

Syndiotactic Styrene Polymerization on a Flat-Surface Deposited Metallocene Catalyst

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Introduction

Syndiotactic polystyrene (sPS) is a semicrystalline polymer having excellent heat and chemical resistances. In our previous work of liquid slurry polymerization of styrene with a silica-supported Cp*Ti(OMe)₃/MAO catalyst [1, 2], fibrillar or worm-like structures were observed. Such morphology is quite different from the multi-grain morphology commonly observed in heterogeneous transition metal catalyzed α -olefin polymerization. The SEM images of sPS indicate that the growth of sPS in a heterogeneous reaction environment may follow a mechanism that might be quite different from that of catalytic olefin polymerization processes with similar solid catalysts.

To understand the development of this peculiar morphology, we consider a polymerization on a flat catalyst surface. There are some reports on the use of a flat silica surface to support catalytically active species for the study of olefin polymerization. For example, Niemantsverdriet et al. [3 – 6] treated silicon wafers to support CrO₃ catalyst and used for olefin polymerization. Loose and coworkers [4] carried out similar experiments with silicon wafers as a catalyst support for ethylene polymerization and AFM results showed that catalyst active sites on the flat surface were molecularly dispersed and they were equally accessible for the monomer [5].

In this work, we designed a novel experimental procedure for syndiospecific polymerization of styrene over metallocene catalyst supported on a silica flat surface to investigate the mechanism of sPS morphology development. The nascent morphology of the sPS grown from the flat catalyst surface has been analyzed using scanning electron microscopy (SEM) and focused ion beam (FIB) techniques.

Experiments

Preparing catalyst-anchored silica flat surface

The surface of a silicon wafer was pretreated with pyranha solution. It was then cleaned with acetone (Pharmco-AAPER) by ultrasonic generator (Cole-Parmer) and calcined in a nitrogen atmosphere at 350 °C for 24 h. To anchor MAO/catalyst onto the treated silica wafer, the wafer surface was treated by MAO (10% Al in toluene, Albemarle) and toluene solution, washed with excess toluene three times, and dried in vacuo for 24 hr. The wafer was treated with a catalyst ($\text{Cp}^*\text{Ti}(\text{OMe})_3$, Strem Chemical) solution, washed with toluene three times, and dried in vacuo for 24 hr. The catalyst anchored onto a silica wafer without MAO was also prepared by the similar method.

Liquid and vapor phase syndiospecific styrene polymerization

The syndiospecific polymerization of styrene was carried out in a reactor assembly illustrated in Figure 1. In the bottom part of the assembly, purified styrene and heptane were charged. Three or four pieces of catalyst deposited silica wafers were added into the lower reaction chamber. In the upper part of the assembly, which is separated from the lower chamber by a sintered glass filter, small pieces of silica wafers were placed. The reactor assembly was carried out in the glove box under argon atmosphere. The reactor was taken out from the glove box and placed in a constant temperature bath (70 °C) to start the polymerization. After 6-8 h of polymerization, silica wafers were removed from the reactor and washed with acidified methanol and 2-butanone. The dried wafers were observed by scanning electron microscopy (SEM) (S-4700, Hitachi).

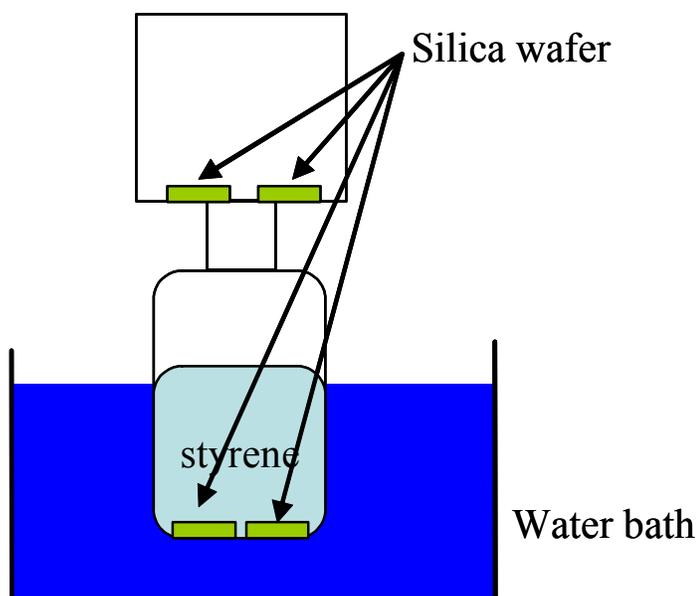


Figure 1. Polymerization reactor for syndiotactic polymerization of styrene.

Results and Discussion

Figure 2 illustrates the chemical anchoring of catalyst-MAO complex onto a surface hydroxyl group of the wafer.

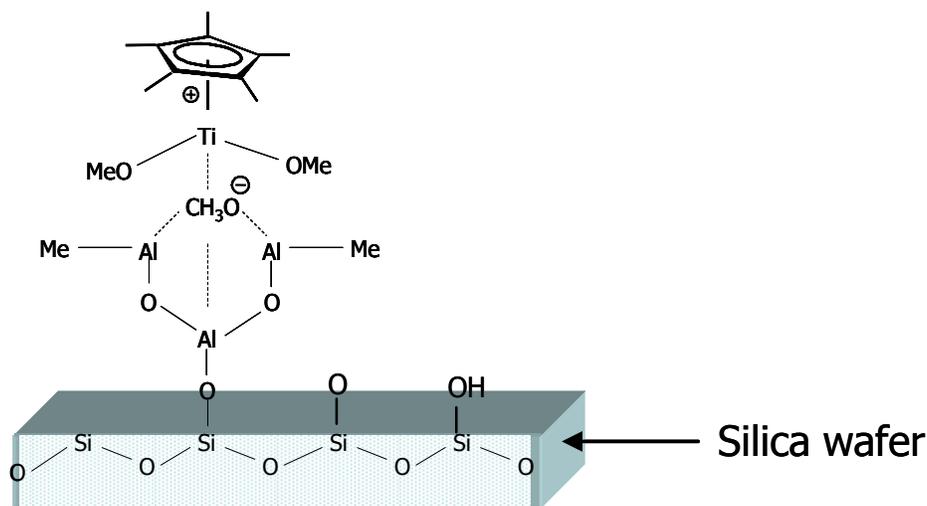
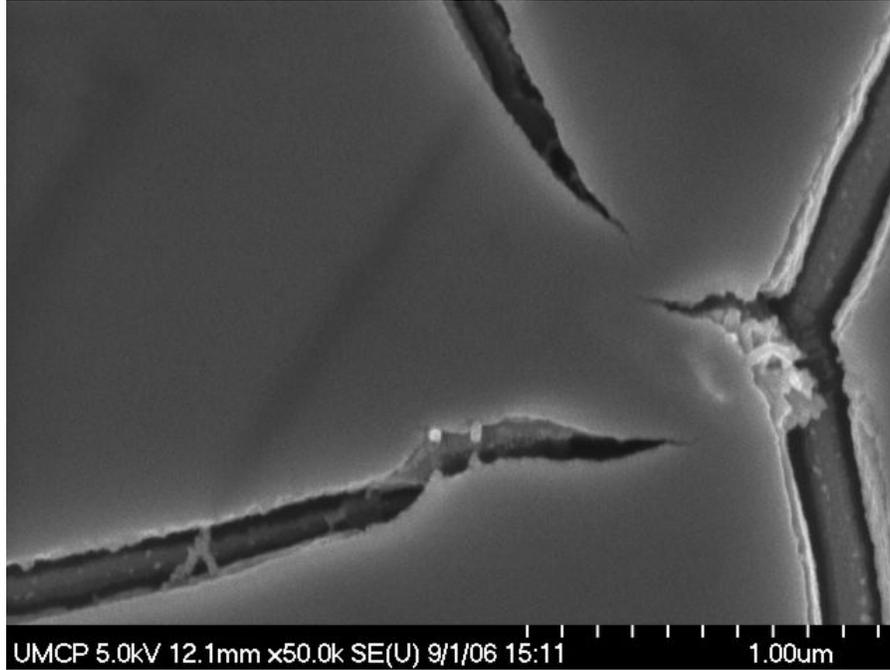


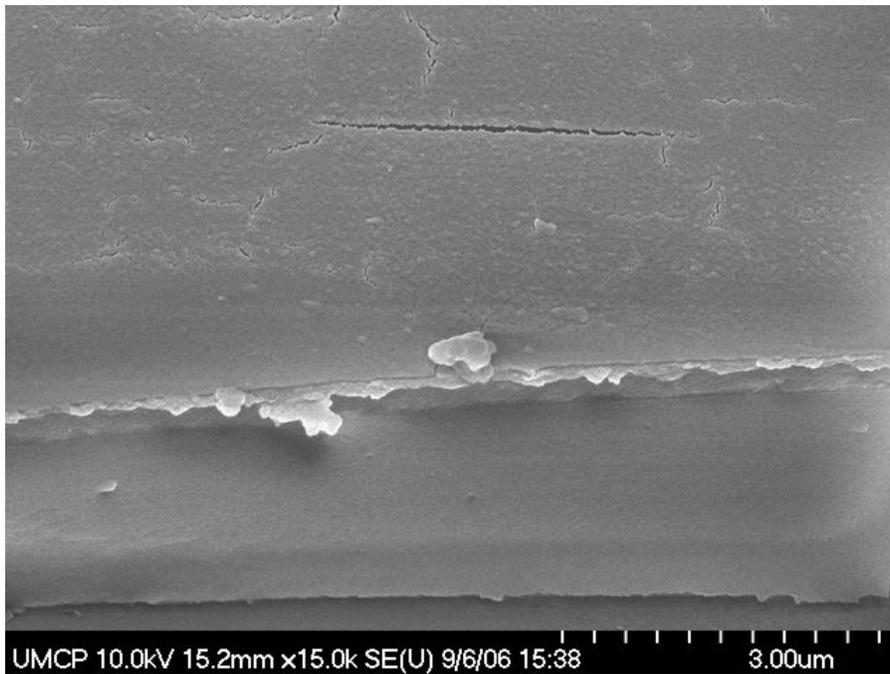
Figure 2. Metallocene/MAO catalyst deposited onto a silica wafer surface.

Figure 3 shows the SEM images of the silica wafers in the liquid and the vapor phases, respectively. Notice that the surface is quite smooth but there are some cracks, probably formed by the removal of solvent during the sample drying. It is interesting to observe that short nano fibrils are seen inside some cracks. Figure 3(b) shows the side view (tilted by 45°) of the sample from the vapor phase reaction chamber. The polymer layer thickness is about 300 nm. The images shown in Figure 3 show that the polymer yield is too large to minimize the entanglement of polymer chains.

Figure 4 shows spherical growth of polymers at the wafer surface. Notice that 100-300 nm size ball-shaped polymers have been formed. The similar polymer growth in ethylene polymerization was reported by Thune and coworkers [5,6]. They explain that when the catalyst loading is slightly more than monolayer coverage, the catalyst/activator does not spread out on the silica wafer. Instead, it precipitates to form flat, roundish islands that grows to form ball-shaped polymers. In our experiments, the spherical polymer particles or clusters were observed only when MAO was added to a liquid phase. It is possible that some catalysts were leached out from the silica but further experimental analysis is needed to fully understand the polymer formation mechanism. More results will be presented at the meeting.



(a) liquid phase reaction



(b) vapor phase reaction

Figure 3. SEM images of silica wafer surface after polymerization (Styrene: 60 v/v%, temp: 70°C, reaction time: 8 hr, MAO solution dipping)

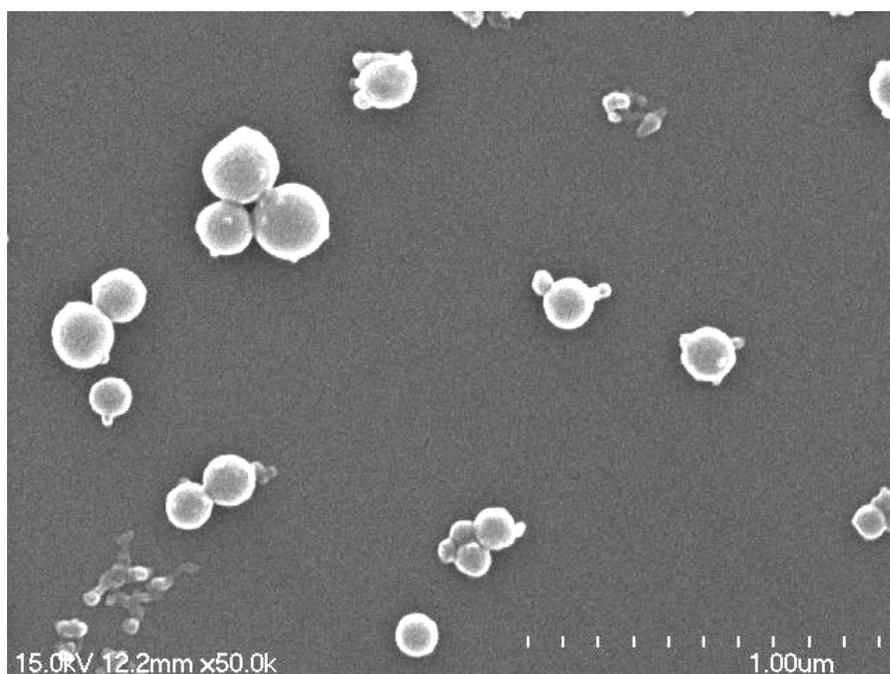


Figure 4. SEM image of silica wafer surface after polymerization (Styrene: 60 v/v%, temp: 50°C, reaction time: 8 hr, MAO dipping, liquid phase)

References

1. Han, J. J.; Choi, K. Y. (2005) AIChE annual meeting, Cincinnati, Ohio.
2. Lee, H. W.; Chung, J. S.; Choi, K. Y. (2005), *Polymer*, 46, 5032-5039.
3. Thüne, P. C.; Werhagen, C. P. J; vandenBoer, M. J. G; Niemantsverdriet, J. W. (1997) *Journal of Physical Chemistry B.*, 101, 8559-8563.
4. Loos, J; Thüne, P. C.; Niemantsverdriet, J. W.; Lemstra, P. J. (1999) *Macromolecules*, 32, 8910-8913.
5. Thüne P. C; Loos, J; Wouters D; Lemstra P. J; Niemantsverdriet J. W. (2001) *Macromolecular Symposia*, 173, 37-52.
6. Thüne, P. C; Loos, J; Weingarten, U; Muller, F; Kretschmer, W; Kaminsky, W; Lemstra P. J; ; Niemantsverdriet J. W. (2003) *Macromolecules*, 36, 1440-1445.