Kinetics and Morphological Development in Syndiotactic Styrene Polymerization over Heterogeneized Metallocene Catalysts

Joongjin Han and Kyu Yong Choi, Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742*

Introduction

Syndiotactic polystyrene (sPS) is a highly heat and chemical resistant engineering thermoplastic that can be synthesized over homogeneous metallocene catalysts in conjunction with methylaluminoxane (MAO). Since sPS is insoluble in its own monomer (styrene) and in many organic solvents at its typical reaction temperatures (40-90^{o}C), sPS precipitates out from the liquid phase during the early stage of polymerization. As monomer conversion increases the polymer precipitates agglomerate and they develop into an immobile 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. The gelation makes the agitation of the reaction mixture difficult with conventional agitators or mixers. Therefore, specially designed reactors such as self-cleaning reactors equipped with intermeshing blades or screws are needed [1,2].

A liquid slurry polymerization is an alternative to a bulk polymerization process to avoid gelation and to produce polymers as discrete particles. To conduct the slurry phase polymerization, a homogeneous catalyst needs to be heterogenized onto an inert support material. In our recent work, we demonstrated the feasibility of heterogenizing the $Cp^*Ti(OMe)_3/MAO$ catalyst onto sPS prepolymer particles (i.e., catalyst embedding) in a liquid slurry sPS process [3,4]. In this technique, styrene is polymerized to sPS to a very low conversion (< 3 vol.%) to incorporate homogeneous catalytic active sites into the prepolymer solid phase. The prepolymer particles (embedded catalysts) as obtained are then used in the subsequent main slurry phase polymerization. sPS was obtained as fine particles without global gelation for certain polymerization conditions. Homogeneous $Cp^*Ti(OMe)_3/MAO$ catalyst can also be immobilized onto a silica support. In this work, we report the styrene polymerization to sPS with three different catalyst systems: homogeneous catalyst, embedded catalyst, and silica-supported catalyst. We compare the intrinsic polymerization rates, physical transitions, and polymer morphology of sPS obtained by different polymerization methods.

Polymerization Kinetics

With homogeneous, embedded, and supported catalysts, we carried out styrene polymerization in a hydrocarbon diluent. The polymerization experiments were carried out in a 100mL agitated glass reactor (working volume = 60 mL) equipped with a three-balde agitator element and a heating/cooling jacket. The catalyst, solvent, and monomer were added into the reactor in a glove box. After the reaction was complete, the reaction mixture was washed with excess amount of methanol containing hydrochloric acid and dried in vacuo.

Figure 1 shows the catalyst activity vs. reaction time profiles for different reaction methods. Like in Ziegler-Natta or metallocene-catalyzed olefin polymerization processes, the catalyst activity declines with reaction time. However, it should be noted that the monomer concentration decreases with reaction time. It is also seen that the embedded catalyst exhibits higher activity than the silica-supported catalyst.

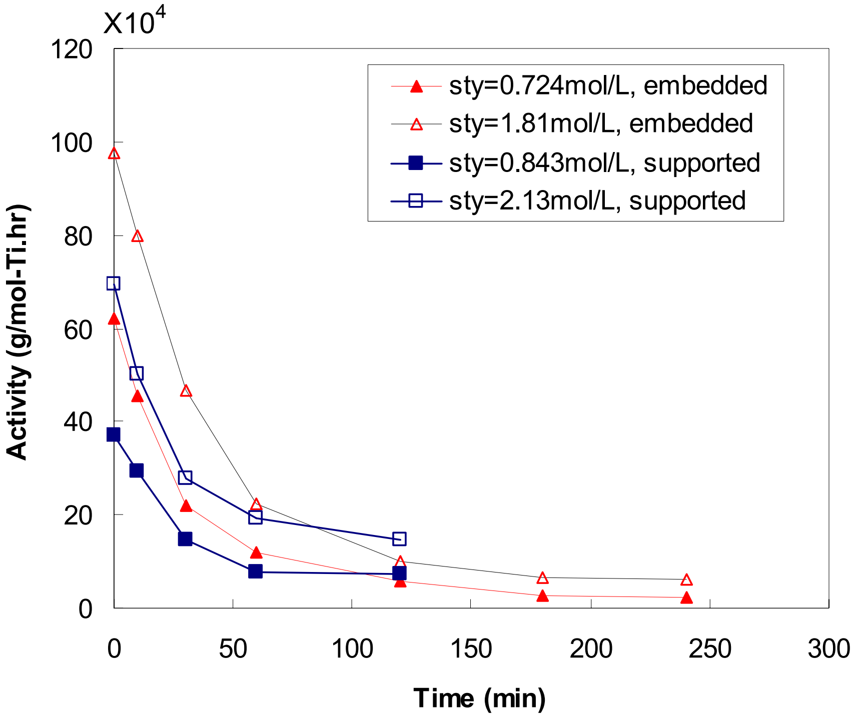


Figure 1. Polymerization rate with embedded and silica-supported catalysts.

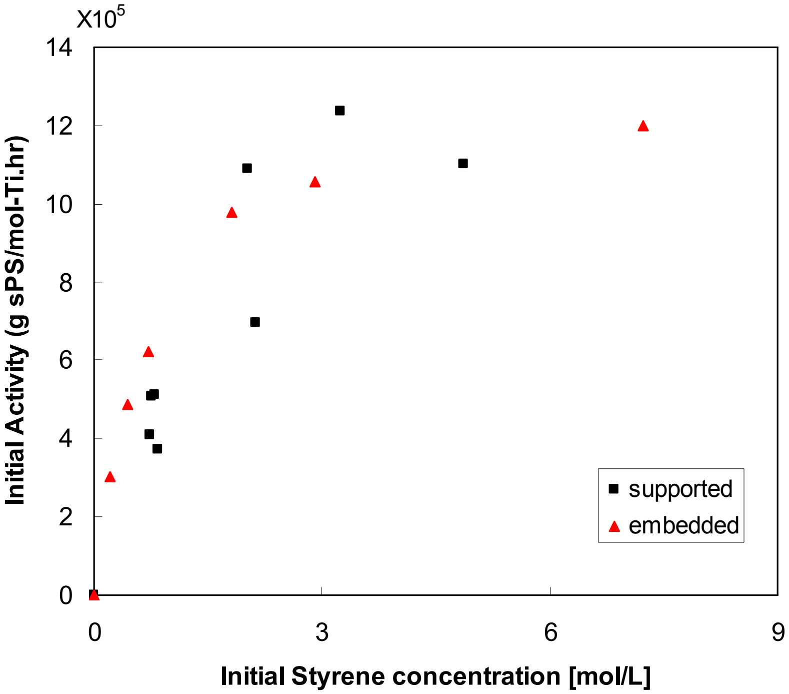
The initial catalyst activity values (i.e., at t = 0 min) are shown in Figure 2(a) for silica-supported Cp*Ti(OMe)$_3$ catalyst and embedded catalyst at different initial monomer concentrations. It is interesting to notice that for the monomer concentration up to about 3.0 mol/L, the initial catalyst activity increases linearly with the monomer concentration; however, at higher monomer concentration, the catalyst activity tends to level off. In other words, a further increase in monomer concentration does not result in higher catalyst activity or polymerization rate. We can express the initial polymerization as follows:

$$R_{p0} = k_p [M]_0 [C^*]_0 \tag{1}$$

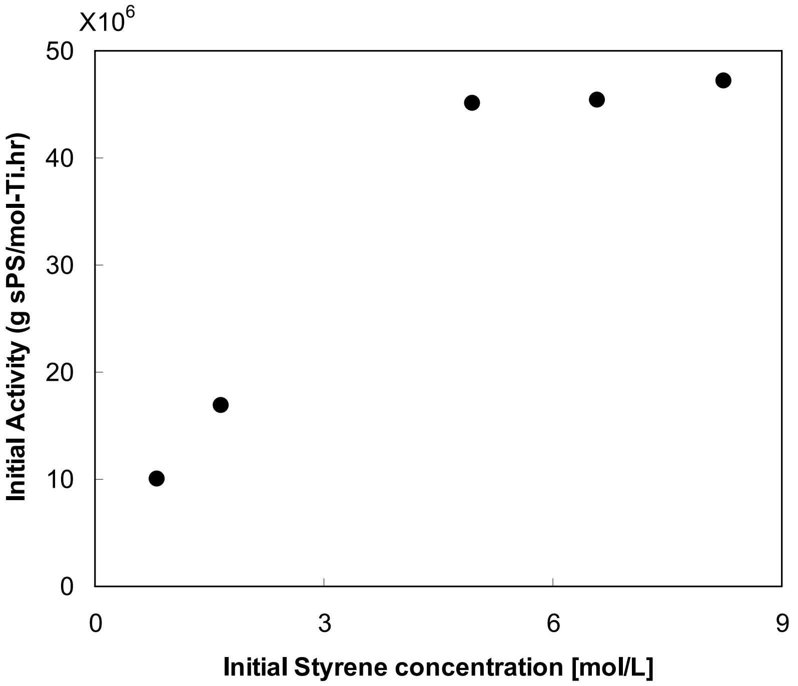
where k_p is the propagation rate constant, $[M]_0$ is the initial monomer concentration in the solid phase, and $[C^*]_0$ is the initial titanium concentration in the solid phase. The initial catalyst activity is defined as:

$$A_0 = \frac{R_{p0}}{[C^*]_0} = k_p [M]_0 \tag{2}$$

The experimental data shown in Figure 2 strongly suggests that the monomer concentration in the solid phase may be affected by the presence of solid phase. For example, the monomer concentration in the solid phase may reach a saturation sorption equilibrium, limiting the styrene concentration to a certain maximum level. Figure 2(b) also shows the initial catalyst activity values for homogeneous catalyst at different initial monomer concentrations. Notice that qualitatively it is very similar to that of supported catalyst but the initial catalyst activity is much higher. It was observed that at high monomer concentrations with the homogeneous catalyst, gelation occurred shortly after the beginning of polymerization. However, the polymerization itself continues even after the gelation.



(a) Supported and embedded catalyst system



(b) Homogeneous catalyst

Figure 2. Initial reaction rate vs. styrene concentration with supported, embedded, and homogeneous catalysts.

Figure 3 illustrates the effective propagation rate constant (k_p) vs. initial monomer concentration. The effective propagation rate constant can be expressed as follows:

$$\frac{R_p}{[M][C^*]_0} = k_p \tag{3}$$

From a pure kinetics point of view, the intrinsic propagation rate constant should be independent of the initial monomer concentration. However, Figure 3 shows that the calculated propagation rate constant decreases with initial monomer concentration, indicating that non-kinetic effects such as mass transfer limitations influence the polymerization kinetics from the early stage of sPS polymerization. The decline in k_p value is modeled as a first order decay of catalyst activity [i.e., $[C^*] = [C^*]_0 \exp(-k_d t)$]:

$$\frac{R_p}{[M][C^*]_0} = k_p e^{-k_d t} \tag{4}$$

If k_d represents the catalyst deactivation rate constant, then the catalyst half-life estimated from the data in Figure 3 is 1.15 hr.

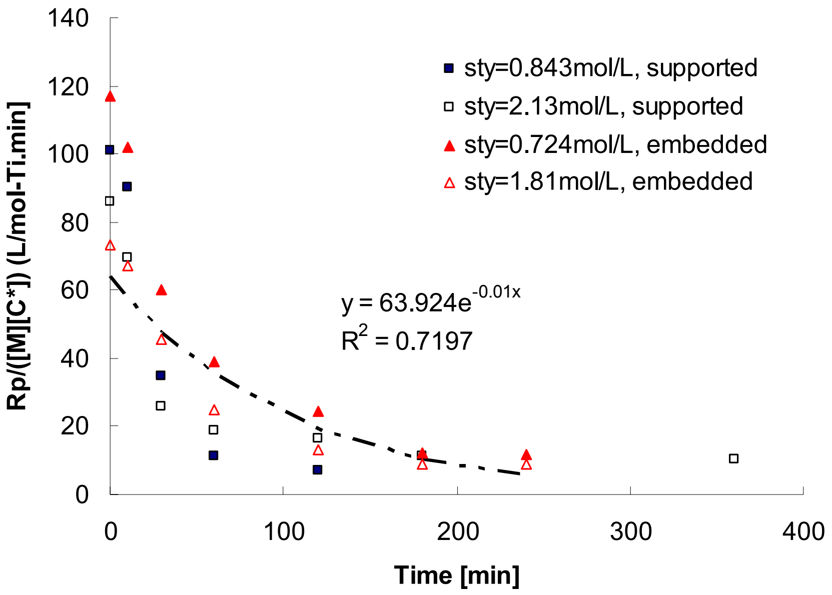
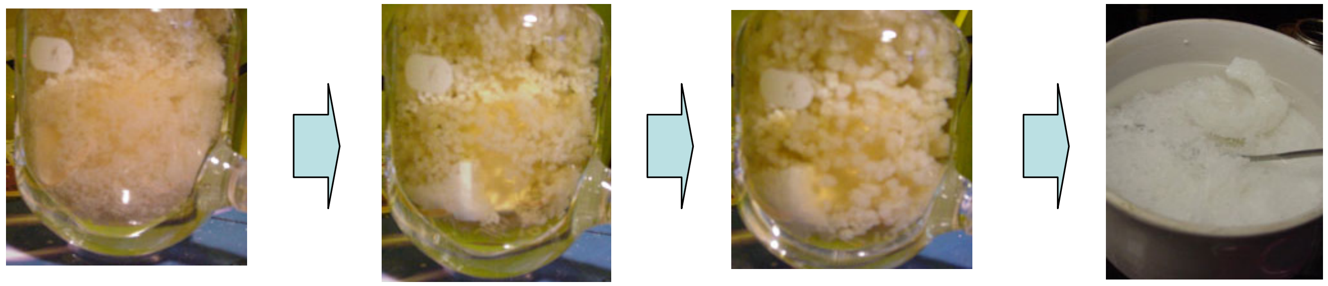


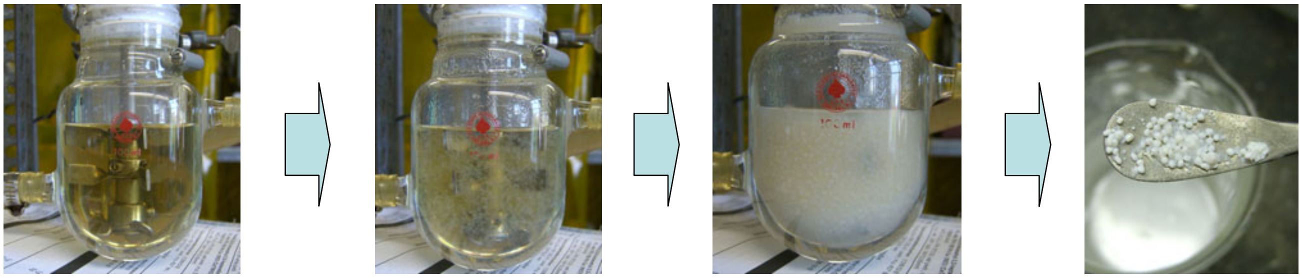
Figure 3. Effective propagation rate constant.

Macroscopic Phase Changes

One of the interesting and complex phenomena in slurry polymerization of styrene is that the reaction mixture undergoes a series of complex phase changes as sPS yield increases. If the purpose of slurry polymerization is to obtain sPS as discrete particles, understanding the phase changes during the polymerization is of great practical importance. Figures 4 (a) and (b) illustrate respectively the observed phase changes during the polymerization at 100% of initial styrene concentration with embedded catalyst and at 80 % initial styrene concentration with silica-supported catalyst. In both cases, no global gelation occurred with the heterogenized catalysts but the entire reaction mixture undergoes a significant phase changes during the reaction.



(a) with embedded catalyst

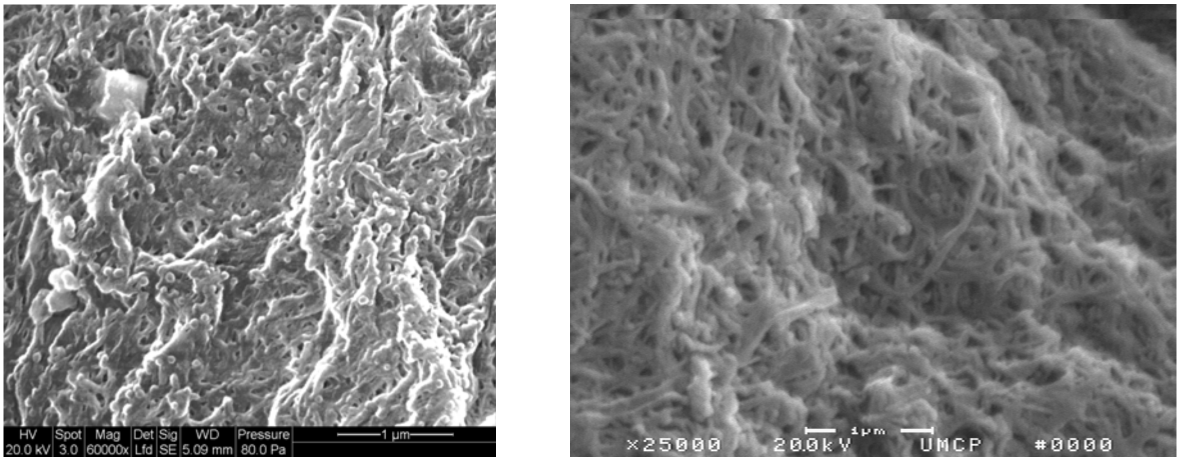


(b) with silica-supported catalyst

Figure 4. Phase changes during sPS polymerization

Nascent Morphology of sPS

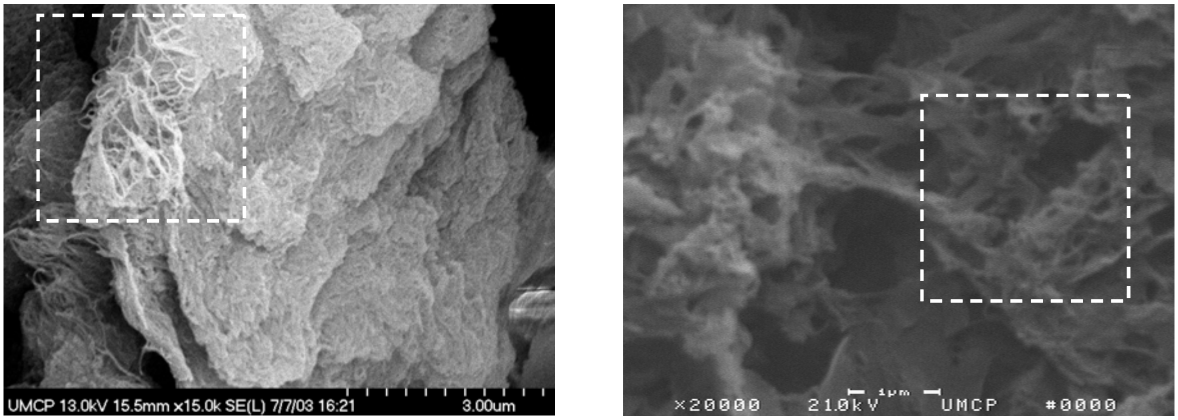
The nascent morphology of sPS has been examined by scanning electron microscopy (SEM). The polymer morphology changes with reaction conditions (ex. styrene concentration, temperature, solvent type, etc.). Unlike in silica-supported α-olefin polymerization processes, sPS particles obtained with either embedded catalyst or silica supported catalyst in our experiments do not show a globular morphology. The globular morphology commonly observed with Ziegler-Natta type catalysts or supported metallocene catalysts in ethylene or propylene polymerization is due to the fragmentation of catalyst into catalyst crystallites and micrograins during the early stage of polymerization. Figure 5(a) shows that such polymer micrograins are not formed in slurry sPS process, suggesting that the particle growth mechanism might differ from that of polyolefins. Figure 5(b) illustrates that a nascent sPS particle consists of long fibers of diameter around 20-50 nm. The formation of short polymer fibrils and fibers has been found in polyolefins made over Ziegler-Natta catalysts. For example, Wristers [5] reports that polypropylene grows as a coil at the active catalyst site because of steric hindrance between methyl groups of neighboring monomer units. These polymer coils crystallize into a composite structure of folded-chain lamellae supported on a core of partially extended chain crystal filaments. Then, these become longer fibers (500nm) and finally, it becomes polyolefin particle. Figure 5(b) shows that sPS fibers are much longer than 500 nm. The mechanism of the particle morphology shown in Figure 5 is under further investigation.



a) 3min

b) 10min

Figure 5. SEM image of sPS synthesized over silica-supported catalyst.



a) Embedded catalyst

b) Homogeneous catalyst

Figure 6. SEM images of sPS with embedded and homogeneous catalyst.

Figure 6 (a) and (b) shows the SEM images of sPS obtained with embedded catalyst and unsupported homogeneous catalyst. Similar fibrils or fibers are seen in both cases but they are not as prominent or clear as in the polymers with silica-supported catalyst.

Crystalline Structure of Nascent sPS

sPS is a semicrystalline polymer that can have 4 different crystalline structures (α, β, γ, and δ forms). Of particular interest is the δ-form sPS with TTGG chain configuration. Figure 7 shows the X-ray diffraction patterns of nascent sPS polymers with supported, embedded and homogeneous metallocene catalysts. All these catalysts produce sPS of δ–form crystals.

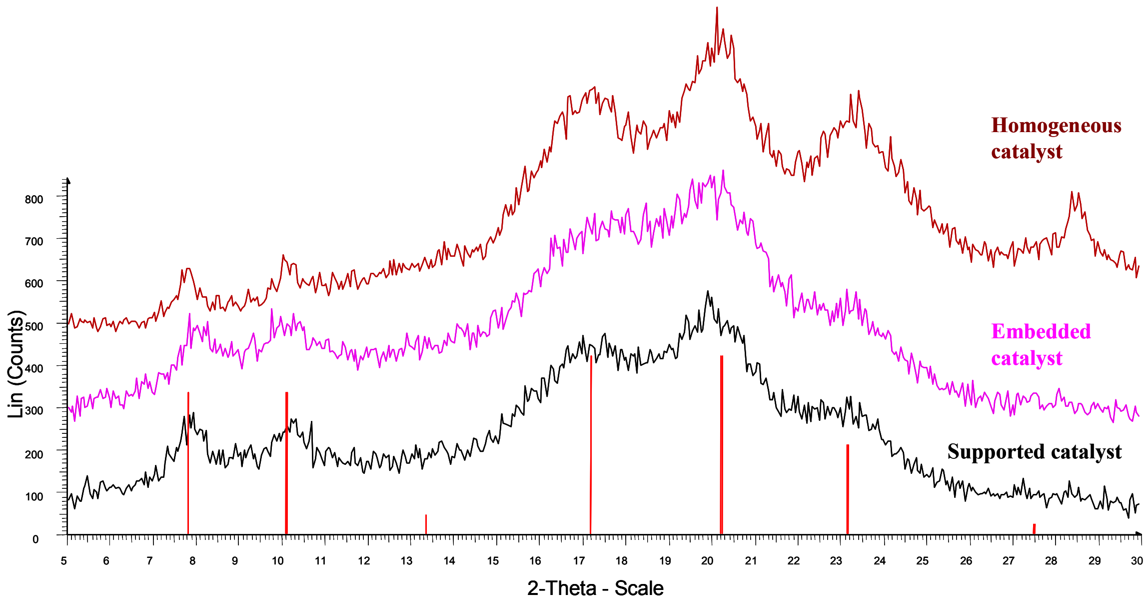


Figure 7. XRD patterns of nascent sPS polymer.

δ form sPS crystals are known to form a clathrate structure with guest molecules in its cavities. It means that the size of cavities in δ form is sufficiently large. Although the interaction between sPS chain and guest molecules is not strong, only vacuum drying cannot remove guest molecules from δ form of sPS. The guest molecules in δ form cavities can be removed by adequate treatments without the change of cavity size.

Concluding Remarks

The polymerization of styrene to sPS with heterogeneous catalysts results in the formation of discrete polymer particles. However, with such catalysts, unless the reaction conditions are well designed, the particles in the reaction mixture may lose the suspension stability and they might form a chunk of agglomerated polymers. The polymerization rate profiles indicate that from the beginning of polymerization the catalyst activity declines possibly due to the intrinsic catalyst site deactivation or the mass transfer limitations in presence of the sPS solid phase. It is also interesting to note that all the sPS samples synthesized with different types of catalysts are of δ form crystals. Such δ form crystalline structure of sPS forms a clathrate with guest hydrocarbon molecules. More results will be presented at the meeting.

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