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Syndiospecific Polymerization of Styrene with Embedded Metallocene Catalysts

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Summary: Syndiotactic polystyrene (sPS) is a highly crystalline polymer with high melting point (270°C). The syndiospecific polymerization of styrene to sPS with metallocene catalysts is characterized by significant phase changes that lead to global gelation. Since sPS does not dissolve in styrene or solvents such as toluene and n-heptane, sPS precipitates out immediately from the liquid phase with the start of polymerization. The polymer crystallites aggregate to primary particles and they develop to a gel. The gelation is not due to cross-linking polymerization but due to strong molecular interactions between the polymer and monomer molecules. In this work, homogeneous $Cp^*Ti(OMe)_3$ catalyst is heterogenized or embedded into sPS prepolymer particles. The embedded catalyst has been tested in a laboratory scale diluent slurry process to illustrate the feasibility of slurry phase polymerization for the synthesis of sPS particles.

Keywords: gelation; metallocene catalysts; phase transition; polymerization; styrene; syndiotactic polystyrene

Introduction

Syndiotactic polystyrene (sPS) is one of the three polystyrene isomers derived from the inexpensive ordinary monomer, styrene, with excellent thermal and chemical resistances, low specific gravity, low dielectric constant, high modulus of elasticity, and low moisture absorption. SPS exhibits the properties that are dramatically different from those of atactic polystyrene (general purpose polystyrene), synthesized by free radical polymerization. SPS is emerging as a new class of engineering polymers suitable for many applications in the automotive, electronic, and packaging industries. The high degree of molecular order of sPS gives rise to the ability of the polymer to crystallize from the melt and form discrete crystalline domains. Unlike isotactic

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polystyrene, sPS crystallizes very fast and sPS can be readily processed into final parts by injection molding, extrusion, and thermoforming. Also, the melting point of sPS (270°C) is higher than the melting point of isotactic polystyrene by 40°C.

Ishihara et al. first reported the synthesis of highly syndiotactic polystyrene in 1986 using titanium based homogeneous metallocene catalysts, based on Group IV metal compounds, like $TiCl_4$ and $CpTiCl_3$ (Cp = cyclopentadienyl).[1,2] Since Ishihara's first report, there have been a large number of publications on the synthesis of sPS using various metallocene catalysts.[3,4] The most commonly used catalysts are homogeneous monotitanocene catalysts with methylaluminoxane (MAO). The syndiotacticity of sPS, synthesized by single site metallocene catalysts, is attributed to phenyl-phenyl repulsive interaction between the last inserted unit of growing polystyrene chain and the incoming styrene monomer.

One of the most prominent phenomena in homogeneously catalyzed sPS synthesis is the complex phase transition that the reaction mixture undergoes during the polymerization. SPS is insoluble in its own monomer (styrene) or organic solvents, such as toluene, at a typical reaction temperature (e.g., 50-90°C). Therefore, sPS particles precipitate out immediately from the bulk liquid phase as soon as the polymerization starts. With an increase in conversion to about 10-15% (in bulk polymerization), these precipitates form aggregates that eventually develop into a gel. The sPS gel is not a covalently crosslinked gel, but a physical gel in which monomer and solvent molecules are intercalated between the polymer molecules with strong intermolecular forces. According to Domszy et al., the gelation occurs as a consequence of polymer crystallization from a dilute, or moderately dilute, solution of sPS particles, with the formation of a three dimensional network where primary molecules of finite molecular weight are bound together by crystallites.[5] Unreacted styrene or solvent molecules are imbibed in the polymer matrix. Once the gel is formed, the mechanical mixing of the reaction mixture becomes very difficult with ordinary means of agitation. The use of specially designed screw-type or self-cleaning reactors is described in patent literature.[6,7] Factors that affect the formation of sPS gel are, for example, the amount of sPS in the reaction mixture, crystallinity of sPS, agitation speed, temperature, etc. Undoubtedly, the formation of sPS gels will pose a great challenge in designing a polymerization reactor.

In a recent study, we investigated the kinetics of bulk polymerization of styrene with a $Cp^*Ti(OCH_3)_3$/MAO [pentamethyl cyclopentadienyl titanium trimethoxide/ methylaluminoxane] catalyst system. The catalyst activity was in the range of $10^6 \sim 10^7$ g/mol-Ti.hr at 70°C. It was observed that the catalyst activity was very high at the beginning of polymerization but it decreased as catalyst sites were occluded in the solid phase.[8] Interestingly, it was also shown that styrene conversion continued to increase to near 100% even after the formation of hard sPS gels (Figure 1). The reaction mixture became a gel after about 2-3 min but as shown in the figure, monomer conversion continued to increase until it reached a plateau.

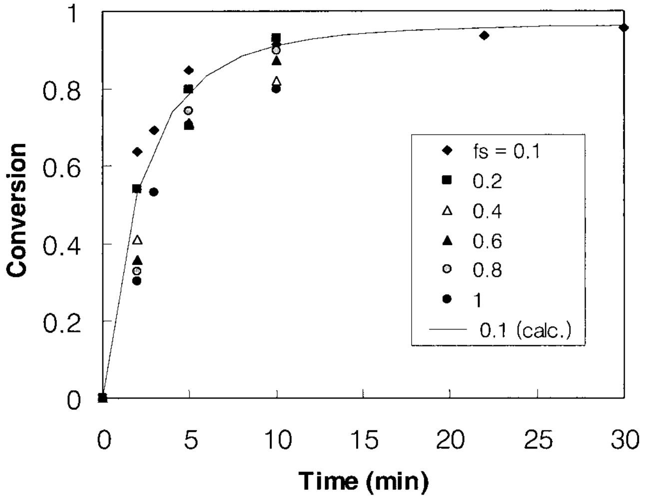

Figure 1. Styrene conversion at different initial styrene volume fractions (solvent: n-heptane) at 70°C with homogeneous Cp*Ti(OCH_3)$_3$/MAO catalyst.

A liquid slurry process has many advantages over a bulk process for industrial sPS manufacturing. For example, sPS can be recovered as discrete particles. To carry out the slurry polymerization of styrene, a catalyst needs to be heterogenized by supporting active titanium compounds onto a solid carrier material.[9-15] When Ti catalyst supported on Mg is used, Ishihara[9] reports that isotactic polystyrene is obtained from the supported catalyst, whereas, sPS is obtained from the solution in which Mg-supported catalyst is prepared. He attributes the change in the catalytic selectivity to the migration of a part of Ti on the carrier material in solution on reaction with

MAO. He also shows that the amount of Ti migrating from the solid phase to the liquid phase depends on the molar ratio of Al to Ti. Soga and Monoi[16] report similar results with $MgCl_2/Ti(O^nBu)_4/MAO$ catalyst. They suggest that the presence of chlorine in the carrier affects the tacticity of sPS obtained with supported catalysts. There are also reports that other supported Ti catalysts exhibit little difference in syndiotacticity from homogeneous catalysts.[14]

In this work, we investigate the feasibility of styrene polymerization to sPS by a liquid slurry process, using $Cp^*Ti(OCH_3)_3/MAO$ catalyst embedded onto sPS prepolymer. Here, the active Ti compound is first embedded into an sPS prepolymer by polymerizing styrene at low reaction rate. Then, the solid embedded catalyst is used to polymerize styrene in a main reactor. The use of sPS as a carrier for the catalyst has an advantage in that no foreign materials such as silica or alumina will be present in the final polymer.

Experimental

Preparation of embedded catalyst: Styrene monomer and n-heptane (diluent) were purified by vacuum distillation over CaH_2 and stored over activated alumina under nitrogen blanket. To prepare the embedded catalyst, polymerization was first carried out in a small agitated glass reactor at room temperature for 1 hr, in n-heptane, at very low styrene concentration (< 4 vol.%) using $Cp^*Ti(OCH_3)_3$/methylaluminoxane (MAO, Akzo Novel, Type 3A) catalyst, with Al/Ti mole ratio of 20-500. Very fine sPS particles were obtained without gelation. After the reaction, the solid fraction (embedded catalyst) was isolated from the liquid phase by vacuum drying. The catalyst particles were classified using sieve trays in a glove box.

Polymerization: The styrene polymerization was carried out using a 12 Oz glass reactor equipped with a two-blade impeller. In a glove box, a predetermined amount of styrene monomer and n-heptane were injected into the reactor. Then, a predetermined amount of MAO was injected into the reactor before a predetermined amount of embedded catalyst was added. The reactor was taken out of the glove box and immediately immersed in a constant temperature bath (70°C). After polymerization, an excess amount of methanol was injected into the reactor. The polymer obtained was washed with HCl/methanol solution (10 vol.%) and dried *in vacuo* for 24 hr. Tacticity was measured by Soxhlet extraction in a boiling methylethyl ketone (MEK) and the polymer's crystallinity was measured by differential scanning calorimetry.

Results and Discussion

The results of styrene polymerization using embedded catalyst and homogeneous catalyst are summarized in Table 1. The catalyst activity of the embedded catalyst is slightly lower than the homogeneous catalyst, and the syndiotacticity is almost same for both catalysts. It is possible that not all the titanium catalyst molecules were embedded into a solid phase during the catalyst immobilization process, and hence, some loss of active sites might have occurred. The most notable experimental result shown in Table 1 was that sPS was recovered as discrete particles after 60 min of reaction with the embedded catalyst whereas a gel was obtained after 36 min with the homogeneous catalyst. Some agglomerates were formed with embedded catalyst but they were not hard and easily broken. In our experiment, we observed that a small amount of gel was formed at the surface of agitator shaft with the embedded catalyst, but the overall reaction mixture maintained a slurry phase during the polymerization. Interestingly, the embedded catalyst produced sPS of higher crystallinity than the homogeneous catalyst.

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

Catalyst	Conversion# (%)	Specific Activity*	Tm (°C)	Xc (%)	Syndiotacticity** (%)	Polymer morphology
Embedded catalyst	29.7[a)]	1.54×10^6	281.2		92.8	discrete particles
	24.1[b)]	1.25×10^6	271.2	43.3		fine particles & agglomerates
	13.1[c)]	6.78×10^5	298.5	36.2	92.6	fine particles
Homogeneous catalyst	20.9	1.74×10^6	278.5	34.2	92.8	gel

embedded catalyst: 60 min, homogeneous catalyst: 36 min

* in g-polymer/mol Ti-hr, catalyst: Cp*Ti(OCH_3)$_3$/MAO, Al/Ti = 500, 70°C, styrene concentration: 4.33 mol/L

** % insolubles in boiling methylethylketone (MEK)

Xc: crystallinity (measured by differential scanning calorimetry)

a) Catalyst particle size: > 300 μm, b)& c) Catalyst particle size: 177-300 μm

c) With triisobutylaluminum (TIBAL) (1.4 mL)

Morphology of embedded catalyst particles: The scanning electron microscope images of the heterogenized catalyst (embedded catalyst) are shown in Figure 2. Notice in Figure 2(a) that particle agglomerate consists of smaller but near-spherical particles of about 2-3 μm. Figure 2(b) shows an interesting image of the embedded catalyst particles.

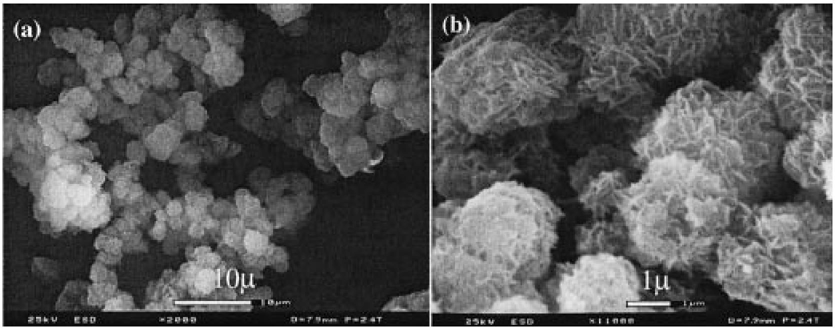

Figure 2. Scanning electron microscopic images of embedded catalyst.

The embedded catalyst particles were also analyzed using Scanning Electron Microscopy-Wavelength Dispersive Spectroscopy (SEM-WDS). Figure 3 shows the images of aluminum distribution map of the embedded catalyst particles. Here, red-white zones represent the areas of high aluminum atom concentration in MAO and green-blue zones represent the thin polymer matrix. Note that each particle contains one or two highly concentrated zones of aluminum. Since the titanium concentration in a catalyst particle was far smaller than the aluminum concentration (i.e., Al/Ti = 200-500), titanium was not detected by WDS analysis. Figure 3 suggests that each primary particle of embedded catalyst is grown from one or two Cp*Ti(OCH$_3$)$_3$ molecules complexed with MAO.

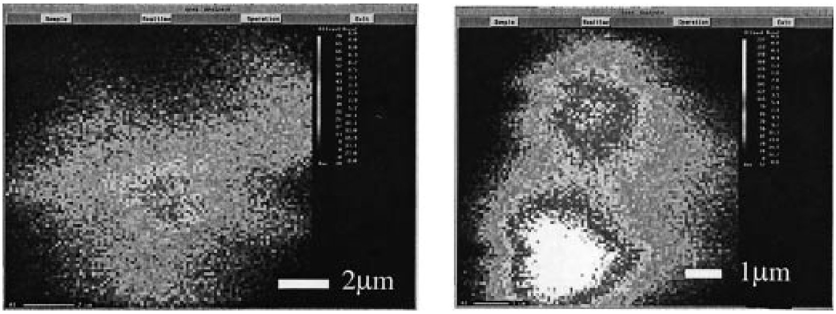

Figure 3. WDS element distribution map of embedded catalyst particles.

Morphology of sPS: Figure 4 shows the SEM images of sPS obtained by homogeneous catalyst (a) and embedded catalyst (b). It is seen that unlike the sPS synthesized with homogeneous catalyst, the sPS with embedded catalyst shows a porous morphology with small microparticles of size about 1 µm or less. These microparticles are not as discrete as in polyolefins made with Ziegler-Natta or supported metallocene catalysts, but they are quite similar.

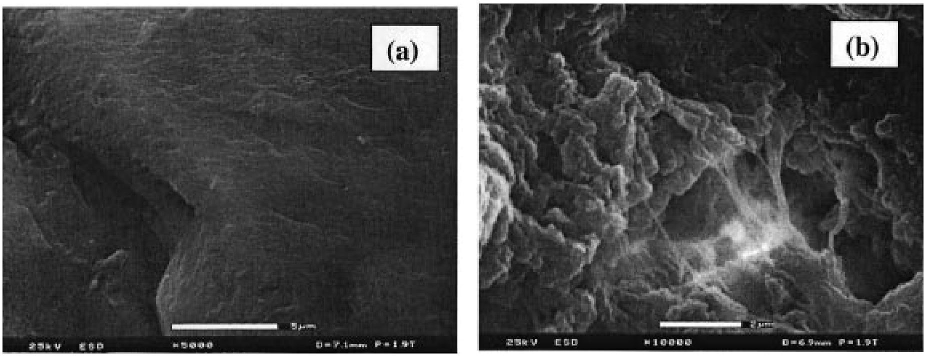

Figure 4. Morphology of syndiotactic polystyrene: (a) with homogeneous $Cp^*Ti(OCH_3)_3/MAO$ catalyst; (b) with embedded catalyst.

Conclusions

A new catalyst immobilization (embedding) technique has been developed to polymerize styrene to syndiotactic polystyrene with $Cp^*Ti(OCH_3)_3/MAO$ catalyst by slurry polymerization. Active titanium sites are first embedded onto sPS prepolymer matrix at low concentration styrene polymerization, and the resulting catalyst/sPS particles are used for styrene polymerization. Our experimental results indicate that it is feasible to obtain sPS as discrete particles by slurry phase polymerization using the embedded catalyst without global gelation. The catalyst activity and polymer syndiotacticity are quite comparable to those of the homogeneous catalyst. The WDS image analysis indicates that each primary particle contains one or two catalytically active sites. The morphology of sPS obtained with embedded catalyst is quite similar to that of polyolefins made with heterogeneous catalysts. The kinetics of sPS polymerization with embedded $Cp^*Ti(OCH_3)_3/MAO$ is currently under investigation.

Acknowledgements

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