

Full-Range Kinetic Study on Bulk Syndiotactic Polymerization of Styrene with Homogeneous Metallocene Catalysis

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ABSTRACT: By choosing a proper agitator and reinforcing its stirring shear, powdery syndiotactic polystyrene (sPS) is prepared in a bulk precipitation process with two homogeneous metallocene catalyst systems [Cp*TiX₃/MAO/TIBA (X = Cl or OPhOMe)]. A full-range kinetics study of the heterogeneous polymerization is performed in detail to produce this kind of powdery sPS in an industrial process. A typical curve of conversion versus time takes an S shape and an obvious acceleration phenomenon occurs in the middle stage of the polymerization, although the polymer–monomer gel is avoided. The viscous-average molecular weight of sPS goes through a peculiar increasing–decreasing–increasing change during the bulk polymerization process. These phenomena are viewed in terms of the two-phase polymerization mechanism and the overheating in particles during polymerization. The influence of the metallocene catalyst type and concentration, MAO/Ti ratio, triisobutyl aluminum (TIBA)/Ti ratio, and polymerization temperature on the polymerization kinetics are investigated. TIBA has dual effects on the polymerization. A small amount of TIBA in the catalyst system promotes polymerization, but more TIBA leads to a low molecular weight sPS. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2635–2643, 2002

Key words: syndiotactic polystyrene; kinetics; polymers; metallocene catalysts

INTRODUCTION

In 1985 Ishihara et al.¹ first synthesized syndiotactic polystyrene (sPS) by using homogeneous metallocene catalysts. With a melting point of 270°C, which is the highest of all the homopolymers, and a crystalline nature, sPS has excellent

heat resistance, chemical resistance, water/steam resistance, and insulating properties. Moreover, the crystallization rate of sPS is much faster than isotactic PS (iPS), which allows the practical use of sPS in many forming operations, such as injection molding, extrusion, and thermoforming. sPS is thought of as a potential engineering polymer and it has aroused wide attention and research interest.

Bulk polymerization has been chosen as the main polymerization method in many recent patents^{2–4} for sPS polymerization technology, because its reaction apparatuses are relatively small and the posttreatment is relatively simple. In the

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bulk syndiotactic polymerization of styrene with homogeneous metallocene, the reacting mixture is first in a slurry state and becomes a wet and then dry powder because of the crystallization of the sPS. The polymerization proceeds further in the solid phase and the conversion increases. Thus, a homogeneous high viscous period does not occur as in the radical polymerization of styrene.

However, as reported in our previous articles,⁵ the original sPS product has a complex morphology. It may form a gel with the monomer itself in the bulk polymerization. Also, the final polymerization conversion limit is 10%. During the polymerization, the greater the metallocene activity and thus the polymerization rate, the more critical is the control of gel formation. Strong agitation is of the utmost importance to avoid this harmful network structure. Using a proper type of agitator and the right stirring speed, powdery sPS can be obtained under appropriate polymerization conditions. In addition to easy posttreatment, a powdery product is propitious to run the polymerization up to a high conversion and to develop an industrial process.

Few articles have dealt with the kinetics of this polymerization. By tracing a temperature change during the bulk polymerization, Liu et al.⁶ and Shan et al.⁷ investigated polymerization kinetics in a resonance ionization mass spectrometry process. However, the resulting product is in the block form. Chien and Salajka⁸ also studied syndiotactic solution polymerization kinetics, which concentrated on the dilute solution polymerization. Our work focuses on powdery sPS, and we report on full-range polymerization kinetic studies on the above-mentioned bulk polymerization process in which highly active tertiary metallocene catalyst systems [$\text{Cp}^*\text{TiX}_3/\text{MAO}/\text{TIBA}$ ($\text{X} = \text{Cl}, \text{OPhOMe}$)] are used.

EXPERIMENTAL

Materials

The styrene used was polymerization grade; it was purified by successive washing over water and NaOH solution, storage on CaH_2 , and distilling under nitrogen at reduced pressure just before use. The triisobutyl aluminum (TIBA) solution (60 g Al/mL) was provided by Shanghai Gaoqiao chemical plant and used without further purification. Toluene was distilled after refluxing over potassium for 48 h just before use. MAO (10

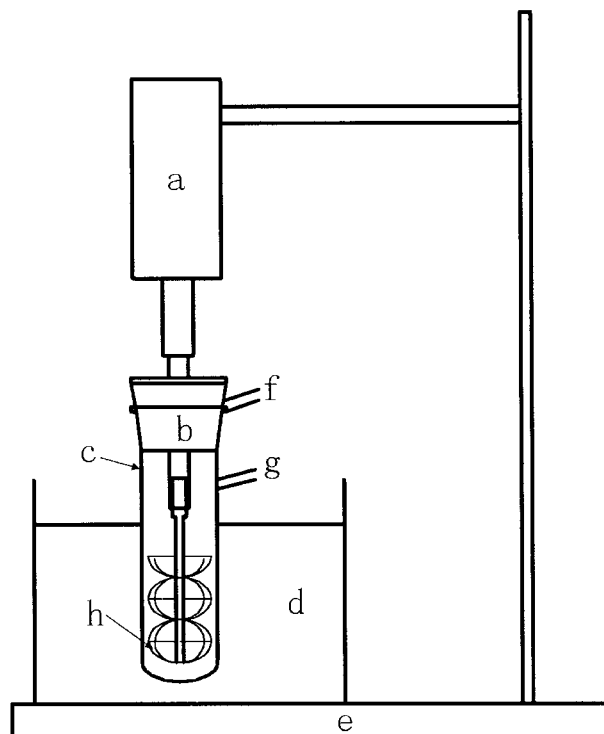


Figure 1 A schematic plot of the polymerization apparatus.

wt % toluene solution) was purchased from Albe-marle Corporation and used without further treatment. The Cp^*TiCl_3 and $\text{Cp}^*\text{Ti}(\text{OPhOMe})_3$ were supplied by the Shanghai Research Institute of Petrochemical Technology and used in their toluene solution. The overall concentration of toluene in the polymerization system is less than 0.5%, so the polymerization is still characterized by the bulk process.

Polymerization

A 100-mL Sulenck tube equipped with an impeller was designed for this polymerization, as shown in Figure 1. Several agitators in different shapes and with various stirring speeds were used for good mixing and a strong shear to produce a powdery product. Before polymerization, the glass tube was evacuated and charged many times with highly pure N_2 . The styrene, TIBA, MAO, and Cp^*TiCl_3 solutions were successively added through syringes. After a given time, the polymerization was stopped by the addition of acidified ethanol. The resulting polymer was weighed, washed with ethanol several times, filtered, and dried in a vacuum at 80°C to a constant weight.

Table I Effect of Agitator Type (40-mm Diameter)

Agitator	Polymer Morphology	Conversion (%)
Two-screw ribbon anchor	Powder	50.21
Symmetry frame anchor	Gel + powder	<10
Asymmetry frame anchor	Gel + powder	<10
Inner and outer two-screw ribbon anchor	Gel	<10
Multilayer anchor	Gel	<10

Polymerization conditions: $[Cp^*TiCl_3] = 1.2 \times 10^{-4} M$, MAO/Ti = 400, Al/Ti = 800, $T_p = 60^\circ C$, 2 h, 800 rpm.

The polymerization conversion was calculated from the solid content. According to the experimental results as shown in Table I, a two-screw ribbon-anchor agitator with an agitation speed of more than 800 rpm was adopted in the kinetic study.

Characterization

The intrinsic viscosity ($[\eta]$) was measured by a modified Ubbelohde viscometer at $135 \pm 0.2^\circ C$ using 1,2-dichlorobenzene (DCB) as a solvent, and the viscosity-average molecular weight (M_η) was calculated by the Mark-Houwink equation:

$$[\eta] = K \times M^\alpha$$

where the constants K and α were taken from atactic PS at $135^\circ C$ in DCB, in which $K = 1.38 \times 10^{-4}$ and $\alpha = 0.7$. The polymer morphology was observed with an S-600 SEM. The syndiotacticity was approximately replaced by an insoluble ratio in 2-butanone. The crystallinity of the sPS sample was measured by DSC with the same method as described in a previous article.⁵

RESULTS AND DISCUSSION

Two Different Morphologies: Powder and Gel

Using the two-screw ribbon-anchor agitator, a series of experiments were done in the Sulenck tube at different agitation speeds. It was found that when the agitation speed is below 800 rpm, the polymer product is a gel-like block, as seen in the micrographs shown in Figure 2. In this case, the syndiotacticity is higher than 95.0%, but the crystallinity of the polymer is less than 2%. However, when the speed exceeds 800 rpm, a product with a powdery morphology can be obtained, although its syndiotacticity is almost the same as the gel-

like product and the crystallinity of the polymer is higher than 50%.

Powder and gel are two distinct polymer morphologies in sPS production. When the polymer

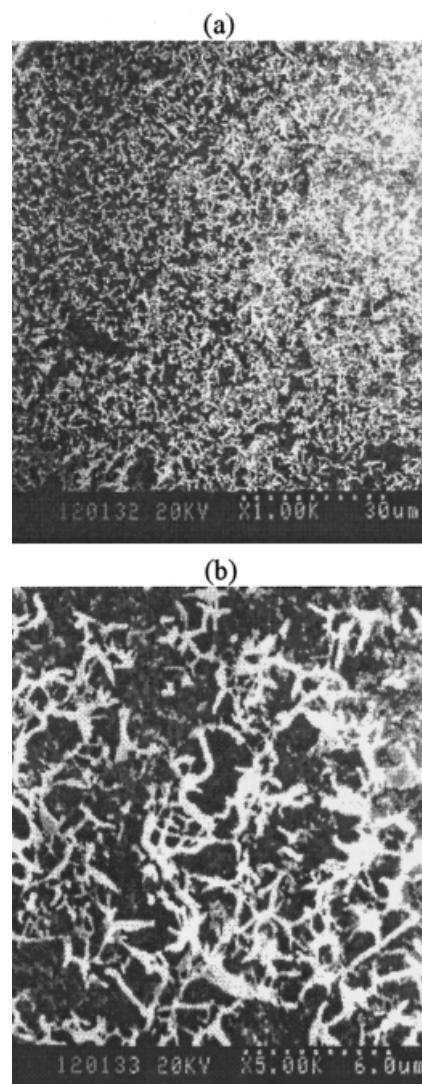


Figure 2 SEM photos of the sPS gel.

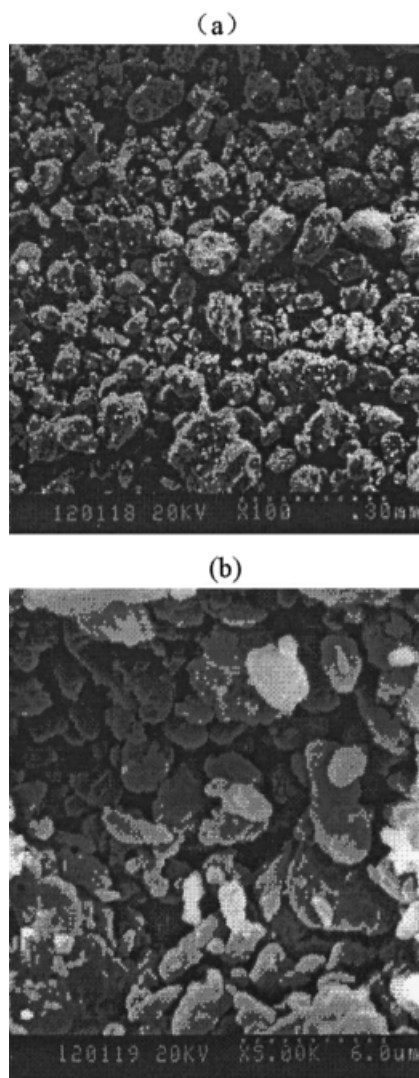


Figure 3 SEM photos of the powdery sPS.

takes the morphology of a powder, the gel has been avoided.

It can be seen clearly from Figure 2 that the gel has a network structure. A large amount of monomer is swollen in this network and the reaction mixture becomes a solid block at around 10% conversion. Serious problems in the mixing and heat transfer result in the loss of control of the polymerization. On the other hand, as shown in Figure 3, the powdery sPS is highly porous and has an irregular shape. Each particle is aggregated by many small nuclei. The particles have much higher crystallinity than the gel, so a small amount of monomer is swollen in the particles. The final conversion of polymerization can reach more than 80%. The comparison of the particles and gel polymerization performance is summa-

Table II Difference Between Two Morphologies of sPS

	Particle	Gel
Final conversion	High	Low
Viscosity in reactor	Low	High
Crystallinity	High	Low
Agitation shear needed	High	Low

rized in Table II. Therefore, a polymerization process to produce a powdery sPS is really feasible for industrialization and the polymerization kinetics is valuable.

Influences of Metallocene Types

Figures 4 and 5 show the kinetic behavior of two kinds of metallocene catalysts, $\text{Cp}^*\text{Ti}(\text{OPhOMe})_3$ and Cp^*TiCl_3 . All of the curves of monomer conversion versus the reaction time (Fig. 4) are S shaped. It is obvious that the activity of $\text{Cp}^*\text{Ti}(\text{OPhOMe})_3$ is much higher than the activity of Cp^*TiCl_3 . The beginning time of acceleration period with the previous catalyst is earlier and the final conversion is much higher.

The S-shaped kinetic curves observed in this work are apparently similar to the Tromsdorff effect in radical precipitation polymerization, but

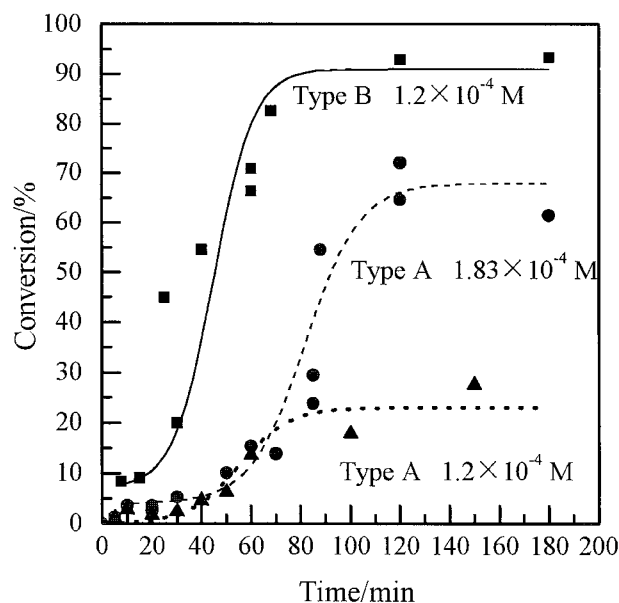


Figure 4 The time evolution of the polymerization conversion using different kinds of metallocene catalysts.

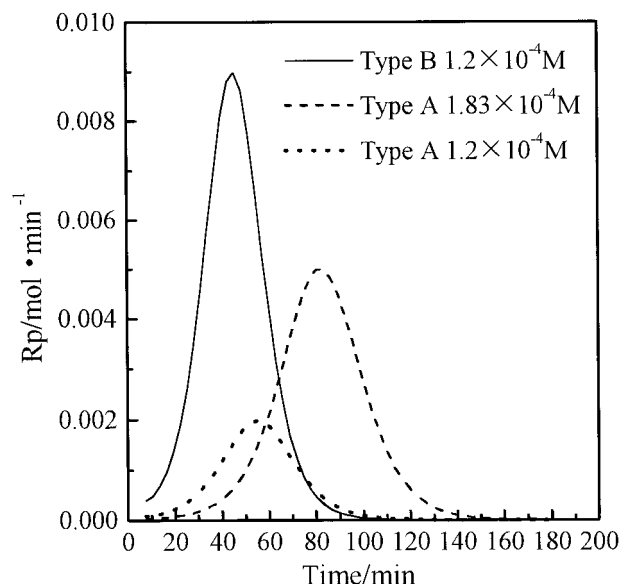


Figure 5 The time evolution of the polymerization rate using different kinds of metallocene catalysts.

the reason is quite different. The reason for the S curve occurring in the polymerization might lie in the following two facts. First, according to our previous research on the nucleation mechanism and particle morphology,⁵ the syndiotactic bulk polymerization processes can be divided into five stages: macromolecular chain formation in the homogeneous phase, macromolecular chain crystallization and precipitation, splaying multilayer lamellae formation, wet particles agglomeration and dispersion, and dry particles fluidization. Once the particle phase is formed from the mixture phases, the polymerization is in progress in the two phases. The kinetic parameters on the particle phase are different from those on the continuous phase. The S-shaped kinetic curve might be caused by the sum of the two-phase polymerizations. Second, the temperature of the reaction mixture might rise after the conversion is more than 20%. Because the reaction mixtures become a wet powder during this stage, the polymerization heat has to transfer through the continuous gas phase rather than through the liquid phase. The heat transfer rate may not keep up with the reaction rate; thus, the temperature in the particle phase increases, leading to the acceleration of the polymerization.

The changing rule of the M_n of the sPS powder was observed in the bulk polymerization, as shown in Figure 6. The molecular weight goes through an increasing–decreasing–increasing

change during the polymerization. In catalyst type B, the M_n of the obtained sPS samples decrease from about 400,000 to 150,000 in the middle of the polymerization and then rally at the end of the polymerization. The decreasing period of the molecular weight appears at the acceleration period of polymerization, as shown in Figure 7. This phenomenon may also result from the temperature rising inside the powder discussed above. A large amount of macromolecules with relatively small molecular weight is produced in a short period of time and this makes the average molecular weight decrease.

Influences of Cp^*TiCl_3 Concentration

The influence of the Cp^*TiCl_3 concentration on the conversion–time and polymerization rate–time curves are shown in Figures 8 and 9. An increase in the metallocene concentration causes the final monomer conversion to rise and the activity to be maintained longer. When the concentration grows to 1.83×10^{-4} mol/L, the final conversion is more than 60%. However, if the concentration is less than 1×10^{-4} mol/L, the final conversion is less than 10%.

The different molecular weight versus time curves at different metallocene concentrations are shown in Figure 10. The higher the Cp^*TiCl_3 concentration is, the more active centers that are

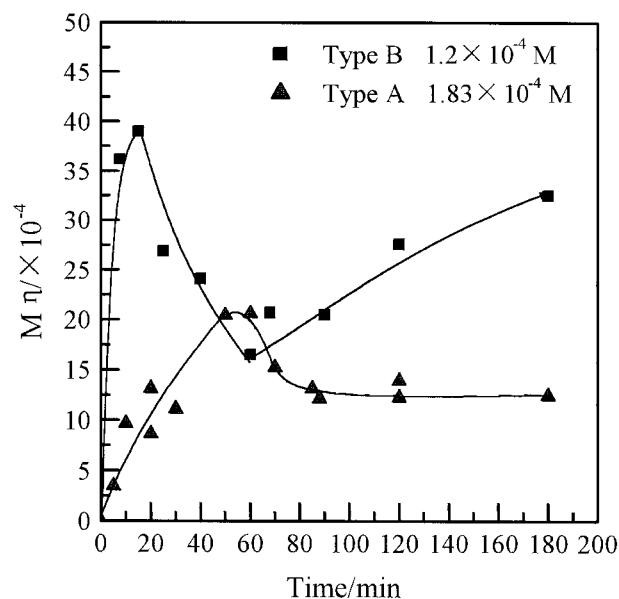


Figure 6 The time evolution of the viscosity-average molecular weight using different kinds of metallocene catalysts.

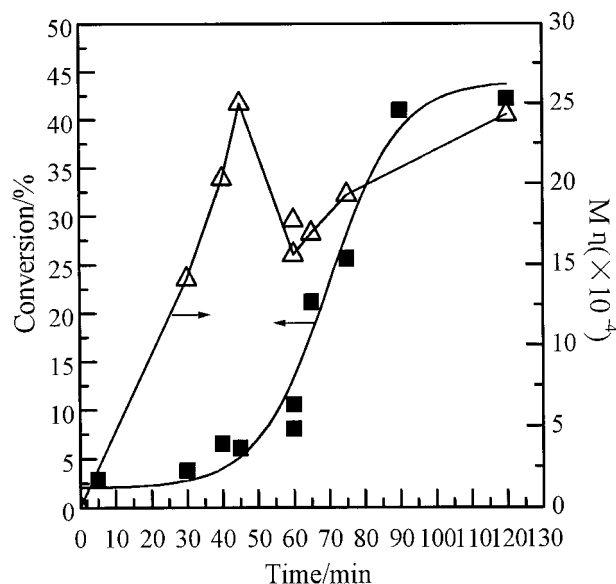


Figure 7 The typical time evolution polymerization conversion and viscosity-average molecular weight curves.

formed and thus the lower the M_n values of the obtained sPS samples. When the Cp^*TiCl_3 concentration is $0.9 \times 10^{-4} \text{ M}$, the acceleration does not occur and no obvious decrease of the M_n is observed.

Influences of Polymerization Temperature

Figure 11 gives conversion–time curves at various polymerization temperatures. The reaction tem-

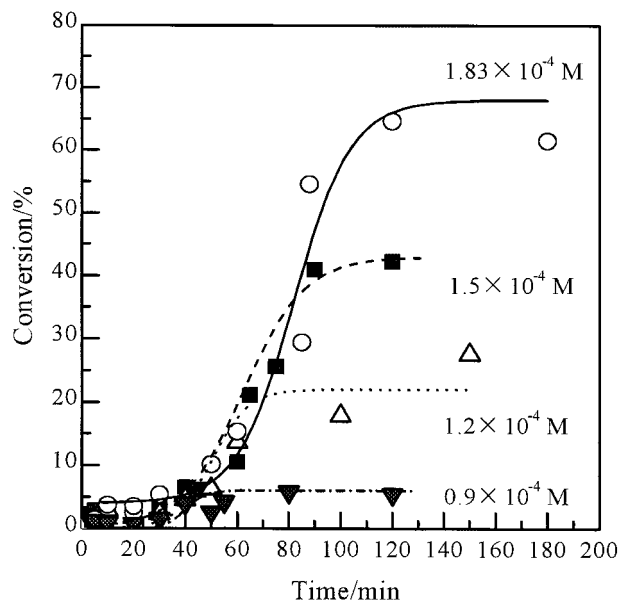


Figure 8 The time evolution of the polymerization conversion at different Cp^*TiCl_3 concentrations.

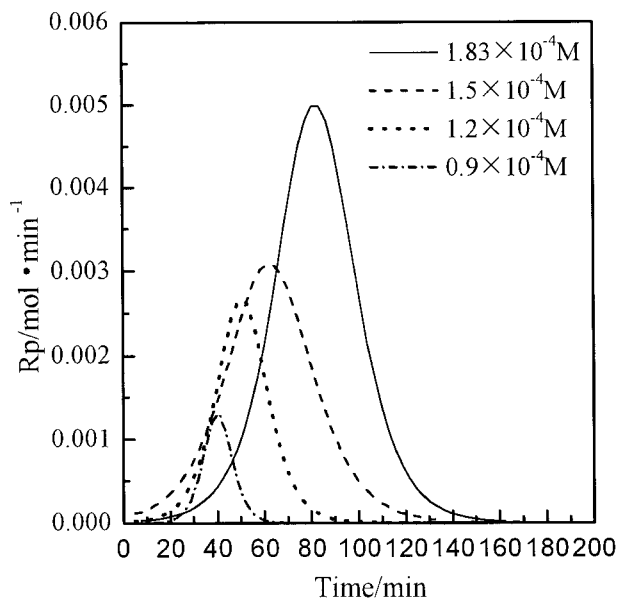


Figure 9 The time evolution of the polymerization rate at different Cp^*TiCl_3 concentrations.

perature also has a strong effect on the kinetic behavior of syndiotactic bulk polymerization of styrene. When the temperature is at 50°C , the final conversion of the monomer is less than 10%. However, if the temperature reaches 70°C , then the final conversion will be more than 80%. Moreover, at a high temperature the onset point of the

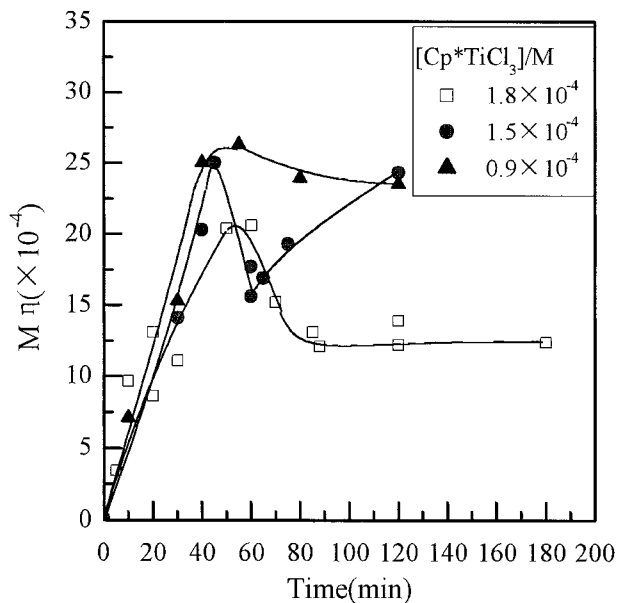


Figure 10 The time evolution of the viscosity-average molecular weight at different Cp^*TiCl_3 concentrations.

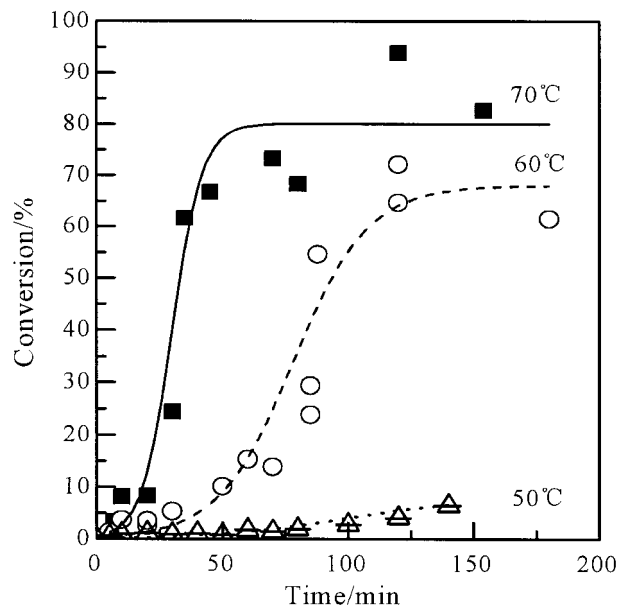


Figure 11 The time evolution of polymerization conversion at different polymerization temperatures.

acceleration in the kinetic curve is brought forward obviously whereas at a low temperature the kinetic curve is close to a linear line. In addition to the final conversion and the onset point of the acceleration, as shown in Figure 12, the maximum polymerization rate increases greatly with the rising of the reaction temperature. Figure 12 shows the polymerization rate curves at different

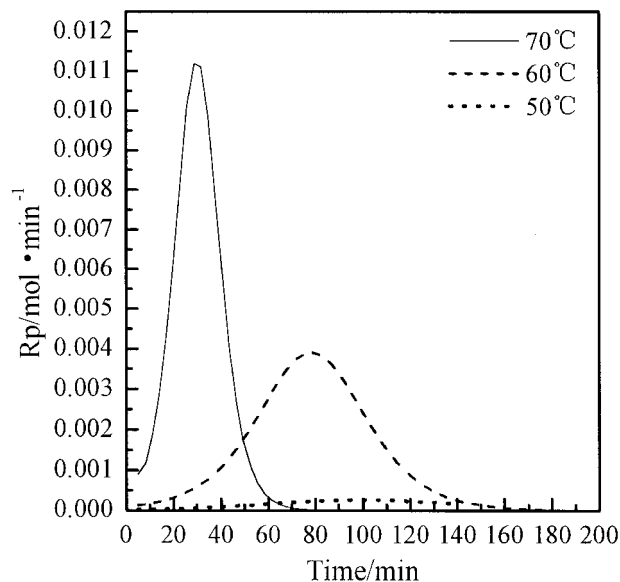


Figure 12 The time evolution of the polymerization rate at different polymerization temperatures.

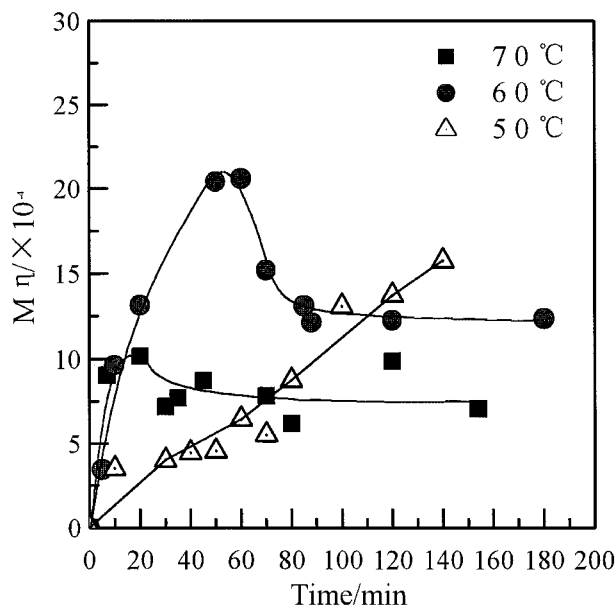


Figure 13 The time evolution of the viscosity-average molecular weight at different polymerization temperatures.

polymerization temperatures. It can be observed that at a high temperature the catalyst's activity in the initial period of polymerization increases very fast; however, it lasts a very short time because of the serious chain transfer reactions and deactivation reactions. Furthermore, the drastic change of catalyst activity is harmful to the control of the polymerization process. Considering all these factors, the best polymerization temperature is chosen to be 60°C.

The molecular weight is greatly influenced by the polymerization temperature, as shown in Figure 13. High temperature leads to low molecular weight; for example, the M_η is only less than 100,000 when the polymerization temperature is at 70°C. However, when the polymerization is done at 50°C, the molecular weight grows linearly with the polymerization temperature.

Influences of MAO/Ti Ratio

MAO is a necessary cocatalyst for this metallocene catalytic system. It participates in the formation of active centers.^{9,10} The effect of the MAO/Ti ratio on the conversion–time curve and polymerization rate–time curves are shown in Figures 14 and 15, respectively. It can be found that more MAO results in a higher final conversion. The MAO/Ti ratio does not affect the lives of the catalysts. The onset points of acceleration at different MAO/Ti ratios are almost the same.

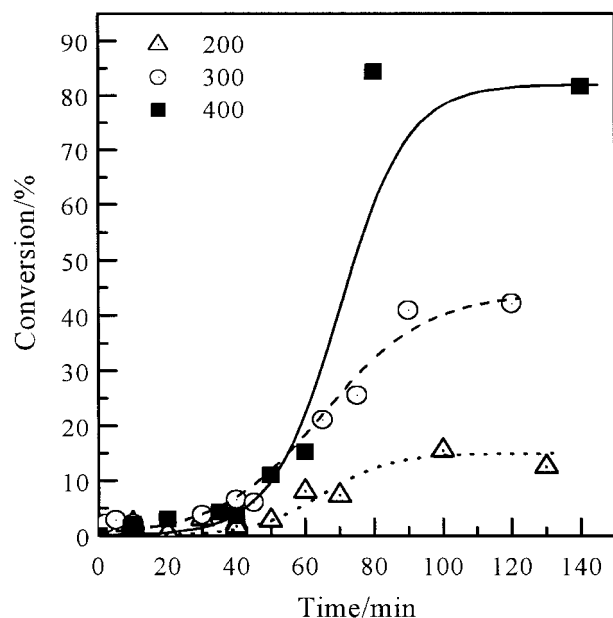


Figure 14 The time evolution of the polymerization conversion at different MAO/Ti ratios.

The MAO/Ti ratio influences the molecular weights of the sPS samples through the number of active centers that are formed. At a high MAO/Ti ratio, such as 400, the molecular weight is relatively lower, as shown in Figure 16.

Influences of TIBA/Ti Ratio

The effect of the TIBA/Ti ratio on the conversion-time curves and polymerization rate-time curves

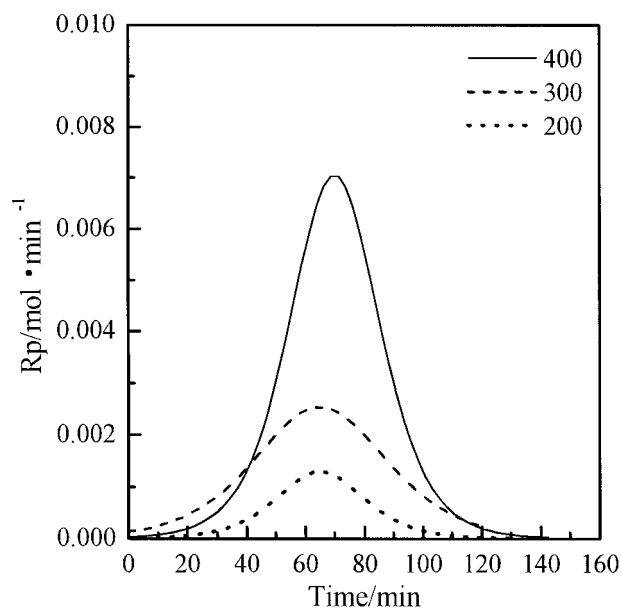


Figure 15 The time evolution of the polymerization rate at different MAO/Ti ratios.

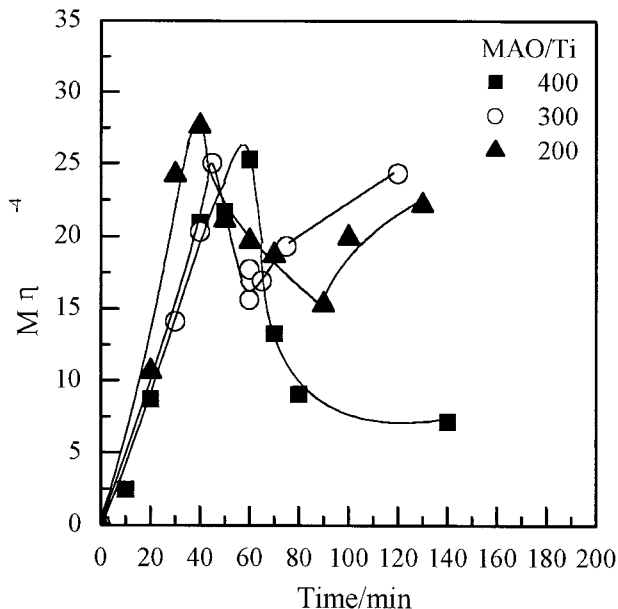


Figure 16 The time evolution of viscosity-average molecular weight at different MAO/Ti ratios.

are shown in Figures 17 and 18, respectively. It can be observed that at a TIBA/Ti ratio of 100, the polymerization system shows higher activity than the other TIBA/Ti ratios. This agrees well with the report that 25–35 mol % of free TIBA is necessary for the titanocene/MAO catalyst to exhibit the highest activity in styrene polymerization.¹¹ The reason may lie in the fact that adding the

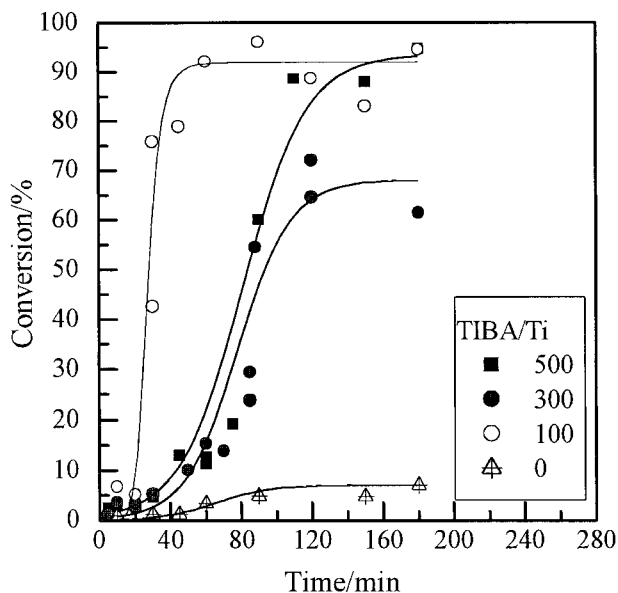


Figure 17 The time evolution of the polymerization conversion at different TIBA/Ti ratios.

right amount of TIBA makes the metallocene form the largest proportion of the active Ti^{3+} catalyst site. However, alkylaluminum is also a good chain transfer agent for this polymerization. Thus, with the addition of more TIBA, the M_w of the polymer decreases, as shown in Figure 19.

CONCLUSIONS

Using a two-screw ribbon-anchor type agitator with an agitation speed exceeding 800 rpm, a powdery sPS can be prepared in a bulk precipitation polymerization with a $Cp^*TiX_3/MAO/TIBA$ ($X = Cl$ or $OPhOMe$) metallocene catalyst system. The gel-like sPS product was successfully avoided. A full-range kinetic study shows that the metallocene type, metallocene concentration, polymerization temperature, MAO/Ti ratio, and TIBA/Ti ratio have a strong influence on the polymerization kinetics. During the polymerization process, S-shaped conversion versus time curves can be observed, which is due to the two-phase polymerization mechanism and the overheating in particles during the wet powder period. It was also found that the viscosity-average molecular weight of sPS decreases greatly in the middle of polymerization, which further verifies that a higher reaction temperature may occur in the

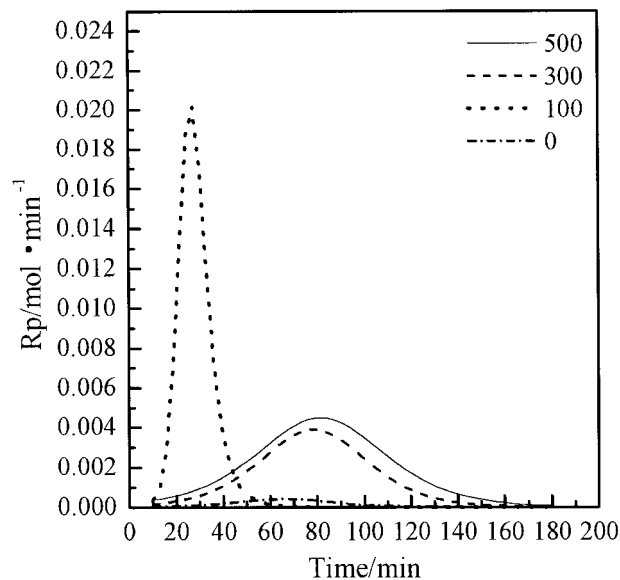


Figure 18 The time evolution of the polymerization rate at different TIBA/Ti ratios.

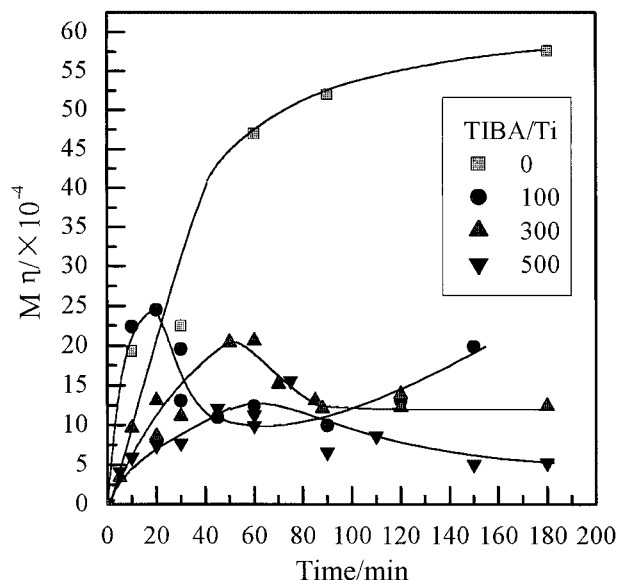


Figure 19 The time evolution of the viscosity-average molecular weight at different TIBA/Ti ratios.

particle phase in the wet powdery stage. Adding a kind(s) of inert solution with a low boiling point(s) to the bulk polymerization system can promote the removal of reaction heat, and then the polymerization can be carried out smoothly. Research work on this field is in progress.

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