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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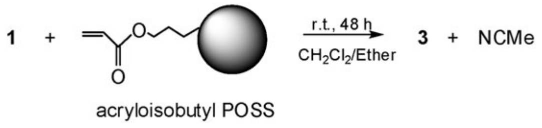
A POSS-supported Pd–diimine complex, an homogeneous analog of a supported catalyst, was synthesized and applied for the unique synthesis of narrow-distributed polyethylene chains containing an end-tethered POSS nanoparticle by ethylene "living" polymerization.

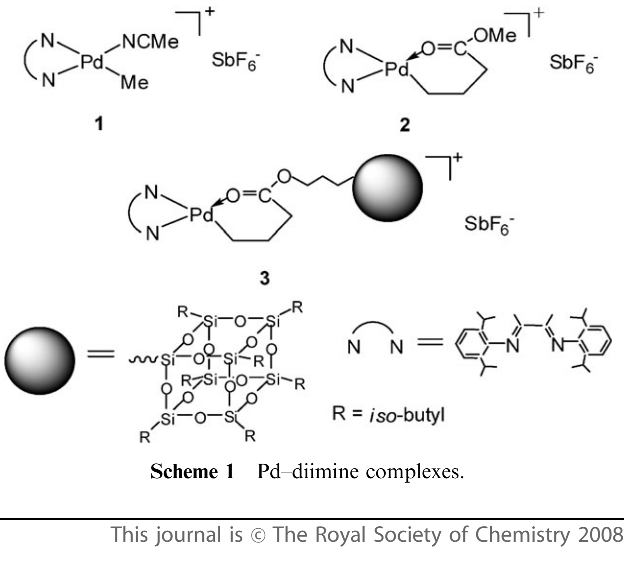
Due to its unique structure and superior properties, polyhedral oligomeric silsesquioxane (POSS) has recently received extensive research attention as a nanoscaled building block for construction of inorganic–organic polymer nanocomposite materials.[1] A variety of polymerization strategies have been successfully developed for design and synthesis of various polymers containing covalently tethered POSS nanoparticles, which show remarkably enhanced thermal and mechanical properties.[1c] Resembling surface feature of silica, incompletely condensed POSS has also been extensively studied as a homogeneous model support for immobilization of various homogeneous metal catalysts, including metallocene catalysts for coordination polymerization of olefin.[2] Such homogeneous model supported catalysts have afforded the molecular level insights into the chemistry of commercial silica-supported heterogeneous catalysts.[2]

Chain walking cationic Pd–diimine catalysts (such as acetonitrile adduct **1** and chelate complex **2** shown in Scheme 1) are a novel class of late transition metal catalysts for catalytic olefin polymerization.[3] Besides possessing the unique chain walking mechanism,[4,5] the catalysts are able to catalyze olefin "living" polymerization[6] and olefin copolymerization with functional monomers.[7,8] They thus enable design and synthesis of novel polyolefins with unique chain structures and architectures, such as dendritic/hyperbranched polyethylenes (PE),[4,5] telechelic PE, block copolymers,[6] and copolymers of olefin with functional monomers.[7,8] We report in this communication a novel homogeneous POSS-supported Pd–diimine catalyst, **3** shown in Scheme 1, and its capability to catalyze ethylene "living" polymerization for unique synthesis of telechelic PEs end-tethered with a POSS nanoparticle.

The POSS-supported complex, **3**, was synthesized conveniently in one step by reacting **1** with acryloisobutyl-POSS (1.2 equiv.), a completely condensed POSS macromonomer bearing an acrylate functionality.



This catalyst immobilization strategy is distinctively different from those reported for POSS-supported metallocene catalysts, where incompletely condensed silsesquioxanes bearing silanol groups as anchoring sites are often used.[2] Herein we utilized the reaction chemistry of the cationic Pd–diimine adduct **1** with acrylate functionality.[3a,7,9] In this reaction, acrylate was inserted into Pd–Me bond of **1** following the 2,1-insertion mechanism and subsequent rearrangement yielded a six-membered cyclic chelate.[3a,7,9] This unique acrylate-insertion chemistry has previously led to the synthesis of chelate complex **2** (with methyl acrylate)[3a] and several functionalized Pd–diimine catalysts bearing different functional substituents on the chelate ring by using different functional acrylates.[9,10] In this immobilization strategy, the acrylate functionality of acryloisobutyl-POSS is the specific anchoring site for the cationic Pd complex **1**. In **3**, the cationic Pd center is thus bonded onto the POSS nanoparticle through the ester linkage.



Scheme 1 Pd–diimine complexes.

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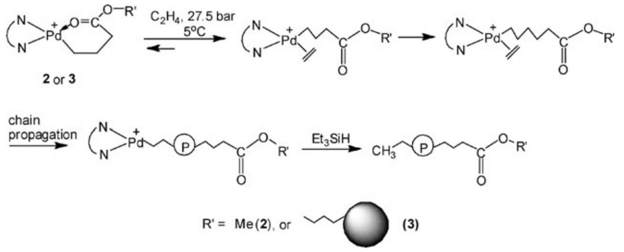
† Electronic supplementary information (ESI) available: Experimental part; ^{1}H and ^{13}C NMR spectra of **3**; MS spectra for **3**, table of polymerization results; ^{1}H NMR spectrum of polymer, TGA curves and DSC thermograms of the polymers. See DOI: 10.1039/b716900k

Complex **3** has limited solubility in ether/alkane, while the POSS macromonomer is highly soluble. This solubility difference allowed a convenient removal of unreacted acryloisobutyl-POSS by using dissolution–precipitation method to obtain pure compounds of **3**. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) analyses confirmed the formation and structure of **3**.[11] The formation of five-membered chelate isomer, resulting from 1,2-insertion of the acrylate group into the Pd–Me bond of **1** followed by rearrangement, has been observed in synthesis of **2**.[7a,10a] However, both ^{1}H and ^{13}C NMR spectra indicated the absence of this isomer in **3**. The structure and high purity of **3** was also confirmed by using electrospray ionisation mass spectrometry (ESI MS) and elemental analysis.[12]

Ethylene polymerization was carried out with **3** (0.12 mmol) in chlorobenzene (300 mL) at 5 °C and under an ethylene pressure of 27.5 bar. Cationic Pd–diimine catalysts (such as **1** and **2**) have been reported[6,9,10] to typically catalyze "living" polymerization of ethylene due to significantly reduced chain transfer reactions at this given condition, leading to a linear increase of polymer molecular weight with time along with low polymer polydispersity index (PDI). More interestingly, in "living" polymerization with the chelate complexes (such as **2**), chain initiation starts by dissociation of the Pd–carbonyl coordination under high ethylene pressure and subsequent ethylene insertion into Pd–CH_2 bond, which introduces the ester functional end cap to the growing polymer chains at the beginning of polymerization (Scheme 2).[6,9,10] Herein, this polymerization chemistry with the POSS-supported chelate complex **3** as the polymerization catalyst should give rise to polyethylene chains end-capped with a POSS nanoparticle through the ester linkage (Scheme 2).

During ethylene polymerization with **3**, aliquots of the polymerization solution in chlorobenzene were removed every hour for six hours for monitoring polymer molecular weight development. The aliquot solutions were quenched with Et_3SiH, which cleaved the Pd–alkyl bond and yielded polymer chains containing a saturated group at one end[6,9] and a POSS nanoparticle at the other end. Fig. 1(a) shows the gel permeation chromatography (GPC) traces of PE samples obtained at different polymerization time, and Fig. 1(b) shows the number-average molecular weight ($M_{n,GPC}$) and PDI, determined from GPC measurements relative to polystyrene standards, *vs.* polymerization time. A close-to-linear increase of polymer molecular weight with time is evident, and the PDI values of these samples are low (within 1.11–1.19), characteristic of "living" polymerization.[6]



Scheme 2 Ethylene "living" polymerization with Pd–diimine chelate complexes.

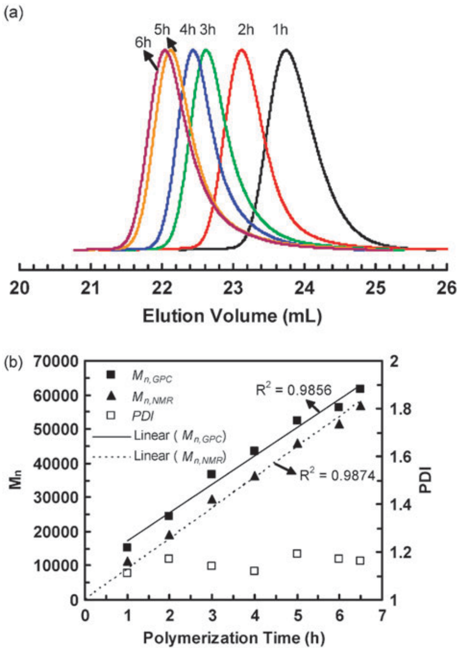


Fig. 1 (a) GPC elution traces, and (b) M_n and PDI for polymer samples obtained after different polymerization time with **3** at 27.5 bar and 5 °C.

^{1}H NMR measurements were performed to elucidate polymer microstructure. The presence of the POSS nanoparticle as chain end functionality was confirmed from the ^{1}H NMR analyses of the polymers.[13] ^{1}H NMR spectra also show the polymers are highly branched. Calculations based on the resonances of methylene, methine, and methyl protons of the ethylene sequence on polymer backbone indicate that the polymers are branched with *ca.* 88 branches per 1000 carbons. Such branched structure is a result of the chain walking mechanism of Pd–diimine catalysts.[4] Based on our prior studies,[5] the polymers, however, should have a linear chain topology with mainly short branches given the polymerization condition of 27.5 bar and 5 °C. The highly branched structure makes polymers soluble in organic solvents like THF and CH_2Cl_2 even at room temperature.

Based on the fact that each polymer chain contains one end-capping POSS nanoparticle, the number-average molecular weights, $M_{n,NMR}$, of the polymer samples were also calculated from their ^{1}H NMR data. These data are also plotted in Fig. 1(b) as a function of polymerization time. Due to the differences in the hydrodynamic volumes of these telechelic branched PEs and polystyrene standards, $M_{n,GPC}$ data determined for these polymers are relative values and do not match $M_{n,NMR}$ data, which reflect the true number-average molecular weight of the polymers. GPC coupled with on-line multi-angle laser light scattering measurement was also utilized to determine the absolute molecular weight of the polymers.[14] The number-average molecular weight data, $M_{n,LS}$, obtained from light scattering measurements match $M_{n,NMR}$ very well, which were determined based on end-group analysis. This also confirms the presence of the end-tethered POSS nanoparticle in each polymer chain. The turnover frequency (TOF) values were calculated from the ^{1}H NMR spectra based on end-group

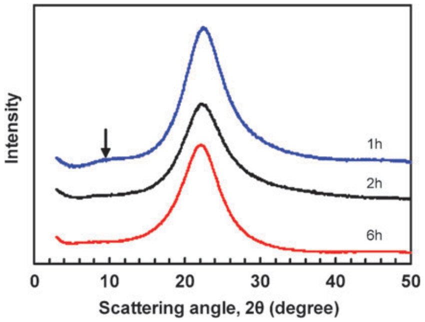


Fig. 2 XRD patterns of POSS-end-tethered polymers obtained after polymerization time of 1 h, 2 h, and 6 h, respectively.

analysis. The average TOF value over 6 h of polymerization was 325 h^{-1}, close to the data for other Pd–diimine chelate complexes.[10] This indicates that the POSS support does not affect the "living" polymerization.

Preliminary characterizations of physical properties of these polymers end-tethered with a POSS nanoparticle were carried out. Thermogravimetric analyses (TGA) were carried out in N_2 on three PE samples obtained after a polymerization time of 1 h, 2 h, and 3 h, respectively.[15] The weight percentage of the end-capping POSS nanoparticle in three polymers is estimated to be 8%, 5%, and 3%, respectively, by calculating from their $M_{n,NMR}$ data and the molecular weight of the POSS nanoparticle. The char yield of the polymers from TGA analyses is 1.7%, 0.30%, and 0.17%, respectively, consistent with their different POSS nanoparticle percentages. The polymers obtained all appear to be oil-like liquids. From differential scanning calorimetry (DSC) studies, the polymers exhibit similar thermal behaviors with a glass transition at about −67 °C and a very weak endotherm centered at about −27 °C, which is possibly a melting endotherm.[16]

Fig. 2 compares the X-ray diffraction (XRD) patterns of three polymers synthesized at 1 h, 2 h, and 6 h, respectively. Owing to the amorphous nature of the polymers at room temperature, the broad amorphous halo centered at $2\theta = 22.4^\circ$ ($d = 4.6$ Å) is the dominant diffraction peak for all three polymers.[17] For the polymer synthesized after 1 h of polymerization, an additional weak and broad diffraction at 9.5° ($d = 10.8$ Å) is found. This diffraction is characteristic of small crystallites resulting from the aggregation of isobutyl-substituted POSS nanoparticles, which further confirms the presence of POSS nanoparticles in the polymer.[17] For the other two samples shown in Fig. 2, however, this diffraction is not clearly observable due to the much lower POSS contents in the polymers.

In summary, we have demonstrated a new catalyst immobilization chemistry specifically for supporting cationic Pd–diimine complex onto homogeneous POSS nanoparticles. The outstanding features of such supported catalysts lie in the ability of the supported cationic Pd centers to initiate "living" polymerization of ethylene and the covalent bonding of the resulting polymer chains onto the supports. We are further applying this immobilization chemistry to graft Pd–diimine complexes onto commercial silica and other supports, which contain surface acrylate groups, to subsequently graft PE chains covalently onto support surface *via* ethylene "living" polymerization.

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11 ^1H and ^{13}C NMR spectra of **3** together with related discussions are presented in Supplementary Information†.

12 ESI MS spectra and elemental analysis results of **3** are shown in Supplementary Information†.

13 A representative ^1H NMR spectrum of the PE sample taken after 1 h of polymerization together with related discussions are presented in Supplementary Information†.

14 The molecular weight and polydispersity index data obtained from GPC with on-line light scattering measurments are listed in Table S1 of Supplementary Information†.

15 TGA traces of the polymers are shown in Supplementary Information (Fig. S5)†.

16 Polymer DSC thermograms are shown in Supplementary Information (Fig. S6)†.

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