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Comparison of Syndiotactic Polystyrene Morphology Obtained Via Heterogeneous and Homogeneous Polymerization with Metallocene Catalyst

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Summary: Supported catalyst system for the slurry phase polymerization of styrene in toluene was prepared by the immobilization of 2-methylindenyltrichlorotitanium(2-MeIndTiCl$_3$) on silica and activation of this catalyst was performed by methylaluminoxane(MAO) in polymerization media. Homogeneous polymerization of styrene with 2-methylindenyltrichlorotitanium activated by MAO was performed in toluene. The morphology of obtained syndiotactic polystyrene (sPS) via heterogeneous and homhgeneous catalyst system was compared. Polymerization of styrene by homogeneous catalyst lead to formation of gel and resultant polymers presented a compact and dense texture while the global gelation do not occur with silica supported catalyst at different Ti/SiO$_2$ mol ratios and sPS was obtained as separated particles. Unlike to the homogeneous catalyst, obtained polymers showed a porous texture. Highly porous texture of sPS was obtained with Ti/SiO$_2$ = 0.5% mol ratio.

Keywords: gelation; metallocene catalyst; slurry polymerisation; styrene; syndiotactic polystyrene

Introduction

In 1986 Ishihara found that half-sandwich catalyst, for example, CpTiCl$_3$ (cyclopentadienyltitaniumtrichloride), produce syndiotactic polystyrene (sPS).[1–2] This phenomenon has spurred an active search for new types of syndiotactic polystyrene catalysts. So far, many new kinds of half-sandwich titanocene such as Cp*TiX$_3$ (Cp* = substituted or unsubstituted Cp or Ind ; X = halogen, alkoxy,hydrocarbyl) complexes have been synthesized and evaluated for their catalytic behavior in syndiotactic styrene polymerisation.[3–9] Syndiotactic polystyrene is a semi crystalline thermoplastic polymer with many advantageous properties. For example, sPS has excellent heat resistance, strong chemical resistance against acids, bases, oils and water and low dielectric constant.[10] sPS is emerging as a new class of engineering polymers suitable for many application in the automotive, electronic and packaging industries.[11,12] These kinds of polymers have high melting points (270 °C) and rapid crystallization rates, making them good injection mold materials. The polymerization of styrene to sPS with either homogeneous or heterogeneous metallocene catalyst is characterized by the precipitation of syndiotactic polystyrene that is insoluble in its own monomer or other common organic solvents at typical reaction temperatures. In sPS polymerization over a homogeneous metalloene catalyst, polymer micro particles agglomerates as monomer conversion increases and these sPS agglomerates become a gel that is a wet cake-like material. The sPS gel is not a covalently cross-linked gel but a physical gel in which monomer and solvent molecule are intercalated between the polymer molecules with strong intermolecular forces.[13–15] Once sPS gel is formed, the reaction mixture becomes extremely difficult to agitate by conventional means. There for, these homogeneous catalysts are unsuitable

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for industrial applications. MAO (methylaluminoxane) is another impediment to industrial scale conditions. This co-catalyst is expensive and improved catalytic activity is only obtained with a very large amount of MAO in homogeneous polymerization process. To overcome these problems, a liquid slurry process that can avoid the gelation and to produce sPS as discrete particles is of important industrial interest. Yong Choi etal. Used embedded metallocene catalyst for syndiospecific polymerization of styrene in slurry polymerization process.[16,17] For slurry process, a homogeneous catalyst must be immobilized onto a solid carrier material. Our previous work, include pretreatment of the $IndTiCl_3$ (indenyltitaniumtrichloride) with MAO and immobilization of the activated catalyst onto a calcinated silica. Then this heterogeneous catalyst system applied for slurry polymerization of styrene.[18] In this present study, 2-(Me) IndTiCl3 (2-methylindenyltrichlorotitaniumi) was synthesized in several steps. Then this catalyst was immobilized onto calcinated silica at 300 °C, followed by activation with MAO in the polymerization media and was used for syndiotactic slurry phase polymerization of styrene. Also homogeneous polymerization of styrene was carried out with this catalyst in toluene. The thermal behaviors and morphology of the obtained polymers were investigated by DSC and SEM methods respectively. The morphology of obtained sPS from homogeneous and heterogeneous catalyst was studied and compared.

Experimental Part

All experiments were performed under inert atmosphere using the Schlenk technique.

Materials

Indene (90% Merck) was purified by vacuum distillation. Titanium tetrachloride ($TiCl_4$ 98%, Merck), n-Butillithium (n-BuLi, 1.6 M in hexane, Merck), Formic acid (88%), Hydrogen peroxide (30%), were used without further purification. Chlorotrimethylsilane (99% Aldrich) was purified by distilling over calcium hydride. Methylaluminoxane (10% in toluene) was provided by Aldrich and used without further purification. Styrene (Tabriz Petrochemical Co.) was purified through distillation under reduced pressure over calcium hydride. 2-(Me) IndTiCl3 was prepared according to methods in the literature with some modification. Silica gel (Grace 646) was used as a catalyst support. All solvents were provided by Merck and were dried according to the usual procedures.

Preparation of 2-(Me) $IndTiCl_3$

2-methylindenyltrichlorotitanium was synthesized by modification of the literature methods.[4,19] A brief description of this method is as follow:

Synthesizes of 2-Indanone

In a three-necked flask fitted with stirrer, dropping funnel and thermometer are placed 70 ml of formic acid (88%) and 14 ml of hydrogen peroxide (30%). The temperature is kept at 40 °C.Then 11.7 ml of Indene is added dropwise, with stirring over a period of 2h. The reaction solution is stirred at room temperature for 7h. Then the excess formic acid is removed under reduces pressure. The residue, after being coold to room temperature, is a yellowish brown crystalline solid (monoformate of 1,2 indanediol). In a tow-necked flask fitted with condenser is placed 200 ml of 7% (by volume) sulfuric acid. The solution is heated to boiling, and the crude monoformate of 1, 2-indanediol is added. Steam is introduced and the mixture is steam distilled. The cold distillate is filtered. The white crystals (2-indanone) were dried further in a vacuum at room temperature for about 12h. The yield is 70–80%.

Synthesizes of 2-Methylindene

Methylmagnesiumbromide(23ml, 3 M) was added dropwise via a syring to a solution of 2-indanone(9g) in 150 ml of diethyl ether-(previously chilled to 0 °C) and contained in a 250 ml side-armed flask fitted with a reflux condenser and overpressure bubbler. The addition was completed, the reaction mixture was heated at reflux for 4h.The solution was coold to 0 °C and 150ml of water was added dropwise.The water layer was washed twice with 50 ml of ether and the ether layers were combined with the original ether layer. The ether was removed at reduced pressure and replaced with 130 ml of benzene. p-toluenesulfonic acid (50 mg) was added to the benzene solution which was then refluxed overnight using a Dean-Stark to remove the water produced. The remaining benzene solution was washed with 60 ml of saturated Na2CO3 solution and deride over magnesium sulfate. The benzene was removed at reduced pressure and the residue was distilled at 47–50 °C/0. 01 mm Hg to yield colorless oil.

Synthesizes of 1-Trimethylsilyl-2-methylindene

2-methylindene (2.9g, 0.02 mol) was dissolved in 70 ml of hexane in a 250 ml side-armed flask fitted with a gas inlet connected to an overpressure bubbler. To this solution, 16.5 ml of 1.4 M n-butyllithium was added dropwise and the mixture was stirred overnight at room temperature. The supernatant liquid was decanted and the white precipitate was washed with hexane. Fresh hexane (60 ml) was introduced to the flask, 3.5 ml of chlorotrimethylsilane was added to the stirred suspension, and the mixture was allowed to stir overnight. The solution was then filtered and the solvent removed under vacuum. The crude product was further purified via distillation at 60–62 °C/0.01 mm Hg to yield colorless oil. Yields: 80%.

Synthesizes of 2-Methylindenyltrichlorotitanium

$TiCl_4$ (1.4 ml, 0.01 mol) was added via syringe to 60 ml of methylene chloride in a 250 ml side-armed flask. 1-Trimethylsilyl-2-methylindene (2.02 g) was then added and the dark burgundy solution allowed reacting overnight at room temperature. After the solvent was removed under vacuum, the burgundy residue was washed with 70 ml of pentane and deried under vacuum. Recrystallization of the residue from a minimum volume of methylene chloride give dark red crystals.

Preparation of Supported Catalyst

Silica gel was calcinated at 300 °C for 12 h. In to a 50 ml vial equipped with a magnetic stirring bar; 1 g calcinated silica was added. In to another 50 ml vial, 0.06g (2.1×10^{-4} mol) 2-(Me) IndTiCl3 was introduced and then toluene was added. The catalyst solution was then transferred into the silica-containing vial through a syringe while the silica was under constant stir. The mixture was stirred for 1h in the 50 °C. Then the solid was separated from the solvent by decantation and was washed with 6mL of dry toluene and the solvent was again decanted. The washing process was repeated until the filtrate solvent was colorless. The solid support was dried at vacuum evacuation to give a red free-flowing powder. The titanium content in the catalyst was determined by the technique of inductivity coupled plasma atomic emission spectroscopy (ICP-AES). The result for Ti was 0.26%. (Ti = 0.26%).

Slurry Phase Styrene Polymerization

The slurry phase styrene polymerization was carried out in a 100 ml glass reactor equipped whit a magnetic stirrer. A predetermined amount of styrene monomer and toluene were injected in to 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 predetermined amount of supported catalyst was added. After polymerization, an excess amount of HCl/methanol solution (10 V %) was injected in to the reactor. The polymer obtained was washed with methanol and derided in a vacuo for 24 h. Tacticity was measured by soxhlet extraction in a boiling methylethylketone. Thermal analysis of obtained polymers was performed using a TA instrument DSC-Mettler 4000 and the scanning electron microscopy (SEM) image of gold-coated polymer powders using Bruker Leo 440i.

Results and Discussion

Homogeneous and heterogeneous syndiotactic polymerization of styrene with IndTiCl3[18],1-(Me) IndTiCl3 (1-methylindenyltrichlorotitanium) and 2-(Me) IndTiCl3 was studied in our laboratory. According to the obtained results, 2-(Me) IndTiCl3 is highly active for syndiotactic polymerization of styrene. Therefore in this work, we investigated syndiotatic polymerization of styrene with 2-(Me) IndTiCl3.

Table 1.
Results of styrene polymerization with heterogeneous catalyst and homogeneous catalyst.

Run	Ti/SiO$_2$ (w %)	[Ti] mol	c)Syndiotacticity(%)	d)Activity	Tm
a)1	1.5	3.1×10^{-5}	93	17.7×10^5	272.1
a)2	1	2.09×10^{-5}	93	15.2×10^5	271.1
a)3	0.5	1.04×10^{-5}	95	12.24×10^5	272.6
b)4	–	1.04×10^{-5}	91	18.7×10^5	271.5

a)Heterogeneous catalyst: 2-(Me) IndTiCl$_3$/SiO$_2$/MAO.
b)Homogeneous catalyst: 2-(Me) IndTiCl$_3$/MAO.
c)(g of polymer insoluble in 2-butanone) / (g of total polymer) ×100.
d)g polymer/mol Ti h.
Al/Ti = 500, T = 50 °C, t = 60 min, [styrene] = 0.043 mol.

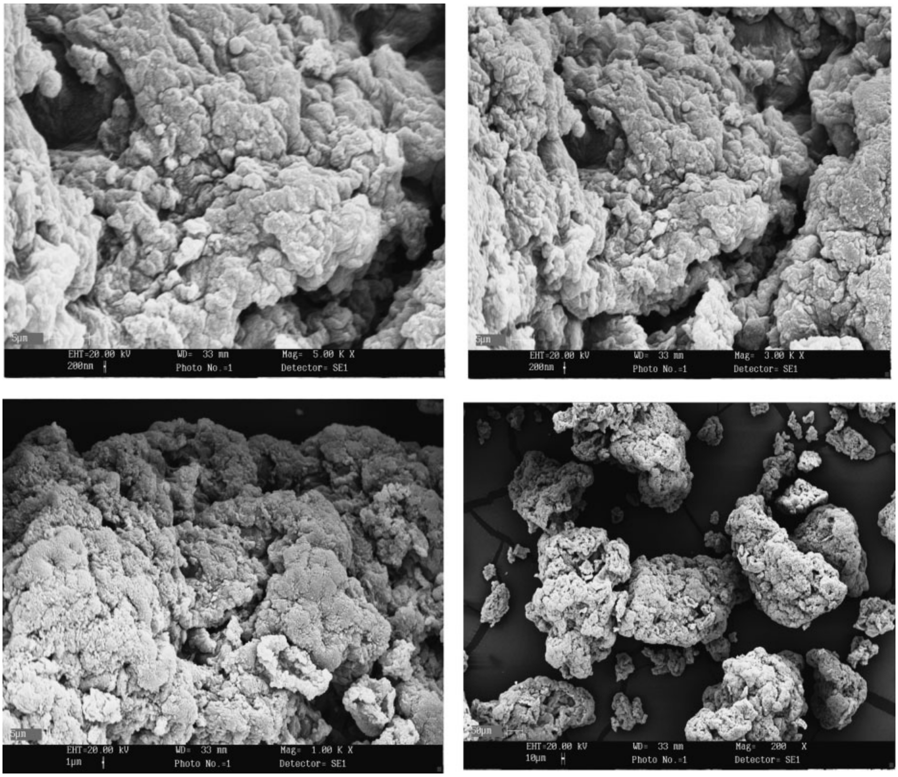

Figure 1.
SEM images of syndiotactic polystyrene obtained with 2-(Me) IndTiCl$_3$/MAO catalyst in homogeneous conditions.

The results of styrene polymerization with heterogeneous and homogeneous catalyst are summarized in Table 1. According to the amount of catalyst, the activity of silica supported catalyst is lower than the homogeneous catalyst, because there is a poisonous effect due to silica surface for the silica supported catalyst.[20–21] Syndiotactic polystyrene that is produced with heterogeneous catalyst, show higher syndiotacticity than homogeneous catalyst.

When the polymerization of styrene carried out with homogeneous catalyst, the sPS particles precipitate from liquid phase and eventually aggregate together, consequently a gel was obtained while silica supported catalyst produce sPS as separated particles. Figure 1 shows the scanning electron microscopic (SEM) images of sPS was obtained by homogeneous catalyst. As shown in these images, the obtained polymer presented a compact and dense texture (chunk) that obtained from agglomerated sPS particles.

Figure 2 shows the SEM images of sPS obtained by silica supported catalyst (Ti/$SiO_2 = 1\%$). Compared with Figure 1, it is seen that sPS was synthesized with heterogeneous catalyst, shows a porous morphology with small particles that they were soft and easily broken. In other word, the global gelation dose not occurs in this case.

We carried out slurry phase polymerization at different Ti/SiO_2 ratios in order to investigation of the influence of this parameter on polymer's morphology. Figure 3 shows the SEM images of sPS obtained by heterogeneous catalyst in tow different Ti/SiO_2 ratios with the same magnitude (5000). As shown in the images, it seems that sPS particles show a highly porous texture with decreasing amount of catalyst on the support (silica).

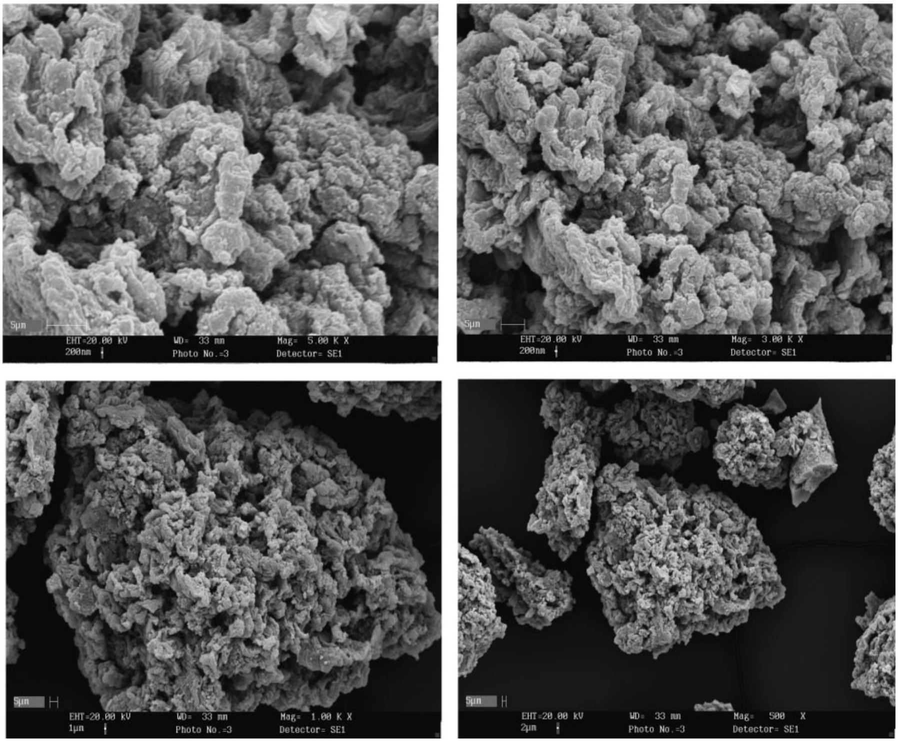

Figure 2.
SEM images of syndiotactic polystyrene obtained with 2-(Me) $IndTiCl_3/SiO_2/MAO$ catalyst (Ti/$SiO_2 = 1\%$) in heterogeneous conditions.

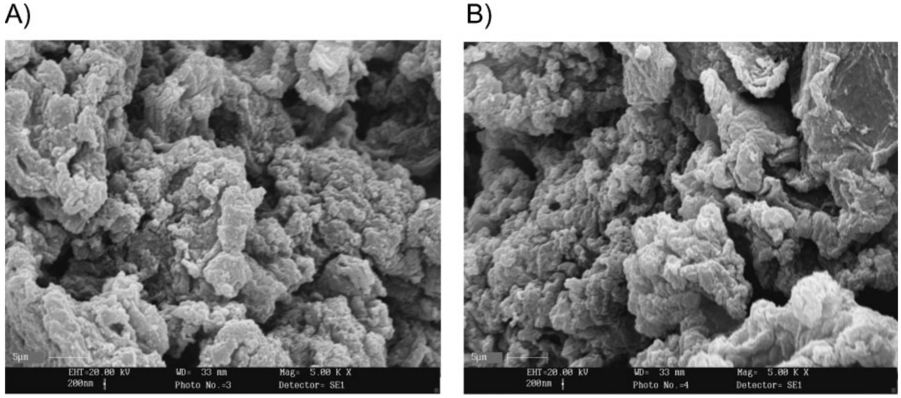

Figure 3.
SEM images of syndiotactic polystyrene obtained with 2-(Me) $IndTiCl_3/SiO_2$/MAO catalyst in heterogeneous conditions. (A): $Ti/SiO_2 = 1\%$, (B): $Ti/SiO_2 = 0.5\%$.

Conclusion

In this work, 2-(Me) $IndTiCl_3$ was supported on silica and used for slurry polymerization of styrene in toluene. According to the experimental and SEM images of sPS with homogeneous and heterogeneous (silica supported) catalyst, we can conclude, in the polymerization of styrene with silica supported catalyst, global gelation does not occur while the polymerization of styrene by homogeneous catalyst lead to formation of gel. By using of silica supported catalyst in a liquid slurry phase polymerization, the sPS particles were obtained as separated particles. Compared to the homogeneous catalyst, the heterogeneous catalyst produced sPS with porous texture. Also, sPS particles with highly porous texture were obtained with lower amount of catalyst on silica in heterogeneous catalyst.

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