 2.25 and 2.24 (s, 3 each, N=C(*Me*)-C′(*Me*)=N), 1.86 (septet, 7H, $SiCH_2CH(CH_3)_2$), 1.40 (t, 2H, PdCH_2), 1.39, 1.38, 1.34, 1.33, 1.29, 1.28, 1.25, and 1.23 (s, 3 each, CH*MeMe*′, C′H*MeMe*′), 0.99, 0.98, 0.95, and 0.94 (s, 42H, $SiCH_2CH(CH_3)_2$), 0.68 (pentet, 2H, $PdCH_2CH_2CH_2C(O)$), 0.63 and 0.59 (s, 14H, $SiCH_2CH(CH_3)_2$).

^{13}C NMR (125 MHz, CD_2Cl_2, rt.) δ 183.0 ($PdCH_2CH_2CH_2C(O)$), 179.5 and 172.4 (N=*C*-*C*′=N), 141.0 and 140.9 (Ar, Ar′, C_{ipso}), 138.9 and 138.4 (Ar, Ar′, C_o), 129.3 and 128.2 (Ar, Ar′, C_p), 125.0 and 124.5 (Ar, Ar′, C_m), 71.0 ($OCH_2CH_2CH_2Si$), 36.3 and 30.3 ($PdCH_2CH_2CH_2C(O)$), 29.6 and 29.3 (*C*HMe_2,*C*′HMe_2), 26.03 and 26.01 ($SiCH_2CH(CH_3)_2$), 24.50 and 24.46 ($SiCH_2CH(CH_3)_2$), 24.0 ($PdCH_2CH_2CH_2C(O)$), 24.3, 24.1, 23.5, and 23.4 (CH*MeMe*′, C′H*MeMe*′), 23.0 ($SiCH_2CH(CH_3)_2$), 22.3 ($OCH_2CH_2CH_2Si$), 21.9 and 20.2 (N=C(*Me*)-C′(*Me*)=N), 8.8 ($OCH_2CH_2CH_2Si$).

Fig. S.1 shows the ^{1}H NMR spectrum of **3** along with those of complex **1**, **2**, and acryloisobutyl-POSS for comparison. The presence of POSS nanoparticle in **3** is evidenced from the resonances (*f*, *g*, *h* in Fig. S.1(a)) of the corner isobutyl groups in the ^{1}H NMR spectrum of **3**, while the resonances of the vinyl double bond disappear, indicating the successful insertion reaction of the acrylate group of POSS macromonomer and the removal of its unreacted residue.[3] The presence of 6-membered chelate is confirmed from the triplet of Pd-CH_2-CH_2-CH_2-C(O)- (*c* at 2.41 ppm in Fig. S.1(a)).[1,4,5] The -C(O)O-CH_2- protons are shifted to 3.17 ppm (*d* in Fig. S.1(a)) from 4.09 ppm in the POSS macromonomer (*d’* in Fig. S.1(c)). Analysis of ^{13}C NMR spectrum as shown in Fig. S.2 also confirmed the structure of **3**. Both NMR spectra indicate the sole presence of a single isomer, the six-membered chelate.

ESI MS measurement was conducted on complex **3**. The results confirm the structure of **3**. Fig. S.3 shows the ESI MS spectrum and comparison with theoretical isotope patterns. The positive ion spectrum shows a strong signal for the cation at m/z 1455, as expected. The observed isotope pattern is in good agreement with the theoretical. Weaker peaks are apparent at m/z 1673 and 1737. M/z 1637 is possibly an adduct with 2 trifluoroacetic acid (TFA) molecules. Similarly, m/z 1737 may be an adduct with 2 TFA + acetic acid. There is no indication of the undissociated complex. The negative ion spectrum shows a strong signal for $SF6^-$, as expected, with an Sb isotope pattern (m/z 113 and 227 are incompletely subtracted TFA background peaks; m/z 471 is an unknown background peak).

Living polymerization of ethylene with 3 at 5 °C and 27.5 bar

Ethylene living polymerizations were carried out at 5 °C under an ethylene pressure of 27.5 bar in a 500 mL Autoclave Engineers Zipperclave reactor equipped with a MagneDrive agitator, a removable heating/cooling jacket, and a sampling port. The reactor temperature was maintained by passing a water/ethylene glycol mixture through the jacket using a refrigerating/heating circulator set at the desired temperature. In a typical run, the autoclave was pressurized with ethylene to 6.9 bar and vented three times. Subsequently chlorobenzene (290 mL) was added into the reactor and it was cooled down to 5°C. 10 mL freshly prepared solution of **3** (0.20 g, 0.12 mmol) in chlorobenzene was injected into the reactor. The reactor was then quickly pressurized to an ethylene pressure of 27.5 bar to start the polymerization. During the polymerization, the temperature and pressure were maintained. Every hour for six hours, a 30 mL aliquot of the polymerization solution was taken from the reactor sampling port and was quenched by adding 0.1 mL of triethylsilane. The viscous polymer product obtained after evaporating the solvent was redissolved in 10 mL THF. To remove black Pd powders in the solution, 2 mL of hydrochloric acid (37%) and 1 mL of hydrogen peroxide (30%) were added in the solution. After stirring for 30 minutes, the polymer was precipitated using 10 mL of methanol. The polymer was redissolved in THF and subsequently precipitated in methanol. This dissolution/precipitation procedure was repeated for three times. Finally the clear polymer sample was obtained after drying in a vacuum oven at 50 °C overnight. The polymer samples were analyzed using ^{1}H NMR and GPC. Table S.1 lists the polymerization results.

^{1}H NMR measurements were performed to elucidate polymer microstructure and confirm the presence of the POSS nanoparticle as chain end functionality. Representatively, Fig. S.4 shows the ^{1}H NMR spectrum of the PE sample taken after 1 h of polymerization. The signals (*f*, *g*, *h* in Fig. S.4) due to the corner isobutyl groups on the POSS nanoparticle are clearly present.[3] The protons (*d*) of -C(O)O-CH_2- shift to 4.02 ppm, and those (*c*) of -CH_2-C(O)O- locate at 2.28 ppm.[3] Peak integration further confirms the consistency with the structure of the POSS end functionality. Similar ^{1}H NMR spectra confirming the presence of an end-capping POSS nanoparticle were found with the other polymers obtained after different polymerization time. Number-average molecular weight data of the polymers were also calculated from ^{1}H NMR spectroscopy based on end-group analysis. The calculated results show very good match with the absolute molecular weight data measured from GPC coupled with on-line multi-angle laser light scattering measurements (see Table S.1). This agreement further confirms that each polymer chain does contain a POSS end group.

References:

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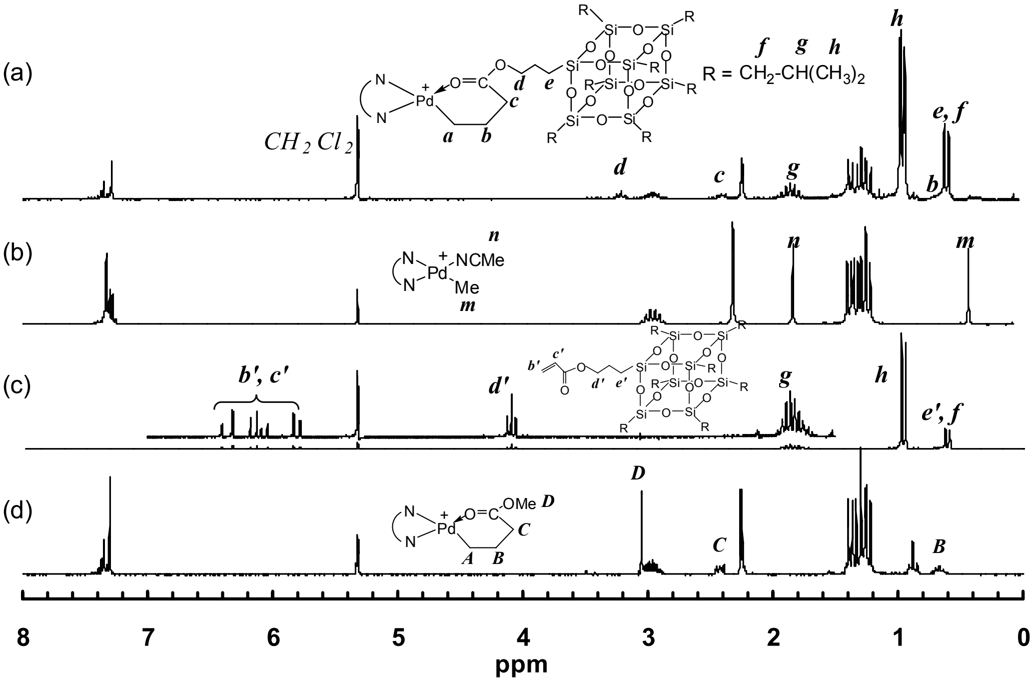


Fig. S.1 ^{1}H NMR spectrum of (a) complex **3**, (b) complex **1**, (c) acryloisobutyl-POSS, and (d) complex **2** ^{5a}.

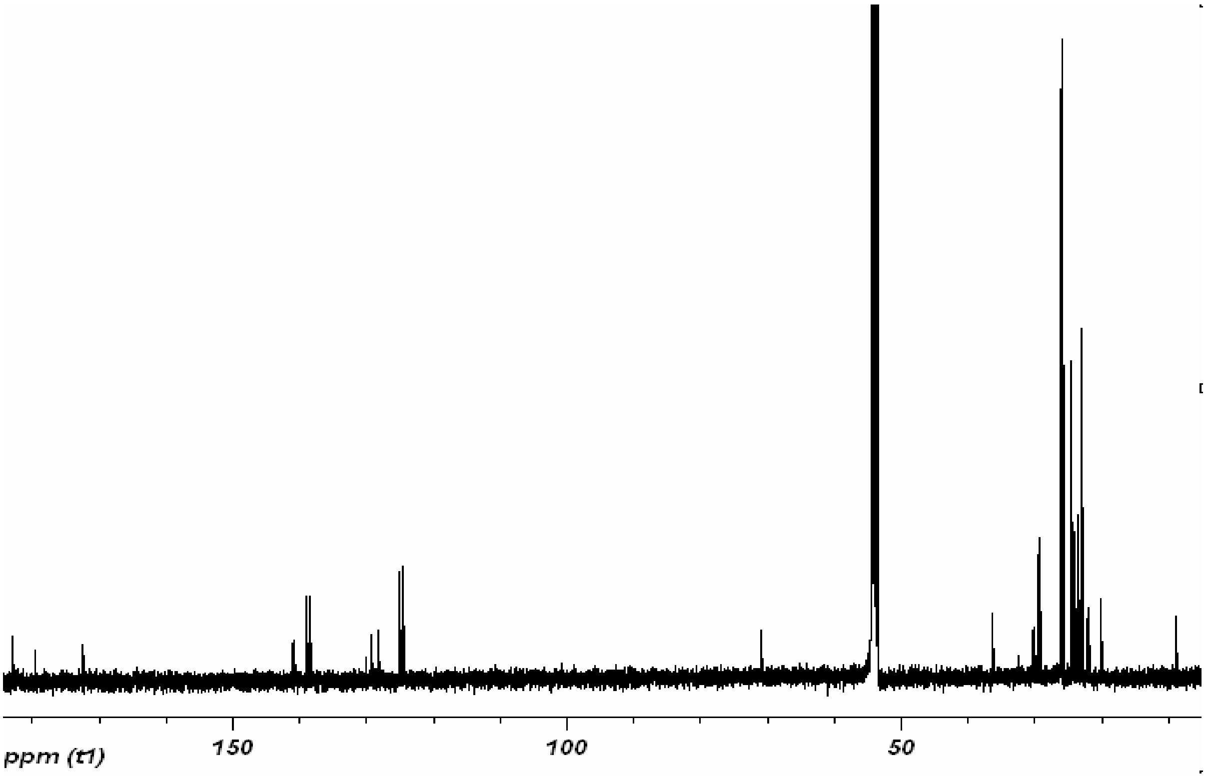
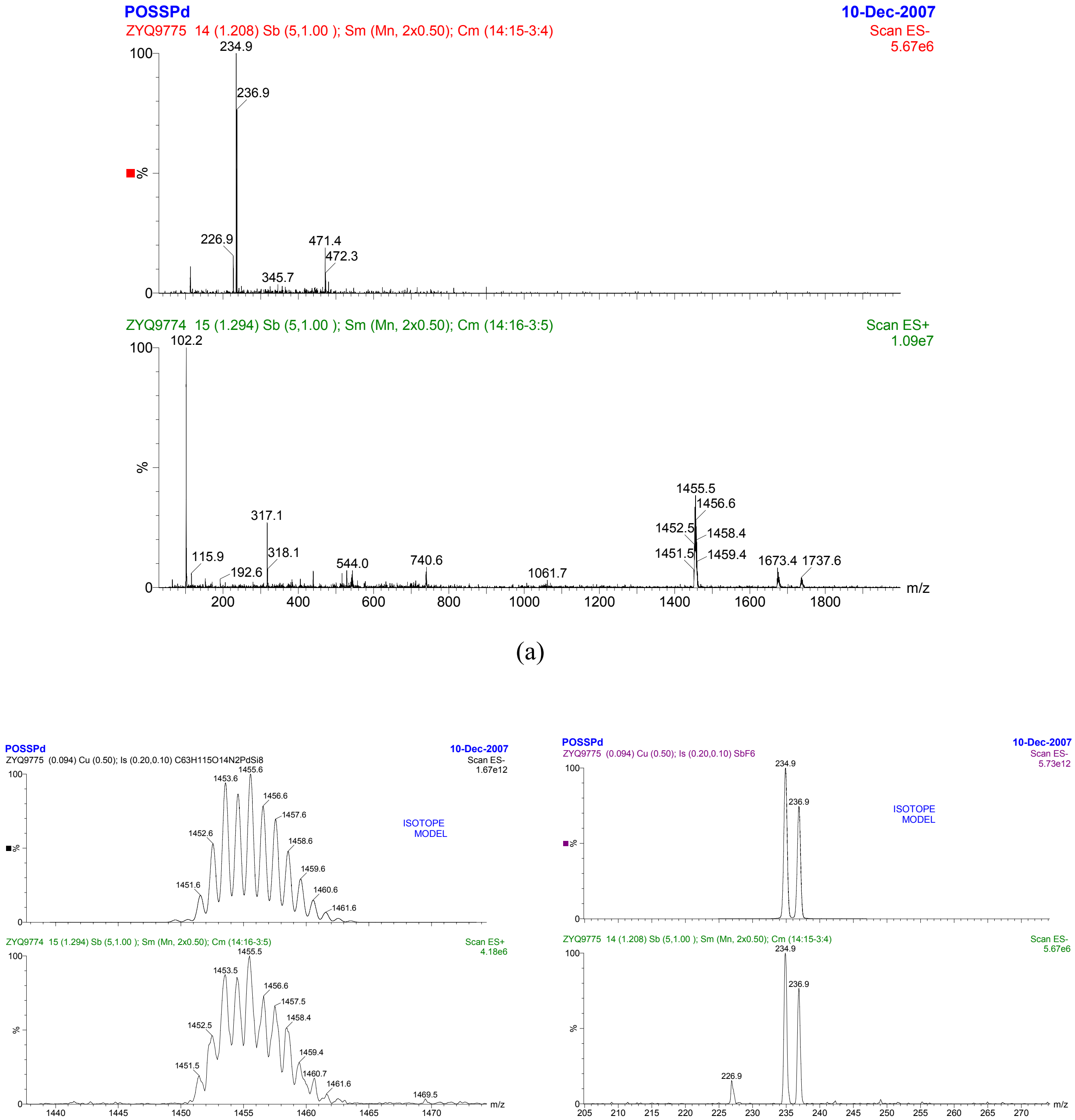


Fig. S.2 ^{13}C NMR spectrum of **3** (with CD_2Cl_2 as solvent)



(a)

(b)

(c)

Fig. S.3 (a) ESI MS spectrum of complex **3**, (b) comparison of observed isotope pattern of positive ion ESI spectrum with the theoretical isotope pattern, and (c) comparison of observed negative ion ESI spectrum with theoretical isotope pattern.

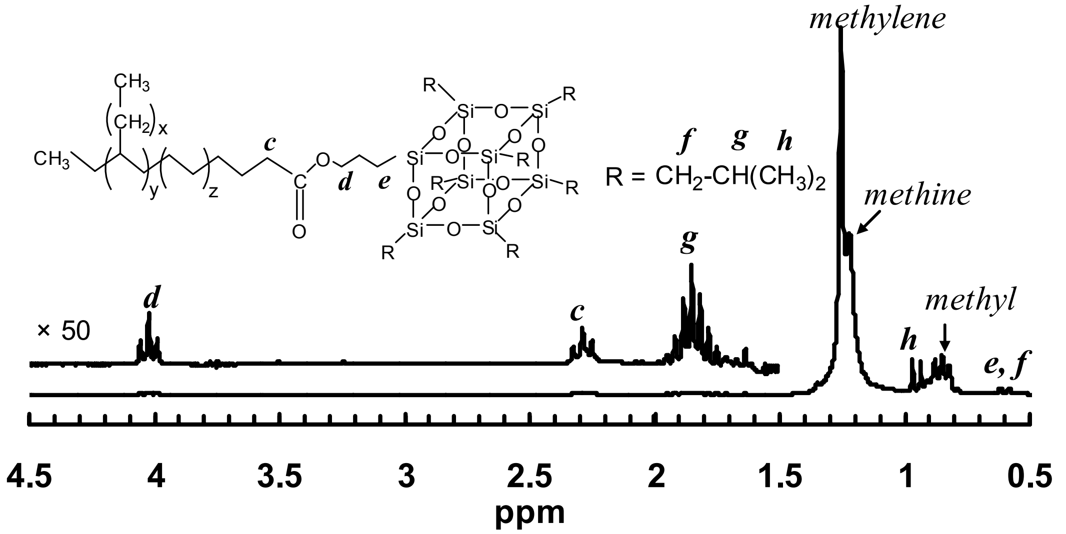


Fig. S.4 ^{1}H NMR spectrum of POSS-ended polyethylene sample obtained after 1 h polymerization with **3** at 27.5 bar and 5 °C.

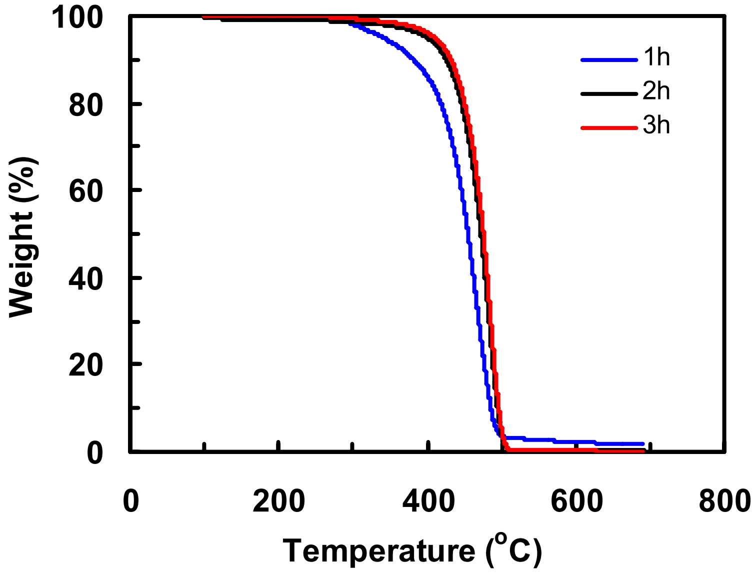


Fig. S.5 TGA curves of polyethylene samples end-tethered with a POSS nanoparticle obtained in ethylene "living" polymerization with **3** after a polymerization time of 1 h, 2 h, and 3 h, respectively. Measurements were conducted in N_2 with a heating rate of 20 °C/min.

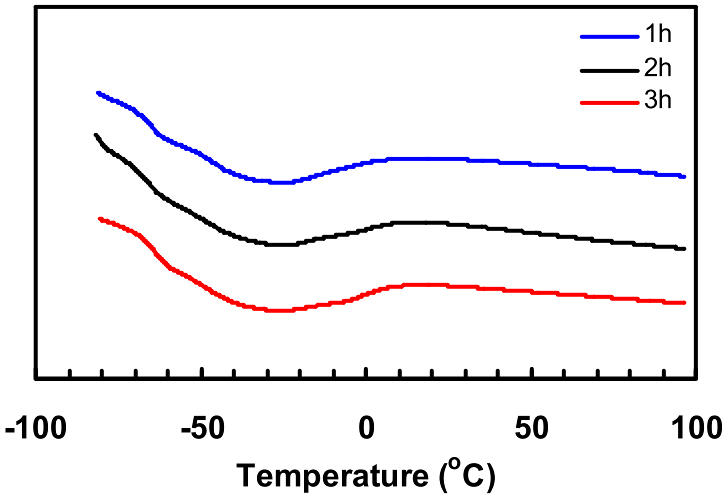


Fig. S.6 DSC thermograms of polyethylene samples end-tethered with a POSS nanoparticle obtained in ethylene “living” polymerization with **3** after a polymerization time of 1 h, 2 h, and 3 h, respectively. DSC heating rate: 10 °C/min.

Table S.1 “Living” polymerization of ethylene with **3** at 5 °C and 27.5 bar in chlorobenzene[a]

Entry	Time (h)	$M_{n,GPC}$ [b] (kg/mol)	PDI_{GPC} [b]	$M_{n,LS}$ [c] (kg/mol)	PDI_{LS} [c]	$M_{n,NMR}$ [d] (kg/mol)	*TOF* [e] (1/h)	Branches [f] (per 1000C)
1	1	15.2	1.11	-	-	11.2	368	89
2	2	24.4	1.17	19.2	1.01	19.1	324	88
3	3	36.6	1.14	30.1	1.01	29.6	342	88
4	4	43.5	1.12	33.4	1.01	36.3	316	87
5	5	52.4	1.19	48.7	1.01	45.9	321	88
6	6	56.4	1.17	49.2	1.03	51.6	302	87

[a] Other conditions: catalyst **3** amount, 0.12 mmol; total volume, 300 mL.

[b] Number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI_{GPC}) determined from GPC vs polystyrene standards.

[c] Number-average molecular weight ($M_{n,LS}$) and polydispersity index (PDI_{LS}) determined from GPC coupled with on-line multi-angle laser light scattering measurement.

[d] Number-average molecular weight ($M_{n,NMR}$) determined from ^{1}H NMR spectroscopy based on end group analysis.

[e] Turn over frequency determined from ^{1}H NMR spectroscopy based on end group analysis.

[f] Total branching determined from ^{1}H NMR spectroscopy.