



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

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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.

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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

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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

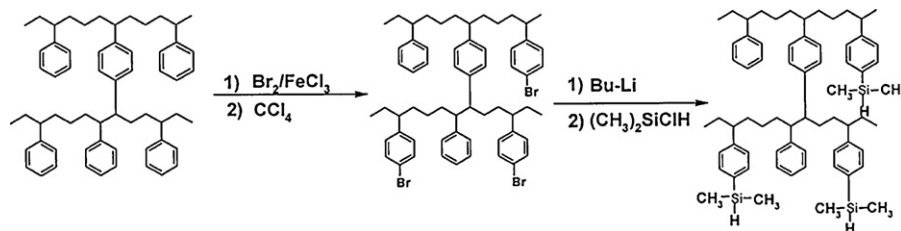


Fig. 1. Synthesis of Me_2SiH -functionalized cross-linked polystyrene.

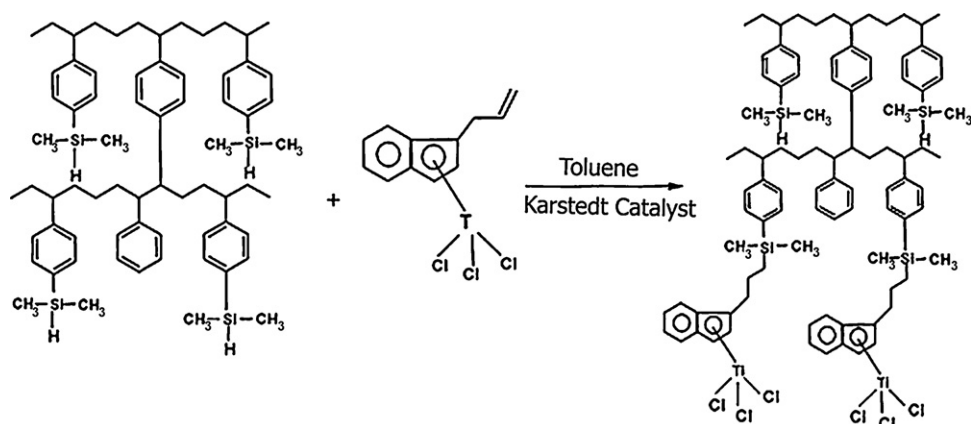


Fig. 2. Immobilization of alkenyl-functionalized indenyltrichlorotitanium complex on functionalized cross-linked polystyrene.

dark red crystals. Yield was 80%. ^1H NMR (CDCl_3): δ 7.78 (m, 2H, aromatic), 7.49 (m, 2H, aroma.), 7.15 (d, 1H, 3-position), 6.97 (d, 1H, 2-position), 6.03 (m, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$), 5.23 (dm, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$ *cis*), 5.14 (dm, 1H, sp^2 , $-\text{CH}_2-\text{CH}=\text{CH}_2$ *trans*), 3.91 (dm, 2H, sp^3 , $-\text{CH}_2-\text{CH}=\text{CH}_2$).

2.3. Washing of cross-linked polystyrene resins

In order to remove surface impurities, the resins were stirred in the following solutions at 60°C for 1 h: 1N NaOH, 1N HCl, 2N NaOH–dioxane (1:2), 2N HCl–dioxane (1:2), H_2O , dimethylformamide. The resins were then washed at room temperature with

the following solutions: 2N HCl in methanol, H_2O , methanol, methanol–dichloromethane (1:3), methanol–dichloromethane (1:10) then dried under vacuum at 70°C [28].

2.4. Preparation of silyl hydride functionalized polystyrene beads

2.4.1. Bromination of 2% cross-linked polystyrene beads

To a suspension of 2 g of washed resin in 50 ml of carbon tetrachloride was added 0.04 g of ferric chloride. The reaction mixture was stirred in the dark for 30 min, and then 3 g of bromine in 10 ml of carbon tetrachloride was added to the reaction mixture. After stirring for 1 h at room temperature in the dark, the mixture was heated to reflux for 2 h. The reaction mixture was collected on filter and washed with carbon tetrachloride, acetone, benzene and methanol. After drying under vacuum, 3.1 g of brown powder was obtained [28]. By elemental analysis the product contained 23.8% Br, corresponding to 2.97 mmol Br/g.

2.4.2. Lithiation of brominated cross-linked polystyrene and treated with chlorodimethylsilane

The lithiation was carried out using 2 g brominated resin (2.97 mmol Br/g) in 30 ml of dry toluene by adding 13 ml of 1.6M n-BuLi and stirring the suspension at 60°C for 4 h. After removal of the liquid phase, a new 30 ml of dry toluene and 4.5 ml (32 mmol) of chlorodimethylsilane was added respectively. After a 2 h time period at room temperature, the polymer was collected on a filter and washed repeatedly with dry toluene to give a yellow powder (1.8 g) which exhibited large Si–H absorption at 2113 cm^{-1} . By elemental analysis the product contained 7.1% Si, corresponding to 2.5 mmol Si/g.

2.5. Preparation of polymer-supported catalyst

2.5.1. Method A

Toluene (15 ml) and 0.3 g of silylated functionalized polystyrene beads (2.5 mmol Si/g) were introduced into a 50 ml side-armed flask fitted with an over pressure and magnetic stirring bar. A toluene solution of the catalyst (1-allylindenyltrichlorotitanium) (0.1 g, 0.32 mmol in 15 ml toluene) was then injected into the reaction mixture. Finally, 15 μl of Karstedt catalyst (2 wt % Pt in xylene) was added and the reaction mixture was stirred at 50°C for 2 days. Then the liquid phase was removed and the solid part was washed with toluene for several times until the filtrate solvent was colorless and dried in vacuum to give a red-orange powder. The content of Ti in the polymer-supported catalyst estimated from ICP analysis was 1.7×10^{-2} mmol Ti/g beads.

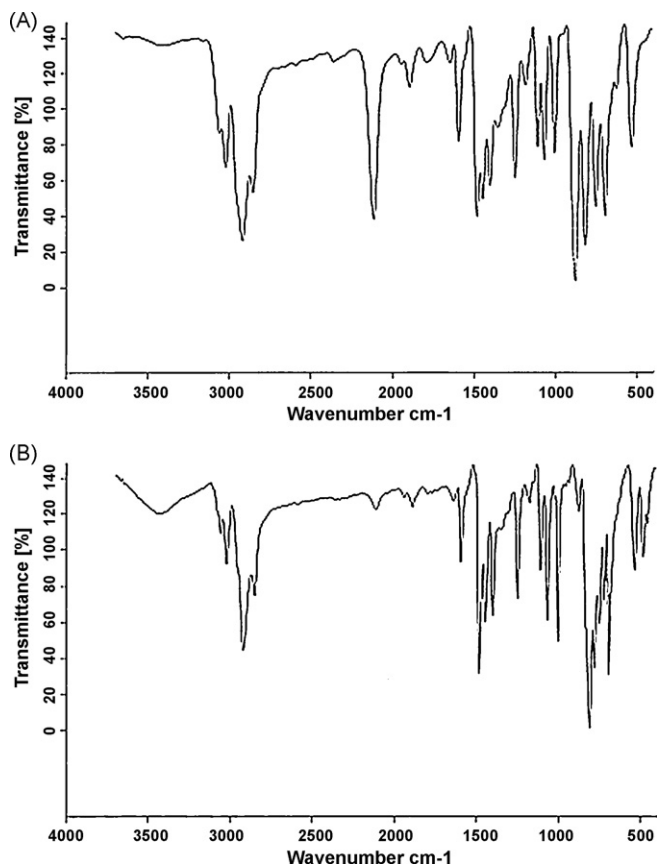


Fig. 3. Infrared spectra of the supported catalyst: (A) Me_2SiH -functionalized cross-linked polystyrene and (B) anchored catalyst.

2.5.2. Method B

2.5.2.1. Tethered 1-trimethylsilyl-3-allylindene on functionalized polystyrene. Toluene (30 ml) and 0.3 g of silylated functionalized polystyrene beads (2.5 mmol Si/g) were introduced into a 100 ml side-armed flask fitted with an overpressure and magnetic stirring bar. 1-Trimethylsilyl-3-allylindene (1 ml) was injected into the reaction mixture and then Karstedt catalyst (15 μ l) was added. The reaction mixture was stirred at 50 °C for 2 days. Then, the resulting solid was separated via filtration, thoroughly washed with toluene and finally dried in vacuum.

2.5.2.2. Synthesis of final half-titanocene complex. TiCl_4 (0.5 ml) was added using syringe to 50 ml of CH_2Cl_2 in a 100 ml side-armed Schlenk flask that was fitted with an over pressure bubbler, magnetic stirring bar and claisen apparatus. Ligand functionalized polystyrene (0.4 g) was then added into the reaction mixture. The dark-red suspension was stirred overnight at room temperature. Then the liquid phase was removed and the solid residue was washed with toluene for several times and dried in vacuum to give a dark-red solid product. The Ti content of the polymer immobilized metallocene catalyst determined from the ICP analysis was 1.1×10^{-2} mmol Ti/g beads.

2.6. Polymerization procedure

The slurry phase styrene polymerization was carried out in a 100 ml glass reactor equipped with a magnetic stirrer. A prede-

termined amount of styrene monomer and toluene were injected into the reactor. Then, a predetermined amount of methylaluminoxane (MAO) was injected into the reactor and the reactor was immersed in a constant temperature bath (50 °C). Then a desired amount of polymer-supported catalyst was added. After polymerization, an excess amount of HCl/methanol solution (10V%) was injected into the reactor. The obtained polymer was washed with methanol and derided in a vacuum for 24 h. Tacticity was measured by soxhlet extraction in a boiling methylethylketone. For analytical purposes, the obtained polymers were dissolved in boiling 1,2,4-trichlorobenzen and the cross-linked polystyrene beads were separated by filtration.

3. Analytical procedures

Ti content of the Si in the cross-linked polystyrene and Ti in the supported catalyst was measured by an inductively coupled plasma spectrometer (ICP Integra XL). 0.05 g of the polymer-supported catalyst was placed in a 100 ml beaker and 4 ml concentrated HNO_3 and 1 ml concentrated HClO_4 was added and covered with a watch glass. The beaker was heated on a oil bath of 100 °C for 5 h. The solid residue was separated and the solution was diluted with distilled water to the mark in a 10 ml volumetric flask. Bromine analysis was performed by Vega 2 CT scan Oxford instrument. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectrum of polystyrene was obtained at 100 °C with a Bruker 400 MHz NMR spectrometer. The polymer solution was prepared by dissolving about 50 mg of the polymer in

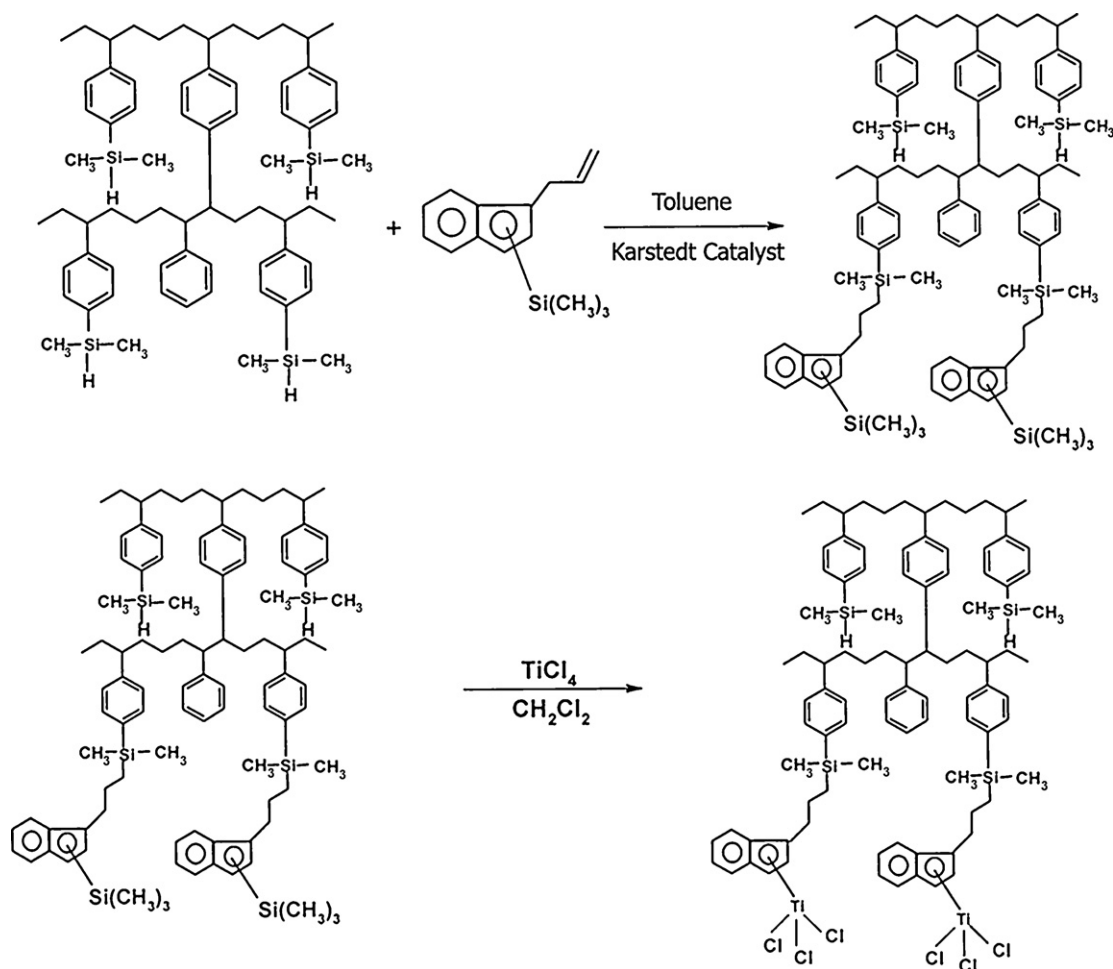


Fig. 4. Synthesis of catalyst on Me₂SiH-functionalized cross-linked polystyrene.

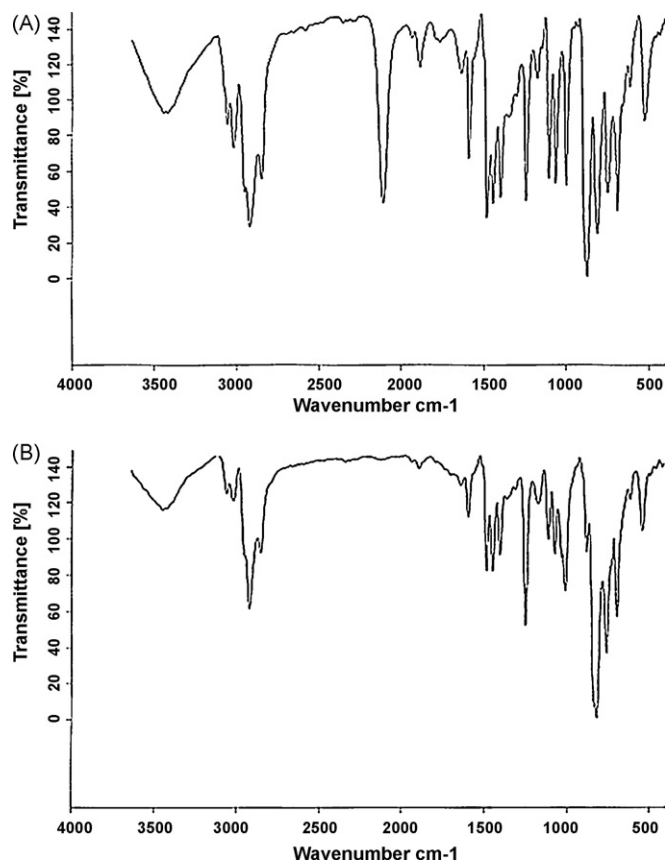


Fig. 5. Infrared spectra of the anchored ligand: (A) Me₂SiH-functionalized cross-linked polystyrene and (B) anchored ligand.

0.5 ml 1,1,2,2-tetrachloroethane-d₂. The solvent peak was observed at 75 ppm. Fourier transform infrared (FTIR) spectra were recorded at room temperature using Shimadzu FTIR-8101 M that cast on KBr. Differential scanning calorimetry (DSC) was carried out using a TA DSC-Mettler 4000 instrument. The morphology of polymer was observed by a scanning electron microscope (SEM, Cambridge S360).

4. Results and discussion

Polymerization of styrene with silica supported half-titanocene catalysts was investigated previously in our laboratory [30,31]. Inorganic supports, such as silica or alumina, have been used in the production of polyolefins, but such acidic supports have relatively reactive surfaces leading to catalyst deactivation while the cross-linked polystyrene beads are non-reactive to the catalyst and amenable to numerous functionalization procedures.

Table 1

Results of styrene polymerization with polymer-supported and unsupported catalysts.

Catalyst	Total yield (g) ^a	Activity ($\times 10^{-7}$) ^b	% sPS ^c	Tm (°C) ^d
1-Allylindenyltrichlorotitanium/MAO	0.41	0.27	78.8	271
P-IndTiCl ₃ /MAO (method A)	0.39	0.25	85.2	272
P-IndTiCl ₃ /MAO (method A) ^e	0.37	0.24	86.1	270
P-IndTiCl ₃ /MAO (method B)	0.27	0.17	71.5	272

Polymerization conditions: Ti = 1.7×10^{-6} mol, styrene = 0.043 mol. Polymerization temperature = 50 °C, polymerization time = 2 h, Al/Ti = 600 mol/mol.

^a Free weight of polymer-supported catalyst.

^b Activity = g bulk polymer/(mol Ti) (mol monomer) (h).

^c % sPS = [(g of 2-butanone insoluble polymer)/(g of bulk polymer)] \times 100.

^d Determined by DSC.

^e Titanium leaching test.

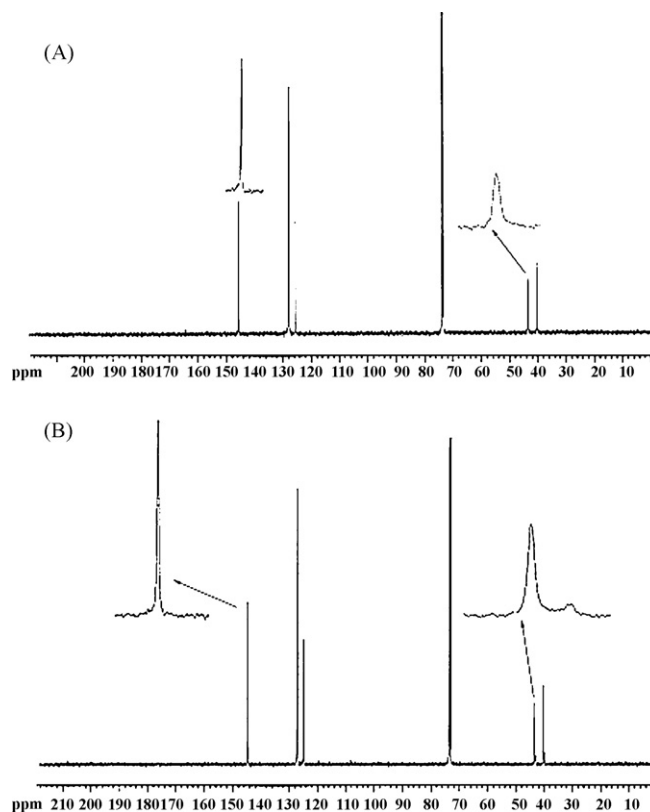


Fig. 6. ¹³C NMR spectra of syndiotactic polystyrene synthesized by: (A) polymer-supported catalyst and (B) unsupported catalyst.

4.1. Polymer-supported catalyst preparation

4.1.1. Method A

An easy access to supported polymerization catalysts is the coupling of the alkene functionalized (1-allylindenyltrichlorotitanium) complex with an Si(CH₃)₂H-functionalized polystyrene beads via hydrosilylation of the alkenyl moiety of the homogeneous pre-catalyst with Si-H groups of the cross-linked polystyrene beads. Therefore, at first step, the cross-linked polystyrene has to be functionalized with Si-H groups. This modification can be performed in two steps as shown in Fig. 1. Brominated resin was prepared by the reaction of polystyrene with bromine in the presence of ferric chloride as a catalyst. The brominated polystyrene was then metallated by n-butyllithium following by reaction with chlorodimethylsilane.

At second step, the alkenyl-functionalized complex (1-allylindenyltrichlorotitanium) can be reacted with the Si-H groups of polystyrene using of Karstedt catalyst as a coupling reagent to yield the covalently tethered indenyltrichlorotitanium complex (Fig. 2).

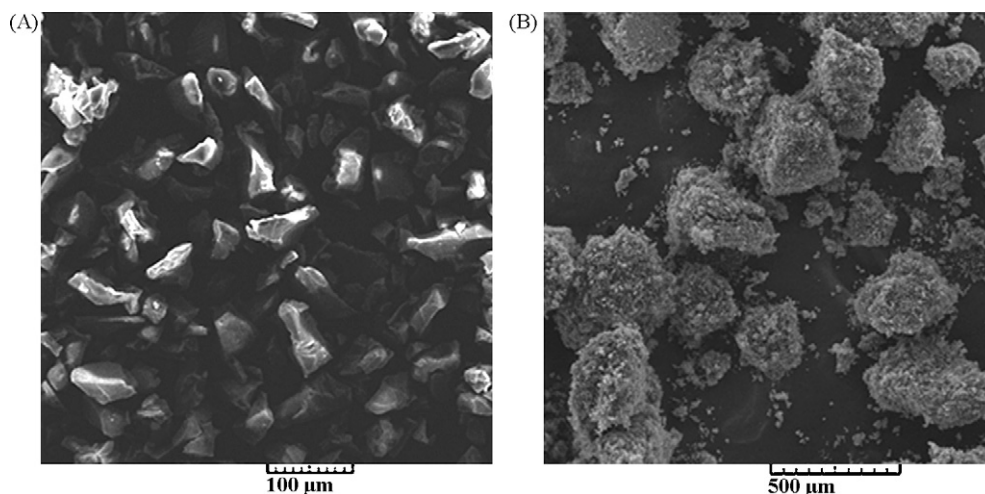


Fig. 7. SEM images of (A) supported catalyst and (B) sPS particles.

Infrared spectroscopy has been applied to insure the intended formation of a covalent bond between the alkenyl-functionalized homogeneous catalyst and the $(\text{CH}_3)_2\text{SiH}$ -functionalized polystyrene via hydrosilylation (Fig. 3). To monitor the covalent immobilization of the catalyst, IR spectra of the SiMe_2H -functionalized support (Fig. 3, spectrum A) and the catalyst (Fig. 3, spectrum B) have been recorded. According to Fig. 3A, the Me_2SiH -functionalized polystyrene shows large absorption attributed to Si–H at 2113 cm^{-1} that confirms the formation of SiH-functionalized polystyrene. This functionalization also was confirmed by ICP analysis (2.5 mmolSi/g beads). The decrease of the intensity of the Si–H band (2113 cm^{-1}) after the immobilization clearly shows the formation of a covalent bond between double bond of the alkenyl-functionalized catalyst and the SiMe_2H -functionalized polystyrene. ICP analysis showed that the amount of Ti in the polymer-supported catalyst was $1.7 \times 10^{-2}\text{ mmol Ti/g}$ beads.

4.1.2. Method B

In this method, 1-trimethylsilyl-3-allylindene can be reacted with the Si–H groups of polystyrene using Karstedt catalyst as a coupling reagent to yield the covalently tethered ligand (Fig. 4).

Fig. 5 shows FTIR spectra of the SiMe_2H -functionalized support (spectrum A) as well as the covalently tethered ligand (spectrum B). The covalent tethered of the ligand was confirmed by the same criteria presented in the previous section. The tethered ligand was then reacted with TiCl_4 to form a tethered catalyst (Fig. 4). ICP analysis showed that the amount of Ti in the polymer-supported catalyst was $1.1 \times 10^{-2}\text{ mmol Ti/g}$ beads.

4.2. Polymerization

Polymerizations of styrene with polymer-supported catalysts (methods A and B) in the presence of MAO were performed in toluene solution. In order to compare the catalytic activity, polymerization of styrene also was carried out by 1-allylindenytrichlorotitanium/MAO as a homogeneous catalyst system under the same polymerization conditions. The polymerization results are summarized in Table 1. These results show that both polymer-supported catalyst (methods A and B) are active in syndiospecific polymerization of styrene but the supported catalyst prepared with method (A) (i.e. reaction of 1-allylindenytrichlorotitanium with functionalized polystyrene) shows higher activity than supported catalyst prepared with method B (i.e. synthesis of catalyst on functionalized polystyrene).

Also according to Table 1, the activity of supported catalyst (method A) is comparable with homogeneous catalyst.

According to these results, preparation of polymer-supported catalyst by method A is a more useful and effective approach. In this way, the immobilization of catalyst involves the reaction of purified catalyst possess reactive allyl functional group with functionalized polystyrene in one step without complexity while the synthesis of catalyst on support (method B) needs rigorous purification to remove byproduct from the support that is responsible of low activity of catalyst. Also characterization of final complex seems to be difficult. In order to evaluate titanium leaching from support into toluene, polymer-supported catalyst (P-IndTiCl_3) was stirred in toluene for 24 h at $50\text{ }^\circ\text{C}$. Then the liquid phase was removed and the solid residue was dried under vacuum and used for styrene polymerization. Table 1 shows that the metal was not washed out by solvent indicating that the prepared supported catalyst was anchored on the polymer support by covalent bond. Because the activities of polymer-supported catalysts (before and after washing) are not changed under the same reaction condition. The synthesized polystyrene with polymer-supported catalyst ($\text{P-IndTiCl}_3/\text{MAO}$) and unsupported catalyst (1-allylindenytrichlorotitanium/MAO) were characterized by ^{13}C NMR spectroscopy (Fig. 6). The characteristic peak (phenyl C-1 carbon at 145.5 ppm) in each spectrum is single and sharp confirming the obtained polymers are syndiotactic polystyrene and the entire spectrum matches closely with those of sPS in previous reports [1,15].

Methylene region in ^{13}C NMR spectra reveals that the syndiotacticity of the obtained polystyrene from polymer-supported catalyst is high. Because single peak is observed at 44.3 ppm that is related to *rrr* tetrad. There is not any other peaks which correspond to different tetrads such as *rrm* and *mmm* in the around of this peak [32]. The morphologies of supported catalyst and resultant polystyrene were studied with SEM. From Fig. 7, it can be seen that sPS particles are well grown on the cross-linked polystyrene beads and the shape of the polymer particles replicates that of the catalyst particles.

5. Conclusions

In this work, two synthetic procedures were used to immobilization of 1-allylindenytrichlorotitanium on silyl hydride functionalized polystyrene beads. In one approach, 1-allylindenytrichlorotitanium covalently anchored on the functionalized polystyrene by applying hydrosilylation chemistry (method A). In other way, the half-titanocene complex was syn-

thesized on the functionalized polystyrene (method B). These polymer-supported catalysts were tested for styrene polymerization using methylaluminoxane (MAO) as a cocatalyst. It was found that the preparation of polymer-supported catalyst by method (A) is an effective approach and displays higher activity and syndiotacticity than supported catalyst obtained by method (B).

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