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Facile high-temperature synthesis of weakly entangled polyethylene using a highly activated Ziegler-Natta catalyst

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ABSTRACT

A Polyhedral oligomeric silsesquioxane (POSS) modified Ziegler-Natta catalyst is reported to synthesize the weakly entangled ultra-high molecular weight polyethylene at a high temperature and with a high activity. Incorporation of POSS can form numbers of aggregates with a mean size of 48 nm adsorbing on the surface of SiO_2. The structure of nanoaggregates is evidenced by the experiments and theoretical calculations where one POSS can coordinate with multiple $MgCl_2$ molecules serving as an electric donor to the further immobilized $TiCl_4$. The catalyst is thus featured by two distinct active regions positioned in the POSS/$MgCl_2$ nanoaggregates and δ-$MgCl_2$, respectively. The former regions present extremely low activity on ethylene polymerization, which function as horizontal separators for isolating the active $TiCl_4$ sites and the growing chains. This catalyst exhibits an exceptional activity (*i.e.* 1.3×10^6 gPE mol_{Ti}^{-1} h^{-1} bar^{-1}) for the synthesis of weakly entangled polyethylene at 60 °C.

1. Introduction

The balance of mechanical and processable property is one of the key issue for developing high performance polyolefin. To this end, numerous studies have focused on the precise control of microstructures such as molecular weight and distribution, branch degree and distribution [1]. Recently, the chain entanglement of nascent polymers, caused by the intertwined chains during the polymerization, is highlighted and is proved to show significantly influence on the mechanical, thermal and processable properties of the final products [2].

Some approaches have shown validity to synthesize the nascent polyethylene (PE) with a weakly entangled state, where the growing chains are separated from each other by diluted, compartmented or isolated active species [2]. For instance, our group employed a polyhedral oligomeric silsesquioxane (POSS) modified silica for immobilizing fluorinated bis(phenoxyimine)Ti complexes. The POSSs were chemically bonded on the silica surface, serving as horizontal spacers between the active sites to reduce the chain overlap in polymerization [3]. By this modification, the weakly entangled polyethylene (PE) can be synthesized by the heterogeneous catalyst with a considerable activity. To date, all the strategies for synthesizing the weakly entangled polyethylene are conducted below 30 °C at which a fast crystallization rate (even faster than the chain growth rate) can be achieved [2]. This fast crystallization rate can make the growing chains to be crystallized as soon as they are growing out, controlling a single chain to form a single crystal [2a,2b]. However, this low temperature will either lower the catalytic activity or harden the removal of heat transfer, making the process highly energy-consuming and difficult to be scaled-up [4]. Importantly, the growth rate of the polyethylene crystal presents exponential decrement when the temperature is increased from 30 to 90 °C [2b,5]. This fact takes a big challenge for synthesizing the weakly entangled polyethylene above 60 °C which is the economically critical temperature for industrial polymerization process.

Heterogeneous catalysts play a very important role in the synthesis of polyolefin and show great potential of being transferred to industrial continuous processes thanks to its efficiency of directing the polymers morphology and preventing reactor fouling [4,6]. The active species are dispersed randomly on the porous supports depending on the location of nucleophilic groups [2a]. It was reported that the onset of chain folding was from 65 to 150

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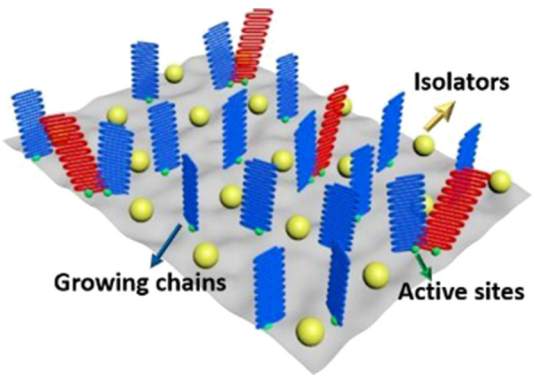
carbon atoms for solution-crystallized linear *n*-alkanes [5]. Thus, the close distance between active species will result in a higher probability of chain overlap, especially before the formation of crystals [2,3]. We report here a facile method of modifying the traditional Ziegler-Natta (ZN) catalyst by the POSS, which has been proven effective in producing the weakly entangled PE at a high temperature with an exceptional activity (Scheme 1). The POSS molecule has a large molecular weight (*i.e.* 891.72 g/mol) and contains only two —OH groups (See Fig. S1 for the structure of POSS which is an incompletely condensed silsesquioxane). The incorporation of POSS contributes a large weight fraction but only a small increment of the mole fraction of nucleophilic groups (*i.e.* hydroxyl). We show that the POSS can capture the $MgCl_2$ and form POSS/$MgCl_2$ nanoaggregates which can isolate the active sites and hinder the chain overlap. Considering the critical length scale of polymer chains for crystallization (ranging from 8.5 nm to 19.3 nm) [5], the size and the density of the obstructer must reach a certain level to be able to effectively prevent the formation of entanglement. A macropores SiO_2 with an open-framework structure (Macro-SiO_2) is chosen as the support [7], since its open structure is helpful for (*i*) observing the assembly of POSS/$MgCl_2$ nanoaggregates, and (*ii*) imposing less confinement to the chain crystallization and propagation [7], thus amplifying the influence of obstructers on the entanglement formation (See Fig. S2 for the morphology of Macro-SiO_2).

2. Experiments

2.1. Materials

All manipulations of air-sensitive and moisture-sensitive compounds were conducted under an inert nitrogen atmosphere using standard Schlenk techniques or in a glovebox. The macropores-silica (average pore diameter = 0.9 μm, porosity = 90.8%), was synthesized following our previous work and was marked as Macro-SiO_2 [7]. 955 silica was purchased from Grace Davison Company (China). Disilanolisobutyl POSS was purchased from Hybrid Company (USA) and dried for 24 h before use. The Macro-SiO_2 and 955 silica were activated at 600 °C for 5 h with nitrogen flow before use. The titanium (IV) chloride ($TiCl_4$, 99.9 wt%) was supplied by the Acros Organics. The anhydrous magnesium chloride ($MgCl_2$) was purchased from the Aladdin Chemical Reagent. The 1,4-butanediol (BD) was obtained from the Aladdin Chemical Reagent, and was dried over molecular sieves for 2 days before use. The triethylaluminium (TEA) (1 mol/l in hexane) was purchased from the J&K Chemical Corp. The tetrahydrofuran (THF), *n*-heptane and *n*-hexane were distilled over the sodium/diphenyl ketone before use.



Scheme 1. POSS modified ZN catalysts for synthesizing weakly entangled PE.

2.2. Catalyst preparation

0.5 g of $MgCl_2$ and POSS were stirred with 30 ml of THF at 60 °C for 2 h, achieving $MgCl_2$/POSS/THF solution. The 0.5 g of Macro-SiO_2 was mixed with 0.25 ml of BD and 20 ml of THF in another Schlenk flask at 40 °C for 2 h, obtaining Macro-SiO_2/BD/THF. The weight fraction of POSS to the Macro-SiO_2 was varied as 0, 10, 20, 30, 50 wt%. The corresponding mole ratio of [POSS]/[$MgCl_2$] was 0, 0.01, 0.02, 0.03 and 0.05, respectively. The prepared $MgCl_2$/POSS/THF solution was then added into the Macro-SiO_2/BD solution. The mixture was stirred for another 2 h. The obtained solids were filtered and washed three times with 30 ml of *n*-hexane, and dried under vacuum for 3 h, achieving the supports (Sup-POSS-X, where X (=0, 10, 20, 30 and 50) represented the nominal loading of POSS). Subsequently, 30 ml of *n*-hexane and 5 ml of TEA were mixed with 1.0 g of Sup-POSS-X to remove the coordinated BD. The slurry was stirred at 60 °C for 2 h and washed with 30 ml of *n*-hexane three times. Finally, 30 ml of *n*-hexane and 1 ml of $TiCl_4$ were added and stirred for another 2 h at 60 °C in order to synthesize the catalyst. The catalyst, labelled as Cat-POSS-X, was washed three times with 30 ml of *n*-hexane to remove the extra $TiCl_4$ and then dried under vacuum for 3 h. For the synthesis of 955 silica supported catalyst, all the procedure was the same with Cat-POSS-10, only changing the Macro-SiO_2 to this commercial 955 silica.

In order to study the reaction between the POSS, $MgCl_2$ and $TiCl_4$, the POSS/$MgCl_2$ adducts and POSS/$MgCl_2$/$TiCl_4$ adducts were synthesized with equimolar quantity of these molecules. For synthesizing the POSS/$MgCl_2$ and the POSS/$MgCl_2$/$TiCl_4$, 1 mmol of $MgCl_2$ was dissolved into 30 ml of THF and was then added droplets into the POSS solution (1 mmol of POSS solved into 30 ml of THF). The mixture was further stirred for 2 h at 60 °C. The solution was dried under vacuum for another 3 h at 60 °C achieving solids. The solids were dissolved into 30 ml of *n*-hexane again and then filling out the unsolvable solids in order to remove the uncoordinated $MgCl_2$. The solution was dried achieving a solid named as POSS/$MgCl_2$. The POSS/$MgCl_2$ was dissolved into 30 ml of *n*-hexane achieving a transparent solution. 1 mmol of $TiCl_4$ was added into the solution. The solution was transferred to the yellowish supernatant and some solids was seed out after 4 h. The solid was washed by the *n*-hexane 3 times to remove the POSS/$TiCl_4$ (formed by the chemical bonding between hydroxyl and Ti—Cl bonds). This solid was further dried under vacuum for 3 h at 50 °C, achieving the POSS/$MgCl_2$/$TiCl_4$ catalysts (Cat-1). An excessive amount of $TiCl_4$ is incorporated (*i.e.*, 8 mmol) for synthesizing the Cat-2. The POSS/$TiCl_4$ catalysts were synthesized as following and used for a benchmark. 1 mmol of POSS and 2 mmol of $TiCl_4$ are mixed with 30 ml of *n*-hexane, achieving a homogenous solution. This solution was directly used as a homogenous catalyst for ethylene polymerization. The catalyst (*i.e.*, $TiCl_4$ immobilized on the POSS/$MgCl_2$ modified Macro-SiO_2) was synthesized following the preparation method of Cat-POSS-X. 0.2 g of the POSS/$MgCl_2$ was dissolved into 30 ml of THF, instead of the excessive $MgCl_2$ in the Sup-POSS-X. 0.2 g of Macro-SiO_2 and 0.1 ml of BD were also used.

2.3. Ethylene polymerization

Ethylene polymerization was carried out in a 1.0 L Buchi stainless steel autoclave reactor, equipped with a mechanical stirrer and a temperature control equipment. The reactor was heated above 130 °C under vacuum for more than 3 h and repeatedly purged with nitrogen before polymerization. Then, the reactor temperature was reduced to 60 °C. 350 ml of *n*-heptane was added to the reactor. After the introduction of TEA as the cocatalyst, 12 ± 2 mg of the catalyst (0.025 mmol of [Ti]) was injected into the reactor.