

Physical transitions and nascent morphology of syndiotactic polystyrene in slurry polymerization with embedded $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{methyl aluminoxane}$ catalyst

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Abstract

The physical transitions and nascent morphology of syndiotactic polystyrene (sPS) synthesized over heterogeneized embedded $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$ catalyst in *n*-heptane slurry polymerization have been investigated. The homogeneous metallocene catalyst is heterogeneized by embedding active titanium sites into an sPS prepolymer phase. At low styrene concentrations, the reaction mixture is well-dispersed slurry of sPS particles and at high styrene concentrations, swollen sPS particles form aggregates that become a wet powder phase. For a wide range of styrene concentrations, no global gelation occurs with the embedded catalyst. Complex nascent morphology of sPS polymers is also presented. Scanning electron microscopic images show that spherical as well as irregular-shaped microparticles, films, and fibers are formed and that particle generation and growth mechanisms are different from that of heterogeneously catalyzed α -olefin polymerization processes.

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1. Introduction

Syndiotactic polystyrene (sPS) is a new class of highly heat resistant and chemical resistant engineering thermoplastic polymer that can be synthesized over titanium-based homogeneous metallocene catalysts (e.g., $\text{CpTiCl}_3/\text{MAO}$ or $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$) [1–17]. The bulk polymerization of styrene to sPS is characterized by the precipitation of syndiotactic polystyrene that is insoluble in its own monomer or other common organic solvents at typical reaction temperatures (40–90 °C). As the amount of precipitated polymer increases, these precipitates form aggregates that eventually develop into an immobile gel. 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 [18–20]. Once sPS gel is formed, mechanically agitating the reaction mixture becomes impossible by conventional means.

A liquid slurry process might be an interesting alternative to bulk polymerization process to avoid gelation and to produce sPS as discrete particles. To carry out slurry polymerization, a homogeneous catalyst must be immobilized or heterogeneized onto a solid carrier material. In our previous work, we developed a catalyst embedding technique for slurry polymerization of styrene [17]. The embedded catalyst is prepared by prepolymerizing styrene to sPS in fine particulate form using homogeneous catalyst ($\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$) at low polymerization rate. With initial styrene concentration lower than 3 vol%, the conversion of styrene is kept low (<20%) to keep the total solid content in the reaction medium less than 1%. Under such reaction conditions, slurry of fine sPS particles (prepolymers or embedded catalysts) is obtained. The prepolymer particles can be separated from the liquid phase and dried or the slurry of prepolymer can be directly used in the subsequent main polymerization stage.

When embedded catalyst is used in the slurry

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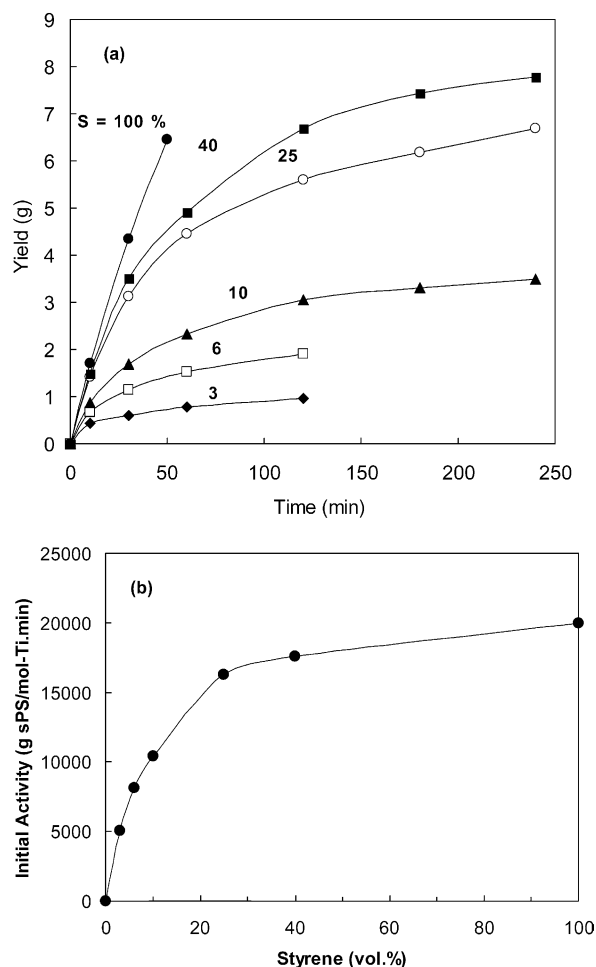


Fig. 1. Polymer yield and initial polymerization activity with reaction time (70 °C).

polymerization of styrene with *n*-heptane as a diluent, the reaction mixture undergoes a series of interesting physical transitions and morphology. We investigated the physical transitions of the reaction mixture and the resulting sPS particle morphology at different styrene concentrations in *n*-heptane diluent at 70 °C with Al/Ti mole ratio of 500. This work is the first to report the physical transitions of sPS slurry and the nascent morphology of the polymer.

2. Experimental

Styrene (Aldrich) was vacuum distilled over calcium hydride. Inhibitor in styrene was removed using activated alumina. $\text{Cp}^*\text{Ti}(\text{OMe})_3$ [Pentamethyl cyclopentadienyl titanium trimethoxide] (Strem Chemical) and modified methyl aluminoxane (MMAO, Akzo Nobel) were used as supplied without further purification. The embedded catalyst was prepared using the procedure described in [17]. To prepare the embedded catalyst, polymerization was first carried out in a small agitated glass reactor at room temperature for 1 h at very low styrene concentration



Fig. 2. SEM image of embedded catalyst (sPS prepolymer). (a) Slurry polymerization at 10 vol% styrene, 30 min; (b) 60 min.

(<4 vol%) using *n*-heptane as diluent [17]. The inductively coupled plasma (ICP) spectroscopy analysis was used to measure the amount of titanium and aluminum in the embedded catalyst. It was found that about 48 mol% of titanium and 33 mol% of aluminum in the catalyst solution were embedded into the solid phase (sPS prepolymer).

The slurry phase styrene polymerization was carried out in a 100 ml glass reactor (working volume = 60 ml) equipped with a three-blade agitator element and a heating/cooling jacket. Predetermined amounts of solvent (*n*-heptane), monomer, embedded catalyst, and MMAO were charged into the reactor. Polymerization was carried out at 70 °C with agitation speed of 700 rpm. After the reaction was complete, the reaction mixture was washed with excess amount of methanol containing hydrochloric acid. The boiling xylene insolubles were determined by Soxhlet extraction. The fractions of boiling xylene insolubles were mostly in the range of 93–95%. It should be noted that the fraction of boiling xylene (or methylethylketone) insolubles is not identical to the syndiotacticity measured by ^{13}C -NMR spectroscopy because boiling solvent washes out low molecular weight sPS as well as atactic polystyrene. Thus, the fraction of boiling xylene insolubles is an approximate measure of polymer

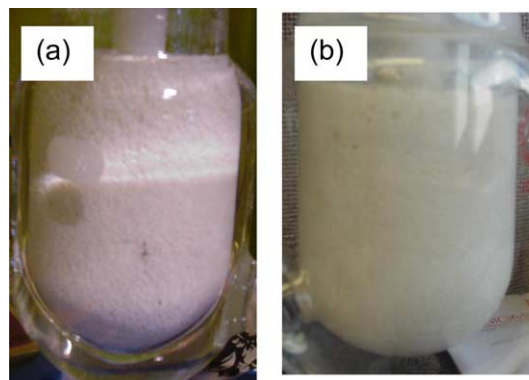


Fig. 3. (a) Slurry polymerization at 10 vol.% styrene, 30 min; (b) 60 min.

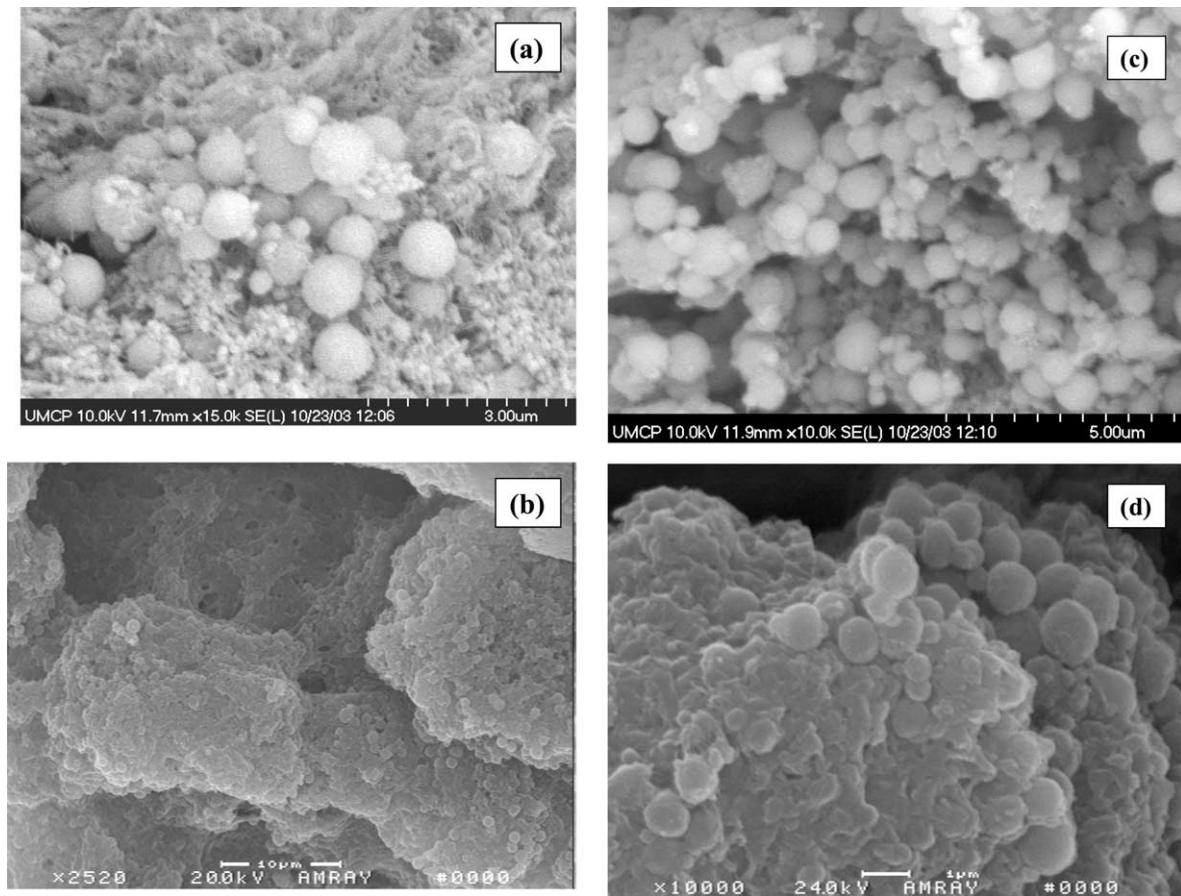


Fig. 4. SEM images of sPS particles at 10% styrene, 10 min.

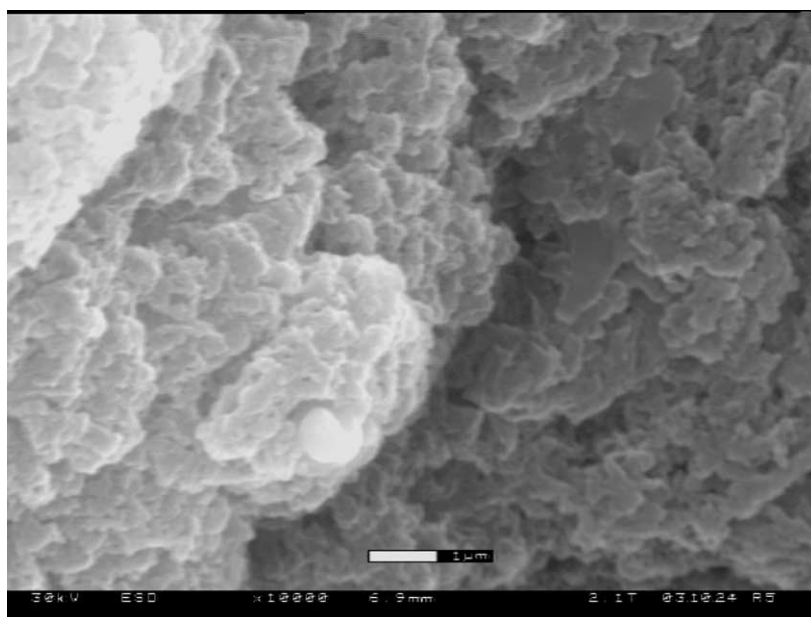


Fig. 5. SPS morphology after 1 h of polymerization, 10 vol% styrene.

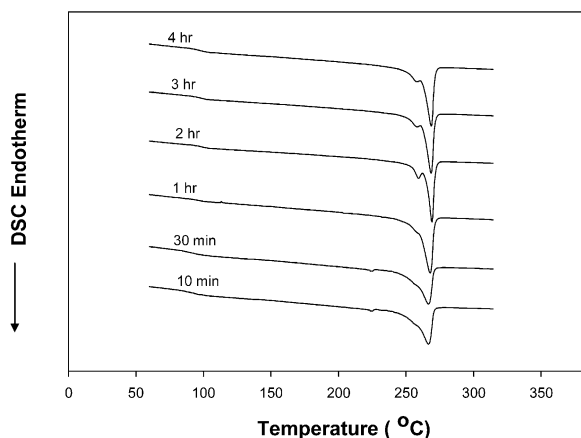


Fig. 6. DSC thermograms of sPS at different reaction times (initial styrene concentration = 10 vol%, 70 °C, scanning rate: 20 °C/min).

syndiotacticity [10]. Most of the sPS samples examined by scanning electron microscopy were not purified in boiling xylene to observe the nascent morphology with minimal effect of post-reaction treatment.

3. Results and discussion

3.1. Catalyst activity

We carried out slurry phase polymerization experiments at several different initial styrene concentrations. In all these experiments, no global gelation occurred and sPS was obtained as particles. Near the bottom of the reactor where mixing was relatively ineffective, soft polymer chunks were often formed but they were easily broken into discrete particles. Fig. 1 shows the polymer yield vs. time and the initial polymerization activity vs. time plots at different initial styrene concentrations (vol%). Here the initial activities are plotted because they are considered as a better measure of catalyst activities in the current polymerization system where styrene concentration decreases with reaction time. The initial polymerization activity values in Fig. 1(b) were estimated by extrapolating the polymer activity profiles to $t=0$. It is interesting to note that initial

polymerization activity is proportional to styrene concentration at low styrene concentrations but it deviates from the linearity as the monomer concentration is increased.

We can express the initial polymerization rate (R_{p0} , g/l min) as follows:

$$R_{p0} = k_p[M]_{s0}[C^*]_{s0} \quad (1)$$

where k_p = propagation rate constant, $[M]_{s0}$ = initial monomer concentration in the solid phase (sPS prepolymer; embedded catalyst) and $[C^*]_{s0}$ = initial active titanium concentration in the solid phase (sPS prepolymer; embedded catalyst). The initial polymerization activity (g sPS/mol-Ti min) is then defined as

$$A_0 \equiv \frac{R_{p0}}{[C^*]_{s0}} = k_p[M]_{s0} \quad (2)$$

Here, the monomer concentration in the solid phase can be correlated to the bulk phase monomer concentration ($[M]_b$) by the following form:

$$[M]_s = f([M]_b) \quad (3)$$

The polymerization activity data shown in Fig. 1 and Eq. (2) suggest 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 not be linearly proportional to the monomer concentration in the bulk liquid phase. Fig. 1(b) suggests that perhaps the monomer concentration may reach a saturation equilibrium in the solid sPS phase. The understanding of phase transitions and polymer morphology during the polymerization will be needed to quantify the kinetics of heterogeneous polymerization of styrene in slurry.

3.2. Catalyst morphology

Fig. 2 shows a scanning electron microscopic (SEM) image of the embedded catalyst used in our experiments. Recall that the embedded catalyst is a prepolymer of sPS with very low content of polymer. First of all, we see that the embedded catalyst has a rather unique morphology. Notice that approximately 3–5 μm size pseudo-spherical

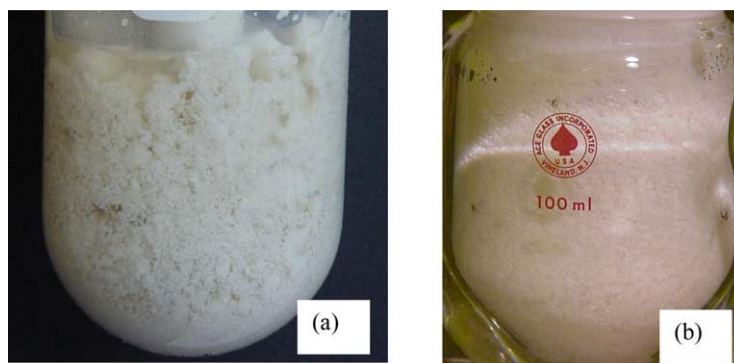


Fig. 7. (a) Slurry polymerization at 25 vol% styrene, 1 h ; (b) 2 h.

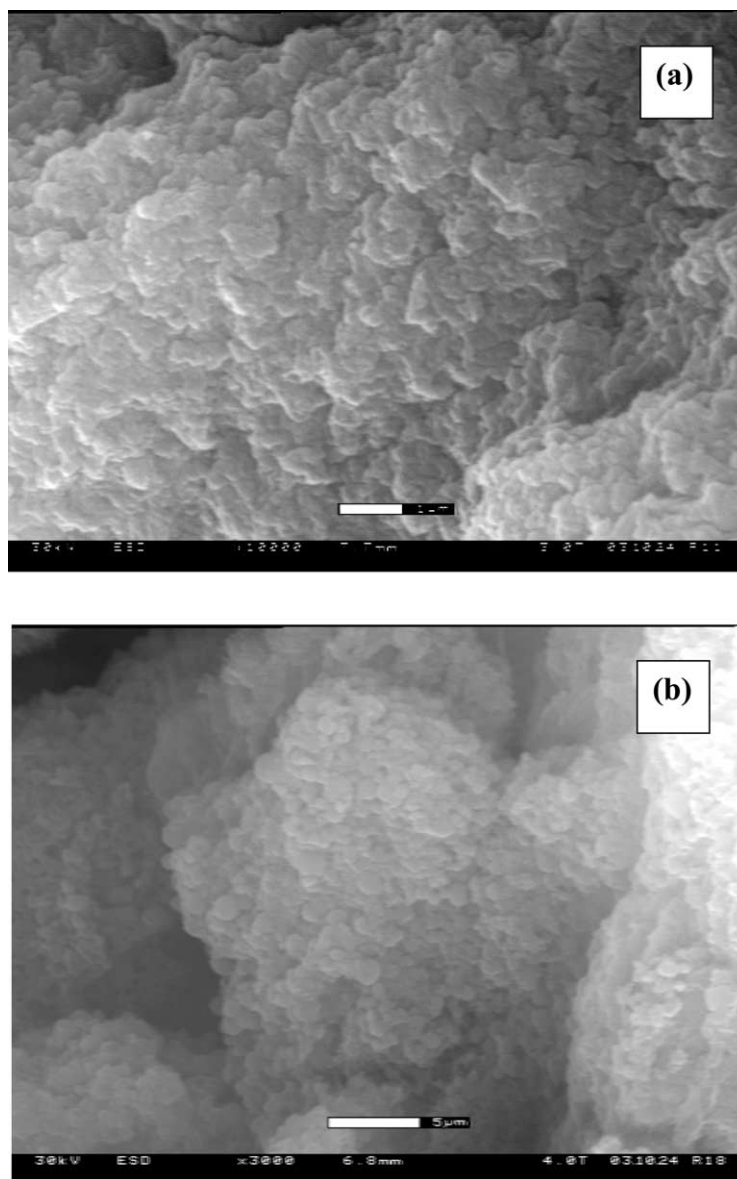


Fig. 8. SEM images of sPS at 25 vol% styrene: (a) 10 min, (b) 1 h.

microstructures are present and that they consist of ‘cabbage leaf’-like thin layers of about 40–100 nm thickness. Since monomer concentration was very low (e.g., <3 vol%) and polymerization rate was also very low (room temperature reaction) during the preparation of the embedded catalyst, sPS crystallites precipitated out from the liquid phase did not seem to have grown to a dense aggregate of primary particles. Scanning electron microscopy-wavelength dispersive spectroscopy (SEM-WDS) analysis indicates that each microstructure (approximately spherical) of embedded catalyst is grown from one or two $\text{Cp}^*\text{Ti}(\text{OCH}_3)_3$ molecules complexed with MAO [17].

3.3. Polymerization at low styrene concentrations

At low styrene concentrations, sPS particles formed in

slurry polymerization with embedded catalyst do not develop into a gel. Fig. 3(a) shows a photograph of stable slurry of sPS particles at $t=30$ min when the initial styrene concentration is 10 vol%. Although the solid content is small in the liquid phase (<3%), the entire reaction mixture is a stable slurry of particles and it looks very dense. Fig. 3(b) shows the reaction mixture at 1 h of reaction. No gelation occurred and the whole reaction mixture is slurry of well-dispersed sPS particles.

Fig. 4(a)–(d) show the SEM images of the sPS particles recovered from the reactor at $t=10$ min. These pictures show some interesting morphology of the sPS polymer. Some sPS particles are near-perfectly spherical particles of about 1 μm diameter or less but other portions of the picture shows irregular-shaped sPS polymers (Fig. 4(a)). Fig. 4(b) shows that aggregates of small microparticles such as shown

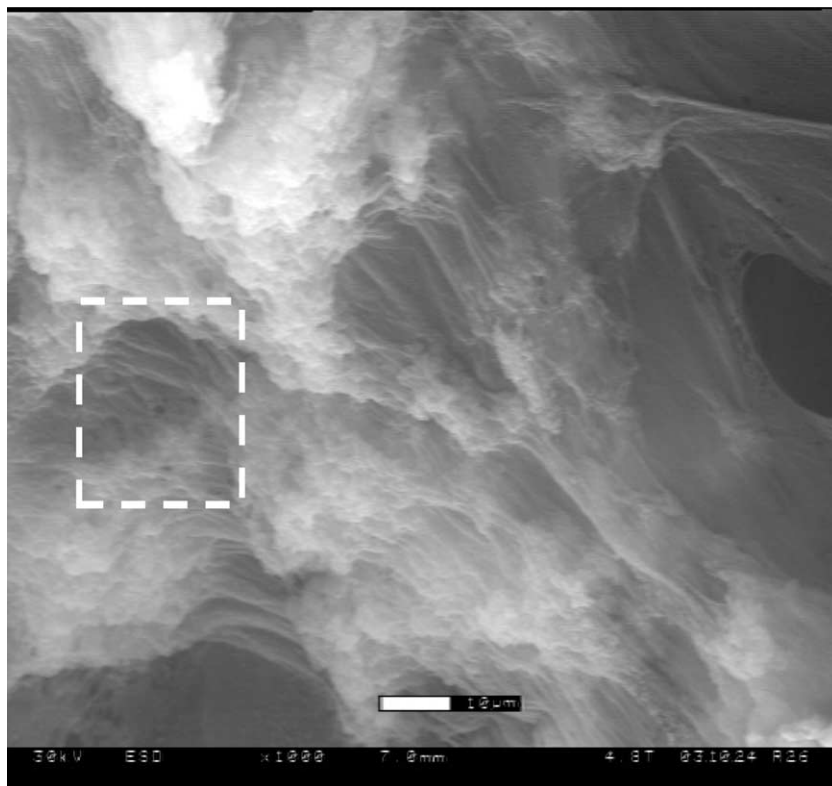


Fig. 9. SEM image of sPS at 25 vol% styrene: chunk.

in Fig. 4(a) are not quite spherical. In heterogeneously catalyzed olefin polymerization processes with supported Ziegler-Natta or metallocene catalysts, microparticles are formed by the fragmentation of original catalyst particles and these microparticles constitute the macroparticles that eventually grow to several hundred microns. The overall shape of the resulting olefin polymer particles is generally a close replica of original catalyst particles (shape replication phenomena) and the polymer macroparticles are nearly spherical. A question we can ask is whether such particle fragmentation and growth can occur in heterogeneous polymerization of styrene. Fig. 4(c) and (d) shows the images of other sections of the sPS particle samples.

Fig. 5 shows the SEM image of sPS particles obtained after 1 h of reaction. The texture of particle surfaces shows very irregular shaped microparticles. The overall morphology of the sPS particles looks quite different from that of α -olefin polymers made over heterogeneous Ziegler-Natta type catalysts. It should be pointed out that active titanium sites in the embedded catalyst are not chemically anchored onto the solid phase but they are physically trapped or embedded in the sPS prepolymer phase. During the polymerization, live polymer chains are detached from the active titanium sites by chain transfer reaction and they become dead polymer chains. Some fractions of vacant titanium sites may leach out from the solid phase into the bulk liquid phase and initiate homogeneous polymerization in the liquid phase. If the concentration of the leached

homogeneous titanium catalysts is low in the liquid phase, it may be possible that the polymer molecules produced in the liquid phase do not grow to large polymer particles.

Syndiotactic polystyrene is known as a semicrystalline polymer. Fig. 6 illustrates the differential scanning calorimetry thermograms for the nascent sPS samples obtained at different reaction times (initial styrene concentration: 10 vol%). During the early reaction period (<1 h), the DSC thermogram of sPS sample shows single melting peak. But the sPS samples obtained after 2 h reaction time show two melting peaks at 258 and 268.8 °C, suggesting the occurrence of recrystallization [21].

3.4. Polymerization at high styrene concentrations

As initial styrene concentration is increased to 25 vol%, initial polymerization rate also increases and the precipitated sPS particles become visibly larger than the particles obtained at lower styrene concentrations. Fig. 7(a) and (b) show the photographs of the reaction mixture at 1 and 2 h, respectively.

Fig. 7(a) shows that a small amount of separate liquid phase is still present. As styrene conversion increases, the slurry becomes a wet cake-like material with no visible separate liquid phase. However, the particles do not agglomerate to a chunky polymer mass. When the resulting polymer wet cake is dried, fine discrete particles are obtained. Fig. 8 shows the SEM image of the polymer.



Fig. 10. (a) Slurry polymerization with 100% styrene (10 min). (b) Slurry polymerization with 100% styrene (45 min). (c) Slurry polymerization with 100% styrene (55 min).

Near the bottom of the glass reactor, mixing was not as effective as in the bulk liquid phase at styrene conversion increased. A small amount of chunky polymer was present at the bottom of the reactor and Fig. 9 shows the SEM image of the polymer. Notice that the polymer morphology shown in Fig. 9 is quite different from that shown previously; dense polymer particles are loosely connected through film-like

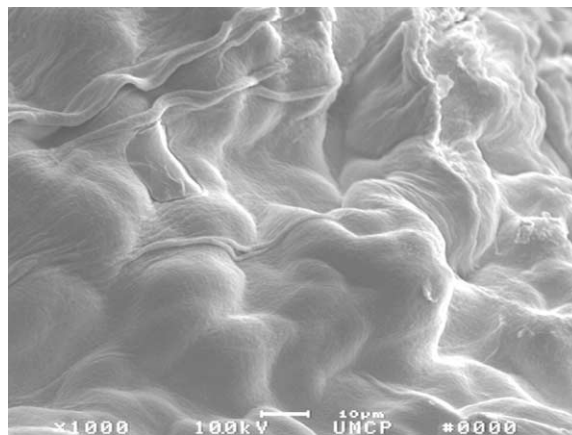


Fig. 11. SEM image of sPS chunk sample (100 vol% styrene, 50 min).

thin layers. It is also interesting to observe that particles are connected by fiber- or bone-like structures of about 40 nm in diameter (dotted square).

When styrene was polymerized in the absence of *n*-heptane, we observed interesting physical transitions of the reaction mixture. Fig. 10(a) shows the photograph of the reaction mixture taken at 10 min of reaction time. Notice that fluffy liquid-swollen sPS particles have been formed. The overall particle population seems to be low. As reaction continues, the reaction mixture undergoes an interesting transition. Fig. 10(b) shows the reaction mixture at 45 min of reaction time. Compared with Fig. 10(a), sPS particles shown in Fig. 10(b) are swollen into much larger size. Furthermore, the sPS particles are not quite spherical but rather irregular. They even look like marshmallows. Fig. 10(c) shows the reaction mixture at 55 min. At this point, very little liquid phase was present in the liquid phase. When these swollen sPS particles were recovered from the reactor and dried, the aggregate of sPS particles collapsed and the particles were surprisingly easy to break into fine particles.

Fig. 11 shows the SEM image of sPS chunk sample. The texture of the polymer sample is quite different from that of other samples obtained at different reaction conditions. It appears that polymer particles are heavily covered with contiguous polymer surface layers.

4. Concluding remarks

In this work, we have presented the visual images of sPS particles produced by liquid slurry polymerization over heterogeneous embedded catalyst $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$ that was prepared by styrene prepolymerization. The reaction mixture undergoes a series of phase transitions such as slurry phase, wet-cake stage, and dry powder stage. In all the experiments with embedded catalyst, no global gelation was found to occur, indicating that embedded catalyst was effective in preventing gel formation. In the bottom region of the reactor where mixing was not effective, polymer

chunks were formed. But these chunks were not hard gels but easily breakable. The morphology of sPS particles has been found to be quite different from that of traditional olefin polymers synthesized over heterogeneous catalysts, suggesting that the particle formation mechanism in sPS polymerization might be different from that in olefin polymerization processes. SEM photographs show that some fractions of sPS produced never develop into discrete particles. For example, both film or fiber shaped polymer fractions were also observed. This work is the first to illustrate complex phase transitions and nascent polymer particle morphology in heterogeneously catalyzed polymerization of styrene to sPS in slurry. The complexity of the particle morphology shown in this work suggests that more in-depth analysis would be needed to understand the growth of sPS particles in slurry polymerization.

Acknowledgements

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