

Synthesis and polymerization behavior of various substituted half-sandwich titanium complexes $Cp'TiCl_2(OR^*)$ as catalysts for syndiotactic polystyrene

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In memory of our respectable and beloved professor Qian Yanlong

Abstract

A new set of chiral alkoxy substituted half-sandwich titanium complexes of $Cp'TiCl_2(OR^*)$ ($Cp' = Cp, CH_3CH(CH_3)Cp, CH_3OCH_2CH_2Cp, CH_3OCH_2CH(CH_3)Cp$; $R^* =$ menthyl, fenchyl) were synthesized, characterized and tested as catalyst precursors for the syndiospecific polymerization of styrene. The structure of complex **8** was confirmed by X-ray crystallography. When chiral alkoxy groups took the place of chlorine atom, it was found that the intramolecular coordination of the oxygen on Cp ring to the titanium disappeared in the solid state. Under the same conditions, complexes **1–4** showed higher activity, and complexes **5–8** showed lower activity than $CpTiCl_3$. The catalytic activity increased in the order **8** < **7** < **6** < **5** < $CpTiCl_3$ < **4** < **3** < **2** < **1**. The highest activity was 7.37×10^7 g s-PS/(mol Ti mol S h) for complex **1**/methylaluminoxane (MAO) at a molar ratio of Al/Ti = 2000. Kinetic measurements of the polymerization were carried out at different temperature for complex **1**. The effects of variation on temperature, Al/Ti ratio for catalytic activity and syndiotactic polystyrene (s-PS)% were also studied.

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1. Introduction

Syndiotactic polystyrene (s-PS) is a relatively new material with a high melting point and rapid crystallization rate, which makes it possible to injection-mold the material. The excellent balances of mechanical, electrical, solvent resistance, and dimensional stability properties combined with a relatively low price (based on styrene monomer) have made it to compete with existing engineering plastics [1]. Ishihara et al. [2,3] in 1986 reported that the s-PS can be prepared using $(\eta^5-Cp)TiCl_3$ /methylaluminoxane (MAO) catalytic system. Since then, many new kinds of half-sandwich titanocene $Cp'TiX_3$ ($Cp' =$ substituted or unsubstituted Cp or Ind; X = halogen, alkoxy, hydrocarbyl) complexes have been synthesized and evaluated for their catalytic behavior in polymerization including the influence on structure

and properties of prepared s-PS [4–10]. Additionally, the catalytic systems for the syndiospecific polymerization of styrene have been reviewed extensively elsewhere [11–14]. Furthermore, the polymerization mechanism [15–17] and the structure of the active site [18–25] were also investigated. According to published reports, to vary in Cp- or Ind-ligand may result in changes of catalytic activity and physico-chemical properties of polymer. For example, half-titanocene catalyst with bulky annulated indenyl ligands may produce polymer with high syndiotacticity and molecular weight [26–29]. In general, these changes in catalyst and polymer are due to the effect of π -donor ligand ($Cp' =$ substituted or unsubstituted Cp or Ind). In addition, the σ -donor X (X = halogen, alkoxy or hydrocarbyl) ligand has been also found to affect both catalytic activities and polymer properties [30–39]. For instance, by application of fluorinated complexes, e.g. $Cp'TiF_3$, and alkoxy ligand substituted complexes, e.g. $CpTiCl_2(OR)$ or $Cp'Ti(OR)_3$, to replace chlorinated counterparts, some research groups have found that the former have much higher activity than

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the latter [30–39]. Previously [40], in a comparison of two catalysts, e.g. $\text{CpTiCl}_2(\text{O-cyclo-C}_6\text{H}_{11})$ and CpTiCl_3 , applied to s-PS, we have found that the activity of the former is about $(6.33\text{--}6.58) \times 10^7$ gPS / (mol Ti mol S h), three times as high as the latter.

In order to study how the changes of π -donor ligand and σ -donor ligand affect the catalytic activity and the properties of s-PS, this work aims to design and prepare a series of $\text{Cp}'\text{TiCl}_2(\text{OR}^*)$ complexes with different substituents in Cp and OR^* , and then to apply them to the production of s-PS.

2. Results and discussion

2.1. Synthesis and characterization of complexes 1–8

The synthetic route for eight new complexes is outlined in Fig. 1.

The molecular structure, selected bond distances and angles for complex **8** were revealed by X-ray crystallography as can be seen in Fig. 2. A comparison of complex **8** with the parent complex $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{CpTiCl}_3$ [41] showed

that the crystal system and space group for the former is in monoclinic and $P2_1/c$ whereas for the latter is in triclinic and $P\bar{1}$. The bond length for complex **8** (Fig. 2) is longer in the Ti–C(1), e.g. of 2.398 Å, and shorter in the Ti–C(3), e.g. of 2.313 Å, than that of $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{CpTiCl}_3$, e.g. 2.370 and 2.400 Å, respectively. The oxygen of substituted Cp ring for complex **8** is found not coordinated as in the parent complex $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{CpTiCl}_3$. In addition, the stretching vibration frequencies of C–O in the IR spectra in the parent complex $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{CpTiCl}_3$ were lower than that in the complex **8**. This also suggests the disappearance of the Ti ← O(1) intramolecular coordination bond in complex **8**. The Ti–O(2) bond has a short length, e.g. 1.729 Å, as compared to the Ti–Cl(2) bond, e.g. 2.265 Å [41], showing that the alkoxy group has a stronger σ -donation possibility than that of the chlorine atom.

2.2. Polymerization of styrene using complexes 1–8

The effect of the temperature on the catalytic activity of complexes **1–8** was investigated. Figs. 3 and 4 shows that

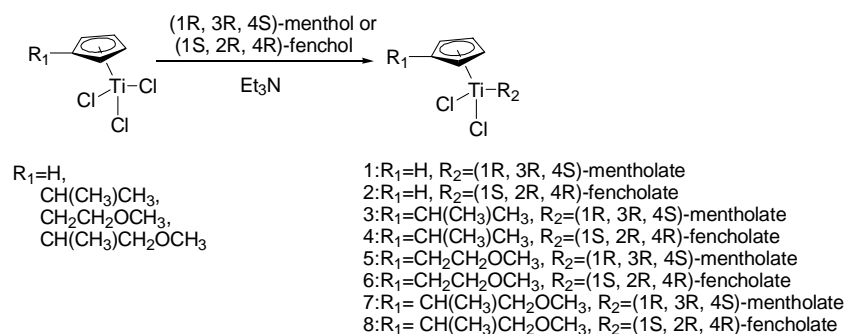


Fig. 1. Route for synthesis of $\text{Cp}'\text{TiCl}_2\text{OR}^*$.

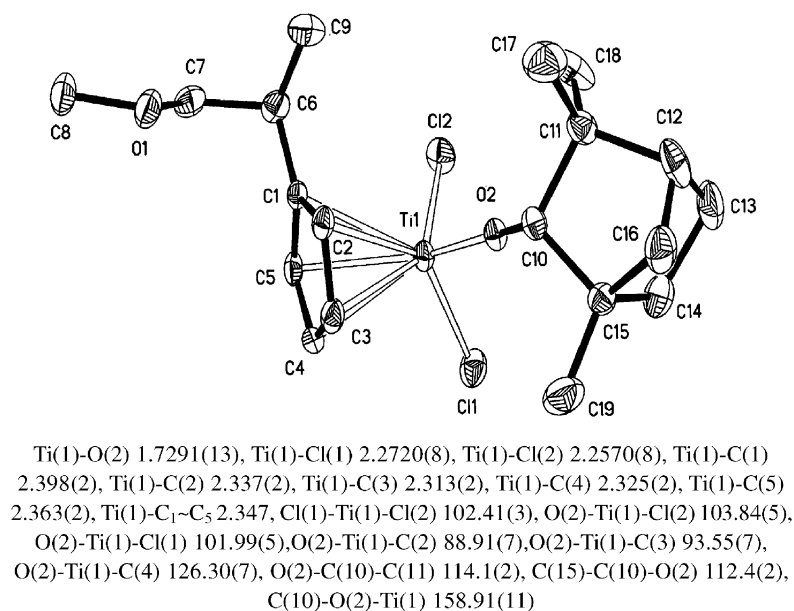


Fig. 2. X-ray structure and selected bond distances (Å) and bond angles (°) for complex **8**.

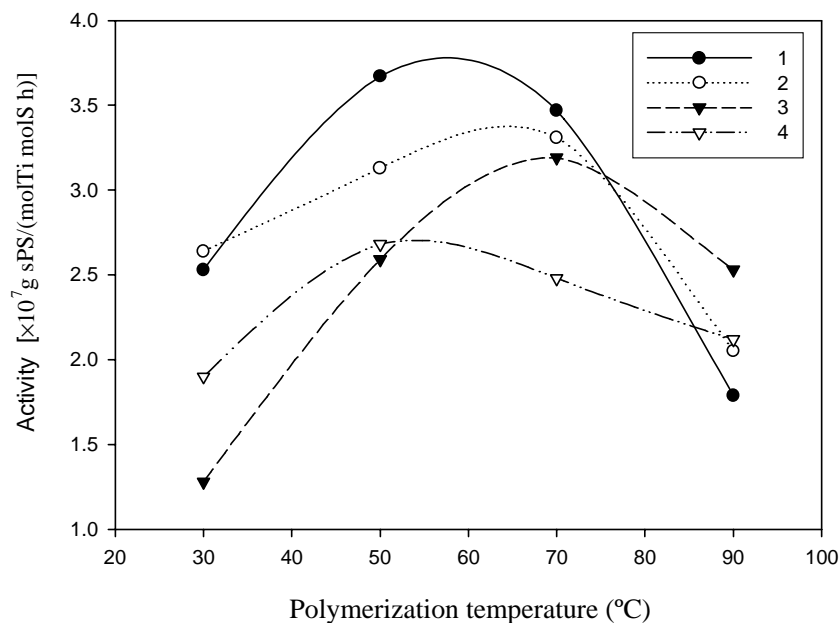


Fig. 3. Activity of complexes 1–4 as different polymerization temperature.

the activity of these complexes 1–8 can be divided into two groups. The complexes 1–4 are about 100 times as active as complexes 5–8. This difference is due to the fact that complexes 1–4 have no *O*-functionalized Cp in contrast to complexes 5–8. Since the coordination of oxygen to titanium decreased the electrophilicity of titanium and impeded the coordination of styrene to titanium sterically, the polymerization rate was decreased [42–46].

In Fig. 3, maximum polymerization activities were found in the range of 50–70°C for complexes 1–4, which decreased at either higher (90°C) or lower (30°C) tempera-

ture. These results were consistent with those reported by Chien and co-workers [21,47]. Cossee's π -complex mechanism [48–51] and Chien's ion-pair model [52,53] can be employed to explain this phenomenon. At low temperature of 30°C the stability of ion-pair and π -complex leads to low activity. Increasing polymerization temperature promotes ion-pair dissociation with a consequent increase in activity. However, at high temperature the π -complex was dissociated, and the activity declined due to the deactivation of active species. In contrast to complexes 1–4, the activity of complexes 5–8 was increased without a decrease at the

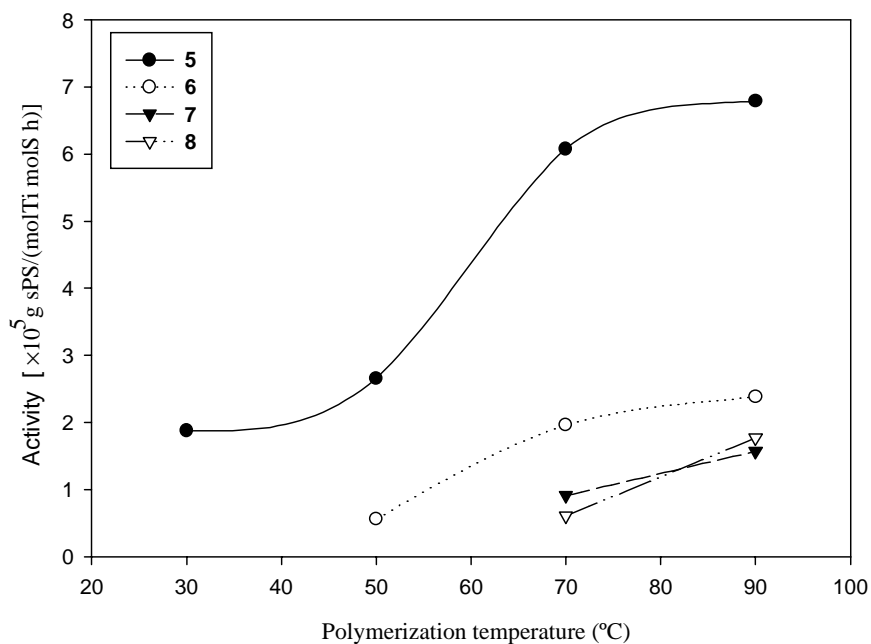


Fig. 4. Activity of complexes 5–8 as different polymerization temperature.

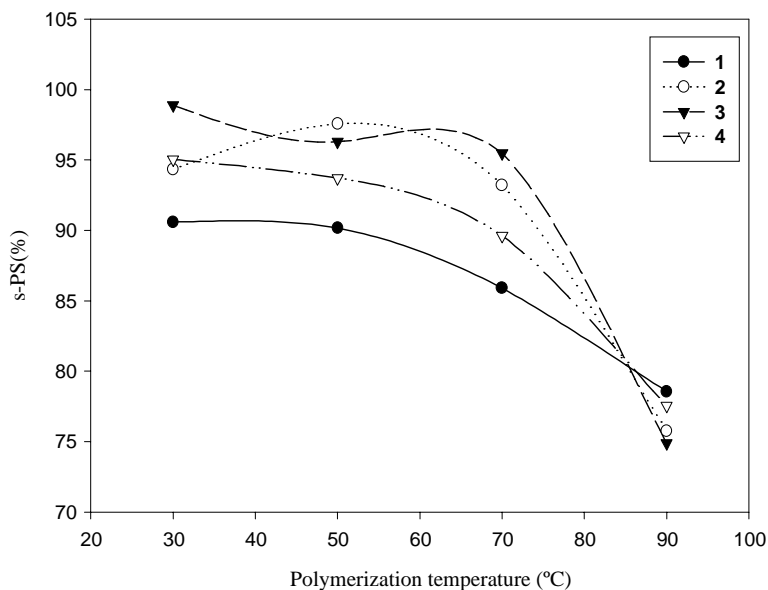


Fig. 5. The relationship between the s-PS% and polymerization temperature for complexes 1–4.

temperature level up to 90 °C (Fig. 4). This means that the complexes 5–8 can fit a high temperature polymerization condition. The reason might be ascribed to the decrease in the coordination possibility for Ti ← O and Al ← O.

The comparison of the catalytic activity for complexes 1 and 3 indicated that the former is higher in the range of 30–70 °C, and lower at 90 °C, than that of the latter (Fig. 3). This phenomenon is most probably due to the steric effects which protect the metal center from thermal decomposition. For the same reason, catalytic activities of complexes 2, 5 and 6 were higher than those of complexes 4, 7 and 8.

Fig. 5 shows that the increase in the temperature usually results in the reduction of the yield of s-PS in solution polymerization. This behavior was mainly due to the decomposition of the active species and reduction of stereochemical control at high temperature, which also led to the decrease in the yield of s-PS fraction. When the temperature increased from 30 to 70 °C, the s-PS% were decreased slightly from 98.9 to 95.5%, whereas when the temperature reached 90 °C, the s-PS% was decreased to 74.9%.

As showed in Fig. 6, the polymerization rate changed with the variation of time and temperature for the catalytic system of complex 1/MAO. Fast initiation and deactivation were

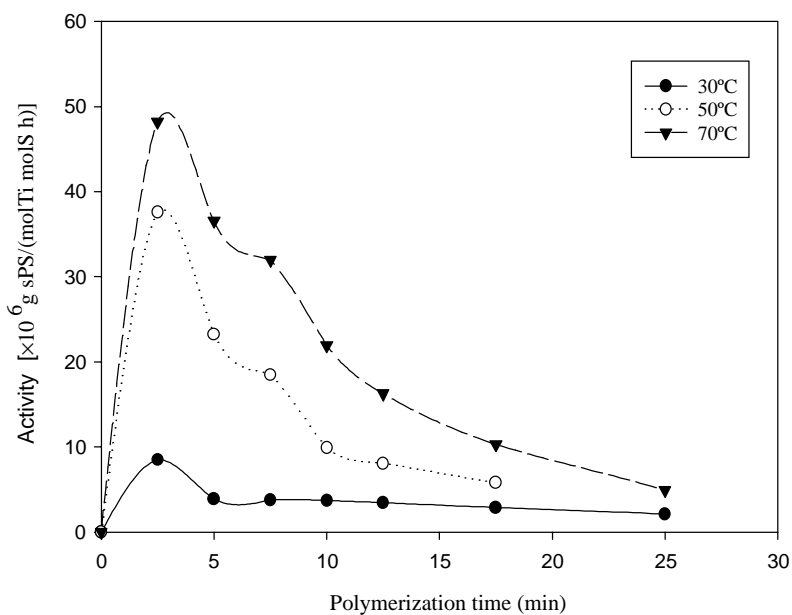


Fig. 6. Kinetic data for each polymerization temperature for complex 1.

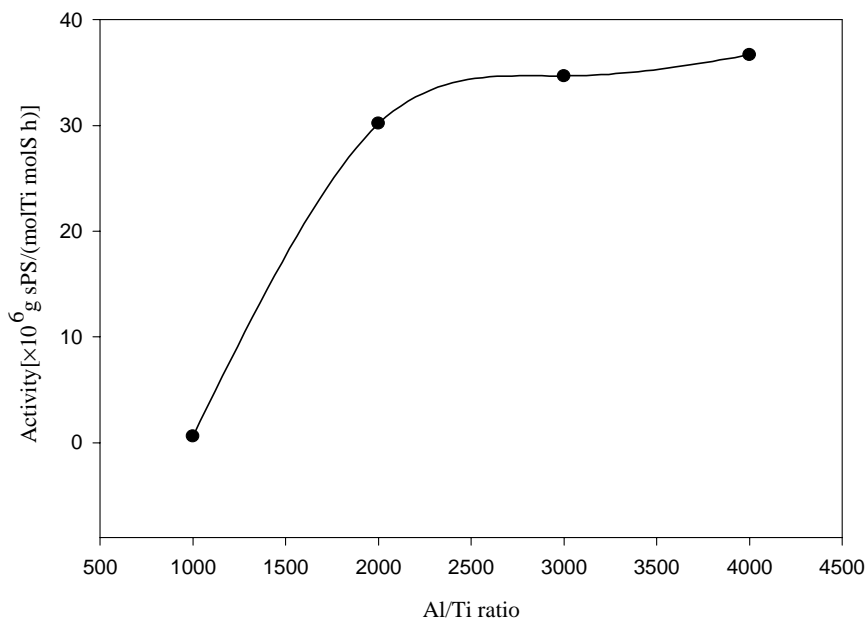


Fig. 7. Dependency of the activity on the Al/Ti ratio for complex **1**.

found at 50 and 70 °C, in contrast to the catalytic activity maintained nearly constant at 30 °C. Catalytic activities increased sharply with increased polymerization temperature at the initial period of polymerization. The highest activities can be observed at 2.5 min for all polymerization temperatures. The highest activity is about 4.82×10^7 g/(mol Ti mol S h) at 70 °C, whereas activity is about 3.75×10^7 g/(mol Ti mol S h) at 50 °C and 8.46×10^6 g/(mol Ti mol S h) at 30 °C.

Fig. 7 shows that the ratio of Al/Ti ranging from 1000 to 2000 greatly influenced the activity of **1**/MAO. However, the further increase in the ratio of Al/Ti only slightly influenced the activity. This phenomenon is in agreement with the findings by Ishihara et al. for the CpTiCl₃/MAO system [3].

Although the nature of the active species in syndiospecific polymerization of styrene is still under debate amongst researchers, the compelling opinion is that the Ti(III) cationic specie played a very important role in this process [18,26,54–57]. Based on it, we assumed that Cp'TiCl₂(OR*)/MAO catalytic systems have formed the nine-electron active species [Cp'TiCH₃]⁺ through two routes. In route one, the complex of Ti(IV) is alkylated to [Cp'Ti(CH₃)₂(OR*)], then decomposed to produce 10-electron species [Cp'Ti(CH₃)(OR*)], and the active species [Cp'TiCH₃]⁺ is obtained in the last step [58]. Route two is analogize to the proposed mechanism described in the literature [59]. The effect of OR* in the Cp'TiCl₂(OR*)/MAO system are mainly divided into two parts: (1) the OR* ligand directly affected the production of the active species [58], (2) the OR* ligand constituted a steric factor in the outer shell of [MAO(OR*)Cl₂]⁻·nMAO of active species {[CpTiMe]⁺·[MAO'X]⁻·nMAO} [34].

In order to investigate the steric effect of OR, we carried out several experiments for complexes **1** and **9** (Fig. 8). At 50 °C, the activity of complex **1** was five times as high as at 30 °C, whereas complex **9** only exhibited a two-fold increase. This is probably due to 1-isopropyl-4-methyl cyclohexane being more electron-donating than cyclohexane. In addition, 1-isopropyl-4-methyl cyclohexane seems to be providing more appropriate bulkiness than cyclohexane for the polymerization of styrene.¹³C NMR of the new polymers were measured in 1,2-dichlorobenzene at 130 °C. The chemical shift of the phenyl C-1 carbon appeared at 145.16 ppm, and the peak was single and sharp. We assigned this peak to *rr* triad or *rrrr* pentad configuration, which agreed with the Ishihara et al.'s report [2].

Thermal property of new polymers produced by Cp'TiCl₂(OR*)/MAO were measured using differential scanning calorimetry (DSC). Figs. 9 and 10 show DSC curves of samples in the first and second heating cycles, respectively. The melting points of polymers increase in this order: Cp > CH₃(CH₃)CHCp > CH₃OCH₂CH₂Cp > CH₃OCH₂(CH₃)CHCp. This shows the same sequence as the stereoselectivity trends. During the first heating, one glass transition temperature and one melting point were found in the curves. The glass transition temperature is about 105 °C and the melting point is around 260 °C for these samples. Kaminsky and co-worker have reported that the s-PS produced by BzCpTiCl₃/MAO have three melting points during the second heating [60]. In our study, polymer produced by the complexes with unsubstituted Cp show only one melting point. However, the complexes with substituted Cp prepared polymers having two melting points during the second heating. On the basis of these observations, we pre-

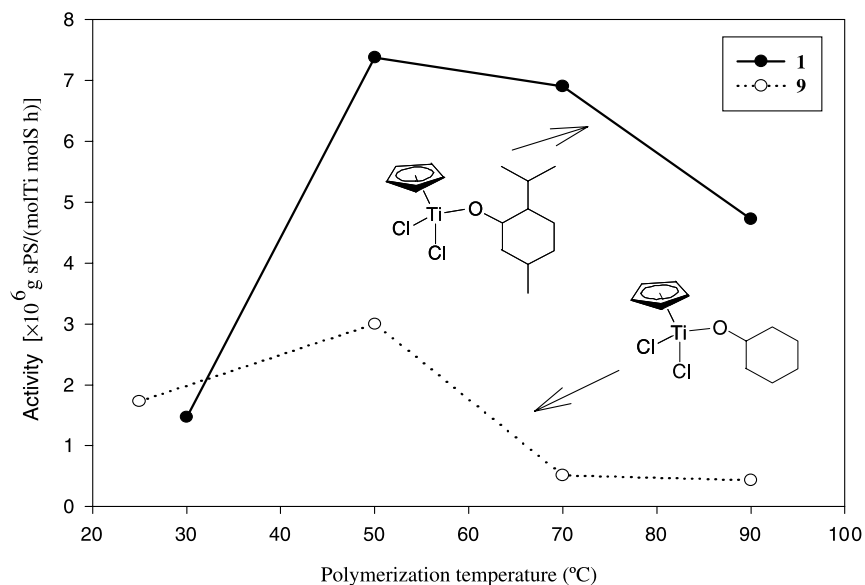


Fig. 8. The steric effect of OR on the catalytic activity.

sume this may be owing to different crystalline polymorphic structure of s-PS [61] produced by $\text{Cp}^*/\text{TiCl}_2(\text{OR}^*)/\text{MAO}$ catalytic systems. A melting point of 268 °C and a melting enthalpy of about 29.9 J/g observed for polymer produced by complex **1** at 50 °C. According to the GPC, s-PS produced by complexes **5** with *O*-functionalized Cp exhibit lower M_w , e.g. 1.11×10^5 , and higher MWD, e.g. 2.25, than

that produced by complex **1**, e.g. 3.03×10^5 and 1.90, respectively. The decreasing order of M_w is **1** (3.03×10^5) > **3** (2.37×10^5) > **5** (1.11×10^5) > **7** (0.84×10^5) (Fig. 11). The trend of M_w is consistent with the melting point of s-PS. This fact furthermore confirms that the stereoselectivity increases in the following order: Cp > $\text{CH}_3(\text{CH}_3)\text{CHCp}$ > $\text{CH}_3\text{OCH}_2\text{CH}_2\text{Cp}$ > $\text{CH}_3\text{OCH}_2(\text{CH}_3)\text{CHCp}$.

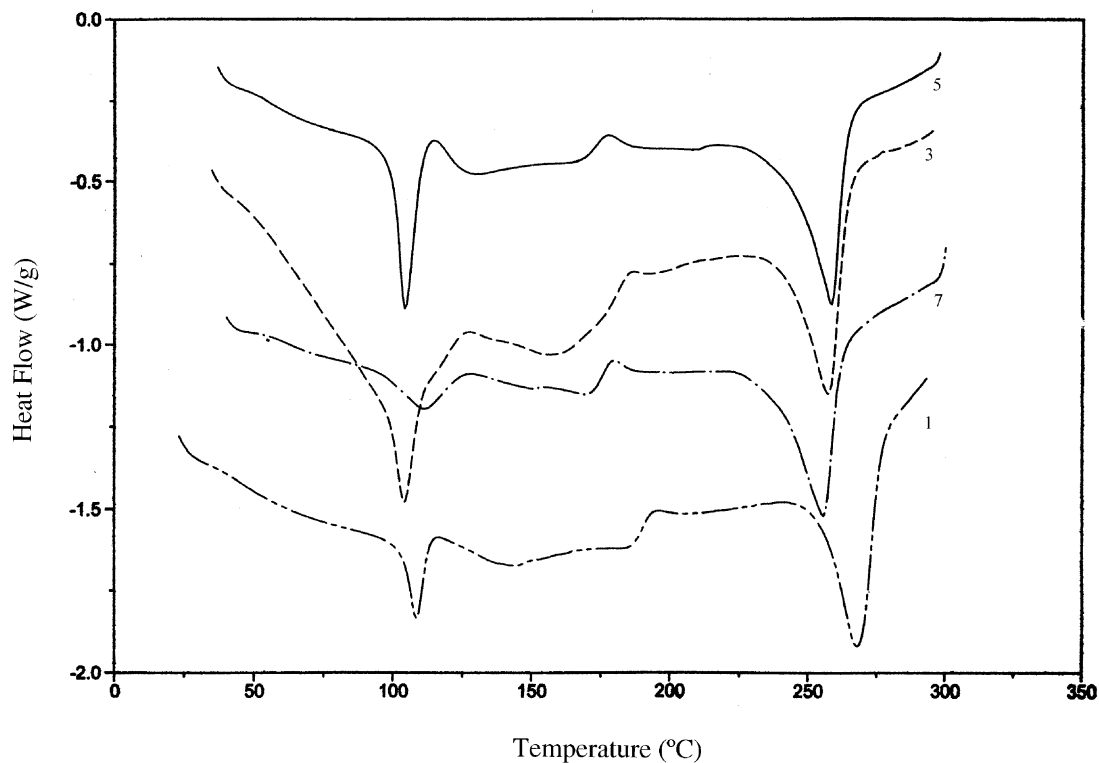


Fig. 9. DSC thermograms first heating of s-PS produced with $\text{Cp}^*/\text{TiCl}_2(\text{OR}^*)/\text{MAO}$ catalytic system.

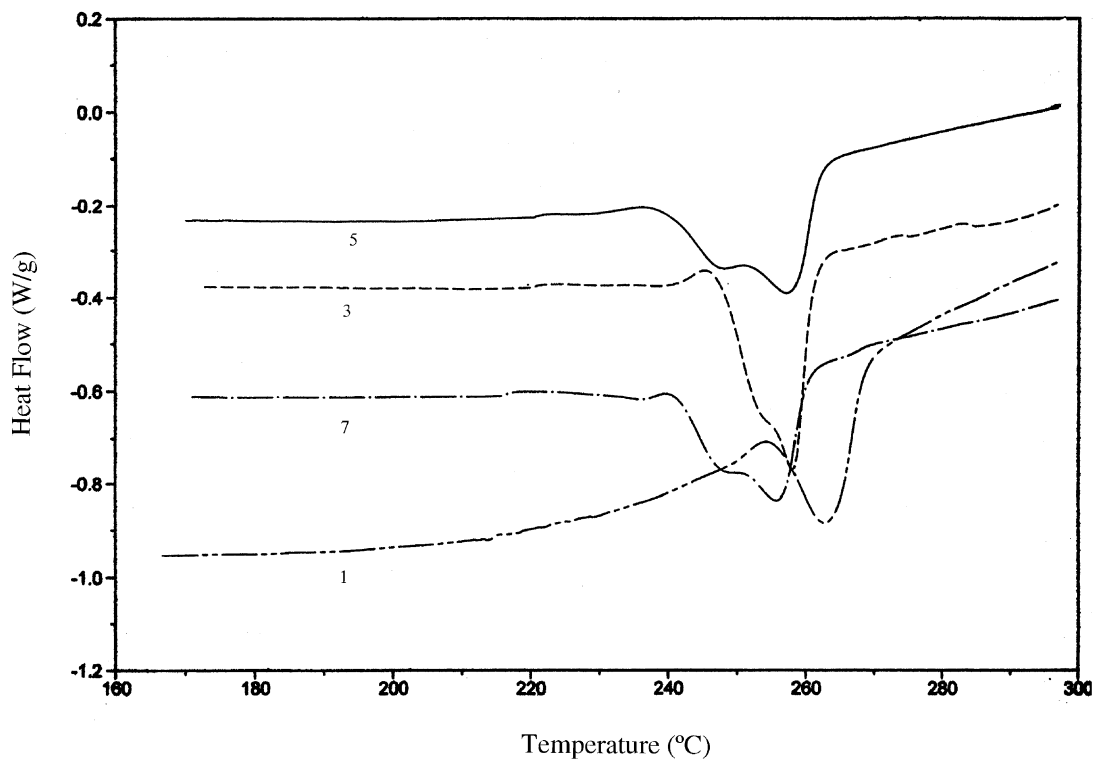


Fig. 10. DSC thermograms second heating of an s-PS produced with $\text{Cp}^*/\text{TiCl}_2(\text{OR}^*)/\text{MAO}$ catalytic system.

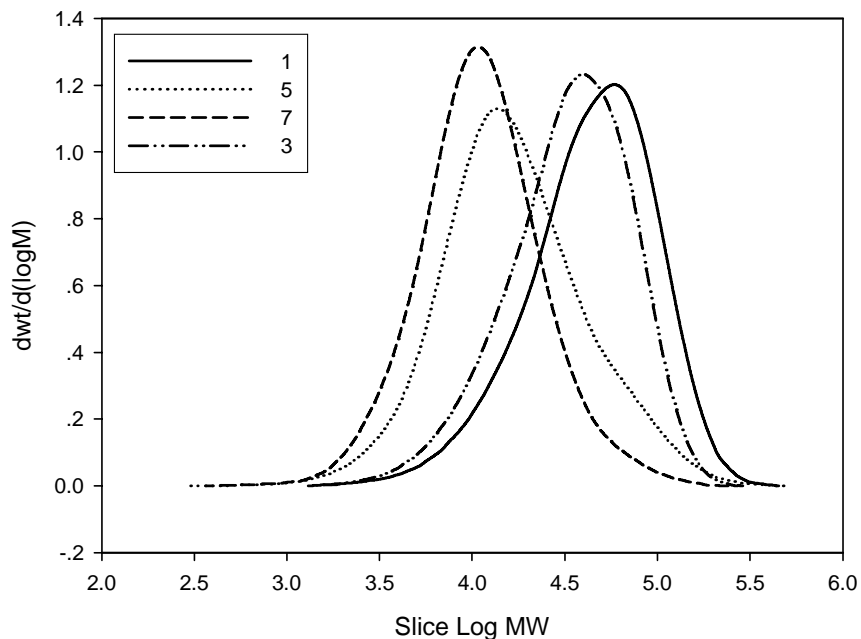


Fig. 11. GPC trace of s-PS produced with complexes 1, 3, 5 and 7.

3. Conclusion

It is obviously shown that the catalytic activity increased in the order $8 < 7 < 6 < 5 < \text{Cp}^*/\text{TiCl}_3 < 4 < 3 < 2 < 1$.

Through the polymerization testing we can conclude that the environment of cyclopentadiene plays a major role in the series of $\text{Cp}^*/\text{TiCl}_2(\text{OR}^*)/\text{MAO}$ catalytic systems, and that the influence of OR^* is relatively weak.

4. Experimental

4.1. Synthesis of complexes 1–8

All operations were carried out under an argon atmosphere using the standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, toluene and *n*-hexane were freshly distilled from sodium benzophenone ketyl under argon prior to use. Styrene was purified by washing several times with dilute NaOH solution, dried over CaH₂, distilled under reduced pressure and stored at –20 °C in the darkness. Methylaluminoxane was purchased from Wittco. CH₃OCH₂CH₂CpTiCl₃ [62], CH₃OCH₂CH(CH₃)CpTiCl₃ [41] were prepared according to the literatures.

All complexes were characterized by ¹H NMR, FTIR, EA and MS. ¹H NMR spectra were recorded on a Varian GRMINI-300 spectrometer in CDCl₃. IR spectra were recorded on a Nicolet MAGNA-IR 550 spectrometer as KBr pellets. Mass spectra were obtained at 70 eV using a HP 5989A mass spectrometer. Elemental analyses were performed on an EA-1106 spectrometer. X-ray structure was determined by an XP-molecular graphics diffractometer with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) and a 12 W rotating anode generator. The structure was solved by direct methods. Refinement was by full-matrix least-squares based on F^2 using SHELXL-93. The optical activity was determined using 241 MC polarimeter in THF at 589 nm.

4.1.1. Synthesis of complex 1

All eight complexes were synthesized via the same route. To a solution of CpTiCl₃ (1.78 g, 8.16 mmol) in 60 ml dry benzene, was added gradually (1R, 3R, 4S)-menthol (1.27 g, 8.16 mmol) and NEt₃ (0.83 g, 8.16 mmol) in this order. The reaction mixture was stirred for 2 h at room temperature, and then was filtered. The residue was washed with dry ethyl ether (2 \times 20 ml), all filtrates were combined and solvents were removed to give a yellow solid. This solid was dissolved in toluene/*n*-hexane (1:1) and stored at –20 °C for 4 h. After filtration, the filtrate was concentrated under vacuum to remove the solvent and was further washed with *n*-hexane twice. The remaining small amount of solvent was removed in vacuo to give needle yellow solid (2.30 g, 82%), mp = 98–100 °C. ¹H NMR (CDCl₃): δ 7.03–6.70 (m, 5H), 4.49 (m, 1H), 2.28 (m, 1H), 2.13 (m, 1H), 1.64 (m, 2H), 1.45 (m, 2H), 1.25 (m, 1H), 0.95 (m, 3H), 0.91 (m, 3H), 0.88 (m, 2H). IR (KBr, cm⁻¹): 3108w, 2955m, 2928m, 2968m, 1454w, 1439w, 1369w, 1105m, 1047s, 1027m, 1020m, 846m, 818s. MS (m/z): 338 (M , 100). Anal. calcd. for C₁₅H₂₄Cl₂O₂Ti: C, 53.12%; H, 7.13%. Found: C, 52.33%; H, 7.09%.

4.1.2. Synthesis of complex 2

Following the procedure described for **1**, CpTiCl₃ (1.60 g, 7.29 mmol), (1S, 2R, 4R)-fenchyl (1.12 g, 7.29 mmol) and NEt₃ (1.02 ml, 7.29 mmol) were used to give a yellow

solid (2.37 g, 96%), mp = 128–130 °C. ¹H NMR (CDCl₃): δ 7.03–6.68 (m, 5H), 4.50 (d, $J = 1.93$, 1H), 1.93 (m, 1H), 1.70 (m, 2H), 1.43 (m, 2H), 1.19 (s, 3H), 1.17 (m, 2H), 1.09 (s, 3H), 0.96 (s, 3H). IR (KBr, cm⁻¹): 3109m, 2954m, 2871m, 1462w, 1444w, 1377w, 1346w, 1110s, 1088s, 1016m, 850m, 826s, 770m, 594w. MS (m/z): 335 ($M - 1$, 4), 301 ($M - Cl$, 15), 183 ($M - OR^*$, 8), 153 (OR^* , 15), 137 (R^* , 58), 81 (C₆H₉, 100). Anal. calcd. for C₁₅H₂₂Cl₂O₂Ti: C, 53.44%; H, 6.58%. Found: C, 53.41%; H, 6.53%.

4.1.3. Synthesis of complex 3

Following the procedure described for **1**, CH₃CH(CH₃)CpTiCl₃ (0.61 g, 2.33 mmol), (1R, 3R, 4S)-menthol (0.37 g, 2.33 mmol) and NEt₃ (0.33 ml, 2.36 mmol) were used to give a yellow solid (0.71 g, 80%), mp = 88–90 °C. $[\alpha]_D^{21} = -57.1^\circ$ ($c = 2.45 \times 10^{-3}$, THF). ¹H NMR (CDCl₃): δ 6.91–6.53 (m, 4H), 4.49 (m, 1H), 3.21 (m, 1H), 2.30 (m, 1H), 2.13 (m, 1H), 1.64 (m, 2H), 1.45 (m, 2H), 1.28 (d, $J = 2.08$, 6H), 1.25 (m, 2H), 0.91 (m, 8H), 0.82 (m, 3H). IR (KBr, cm⁻¹): 3100w, 2961m, 2870w, 1489w, 1461w, 1365w, 1317w, 1261w, 1038m, 930w, 796s, 681w. MS (m/z): 345 ($M - Cl$, 64), 295 ($M - 2Cl - Me$, 48), 225 ($M - OR^*$, 31). Anal. calcd. for C₁₈H₃₀Cl₂O₂Ti: C, 56.71%; H, 7.93%. Found: C, 56.35%; H, 7.82%.

4.1.4. Synthesis of complex 4

Following the procedure described for **1**, CH₃CH(CH₃)CpTiCl₃ (0.78 g, 2.97 mmol), (1S, 2R, 4R)-fenchyl (0.46 g, 2.97 mmol) and NEt₃ (0.41 ml, 2.97 mmol) were used to give a yellow solid (0.99 g, 88%), mp = 56 °C. $[\alpha]_D^{21} = -9.3^\circ$ ($c = 1.78 \times 10^{-3}$, THF). ¹H NMR (CDCl₃): δ 6.55–6.45 (m, 4H), 4.50 (d, $J = 1.92$, 1H), 3.20 (m, 1H), 1.95 (m, 1H), 1.73 (m, 2H), 1.46 (m, 2H), 1.29 (d, $J = 0.77$, 6H), 1.23 (s, 3H), 1.13 (m, 2H), 1.08 (s, 3H), 0.96 (s, 3H). IR (KBr, cm⁻¹): 3103w, 2960s, 2927s, 2869s, 1846w, 1640w, 1490m, 1460s, 1371w, 1365m, 1111s, 1084s, 1038m, 993w, 830s, 802s, 769s, 679m. MS (m/z): 343 ($M - Cl$, 8), 306 ($M - 2Cl$, 6), 207 ($M - Cl - R^*$, 9). Anal. calcd. for C₁₈H₂₈Cl₂O₂Ti: C, 57.01%; H, 7.44%. Found: C, 56.86%; H, 7.48%.

4.1.5. Synthesis of complex 5

Following the procedure described for **1**, CH₃OCH₂CH₂CpTiCl₃ (0.55 g, 2.0 mmol), (1R, 3R, 4S)-menthol (0.31 g, 2.0 mmol) and NEt₃ (0.29 ml, 2.0 mmol) were used to give a yellow solid (0.68 g, 86%), mp = 59–60 °C. $[\alpha]_D^{21} = -56.5^\circ$ ($c = 2.14 \times 10^{-2}$, THF). ¹H NMR (CDCl₃): δ 6.58–6.54 (m, 4H), 4.52 (m, 1H), 3.66 (t, $J = 6.20$, 2H), 3.37 (s, 3H), 3.04 (t, $J = 6.20$, 2H), 2.28 (m, 1H), 2.13 (m, 1H), 1.65 (m, 2H), 1.45 (m, 2H), 1.26 (m, 1H), 0.96–0.91 (m, 8H), 0.83 (d, $J = 6.20$, 3H). IR (KBr, cm⁻¹): 3091w, 2930m, 1492w, 1455w, 1250w, 1184w, 1116s, 1063m, 1049m, 977w, 854s, 800s, 728m, 687m, 592w. MS (m/z): 361 ($M - Cl$, 72), 241 ($M - OR^*$, 58). Anal. calcd. for C₁₈H₃₀Cl₂O₂Ti: C, 54.43%; H, 7.61%. Found: C, 53.89%; H, 7.58%.

4.1.6. Synthesis of complex 6

Following the procedure described for **1**, CH₃OCH₂CH₂CpTiCl₃ (0.56 g, 2.03 mmol), (1S, 2R, 4R)-fenchyl (0.33 g, 2.11 mmol) and NEt₃ (0.29 ml, 2.08 mmol) were used to give a yellow solid (0.67 g, 84%), mp = 52–53 °C. $[\alpha]_D^{21} = -17.5^\circ$ ($c = 8.66 \times 10^{-3}$, THF). ¹H NMR (CDCl₃): δ 6.79–6.50 (m, 4H), 4.52 (m, 1H), 3.65 (m, 2H), 3.37 (s, 3H), 3.04 (m, 2H), 1.92 (m, 1H), 1.74 (m, 2H), 1.44 (m, 2H), 1.17 (s, 3H), 1.11 (m, 2H), 0.99 (s, 3H), 0.86 (s, 3H). IR (KBr, cm⁻¹): 3100w, 2957s, 2921s, 2866s, 2822m, 2805m, 2725w, 1492m, 1459m, 1378m, 1356m, 1256w, 1209m, 1112s, 1083s, 1037m, 1014m, 916w, 840s, 822s, 803s, 686w. MS (*m/z*): 358 (*M* – Cl, 26), 322 (*M* – 2Cl, 19), 277 (*M* – Cl – Cp – Me, 64), 241 (*M* – OR*, 100), 153 (OR*, 48), 81 (CH₂Cp, 71). Anal. calcd. for C₁₈H₂₈Cl₂O₂Ti: C, 54.71%; H, 7.14%. Found: C, 54.70%; H, 7.23%.

4.1.7. Synthesis of complex 7

Following the procedure described for **1**, CH₃OCH₂CH-(CH₃)CpTiCl₃ (0.46 g, 1.58 mmol), (1R, 3R, 4S)-menthol (0.25 g, 1.58 mmol) and NEt₃ (0.22 ml, 1.58 mmol) were used to give a yellow solid (0.53 g, 82%), mp = 64–66 °C. $[\alpha]_D^{21} = -52.9^\circ$ ($c = 3.59 \times 10^{-3}$, THF). ¹H NMR (CDCl₃): δ 6.81–6.47 (m, 4H), 4.50 (m, 1H), 3.48 (t, *J* = 6.32, 2H), 3.42 (m, 1H), 3.34 (s, 3H), 2.30 (m, 1H), 2.13 (m, 1H), 1.65 (m, 2H), 1.45 (m, 2H), 1.27 (m, 1H), 1.35 (d, *J* = 0.98, 3H), 0.96–0.91 (m, 8H), 0.82 (m, 3H). IR (KBr, cm⁻¹): 3105w, 2961w, 2925m, 2871w, 2827w, 1632w, 1453w, 1369w, 1261w, 1195w, 1105m, 1043m, 966w, 922w, 851m, 806m, 797s, 710w. MS (*m/z*): 375 (*M* – Cl, 15), 334 (*M* – Cl – OMe, 12), 255 (*M* – OR*, 48), 237 (*M* – Cp' – Cl, 21), 219 (*M* – Cl – OR*, 19). Anal. calcd. for C₁₉H₃₂Cl₂O₂Ti: C, 55.49%; H, 7.84%. Found: C, 55.17%; H, 7.84%.

4.1.8. Synthesis of complex 8

Following the procedure described for **1**, CH₃OCH₂CH-(CH₃)CpTiCl₃ (0.38 g, 1.30 mmol), (1S, 2R, 4R)-fenchyl (0.20 g, 1.30 mmol) and NEt₃ (0.18 ml, 1.30 mmol) were used to give a yellow solid (0.39 g, 74%), mp = 78–80 °C. $[\alpha]_D^{21} = -13.1^\circ$ ($c = 2.09 \times 10^{-2}$, THF). ¹H NMR (CDCl₃): δ 6.65–6.43 (m, 4H), 4.53 (d, *J* = 1.71, 1H), 3.48 (m, 2H), 3.35 (d, *J* = 1.95, 3H), 1.96 (m, 1H), 1.72 (m, 2H), 1.45 (m, 2H), 1.35 (m, 3H), 1.20 (s, 3H), 1.15 (m, 2H), 1.09 (m, 3H), 0.97 (s, 3H). IR (KBr, cm⁻¹): 3104w, 2956s, 2924s, 2868s, 2825m, 2729w, 1639w, 1488m, 1462m, 1384w, 1351w, 1260w, 1196w, 1105s, 1079s, 1015m, 920w, 849m, 827s, 803s, 769s, 682w. MS (*m/z*): 373 (*M* – Cl, 34), 336 (*M* – 2Cl, 8), 255 (*M* – OR*, 100), 220 (*M* – Cl – OR*, 81). Anal. calcd. for C₁₉H₃₀Cl₂O₂Ti: C, 55.76%; H, 7.39%. Found: C, 55.43%; H, 7.33%.

Crystals for the X-ray crystal structure analysis were obtained by recrystallizing the solid **8** from toluene/*n*-hexane at –20 °C for 2 days. Crystal data and relevant structural parameters were listed in Table 1.

Table 1

Crystal data and structure refinement for **8**

Empirical formula	C ₁₉ H ₃₀ Cl ₂ O ₂ Ti
Formula weight	409.23
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 12.588(2) Å, α = 90° <i>b</i> = 12.726(2) Å, β = 91.293(13)° <i>c</i> = 13.166(4) Å, γ = 90°
Volume (<i>z</i>)	2108.7(7) Å ³ , 4
Density (calculated)	1.289 Mg/m ³
Absorption coefficient	0.667 mm ⁻¹
<i>F</i> (000)	864
Crystal size	0.34 mm × 0.22 mm × 0.22 mm
θ range for data collection	2.23–26.00°
Limiting indices	–14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 16
Reflections collected	4677
Independent reflections	3972 (<i>R</i> _{int} = 0.0000)
Completeness to $\theta = 26.00^\circ$	99.8%
Absorption correction	Semi-empirical
Max. and min. transmission	1.000 and 0.923
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3972/0/305
Goodness-of-fit on <i>F</i> ²	0.900
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0456, <i>wR</i> 2 = 0.1081
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1646, <i>wR</i> 2 = 0.1508
Extinction coefficient	0.0000(2)
Largest diff. peak and hole	0.423 and –0.280 eÅ ⁻³

4.2. Polymerization and polymer characterization

Polymerization was carried out in a sealed ampoule tube with a rubber stopper. Styrene, various proportions of toluene, MAO, and various proportions of 0.05 mol/l Ti compound in toluene were injected into the bottle in this order under an argon atmosphere. Polymerization was carried out at a constant temperature in an oil bath for a selected period of time. After the reaction finished, the ampoule was opened and ethanol containing 10% HCl was introduced to terminate the reaction, then the polymer was precipitated out. Afterwards, it was filtered, washed and dried in a vacuum oven at 80 °C for 24 h to a constant weight. The polymer was then extracted with 2-butanone for 2 h to remove any atactic polymer. The syndiotactic polymer was determined as the amount of polymer insoluble in 2-butanone. Melting points were determined by DSC. The thermograms were recorded with a DSC 2910 Modulated DSC Universal V1.10B TA Instruments at a heating and cooling rate of 10 °C/min. ¹³C NMR spectra were recorded on a Varian GRMINI-500 spectrometer in 1,2-dichlorobenzene at 130 °C. Molecular weight and molecular weight distribution (*M*_w/*M*_n) values were obtained from Waters-208 LC/GPC chromatograms employing polystyrene standards for calibration. Analysis was carried out using 1,2-dichlorobenzene at high temperature (140 °C).

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