



Preparation of tethered half-titanocene complex on cross-linked polystyrene beads for using in syndiospecific polymerization of styrene

Sohrab Rahmani, A.A. Entezami*

Lab. of Polymer, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:

Received 16 November 2009
Received in revised form 9 December 2009
Accepted 2 January 2010
Available online 11 January 2010

Keywords:

Syndiotactic polystyrene
Tethered metallocene
Half-titanocene
Cross-linked polystyrene
Functionalization

ABSTRACT

In this work the cross-linked polystyrene beads were functionalized with silyl hydride groups. Two synthetic procedures were employed to tether of indenyltrichlorotitanium (IndTiCl_3) on the functionalized polystyrene beads. In one approach (method A), the half-titanocene catalyst bearing an allyl group (1-allylindenyltrichlorotitanium) was synthesized and covalently anchored on the functionalized polystyrene by using of hydrosilylation chemistry. In the second approach (method B), the half-titanocene complex was synthesized on the functionalized polystyrene beads. The polymer-supported catalysts were tested for styrene polymerization using methylaluminoxane (MAO) as a cocatalyst. The obtained results revealed that the supported catalyst prepared with method (A) has higher catalytic activity and syndiotacticity than the supported catalyst obtained by method (B). In addition the scanning electron microscopy (SEM) images showed that the polymer particle replicates the shape of the carrier. Furthermore, the ^{13}C NMR and differential scanning calorimetry (DSC) studies confirmed the high syndiotacticity of obtained polymers.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Syndiotactic polystyrene (sPS) is a very attractive polymer because of its low specific gravity, low dielectric constant, high melting point (270°C), high modulus of elasticity and excellent resistance to chemicals. Accordingly, the syndiotactic polystyrene has become a promising material for various applications in the automotive, electronic and packaging industries. Both homogeneous and heterogeneous metallocene catalysts, mostly organometallic titanium complexes with methylaluminoxane (MAO) as an activator, have been found to be effective to synthesize sPS with high catalytic activity [1–12]. From an industrial point of view, it is desirable to heterogenize the catalyst by anchoring the catalyst onto a solid support and polymerize styrene in a liquid slurry polymerization process. The supported catalyst can overcome some disadvantages of homogeneous catalysts, such as poor polymer morphology, reaction fouling and low bulk density of polymer. In order to syndiospecific polymerization of styrene in slurry process, a variety of approaches have been adopted for supporting half-titanocen complexes on silica. These methods include direct reaction of silica with a metallocene complex, followed by activation with a cocatalyst (e.g. MAO), or reaction of MAO-modified silica with a metallocene complex

[13,14]. Recently, significant achievements in the preparation of ultrahigh molecular weight sPS nanofibrils in MAO-modified silica nanotube reactors with half-titanocen catalyst have been obtained [15]. Tethering a catalytic complex via a covalent anchoring of metallocene complexes on organic and inorganic supports through metallocene synthesis on the support or reaction of a suitably functionalized metallocene complex with support, represents one of the most varied techniques employed in the immobilization of single site catalyst in ethylene and propylene polymerization [16–20]. In this way, the active centers are firmly anchored to the support at all times with the hope that the catalyst will not leach or have enough freedom to deactivate via a bimolecular species during polymerization. Preishuber-Pflugl and Brookhart [21] have synthesized a variety of nickel α -diimines containing amine or hydroxyl functional groups, which are reacted with TMA-pacified silica to form tethered precatalysts. These tethered complexes show high activity for ethylene polymerization with no reactor fouling. Chung et al. [22] demonstrated the use of hydrosilylation and hydroboration chemistry to form tethered *ansa*-metallocene. The precatalyst formed via the hydroboration procedure when applied in propylene polymerization, resulted in higher activity, higher stereoregularity and a narrower polydispersity than those produced via the hydrosilylation. Cross-linked polystyrene beads possess several attributes to be considered as a good support. They are more chemically compatible supports relative to silica and other inorganic supports. They are also very versatile materials in terms of the incorporation of functional groups, either by copolymerization of styrene with functionalized vinylbenzene or by

* Corresponding author. Tel.: +98 411 3393119; fax: +98 411 3340191/3393119.
E-mail addresses: sohrab_rahmani2002@yahoo.com (S. Rahmani),
aentezami@yahoo.com, aentezami@tabrizu.ac.ir (A.A. Entezami).

post-modification of preformed polystyrene beads, which are commercially available in different sizes and cross-link densities. Jin and coworkers [23,24] have copolymerized styrene with bis(imino)pyridine iron or nickel α -diimine complexes containing a polymerizable allyl functional, which formed a cross-linked support. Ethylene polymerization with the supported catalyst was found to be of comparable activity to the unsupported catalyst and produced polyethylene with narrow molecular weight distribution and good morphology. Huang et al. [25,26] have prepared cross-linked poly(styrene-co-4vinylpyridine) and poly(styrene-co-acrylamide) having functional groups as the support for zirconocene and titanium tetrachloride catalysts respectively and used for ethylene and styrene polymerization. The obtained polystyrene is highly syndiotactic with poly(styrene-co-acrylamide)-titanium complex. In continue a catalyst with porous polystyrene beads supported Cp_2ZrCl_2 was prepared by Huang et al. [27] and tested for ethylene polymerization. This porous polymer-supported catalyst showed higher activity and produced polyethylene with better morphology. To the best of our knowledge, the syndiospecific polymerization of styrene with tethered catalyst on cross-linked polystyrene has not previously been reported in the literature. In this work, we report immobilization approaches to form tethered half-titanocene complex on functionalized cross-linked polystyrene beads by using of hydrosilylation chemistry. These polymer-supported catalysts were examined in styrene polymerization in the presence of MAO.

2. Experimental

All reactions were performed using standard Schlenk tube techniques under dry argon atmosphere.

2.1. Materials

Poly(styrene-co-divinylbenzene) (PS beads, 2% divinylbenzene obtained from Iran Polymer and Petrochemical Institute) was thoroughly washed according to the literature [28].

Indene (90% Merck) was purified through vacuum distillation. Titanium tetrachloride (TiCl_4 98%, Merck) and n-butyllithium (n-BuLi, 1.6 M in hexane, Merck) were used without further purification. Chlorotrimethylsilane (99% Aldrich), 3-bromo-1-propene (98% Merck) and chlorodimethylsilane (98% Aldrich) were purified by distilling over calcium hydride. Karstedt catalyst (solution in xylenes with 2% Pt) purchased from Aldrich and used directly. Styrene (supplied by Tabriz Petrochemical Co., Iran) was purified through distillation under reduced pressure over calcium hydride and stored under N_2 at 0°C . Methylaluminoxane was purchased from Aldrich as a toluene solution (10 wt % aluminum, density 0.87 g/ml) and used without further purification. All solvents were provided by Merck and were dried according to the usual procedures.

2.2. Preparation of 1-allylindenyltrichlorotitanium

1-Allylindenyltrichlorotitanium was synthesized by some modification of the literature methods [29].

2.2.1. Synthesis of 1-allylindene

In a 500 ml side-armed flask fitted with an overpressure bubbler and magnetic stirring bar, 6.5 ml (54 mmol) indene was dissolved in a mixture of 160 ml ether (Et_2O) and 16 ml tetrahydrofuran (THF) and the reaction mixture was cooled to -78°C . n-Butyllithium (34 ml, 1.6 M in hexane, 54 mmol) was added dropwise using a syringe. The solution was allowed to warm up to room temperature and then stirred for 5 h. Allylbromide (4.7 ml, 54 mmol) was added dropwise at -78°C and the reaction mixture allowed being stirred overnight at room temperature and then 50 ml of water was added to the mixture. The water layer was washed twice with 50 ml portions of ether and these ether layers were combined with the original ether layer and dried over sodium sulfate (Na_2SO_4). The solvent removed under vacuum to produce yellow oil. After distillation, colorless oil was obtained. Yield was 85%. ^1H NMR (CDCl_3): δ 7.10–7.44 (m, 4H, aromatic), 6.80 (dd, 1H, sp^2 , 3-position), 6.49 (dd, 1H, sp^2 , 2-position), 6.21–5.58 (complex m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$), 5.20 (d of m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$ trans), 4.95 (m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$ cis), 3.44 (m, 1H, sp^3 , 1-position), 2.46 (complex m, 2H, sp^3 , $-\text{CH}_2-\text{CH}=\text{CH}_2$).

2.2.2. Synthesis of 1-trimethylsilyl-3-allylindene

1-Allylindene (4 g, 0.025 mol) and THF (120 ml) were introduced into a 500 ml side-armed flask fitted with an over pressure bubbler and magnetic stirring bar. The reaction mixture was cooled to -78°C and n-butyllithium (16 ml, 25 mmol) was added dropwise using a syringe. After stirring for 5 h at room temperature, chlorotrimethylsilane (3.4 ml, 25 mmol) was added to the flask using a syringe and the reaction mixture was stirred overnight at room temperature. The THF was removed under reduced pressure, replaced with dry hexane. The hexane solution was filtered and the solvent was removed and the product was distilled to yield 1-trimethylsilyl-3-allylindene as yellow oil. Yield was 70%. ^1H NMR (CDCl_3): δ 7.47–7.22 (m, 4H, aromatic), 6.38 (s, 1H, sp^2 , 2-position), 6.14–6.11 (complex m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$), 5.23 (m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$ trans), 5.12 (m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$ cis), 3.44 (s, 1H, sp^3 1-position), 3.42 (m, 2H, sp^3 , $-\text{CH}_2-\text{CH}=\text{CH}_2$), 0.01 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

2.2.3. Synthesis of 1-allylindenyltrichlorotitanium

1-Trimethylsilyl-3-allylindene (3 g, 0.013 mol) was added to a 50 ml solution of TiCl_4 (1.5 ml, 13 mmol) in CH_2Cl_2 in side-armed round bottom flask (100 ml) fitted with an over pressure bubbler. The dark burgundy solution was stirred overnight at room temperature. The solvent was removed under vacuum and the burgundy residue was washed with 50 ml of pentane and then dried under vacuum. Recrystallization of the residue from pentane produced

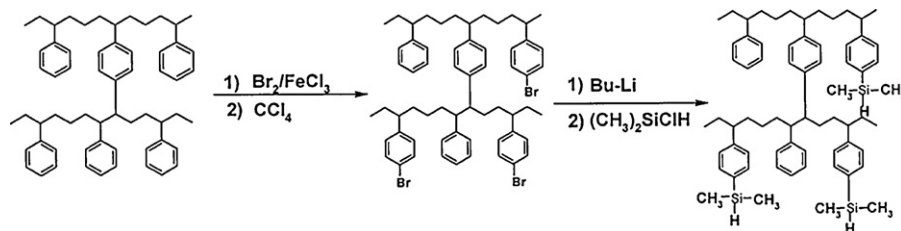


Fig. 1. Synthesis of Me_2SiH -functionalized cross-linked polystyrene.

Download English Version:

<https://daneshyari.com/en/article/66834>

Download Persian Version:

<https://daneshyari.com/article/66834>

[Daneshyari.com](https://daneshyari.com)