

Syndiotactic Polymerization of Styrene: Study of Catalyst Components and Polymerization Conditions

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ABSTRACT: Syndiotactic polystyrene (s-PS) was prepared using monotitanocene catalyst of cyclopentadienyl titanium trichloride (CpTiCl_3) activated by methylaluminoxane (MAO). Solution polymerization was carried out in toluene using different polymerization conditions. Syndiotacticity index (SI) between 68 and 91.6% was obtained. Increasing Al/Ti molar ratio shows an increase in both conversion percentage and SI. The conversion increased linearly with increasing Al/Ti molar ratio in the range studied. The conversion reached to an optimum value of about 65% at styrene/Al molar ratio of 2.83, while no regular behavior of SI was observed with changing the ratio. Effect of temperature of the range 50–80°C on polymerization was studied. The

most favorable temperature for the polymerization regarding activity is 70°C; however SI decreased with temperature up to 80°C. H_2 value to 140 mL/100 mL solvent increased the productivity of the catalyst, however further increase of H_2 reduced the activity of the catalyst. Polymerization time of 15 to 125 min shows a decrease in activity. The decrease was sharper for about 30 min of polymerization than longer time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2216–2221, 2006

Key words: syndiotactic polystyrene; solution polymerization; metallocene; titanocene catalyst

INTRODUCTION

Syndiotactic polystyrene has interesting thermal and mechanical properties. Because of the properties, its use as engineering material has been claimed.^{1–3} In contrast to the isotactic polystyrene, the syndiotactic material shows a fast crystallization rate and high melting point of approximately 275°C, which are similar to those of some expensive engineering plastics. Thus, syndiotactic polystyrene has attracted much attention from polymer scientists.^{4–5}

Stereospecific polymerization of styrene was first reported by Natta et al.⁶ They prepared isotactic polystyrene (i-PS) employing a coordination catalyst derived from TiCl_4 and alkyl-aluminum. Synthesis of syndiotactic polystyrene was reported in 1986.⁷ The polymer could be prepared with high stereoregularity and yield by using organic and inorganic titanium compounds activated with MAO.^{7,8} Syndiospecific polymerization of styrene have greatly expanded the scope of scientific investigation on stereospecific polymerization.

Most of the polymerization catalysts, used to catalyze the syndiotactic polymerization of styrene are half sand-

wich metallocene, mainly titanium compound activated with MAO. Some derivatives of these compounds are also used, such as CpTiCl_3 , $\text{CpTiCl}_2(\text{OR})$, $\text{CpTi}(\text{OR})_3$, IndTiCl_3 , and $\text{IndTiCl}_2(\text{OR})$.^{9–13} Zirconium compounds and MAO are also able to produce syndiotactic polystyrene. Nevertheless, the Zr derivatives in general are less effective than Ti-based catalysts.^{1,14,15} Therefore monotitanocene/MAO catalysts have been found to be the most favorable for syndiospecific polymerization of styrene. The preparation of sPS with Ti-compounds supported in silica and magnesium carrier was also investigated.^{16,17} The activity and syndiospecificity of the catalysts are sensitive to various polymerization conditions, such as the polymerization temperature, the concentration of the catalyst and cocatalyst and their molar ratio, polymerization time, monomer concentration, and so on.^{18,19}

In the present work, catalytic system of CpTiCl_3 /MAO for syndiotactic polymerization of styrene was used. Investigation of the influence of different polymerization condition such as Al/Ti molar ratio, styrene/Al molar ratio, temperature, polymerization time, and H_2 concentration on the activity and syndiotacticity of the catalyst are studied.

EXPERIMENTAL

Materials

Anhydrous grade toluene was refluxed for at least 6 h over CaH_2 , distilled, and kept over sodium wire and

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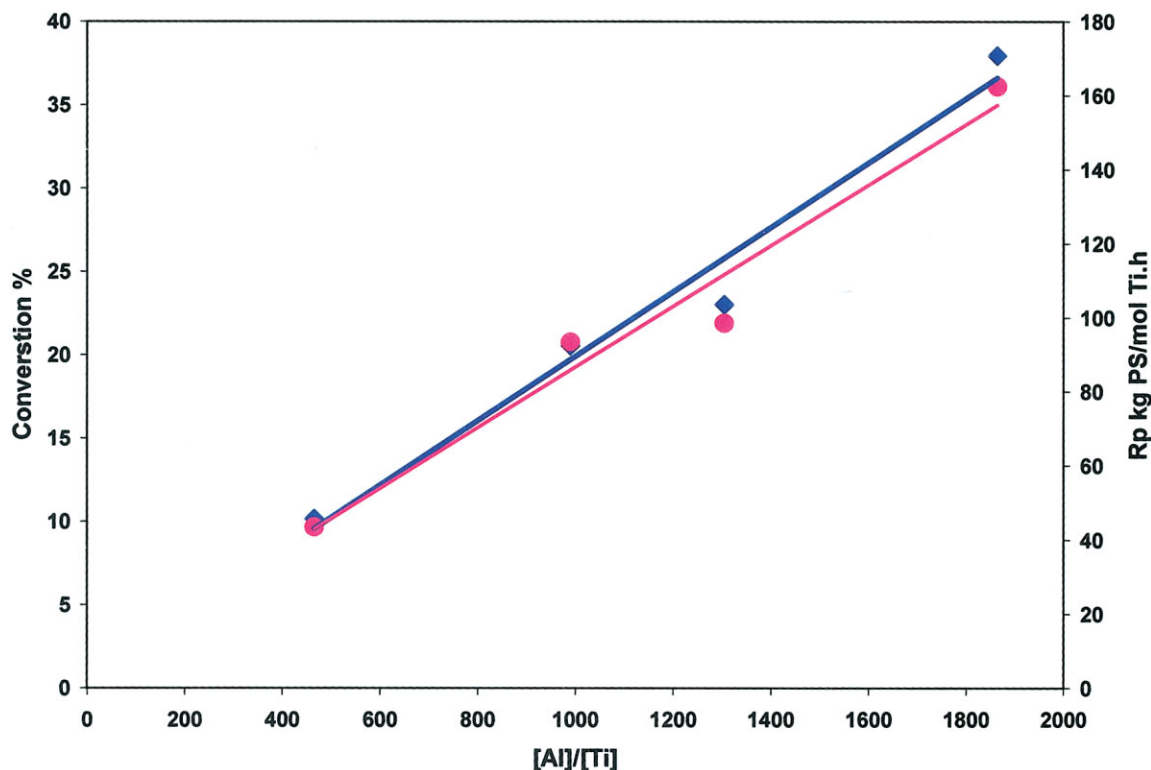


Figure 1 Effect of Al/Ti molar ratio on activity (●) and conversion percentage (■) of the $\text{CpTiCl}_3/\text{MAO}$ catalyst system. Polymerization conditions: $[\text{Ti}] = 1.7 \times 10^{-4}$ mol/L, toluene = 50 mL, time = 2 h, temperature = 60°C , $[\text{styrene}] = 1.45$ mol/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

activated molecular sieves type 4A and 13X. Styrene (99.0% Merck, Germany) was purified by distillation under reduced pressure over CaH_2 and finally stored under nitrogen in a refrigerator. The catalyst and methylaluminoxane (MAO) (10 wt % in toluene) were supplied by Aldrich Chemical Co. (Germany). 1,1,2,2-tetrachloroethane (Merck) was used without further purification. All catalyst and cocatalyst handling were carried out in controlled atmosphere of dry box or dry atmosphere of N_2 by means of a syringe.

Polymerization procedure

Polymerization was carried out in a three-necked flask placed in a thermostat under vacuum and flashed with dry argon several times. Toluene (50–100 mL), appropriate amount of MAO (in toluene), titanium compound (the catalyst) in toluene, and styrene were sequentially injected. The content of the reactor was stirred at a desired temperature and polymerized for a selected time, after which the reaction was quenched with the addition of approximately 25 mL 10% HCl in methanol. The polymer was precipitated using methanol (200 mL). The polymer was filtered and dried under vacuum at 60°C to constant weight.

Polymer characterization

The syndiotacticity index (SI) of the polystyrene was determined as the weight percentage of the insoluble

fraction after extraction of the polystyrene for 6 h with boiling butanone.^{4,18} ^{13}C -NMR spectra were obtained using Bruker 400 MHz AVANCE 400 NMR spectrometer with broad decoupling at 100 MHz. The polymer concentration was 5.0 wt % in 1,1,2,2-tetrachloroethane using 5-mm sample tube. Chemical shifts were referred internally to 1,1,2,2-tetrachloroethane and lock was provided by deuterated benzene. Spectra required more than 1300 scans (equivalent to 3 h) to obtain an appropriate signal-to-noise ratio.

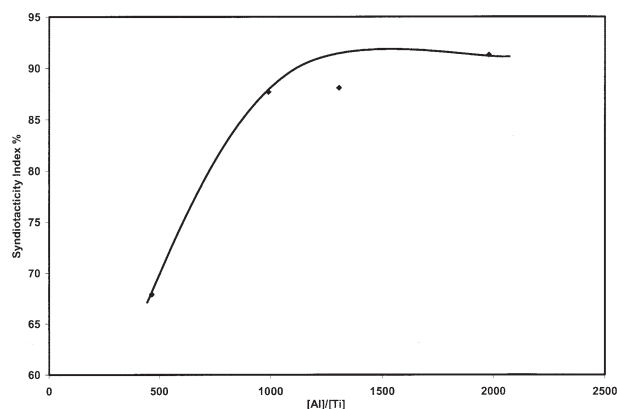


Figure 2 Effect of Al/Ti molar ratio on SI. Polymerization conditions as Figure 1.

TABLE I
Effect of Styrene/Al Molar Ratio on Polymerization Behavior (Concentration of Styrene Was Changed)

[Styrene]/[Al]	g PS	Conversion (%)	R_p [g PS/(mmol Ti h)]	SI (%)
2.35	3.54	48.71	111.25	81.7
2.83	3.87	53.29	146.05	84.1
3.53	2.88	39.66	135.89	81
4.71	2.20	30.25	138.17	78.2

Condition: [Al]/[Ti] = 1980, Toluene = 50 mL, time = 1 h, Temperature = 60°C

RESULTS AND DISCUSSION

Effect of cocatalyst concentration

The cocatalyst compound of Al plays an important role in the formation of catalytic active center for the polymerization. The effect of various amount of Al/Ti molar ratio on conversion, activity, and catalyst selectivity were studied; while the concentration of Ti was kept constant ($[Ti] = 1.7 \times 10^{-4}$ mol/L solvent). As expected, a higher Al/Ti molar ratio has a positive effect on both polymerization activity and syndiospecificity. The activity of the catalyst and conversion percentage increased linearly with increasing the Al/Ti molar ratio in the range studied (Fig. 1). The SI of the polystyrene obtained increased initially with increasing Al/Ti and remained unchanged, 87–90% (Fig. 2). Similar behavior has been reported.^{4,20} The active species in the s-PS polymerization has been

expected to be $[CpTiCH_3]^+ [MAOCl_2]^-$ (cationic species) produced via reduction reaction of Ti(IV) to Ti(III) in the presence of an Al-compound.^{4,21} Because of oligomeric nature of the MAO and weaker reducibility of aluminoxane, the reduction needs high concentration of the aluminum compound used as cocatalyst. Probably the aluminum alkyl group presented in MAO is more responsible to the reduction and formation of the active center.^{18,22} In this case, over reduction of Ti(IV) to Ti(II) may take place at very high Al/Ti ratio to reach the optimum activity of the catalyst that is reported.^{4,21,23,24}

Effect of monomer concentration

The relationship between the monomer/Al molar ratio on the conversion percentage and syndiotacticity of polystyrene was investigated; while the concentration

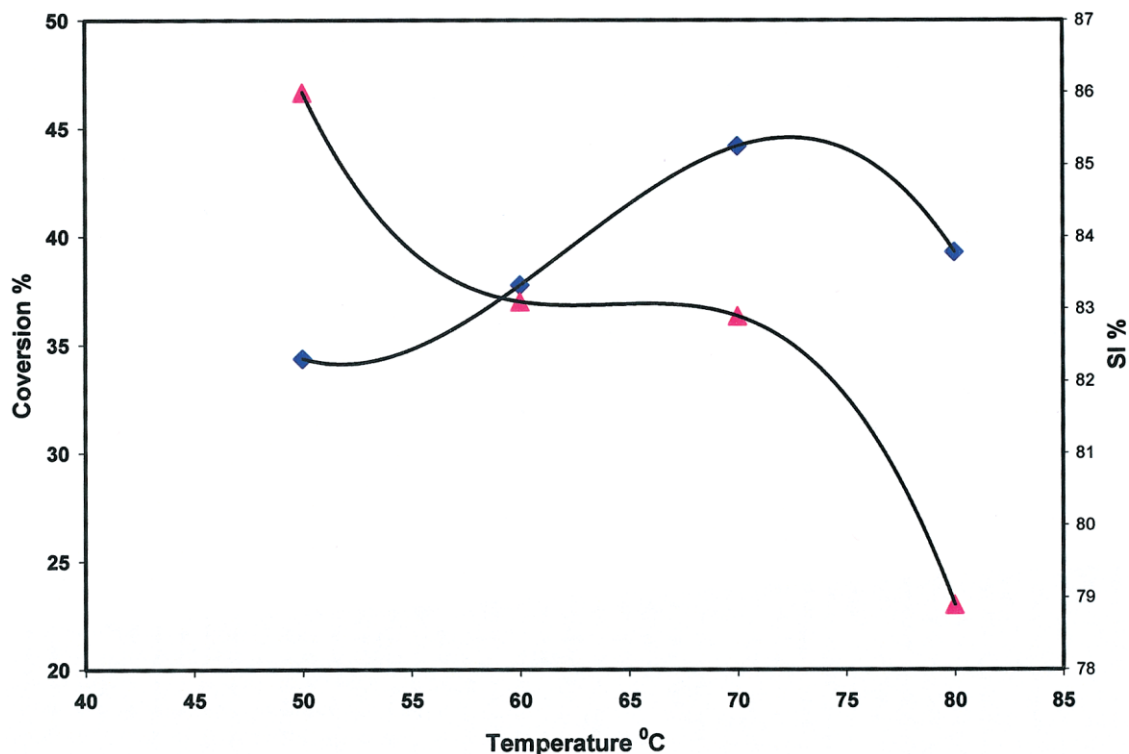


Figure 3 Effect of temperature on the polymerization behavior. Conversion (■) and SI (▲). Polymerization conditions: $[Ti] = 2.08 \times 10^{-4}$ mol/L Al/Ti = 1036, Toluene = 105 mL, time = 2 h. [styrene] = 0.76 mol/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

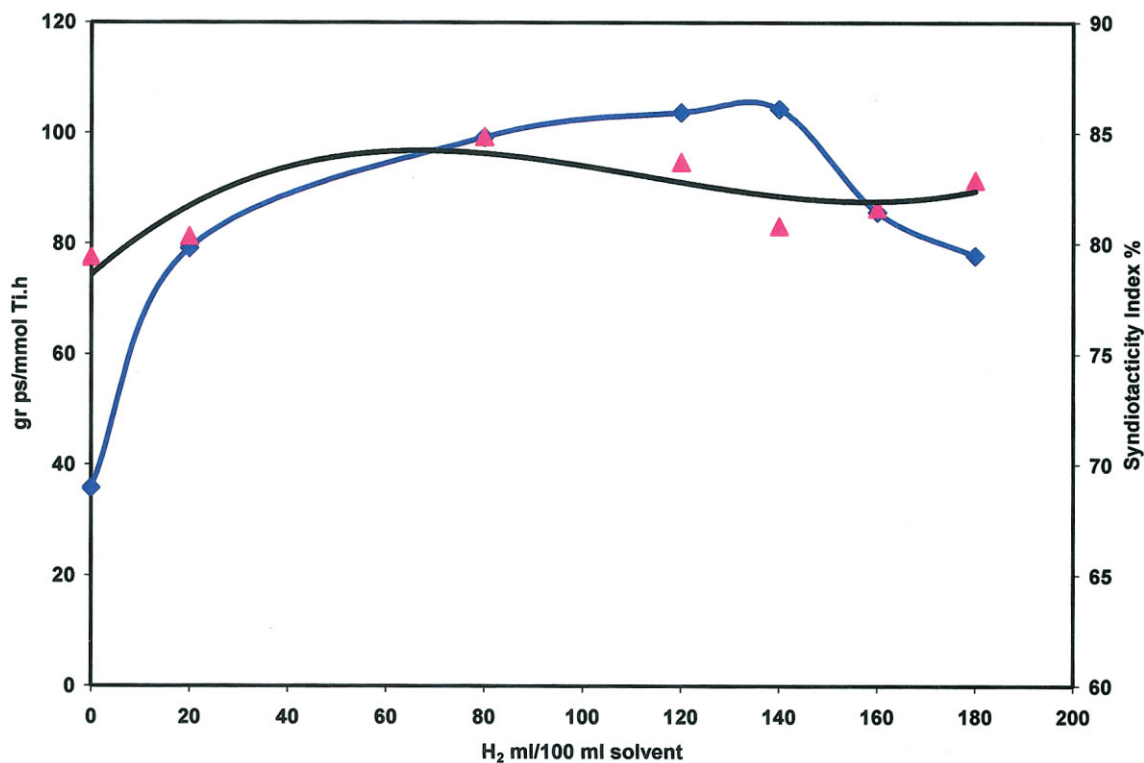


Figure 4 Effect of H₂ on activity (■) and syndiotacticity index (▲) of the polymer obtained, Polymerization conditions: [Ti] = 4.42×10^{-4} mol/L, Al/Ti = 928, toluene = 50 mL, time = 2 h, temperature = 60°C, [styrene] = 1.45 mol/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

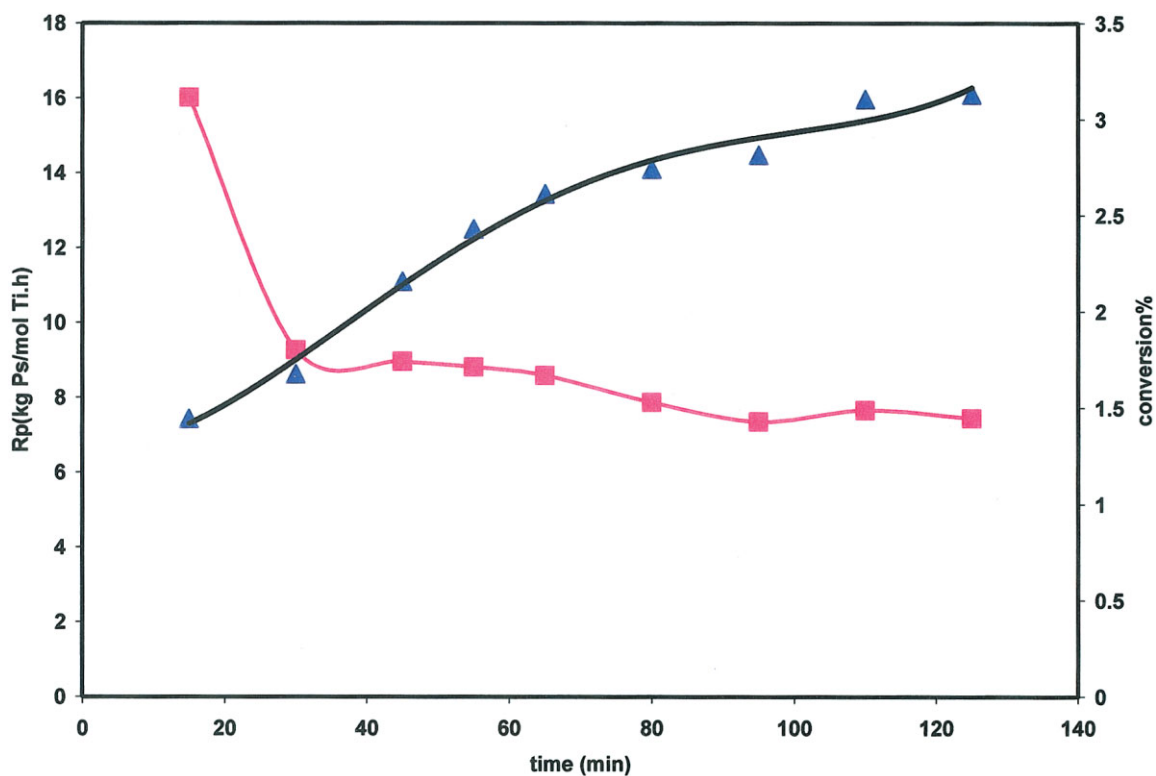


Figure 5 Effect of polymerization time on the conversion and R_p of polystyrene. R_p (■) and conversion % (▲). Polymerization conditions: as Figure 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of MAO was kept constant (Table I). There is an optimum conversion regarding to styrene/Al molar ratio, which took place at styrene/Al = 2.83 mol/mol. At low conversion of the monomer, a first order polymerization reaction with respect to the monomer concentration has been reported.²⁵ In fact, in that report conversion of the monomer was low (<12%), probably because of low temperature used (25°C). At that condition we used a temperature of 60°C, and high concentration of monomer, and a high conversion took place and large amount of solid polymer was produced. Probably active centers occluded in the solid phase,²⁶ which, due to low concentration of MAO chain transfer to the Al, did not take place so much, thus mass transfer limitation to the active center cause decrease in conversion at high monomer/Al ratio. Also no regular behavior of styrene/Al ratio on SI has been observed.

Effect of temperature

The influence of temperature in the range of 50–80°C on the polymerization was studied. Figure 3 indicates that apparent conversion increased with increasing temperature up to 70°C; while higher temperature decreases the conversion obtained. SI of the polystyrene decreased with varying temperature from 50 to 80°C (Fig. 3).

Different catalytic systems show different behavior with respect to the polymerization temperature. Optimum temperature of 50–90°C has been reported regarding the activity of catalysts with no regular behavior in SI.^{4,18,27,28} Activity of the catalyst was shown to be dependent on the degree of the ion-pair $[\text{CpTiCH}_3]^+[\text{MAOCl}_2]^-$ called active center.^{4,21} At low temperature the ion-pair is stable and their activity is low. Probably the activity and the number of active centers decreased at the temperatures higher than the optimum value. Higher temperatures also facilitate overreduction of Ti(IV) and Ti(III) to Ti(II), the species which is not able to produce syndiotactic polymer (only Ti(III) is active species for the syndiospecific polymerization).^{18,21,23,24,29} Increasing temperature seems to favor the formation of active species but it has to be noted that these figures represent an upper limit value only.

Effect of hydrogen concentration

Addition of a small amount of hydrogen as chain transfer agent activates the catalyst initially, but a further increase in its concentration does not affect it anymore. The SI of the polymer is also unaffected by the presence of hydrogen and remains in the 80–85% range (Fig. 4).

Effect of polymerization time

Effect of polymerization time of 15–125 min on the rate of polymerization (R_p) in terms of kg PS/(mol Ti h) and conversion were studied. Figure 5 represents the results obtained. The polymerization was carried out at 70°C, the optimum temperature obtained before.

Rate of polymerization obtained from 15 min which studied sharply decreased with time to about 30 min of the polymerization. Although the rate was decreased further by time but it was not so much pronounced. Huang et al.²⁴ by studying Ti(III) concentration species, the active species for polymerization, with time found that its concentration decrease to almost a constant value. Therefore the concentration of active center could be affected by polymerization time.

¹³C-NMR studies

¹³C-NMR spectrum of s-PS synthesized using Cp-TiCl₃/MAO system was studied. A single peak obtained at 145.5 ppm belong to phenyl carbon confirmed the highly syndiotactic nature of the polymer, which is different from isotactic PS (chemical shift of 146.24 ppm), and atactic PS (five main peaks in the range of 145.1–146.7 ppm).⁷

CONCLUSIONS

Catalyst system of CpTiCl₃/MAO was active for syndiotactic polymerization of styrene. Systematic investigation of polymerization activity was carried out using various polymerization conditions. As result of the study the following conclusions have been obtained:

1. Syndiotacticity index (SI) of 68–91.6% was obtained using various polymerization conditions.
2. Increasing [Al]/[Ti] molar ratio increased activity of the catalyst in the range studied ([Al]/[Ti] = 466–2000).
3. There is an optimum St/Al molar ratio with respect to conversion percentage; while no regular behavior of SI was observed regarding that molar ratio.
4. The optimum temperature of the catalyst system was obtained at 70°C. SI decreased with temperature.
5. Plot of polymerization rate against time was a decay type. The rate decreased sharply with time from 15 to 30 min of the polymerization following to a very slow decay in the rate.
6. Addition of small amount of hydrogen initially increased activity of the catalyst, however high concentration does not affect it anymore. The SI

of the polystyrene is also unaffected by the presence of hydrogen.

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