# Syndiospecific Styrene Polymerization with CpTiCl$_3$/MAO: Effects of the Order of Reactant Addition on Polymerization and Polymer Properties

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**ABSTRACT:** Syndiospecific styrene (St) polymerization, catalyzed by the CpTiCl$_3$/methylaluminoxane (MAO) system, was investigated using two different activation procedures. The polymerization parameters included polymerization time, temperature ($\sim$25–100°C), ratio of [Al]/[Ti] ($\sim$100–1000), and catalyst precursor concentration ($\sim$0.5–10.0 $\times$ 10$^{-4}$ mol Ti/L). It was found that adding reactants in the order of (CpTiCl$_3$ + MAO) + St (Injection of Styrene mode) gave much higher monomer conversion rates, higher weight-average molecular weights, and narrower molecular weight distributions than for the (St + MAO) + CpTiCl$_3$ (Injection of Catalyst mode). The former also yielded significantly higher syndiotacticity fractions. Differential scanning calorimetry measurements showed multiple peaks exhibiting polymorphism in crystalline syndiotactic polystyrene samples. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1449–1455, 2004

**Key words:** syndiotactic polystyrene; metallocene polymerization; methylaluminoxane; titanocene

## INTRODUCTION

Ishihara et al.[1,2] first reported that an organotitanium compound, activated with methylaluminoxane (MAO), can catalyze syndiospecific polymerization of styrene. This finding promoted great interest in the identification of homogeneous organometallic complexes capable of efficient and stereoregular polymerization of styrene. A recent review covers syndiospecific styrene polymerization, especially the catalytic systems.[3] Studies in this field have led to the conclusion that half-sandwich titanium chloride, fluoride, or alkyoxide compounds containing $\eta^5$-C$_5$H$_5$, $\eta^5$-C$_5$Me$_5$, $\eta^5$-C$_5$Me$_4$H, or $\eta^5$-C$_9$H$_7$ ligands are among the favored precursors.[4–13] Kinetic studies of syndiospecific styrene polymerization with various metallocene catalyst systems have been reported by several research groups.[14–21] Full range kinetics and morphology of in situ nascent syndiotactic polystyrene sampels (sPS) were also investigated in recent studies.[22–24] However, there is little coverage of the effects of reactant addition strategy on kinetics.[25]

ESR studies on several pure metallocene catalyst systems and styrene polymerization with CpTiCl$_3$/MAO were reported in our previous work.[26,27] The activation procedure was found to have a dramatic effect on catalyst oxidation. Adding reactants in the order of (CpTiCl$_3$ + MAO) + styrene (St) gave a much higher trivalent titanocene concentration than that of (St + MAO) + CpTiCl$_3$. This finding encouraged us to perform parallel polymerization experiments using the above two different activation procedures. In this paper, we report on the effects of various polymerization parameters and addition orders on polymer yield, catalyst activity, molecular weight, molecular weight distribution, and syndiospecificity ratio. The parameters include polymerization time, temperature ($\sim$25–100°C), ratio of [Al]/[Ti] ($\sim$100–1000), and catalyst precursor concentration ($\sim$0.5–10.0 $\times$ 10$^{-4}$ molTi/L). Differential scanning calorimetry (DSC) and $^{13}$C-NMR were used to characterize the obtained sPS samples.

## EXPERIMENTAL

### Materials and preparation

The metallocene catalyst precursor, cyclopentadienyl titanium trichloride (CpTiCl$_3$), was supplied by Strem Chemical, Inc. Modified MAO (11.5% isobutane, 87.5% methane) was supplied by Akzo Chemical, Inc., as 11.6 wt % Al solution in toluene. The catalyst and cocatalyst were used without further purification. Methylethylketone (MEK, 99%), 1,2,4-trichlorobenzene (99%), and methanol (99%) were purchased from Aldrich without further purification. Anhydrous grade toluene, supplied

by Aldrich Chemical, was refluxed for 6 h over sodium with benzophenone as indicator, until the solution became sky-blue, followed by distillation. Styrene (99.0%) supplied by Aldrich was first reacted with calcium hydride ($CaH_2$) under nitrogen bubbling for 5 days to remove water and then dried using molecular sieves, followed by distillation under reduced pressure over calcium hydride and stored in a refrigerator. All catalyst solution and polymerization samples were prepared in a controlled atmosphere drybox. The injection of catalyst solution or styrene was conducted under a nitrogen atmosphere.

### Catalyst activation procedure

Two different catalyst activation procedures were used to polymerize styrene. In the first procedure, called "Injection of Styrene" mode, ($CpTiCl_3$ + MAO) + St, samples were prepared by first mixing the catalyst precursor solution, toluene and MAO solution, in a drybox (in this case, the catalyst system was activated at this stage during the given aging time). Styrene monomer was then injected to start polymerization. In the second procedure, called "Injection of Catalyst" mode, (St + MAO) + $CpTiCl_3$, samples were prepared by first mixing styrene monomer, MAO solution, and toluene in a drybox. The catalyst precursor, $CpTiCl_3$, was then injected to activate the catalyst system and start polymerization.

### Polymerization

Toluene, styrene, and MAO solution (Injection of Catalyst mode) or toluene, MAO solution, and catalyst precursor solution (Injection of Styrene mode) were mixed in a 10-mL screw-cap tube in the drybox, sealed by a Teflon/silicon septa-lined screw cap, and then transferred out of the drybox. The solution was thermostatted for 10 min at the desired temperature prior to polymerization. The polymerization was initiated either by injecting the catalyst precursor solution (Injection of Catalyst mode) or by injecting styrene (Injection of Styrene mode) into the tube. The polymerization was stopped by adding 10% acidified methanol. Polymers were recovered by filtration, washed three times with fresh methanol, and finally dried at 60°C in a vacuum oven.

### DSC measurement

The melting temperature $T_m$ and enthalpy of the sPS samples were measured using a Dupont Model 910 differential scanning calorimeter calibrated with an Indium standard. A sPS sample of 5.0 ± 0.1 mg was first preheated at a rate of 25°C/min up to 260°C in the first heating cycle. It was quenched to 50°C with compressed air. A second heating cycle was performed

from 50 to 280°C at a heating rate of 10°C/min. The data from the second heating process were used to study the physical property and polymorphism of sPS made under different polymerization conditions.

### GPC measurement

Molecular weight and MWD of sPS were measured using a Waters-Millipore SEC instrument, Model 150-C high-temperature GPC, with a differential refractive index detector. The polymer samples were dissolved in trichlorobenzene at a concentration of about 0.1 wt % and measured at 140°C with a flow rate of 1 mL/min. The GPC was equipped with three linear Shodex AT806MS columns. The retention time was calibrated at 140°C against known monodispersed TSK polystyrene standards from TOYO SODA Mfg. Co.

### $^{13}$C-NMR measurement

$^{13}$C-NMR spectra were obtained at 120°C using a Bruker AC300 pulsed NMR spectrometer with broad decoupling and quadrature detection at 75.4 MHz. The polymer concentration was 8.0 wt % in deuterated $o$-dichlorobenzene ($d$-ODCB) and 1,2,4-trichlorobenzene (TCB) using 10-mm sample tubes. Chemical shifts were referred internally to TCB and lock was provided by $d$-ODCB. Spectra required more than 3000 scans (equivalent to 6 h) to obtain an appropriate signal-to-noise ratio.

### Syndiospecificity (SY) measurement

The fractions of sPS (SY) were measured by extracting atactic PS with boiling MEK with a Soxhlet extractor for 24 h: the soluble portions were atactic PS while the insoluble parts were sPS. The insoluble parts were collected and dried at 60°C under a vacuum overnight to get the syndiospecificity ratio (SY).

## RESULTS AND DISCUSSION

### Polymerization time

The data on styrene conversion, polymerization rate, molecular weight distribution, and melting temperature corresponding to different polymerization time intervals for the $CpTiCl_3$/MAO system using the Injection of Styrene mode are summarized in Table I. The monomer conversion increased continuously with time while the corresponding polymerization rate decreased with time. The rate reduction was attributed to the deactivation of active sites,[27] as well as the consumption of styrene monomer. It may also be attributed to the occlusion of some active sites in precipitating polymers because sPS does not dissolve in

**TABLE I**
**Summary of Data for sPS Polymerization with CpTiCl₃/MAO at 50°C**

| Polymerization time (min) | Conversion (%)[a] | $T_m$ (°C) | | Rate $\times 10^{-4}$ (gPS/gTi · h) | $M_w$ ($\times 10^{-4}$ g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| | | 1st | 2nd | | | |
| Injection of styrene | | | | | | |
| 5 | 3.06 | 241 | 247 | 1.50 | 4.61 | 2.1 |
| 10 | 18.3 | — | 254 | 4.49 | 3.16 | 1.8 |
| 20 | 23.2 | 241 | 253 | 2.85 | 3.04 | 1.9 |
| 30 | 32.4 | 241 | 249 | 2.65 | 3.21 | 1.8 |
| 40 | 35.9 | 242 | 254 | 2.20 | 3.01 | 1.8 |
| 50 | 39.5 | 245 | 254 | 1.94 | 2.93 | 1.8 |
| 60 | 40.6 | 246 | 254 | 1.66 | 3.09 | 1.8 |
| Injection of catalyst | | | | | | |
| 5 | 4.3 | 238 | 251 | 2.11 | 2.70 | 2.4 |
| 10 | 6.0 | 247 | 258 | 1.47 | 2.44 | 1.9 |
| 20 | 7.3 | — | 251 | 0.90 | 2.35 | 2.1 |
| 30 | 8.6 | — | 257 | 0.70 | 2.39 | 2.1 |
| 40 | 9.4 | — | 253 | 0.58 | 2.38 | 2.1 |
| 50 | 10.9 | — | 251 | 0.54 | 2.47 | 2.1 |
| 60 | 13.2 | — | 246 | 0.54 | 2.50 | 2.1 |

*Note.* [Ti] = $10^{-4}$ mol/L, Al/Ti = 500, $T_p$ = 50°C, [St] = 1.88 mol/L, toluene as solvent, Injection of Styrene activation.
[a] This set of conversion versus time data first appeared in Ref. 27.

toluene and the process was a precipitation polymerization. The weight-average molecular weights $M_w$ and molecular weight distributions ($M_w/M_n$) remained almost constant during the course of polymerization. The $M_w$ values were about $3.1 \times 10^4$ except for the first point. The molecular weights of obtained sPS were on the low side because of the given catalyst system and its high concentration. Another possible reason could be chain transfer to solvent.

The parallel experiments using the Injection of Catalyst mode are also summarized in Table I. The Injection of Catalyst mode gave much lower conversions than the Injection of Styrene mode. The differences in the conversion data were dramatic. A possible explanation is that in the Injection of Styrene mode, the catalyst and cocatalyst were mixed first and the alkylation/reduction reactions were accomplished before styrene was added to the system. In the Injection of Catalyst mode, the presence of styrene either inhibited or intercepted these desired reactions to form an inactive complex. Previous ESR studies gave strong evidence that the Injection of Styrene mode generated much higher trivalent titanocene concentrations than the Injection of Catalyst mode.[27]

The Injection of Catalyst mode also gave lower polymer molecular weights than the Injection of Styrene mode: average values of $M_w$'s, about $2.4 \times 10^4$, were over 20% lower than that of the Injection of Styrene mode ($3.1 \times 10^4$). The molecular weight distributions were also broader, with most samples having $M_w/M_n$ = 2.1.

## Ratio of [Al]/[Ti]

Table II summarizes the effect of the Al/Ti molar ratio on the sPS polymerization using the two activation pro-

cedures. The polymerization reactions were carried out for 1 h and the final products were analyzed. The conversion increased monotonously with the Al/Ti ratio up to 1000 in both procedures. However, at all the Al/Ti ratios investigated, the Injection of Styrene mode yielded higher conversions than the Injection of Catalyst mode.

At all the [Al]/[Ti] ratios, the $M_w$ values of the Injection of Styrene mode were higher than those of the Injection of Catalyst mode, while the former mode gave lower $M_w/M_n$ values than the latter. However, the influence of the [Al]/[Ti] ratio on the molecular weight and distribution within each mode was not conclusive. This result was somewhat different from the data of Ishihara et al.[2] They reported a slight decrease of $M_w$ with an increase in the [Al]/[Ti] ratio.

The PS syndiotactic fractions were somewhat different for the two different activation modes. The sPS samples prepared by the Injection of Styrene mode were highly syndiotactic with SY about 97%, while the Injection of Catalyst gave only 87% syndiotacticity.

## Polymerization temperature

The results of the temperature effect on the sPS polymerization are summarized in Table III. At all temperatures, the Injection of Styrene mode gave higher conversion than the Injection of Catalyst mode. Both modes showed a maximum conversion at about 50°C. For the former it was because of the increase in the monomer propagation rate constant $k_p$, while the latter was probably due to the quick deactivation of the catalyst. The ESR studies reported in Ref. 27 also showed that the CpTiCl₃/MAO system deactivated rapidly at temperatures above 50°C.

The temperature had a significant effect on the molecular weight for both activation modes. The $M_w$ value decreased

## TABLE II
### Effect of the [Al]/[Ti] Ratio on sPS Polymerization with CpTiCl$_3$/MAO at 50°C for 1 h—Injection of Styrene versus Injection of Catalyst

| Injection St Al/Ti ratio | Conversion (%) | Activity ($\times 10^{-5}$) (gPS/molTi · [St] · h) | $T_m$ (°C) 1st | 2nd | SY (%) | $M_w$ ($\times 10^{-4}$ g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 100 | 3.8 | 0.40 | | | | | |
| 300 | 17.1 | 1.78 | 250 | 258 | 95.9 | 3.00 | 2.0 |
| 500 | 40.6 | 4.22 | 250 | 257 | 97.5 | 3.09 | 1.8 |
| 800 | 43.2 | 4.49 | 246 | 258 | 97.7 | 2.91 | 1.9 |
| 1000 | 67.4 | 7.01 | 249 | 258 | 96.2 | 3.15 | 2.0 |

| Injection Cat. Al/Ti ratio | Conversion (%) | Activity ($\times 10^{-5}$) (gPS/molTi · [St] · h) | $T_m$ 1st | 2nd | SY (%) | $M_w$ ($\times 10^{-4}$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 100 | 3.3 | 0.34 | | | | | |
| 300 | 9.3 | 0.97 | 243 | 254 | 86.7 | 2.52 | 2.3 |
| 500 | 13.8 | 1.44 | 243 | 255 | 87.8 | 2.50 | 2.1 |
| 800 | 22.8 | 2.37 | 246 | 254 | 87.4 | 2.77 | 2.0 |
| 1000 | 35.9 | 3.73 | 243 | 255 | 86.5 | 2.60 | 2.1 |

*Note.* [Ti], $10^{-4}$ mol/L; [St], 1.88 mol/L; $T_p$, 50°C; time, 60 min; solvent, toluene.

with an increase in temperature. Furthermore, the Injection of Styrene mode yielded higher syndiotacticity than the Injection of Catalyst mode at all temperatures.

## Catalyst precursor concentration

The conversion, catalyst activity, $T_m$, and SY data for the two different activation modes with four catalyst precursor concentrations are summarized in Table IV. The conversions increased quickly with the catalyst precursor concentration. At the highest catalyst concentration (i.e., $10^{-3}$ mol/L), the conversions of the two modes were almost identical.

The catalyst activity in the Injection of Styrene mode decreased dramatically with increasing precursor concentration. Previous ESR studies[26] elucidated linear relationships between the concentration of trivalent titanocene and that of the catalyst precursor. However, their slopes were always smaller than unity, indicating the existence of bimetallic interactions of the active sites. The rate of bimetallic deactivation has a strong dependence on the catalyst concentration: doubling the catalyst concentration should increase the rate by four times. Therefore, the higher the catalyst concentration, the lower the catalyst activity. Similar observations were reported for $\alpha$-olefin polymerization with metallocene catalysts.[28]

In the Injection of Catalyst mode, the activity showed little change with the catalyst concentration. The polymerization system was diluted by styrene monomer prior to the catalyst injection and thus the initial active site concentration was much lower than the Injection of Styrene mode. As a result, the deactivation by bimetallic interactions was slow.

## TABLE III
### Effect of Temperature on sPS Polymerization with CpTiCl$_3$/MAO—Injection of Styrene Versus Injection of Catalyst

| Injection St $T_p$ (°C) | Conversion (%) | Activity ($\times 10^{-5}$) (gPS/molTi · [St] · h) | $T_m$ (°C) 1st | 2nd | SY (%) | $M_w$ ($\times 10^{-4}$ g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 25 | 23.0 | 2.39 | | 260 | 97.9 | 4.78 | 1.9 |
| 50 | 40.6 | 4.22 | 250 | 257 | 97.5 | 3.09 | 1.8 |
| 70 | 37.2 | 3.87 | 237 | 252 | 96.8 | 2.32 | 1.8 |
| 100 | 20.0 | 2.08 | | 243 | 95.2 | 2.10 | 1.8 |

| Injection Cat $T_p$ (°C) | Conversion (%) | Activity ($\times 10^{-5}$) (gPS/molTi · [St] · h) | $T_m$ 1st | 2nd | SY (%) | $M_w$ ($\times 10^{-4}$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 25 | 6.6 | 0.69 | | 258 | 88.4 | 3.28 | 2.2 |
| 50 | 13.2 | 1.37 | 243 | 255 | 87.8 | 2.50 | 2.1 |
| 70 | 8.4 | 0.87 | 235 | 248 | 87.2 | 2.05 | 2.1 |
| 100 | 4.6 | 0.48 | 221 | 238 | 87.4 | 1.78 | 2.0 |

*Note.* [Ti], $10^{-4}$ mol/L; [St], 1.88 mol/L; [Al]/[Ti], 500; time, 60 min; solvent, toluene.

**TABLE IV**
**Effect of Catalyst Precursor Concentration on sPS Polymerization with CpTiCl$_3$/MAO at 50°C for 1 h—Injection of Styrene versus Injection of Catalyst**

| Injection St [Ti] (×10$^4$) | Conversion (%) | Activity (×10$^{-5}$) (gPS/molTi · [St] · h) | $T_m$ (°C) 1st | $T_m$ (°C) 2nd | SY (%) |
|---|---|---|---|---|---|
| 0.5 | 15.3 | 3.18 | 241 | 254 | 96.2 |
| 1.0 | 40.6 | 4.22 | 250 | 258 | 97.5 |
| 5.0 | 78.5 | 1.63 | 248 | 256 | 97.1 |
| 10 | 92.0 | 0.96 | | 242 | 96.8 |

| Injection catalyst [Ti] (×10$^4$) | Conversion (%) | Activity (×10$^{-5}$) (gPS/molTi · [St] · h) | $T_m$ 1st | $T_m$ 2nd | SY (%) |
|---|---|---|---|---|---|
| 0.5 | 4.3 | 0.89 | 240 | 251 | 86.7 |
| 1.0 | 13.2 | 1.37 | 243 | 255 | 87.8 |
| 5.0 | 64.2 | 1.34 | 241 | 253 | 87.3 |
| 10 | 90.1 | 0.94 | 239 | 249 | 86.9 |

*Note.* [Al]/[Ti], 500; [St], 1.88 mol/L; $T_p$, 50°C; time, 60 min; solvent, toluene.

## sPS polymorphism

sPS exhibits extended polymorphism. Its morphology is influenced by thermal, solvent, and/or mechanical treatment.[29–41] Our sPS samples, after extracting atactic PS with MEK, showed several small endotherms in the temperature range 100–190°C during the first heating cycle. The major melting endotherms were asymmetric with shoulders or small peaks, suggesting the presence of more than one crystalline form. A typical first heating DSC curve is shown in Figure 1a. After samples were heated to 260°C and cooled down to room temperature, the second DSC scan exhibited no transitions as in the first cycle, but still showed two melting endotherms in the temperature range 242–259°C (Fig. 1b) lower than the about 270°C typically reported. This can be ascribed to lower molecular weights of the resulting sPS, as indicated in our previous work.[42] Two crystalline modifications were identified by Greis et al.[29,30] using high-energy electron diffraction. The sPS backbone chains were in the planar zigzag conformation. The two modifications were shown to be a hexagonal sPS-$\alpha$ and a monoclinic sPS-$\beta$,[30] with C-centered orthorhombic parent structure. The other two modifications were called $\gamma$ and $\delta$ forms with helical conformation. There could also be some distorted structures of either sPS-$\alpha$ or sPS-$\beta$. The DSC curves showed two peaks indicating the existence of polymorphism in the sPS crystalline.

## NMR results

Figure 2a shows a typical $^{13}$C-NMR spectrum for PS synthesized by CpTiCl$_3$/MAO system using the Injec-

(a) DSC curve of sPS: first cycle at a heating rate 25 °C/min
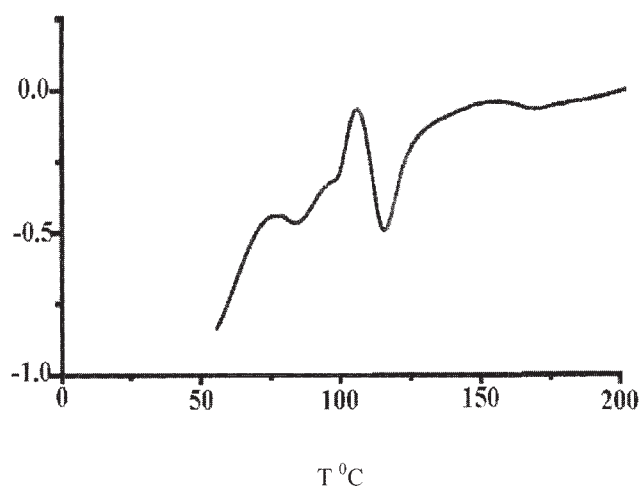
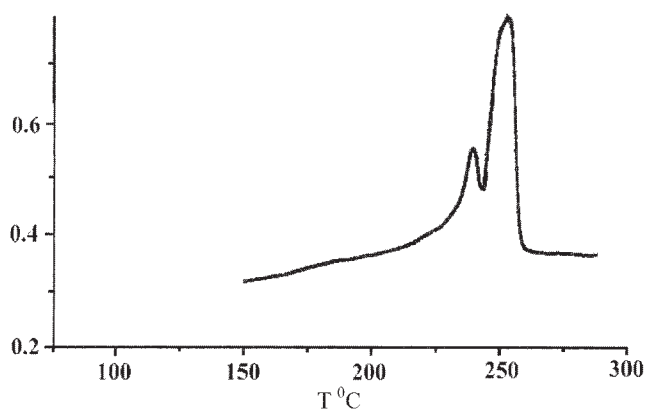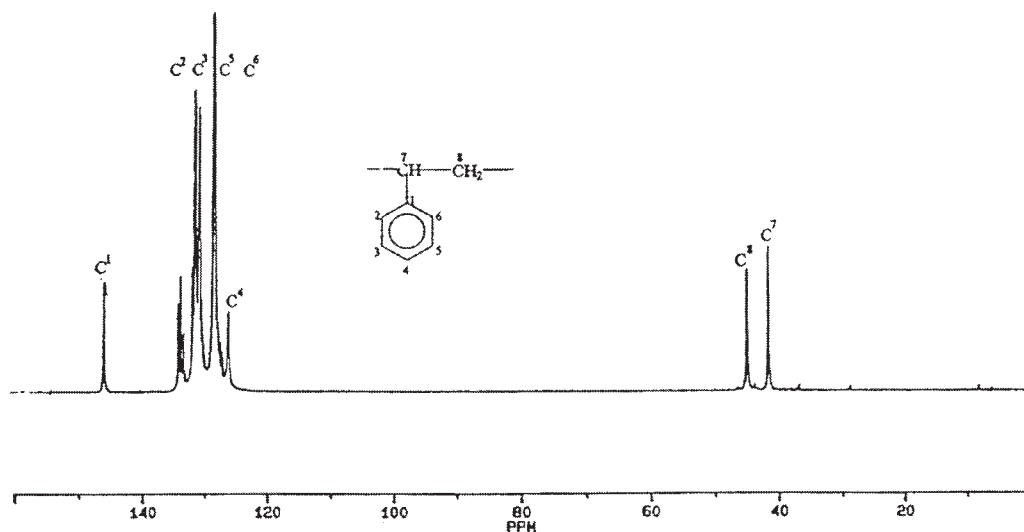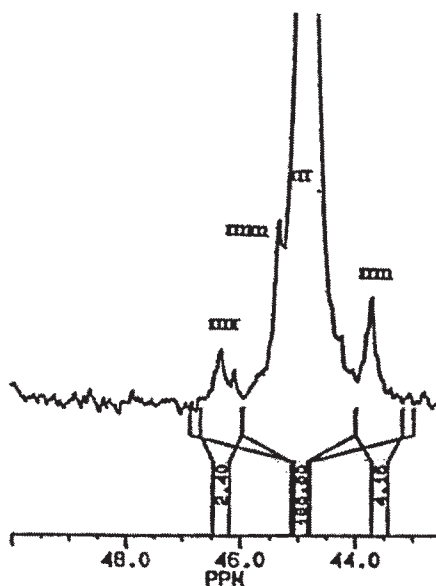(b) DSC curve of sPS: second cycle at a heating rate 10 °C/min



**Figure 1** DSC curve of sPS: (a) first cycle at a heating rate of 25°C/min and (b) second cycle at a heating rate of 10°C/min.

(a) $^{13}$C NMR spectrum of sPS: whole NMR curve



(b) $^{13}$C NMR spectrum of sPS: magnified C$^8$ portion



**Figure 2**    $^{13}$C-NMR spectrum of sPS: (a) whole NMR curve and (b) magnified C$^8$ portion

tion of Styrene mode. The assignments of various carbons are marked in the spectra. sPS was characterized by a specific chemical shift (145.5 ppm) for phenyl $C_1$ carbon that was different from isotactic PS (chemical shift for $C_1$: 146.24 ppm) and atactic PS (five main peaks in the range of 145.1–146.7 ppm).[1,16,43] The single peak at position 145.5 ppm proved that the obtained polystyrene was syndiotactic.

By magnifying the $C_8$ portion of $^{13}$C-NMR spectra, the sequence distribution of sPS and SY value were calculated. A magnified $C_8$ portion is shown in Figure

2b. Integrating different chemical shift peaks corresponding to different sequence distributions gave the following sequence data:

| Chemical shift | Sequence | Percentage |
|---|---|---|
| 46.3 | rmr | 2.4 |
| 45.3 | rmm+mmr | 1.21 |
| 44.8 | rrr | 92.23 |
| 43.7 | rrm+mrr | 4.16 |

and thus

rr = rrr + ½ (mrr + rrm) = 94.31;
mm = mmm + ½ (rmm + mmr) = 0.605;
r = rr + ½ (rm + mr) = 96.85;
m = mm + ½ (rm + mr) = 3.15.

The fraction of SY, 96.85%, agreed with the results obtained by the extraction method (SY: 96–98%).

## CONCLUSION

(1) The influence of the catalyst activation procedure on the syndiotactic styrene polymerization with Cp-TiCl$_3$/MAO system was found to be dramatic. Under all the experiment conditions investigated, the Injection of Styrene mode always gave higher styrene conversions, higher polymer molecular weights, and narrower molecular weight distributions than the Injection of Catalyst model.

(2) The Injection of Styrene mode also produced sPS samples with higher syndiotacticities than the Injection of Catalyst mode. The former gave SY 97% while the latter gave only 87%.

(3) The conversion versus temperature curves showed maxima at about 50°C for both activation modes with the given CpTiCl$_3$/MAO system. The catalyst system experienced significant deactivation at temperatures above 50°C. The sPS molecular weights showed a monotonous decrease with temperature.

(4) The catalyst activity per metal center decreased significantly with an increase in titanocene precursor using the Injection of Styrene mode. This was attributed to bimetallic interactions and thus deactivation of active sites.

(5) The DSC curves always showed multiple peaks that indicated the existence of polymorphism for crystalline sPS. The sPS, with molecular weight in the order of 10$^4$, had melting temperatures in the range of 242–259°C. $^{13}$C-NMR spectra showed a clear peak at the chemical shift 145.5 ppm. The SY values obtained from the sequence distribution analysis agreed with those by the MEK extraction method.

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