

Kinetics of Slurry Phase Polymerization of Styrene to Syndiotactic Polystyrene with Pentamethyl Cyclopentadienyl Titanium Trimethoxide and Methyl Aluminoxane. I. Reaction Rate Analysis

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ABSTRACT: The kinetics of syndiospecific slurry polymerization of styrene in heptane has been investigated with pentamethyl cyclopentadienyl titanium trimethoxide [Cp*Ti(OMe)₃] catalyst with methylaluminoxane. The experimental studies at different styrene/heptane ratios indicate that no global gelation occurs at low styrene/heptane ratios even at high styrene conversion. The effective propagation rate constant tends to decrease as polymerization rate is increased at higher initial styrene concentrations. To analyze the effect of catalyst deactivation, a novel three-stage polymerization experiment has been designed and carried out where monomer is added during the polymerization. The experimental

results show that the catalyst activity is very high at the beginning of polymerization but it decreases significantly as catalyst sites are occluded in the solid phase. We also observe that the catalyst remains active for more than 3 h and the rate decay is not solely due to intrinsic catalyst deactivation. Our experimental data suggests that physical transport effects cause the decay in the polymerization rate. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2132–2137, 2003

Key words: syndiotactic polystyrene; polymerization kinetics; metallocene catalyst; gels

INTRODUCTION

Syndiotactic polystyrene (sPS) is emerging as one of the new engineering thermoplastic polymers derived from inexpensive ordinary monomer (styrene) with excellent thermal and chemical resistances. sPS is a highly crystalline polymer with a melting point of about 270°C. Since Ishihara et al.^{1,2} reported the synthesis of highly syndiotactic polystyrene using titanium catalysts, there have been a large number of publications on the synthesis of sPS using various metallocene catalysts (for review, see refs. 3 and 4). In general, monotitanocene catalysts with methylaluminoxane (MAO) are very effective in obtaining highly syndiotactic polystyrene.

When styrene is polymerized to sPS in bulk with a metallocene catalyst, the entire reaction mixture develops into a global gel with an increase in conversion, making the agitation practically impossible with ordinary means of mixing. The use of screw-type reactors or self-cleaning reactors are described in patent literature.^{5,6} Interestingly, however, the polymerization

continues even in the solid phase (monomer swollen polymer phase) to near complete conversion of styrene. However, very little has been reported on the polymerization kinetics and the physical changes the reaction mixture undergoes during polymerization. It is probably because very low styrene concentrations in solvent (e.g., toluene) were commonly used in many of the reported experimental studies to examine the intrinsic catalyst performance without any solid precipitation effect.

In this work, we report new experimental results of the sPS polymerization kinetics with pentamethyl cyclopentadienyl titanium trimethoxide [Cp*Ti(OMe)₃]/MAO catalyst system using heptane as a diluent. In particular, the effects of monomer concentration on the polymerization rate are analyzed through experimentation.

EXPERIMENTAL

Styrene (Aldrich, WI) and heptane were purified by vacuum distillation over CaH₂ and stored over activated alumina (Alcoa, TX). Polymerization experiments were carried out using 20 mL glass reactors. In a glove box, predetermined amounts of styrene, heptane, and MAO (10 wt % in toluene; Akzo Nobel (NY), Type 3A) were added into a reaction vessel. Then, a predetermined amount of Cp*Ti(OMe)₃ catalyst (Strem Chemicals, MA) in toluene was injected into

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TABLE I
Effect of Styrene/Heptane Ratio on Styrene Conversion and Gelation

Styrene/heptane (v/v)	Reaction time (min)	Conversion (%)	Remarks
1/9	10	91.3	No gelation
1/9	180	96.8	No gelation
2/8	10	93.0	Gelation
6/4	10	92.2	Gelation
8/2	10	88.6	Gelation
10/0	10	79.8	Gelation

the reactor. The initial reaction mixture was a homogeneous solution. In all the experiments, the amount of catalyst used for the polymerization was kept constant at 1.75×10^{-6} mol (or $0.165 \text{ mmol L}^{-1}$). Then, the glass reactor was immersed in a constant temperature bath. All the polymerization experiments were carried out at 70°C . [Although there was a possibility of temperature rise due to polymerization, the reactor temperature was not directly measured. Since the reactor volume is very small, our simple energy balance calculation result shows that the maximum possible temperature rise (i.e., adiabatic reaction) is less than 2°C . And hence, the actual temperature rise might have been much smaller because the reactor was immersed in the bath.] After polymerization, an excess amount of methanol was added to the reactor. The polymer recovered from the reactor was dried *in vacuo* and weighed for conversion measurement. The tacticity of sPS was measured by extraction in a boiling methylketone.

RESULTS AND DISCUSSION

The polymerization of styrene to sPS is characterized by the precipitation of sPS in the bulk liquid phase because of insolubility of sPS in styrene and most of the organic solvents. At low conversion, very small polymer particles are formed, but they quickly aggregate to larger particles. sPS is a highly crystalline polymer, and strong intermolecular interactions occur between styrene and polymer as styrene conversion increases, resulting in global gelation. The sPS gel is not a chemically crosslinked gel but a physical gel where monomer or solvent molecules are intercalated between polymer molecules. In bulk styrene polymerization, gelation commences at about 10–20% conversion of styrene. At very low styrene concentrations, the total amount of solid mass is too small to form a global sPS gel. Due to the formation of solid phase during the polymerization of styrene, it is of practical importance to understand the effect of solid phase on the rate of polymerization.

Effect of monomer concentration

In our study, we first investigated the effect of styrene/heptane volume ratio (S/H) on the polymeriza-

tion rate with the volume of a styrene/heptane mixture fixed at 10 mL. The polymerization temperature was fixed at 70°C . In all the experiments, MAO/Ti mole ratio and the catalyst concentration were fixed at 500 and $1.65 \times 10^{-4} \text{ mol L}^{-1}$, respectively. Table I shows the summary of experimental results. The syndiotacticity of the polymer (96–98%) was similar with the results reported by others.^{4,7} Since the catalyst concentration was relatively high, the polymerization rate was quite large and conversion increased rapidly in all the experiments. With the same catalyst concentration, Table I shows that at a given reaction time (e.g., 10 min), styrene conversion tends to decrease as styrene concentration is reduced. Also, it was observed in our experiments (visual observation) that gelation started faster as higher styrene concentration (i.e., smaller amount of heptane) was used.

We observed that for the initial styrene volume fraction larger than 0.2, the entire reaction mixture turned rapidly into a gel. With a further increase in monomer conversion, the entire reaction mixture turned into a hard solid phase. Interestingly, styrene conversion continued to increase even after the global gelation had occurred. It was found that at low styrene/heptane ratios (e.g., S/H = 1/9 or less), no gelation occurred even at very high styrene conversion. In this case, although the total solid content was only about 10% after the reaction, there was no separate liquid phase and the reaction mixture resembled a soft wet cake with solid polymer phase swollen by the liquid (heptane). The total volume of the reaction mixture remained nearly constant during the polymerization.

The measured styrene conversion data at different monomer volume fractions are shown in Figure 1. Here, f_s is the styrene volume fraction at the beginning of polymerization. In all the experimental runs, Figure 1 shows that styrene conversion rises to above 30% in 2 min of reaction time. (The conversion measurement in less than 2 min was not possible because it took

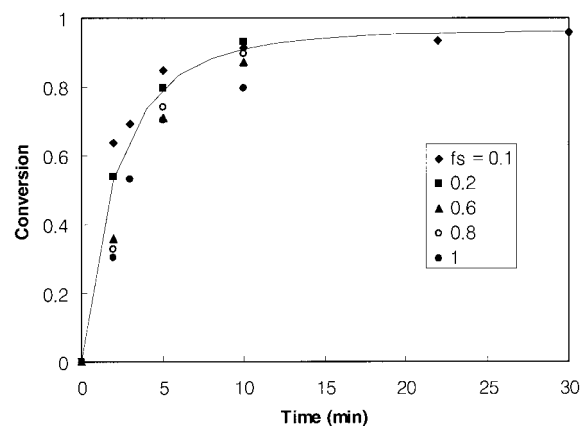


Figure 1 Styrene conversion at different styrene volume fractions.

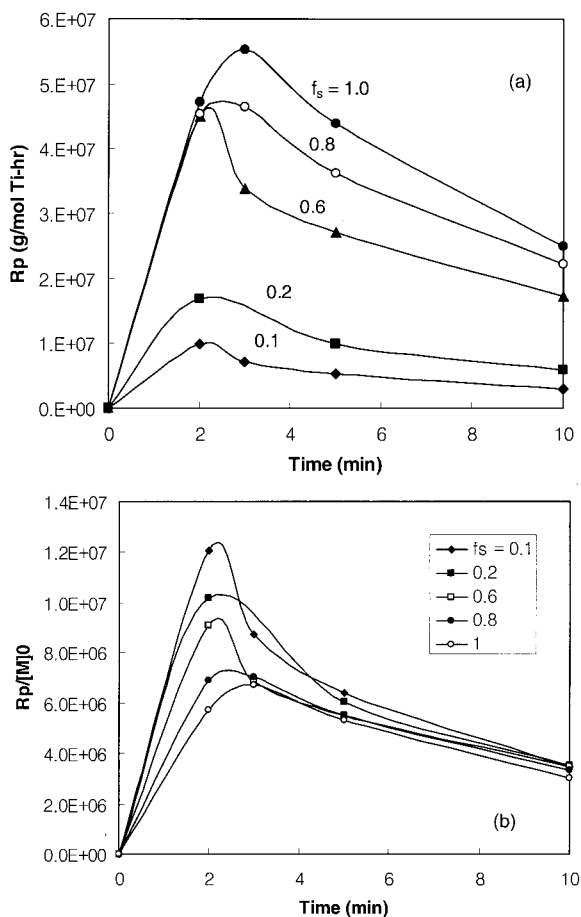


Figure 2 Effect of initial styrene concentration on polymerization rate (f_s = volume fraction of styrene at $t = 0$).

about 1 min for the reactor to reach a reaction temperature in the constant temperature bath.)

Figure 2(a) shows the polymerization rate profiles for different monomer volume fractions (f_s). Here, the polymerization rate (or catalyst activity) is expressed in g sPS mol-Ti⁻¹ h⁻¹. As expected, the polymerization rate is higher at higher styrene concentration, f_s . The polymerization rate declines as monomer is consumed. The polymerization rates normalized by the initial monomer concentration ($[M]_0$) is shown in Figure 2(b). It is interesting to observe in Figure 2(b) that the maximum polymerization rate per mole of styrene is the largest at the lowest styrene concentration, although the difference between the runs diminishes after 10 min.

Reaction rate analysis

Let us consider the polymerization rate (mol L⁻¹ h⁻¹) represented by the following equation:

$$R_p = -\frac{d[M]}{dt} = k_p[M][C^*] \quad (1)$$

where $[M]$ is the monomer concentration and $[C^*]$ is the active catalyst concentration. In a batch polymerization experiment, the polymerization rate decreases with time as styrene is polymerized. If we assume that catalyst deactivation effect is negligible, eq. (1) can be integrated to

$$-\frac{\ln(1-x)}{[C^*]_0} = k_p t \quad (2)$$

where $[C^*]_0$ is the initial catalyst concentration. Then, by plotting $-\ln(1-x)/[C^*]_0$ vs time, a straight line should be obtained and the propagation rate constant is determined from the slope of the line. Figure 3(a) (symbols) shows the test of eq. (2) for $f_s = 0.1$ (S/H = 1/9). Here, we assume that all the titanium sites are active for the polymerization. Notice that eq. (2) is valid only during the initial reaction period (up to 85% conversion or less than 5 min, marked by a dotted line) and the data points after 5 min deviate significantly from eq. (2). Using the linear portion of the curve, the propagation rate constant is estimated as $k_p = 1.432 \times 10^5$ L mol⁻¹ h⁻¹.

Equation (2) was derived with an assumption that no catalyst deactivation occurred. If we assume that catalyst activity decreases following the first-order deactivation kinetics, the polymerization rate is expressed as

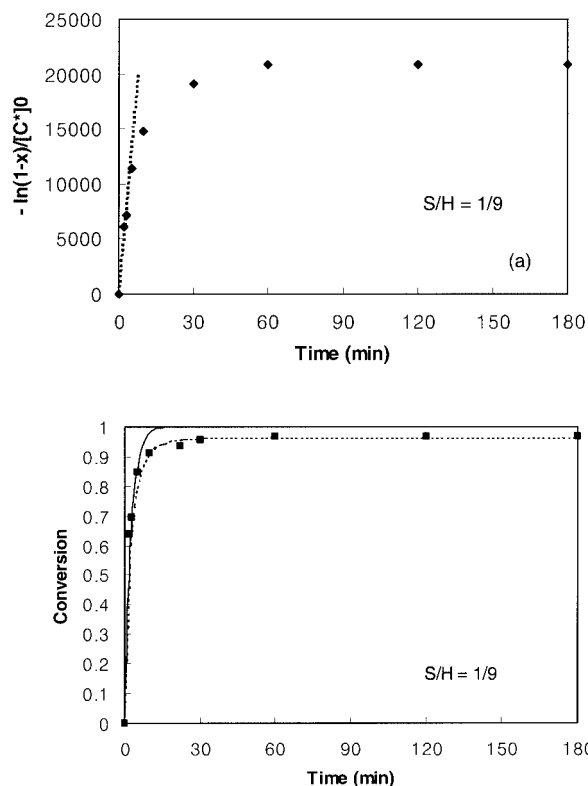


Figure 3 Test of eq. (2): styrene/heptane (v/v) = 1/9.

$$\tilde{R}_p = -\frac{d[M]}{dt} = k_p[M][C^*]_0 \exp(-k_d t) \quad (3)$$

where k_d is the first-order deactivation rate constant. Equation (3) is integrated to

$$-\ln(1-x) = \frac{k_p}{k_d}[C^*]_0(1 - e^{-k_d t}) \quad (4)$$

Equation (4) indicates that as $t \rightarrow \infty$, $-\{\ln(1-x_\infty)/[C^*]_0\} \rightarrow k_p/k_d$. Therefore, once the propagation rate constant is estimated from the initial reaction rate data, the deactivation rate constant can be estimated from the final conversion data. From Figure 3(a), the deactivation rate constant is estimated as $k_d = 6.8 \text{ h}^{-1}$. The rate constants in eq. (3) can also be estimated directly using the regression method: At 70°C and $[\text{MAO}]/[\text{Ti}] = 500 \text{ (mol/mol)}$, $k_d = 7.74 \text{ h}^{-1}$, $k_p = 1.56 \times 10^5 \text{ L mol}^{-1} \text{ h}^{-1}$. The dotted line in Figure 3(b) shows the calculated styrene conversion [with eq. (4)] and excellent fit of the experimental data has been obtained. The solid line in Figure 3(b) is the prediction of styrene conversion without catalyst deactivation effect. Notice that the conversion prediction without deactivation effect also gives a reasonable fit of the data up to about 70% conversion, but the nondeactivating kinetic model yields the overestimated monomer conversion at the monomer conversion larger than 85%. Here, it was brought to our attention that at very high conversions (e.g., >90%), the error might be present in conversion measurements because the amount of polymer sample recovered from the reactor was quite small. Although the deactivation model seems to give a better prediction of conversion than the nondeactivation model, it would be fair to say from Figure 3(b) that it is rather inconclusive to claim the validity of the deactivation model because the difference between the two models is not sufficiently large to discriminate them at high conversions. This issue is discussed in more detail in the next section.

Figure 4(a) shows the test of eq. (2) for five different S/H volume ratios. Here, the slope of each line corresponds to an effective propagation rate constant. Figure 4(b) is a plot of the effective propagation rate constants vs initial styrene volume fractions. Notice that the propagation rate constant decreases with an increase in the styrene volume fraction in the solution. Since it is unlikely that the intrinsic propagation rate constant is dependent on the monomer concentration, the results shown in Figures 4(a) and (b) suggest that the estimated rate constants are the effective rate constant masked by some other effects such as monomer mass transfer limitation in the solid phase.

Catalyst activity

In the foregoing analysis, the first-order catalyst deactivation model was assumed to fit the experimentally

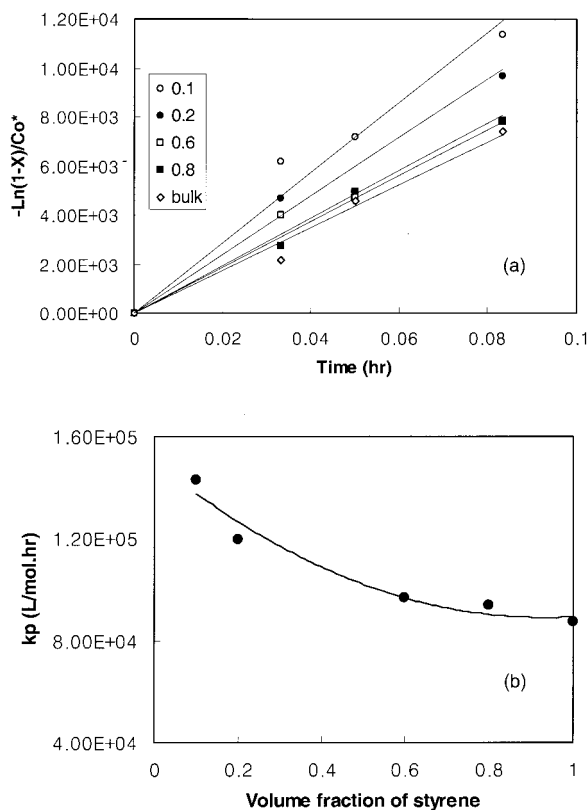


Figure 4 Test of first-order reaction kinetic model at different styrene volume fractions without catalyst deactivation.

measured styrene conversion data. The decrease in the polymerization rate is primarily due mainly to the depletion of monomer, but the catalyst deactivation may also be contributing. If no catalyst deactivation occurs, the rate decline should be solely due to the depletion of monomer and experimental data should be fit by eq. (2). But Figure 3(a) shows that eq. (2) fails to fit the data over the entire reaction period. Recall that with the inclusion of catalyst deactivation effect, the model fits the conversion profile quite well. With the catalyst deactivation rate constant estimated from the data, the catalyst deactivation half-life is calculated as about 5–6 min at 70°C . This means that after 1 h of reaction, the active site concentration becomes nearly zero.

In what follows, we examine the role of catalyst deactivation and see if the deactivation model is indeed valid or if there are some other effects that might also affect the reaction rate. We designed and performed the following three-stage polymerization experiments.

1. *Experiment 1 (period 1)*: One milliliter of styrene and 9 mL of heptane were mixed and reacted for 1 h with catalyst (Ti) concentration of $0.165 \text{ mmol L}^{-1}$. A 95.7% conversion (sPS yield = 0.87 g) was obtained. At $t = 1 \text{ h}$, the reaction mixture looked like a wet cake, but no gelation occurred and no separate liquid phase was present.

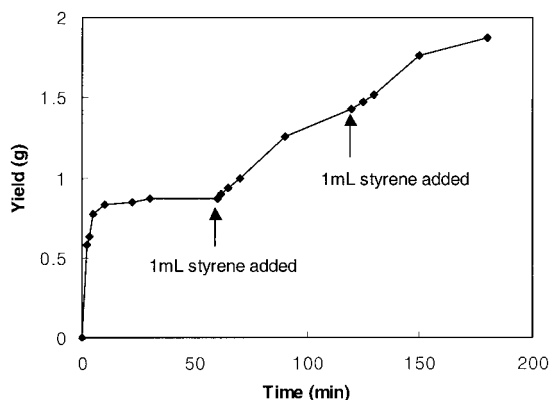


Figure 5 sPS yield profiles in experiments 1–3.

2. *Experiment 2 (period 2)*: One milliliter of styrene and 9 mL of heptane were mixed and reacted for 1 h (same as experiment 1). Then, 1 mL of styrene was added to the reactor and polymerization was continued for 1 h. During the reaction, no visible liquid phase was observed and the total volume of the reaction mixture remained nearly constant. After 2 h of polymerization, 1.43 g of sPS (57.3% conversion of added styrene) was obtained and the reaction mixture still looked like a wet cake.
3. *Experiment 3 (period 3)*: This experiment is an extension of experiment 2. After 2 h of polymerization, another 1 mL of styrene was added to the reactor and the polymerization was continued for one more hour (total reaction time = 3 h). Again, no separate liquid phase was present in the reaction vessel during the polymerization. A total 1.87 g of sPS was obtained after 3 h of reaction and the reaction product looked like a wet cake with a slight sign of gelation.

Figure 5 shows the experimentally measured sPS yield profiles. First of all, it is interesting to observe that the yield profile in the first period is very different from the yield profiles in the second and third periods. Notice that initially styrene conversion increases very rapidly to about 91% in less than 20 min. After 1 h, styrene conversion is 95.7% (0.87g). After 1 mL (0.909 g) of additional styrene monomer was added to the reactor at $t = 1$ h (experiment 2), the polymer yield increases with reaction time, albeit at much lower reaction rate than in the first 20 min reaction period. At $t = 2$ h, the overall polymer yield is 1.43 g, which corresponds to 78.7 % overall conversion (based on the total styrene charged in the reactor) or 59.0% conversion based on the amount of styrene at $t = 1$ h (i.e., 0.948 g).

After adding another 1 mL of styrene at $t = 2$ h (experiment 3), the polymerization still continues to occur, but again at a reduced reaction rate. The final polymer yield at $t = 3$ h is 1.87 g, which corresponds to 68.5% overall conversion or 34.0% conversion based on the amount of styrene at $t = 2$ h. Unlike in the first

period, the polymer yield steadily increases with time in the second and third periods.

Figure 6(a) shows the polymerization rate profiles [Fig. 6(b) is the blow-up view of the reaction rate during the first one hour reaction period]. Initially, the polymerization rate increases almost instantly to about $10,000 \text{ kg mol-Ti}^{-1} \text{ h}^{-1}$ followed by a rapid decrease to about $40 \text{ kg mol-Ti}^{-1} \text{ h}^{-1}$ in 30 min. After an extra 1 mL of styrene is added at $t = 1$ h, the polymerization rate increases again to $486 \text{ kg mol-Ti}^{-1} \text{ h}^{-1}$ and then gradually decreases to $234 \text{ kg mol-Ti}^{-1} \text{ h}^{-1}$ after 2 h. It should be pointed out that the polymerization rate at the beginning of the second period is far smaller than in the first period, albeit with almost the same monomer concentration in the reactor. The rate of decrease in the polymerization rate in the second one-hour period is also much slower than that in the first one-hour period. At the beginning of the third period ($t = 2$ h), the polymerization rate increases to $309 \text{ kg mol-Ti}^{-1} \text{ h}^{-1}$ and then decreases to $126 \text{ kg mol-Ti}^{-1} \text{ h}^{-1}$ at $t = 3$ h. It is also interesting to observe that in the third period, the polymerization rate does not reach its maximum right after the addition of 1 mL of styrene, but it takes some time to reach a maximum polymerization rate. It is probably because it takes time for the added monomer to diffuse to the heptane/styrene-swollen sPS solid phase.

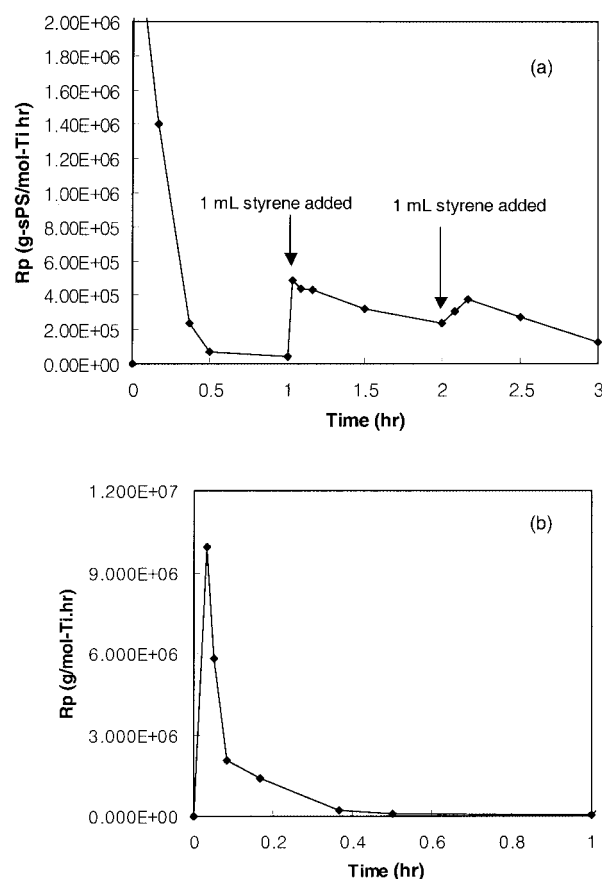


Figure 6 Polymerization rate profiles in experiments 1–3.

If the first-order deactivation rate constant $k_d = 7.74 \text{ h}^{-1}$ obtained from our earlier analysis is used, the calculated catalyst site concentration (assuming all the titanium sites are active) at $t = 1 \text{ h}$ is 0.04% of the initial site concentration. As such, practically no additional polymerization should occur after 1 h. However, the polymerization resumes after adding 1 mL of additional styrene, indicating that active catalyst site concentration must be much larger than 0.04%. Figures 5 and 6 clearly indicate that the catalyst is quite active even after 3 h of polymerization. A relatively small difference in the polymerization rates in the second and third period suggests that the catalyst deactivation is rather slow.

The experimental results presented in the above suggest that the decrease in the polymerization rate is not only due to both monomer depletion and catalytic site deactivation, but some other effects are also responsible. It is possible that the formation of solid phase with an increasing conversion greatly affects the mobility of monomer or the transport of monomer to active site, lowering the overall polymerization rate. Or the occlusion of the catalyst sites in the solid phase limits the access of monomer.

For example, we can consider the polymerization rate expression of the form

$$R_p = k_p[M]_s[C^*] \quad (5)$$

where $[M]_s$ is the styrene concentration at the catalyst site. Since a solid phase is formed immediately after the polymerization is started, the monomer concentration at the catalyst site may depend on the monomer concentration in the bulk phase ($[M]_b$). Initially, styrene in a solution may have a quick access to the active sites and hence the polymerization rate is very high as seen in Figure 5. As the amount of solid increases, a separate liquid phase disappears and the precipitated sPS is swollen by heptane/styrene. Therefore, the mobility of styrene in the solid phase decreases. Then, we can approximate the monomer concentration at the active sites $[M]_s$ by the relation

$$[M]_s = k_m[M]_b \quad (6)$$

Here, $[M]_b$ is the bulk phase monomer concentration. The parameter k_m represents some physical effects that cause the difference in the monomer concentrations at the catalyst site and in the bulk liquid phase. For example, k_m may be dependent on the amount of solid phase formed and the degree of swelling of the polymer. Then, the polymerization rate can be expressed as

$$R_p = k_p k_m [M]_b [C^*] \quad (7)$$

If catalyst deactivation effect is also included, eq. (7) can be expressed as

$$R_p = \eta k_p [M]_b [C^*]_0 \quad (8)$$

where both deactivation and physical transport effects are lumped into a single parameter η .

In our experiments, it was observed after 1 h of reaction that the entire reaction mixture looked like a wet cake. After 1 mL of additional styrene was added at $t = 1 \text{ h}$, styrene was quickly mixed with the reaction mixture, but the overall appearance of the reaction mixture did not change. It is not difficult to expect that the solid phase would affect the diffusion of monomer from the bulk phase to the solid phase where catalyst sites are present. It is also possible that the presence of solid phase and its morphology or structure (e.g., crystallinity) may affect the mobility of the monomer in the solid phase.

CONCLUSIONS

In this work, we investigated the polymerization rate phenomena at different styrene concentrations and observed that no global gelation occurred for the styrene/heptane ratio smaller than 0.1. The kinetics of diluent slurry polymerization of styrene to sPS has never been reported in literature. According to our experimental study, the apparent propagation rate constant tends to decrease with an increase in styrene concentration in the liquid phase. Our experimental data indicates that $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$ catalyst system sustains its activity for more than 3 h at 70°C but the presence of solid phase greatly affects the polymerization rate. It is also possible that the active sites are distributed in the solid and the liquid phases at different concentrations during the course of polymerization. The experimental data also suggests that the decrease in the polymerization rate is not solely due to the depletion of monomer and the active catalytic site deactivation, but probably is due to the mass transfer resistance exerted by the solid polymer phase. All these experimental observation may have to be incorporated into a kinetic modeling to estimate the polymerization rate and polymer properties.

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