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Syndiospecific Polymerization of Styrene Using Half-Titanocene Catalyst Covalently Supported on $MgCl_2/AlEt_n(OEt)_{3-n}$

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Summary

The novel half-titanocene catalyst bearing reactive functional amino group, η^5-pentamethylcyclopentadienyltri(*p*-amino-phenoxyl) titanium [$Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$], was easily synthesized by the reaction of η^5-pentamethylcyclopentadienyltrichloride titanium (Cp^*TiCl_3) with *p*-amino phenol in the presence of triethyl amine (NEt_3). $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ covalently anchored on $MgCl_2/AlEt_n(OEt)_{3-n}$ support obtained from the reaction of triethylaluminium ($AlEt_3$) with the adduct of magnesium chloride ($MgCl_2$) and ethanol (EtOH), has been investigated and used to catalyze syndiospecific polymerization of styrene. Influences of the support structure, cocatalyst, and the molar ratio of Al in methylaluminoxane (MAO) and Ti (Al_{MAO}/Ti) on catalytic activity, syndiotacticity and molecular weight of the resultant polystyrene were investigated. Compared with the corresponding $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ homogeneous catalyst, a considerable increase in activity and molecular weight of syndiotactic polystyrene (sPS) was observed for the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3\text{–}MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst even at a relatively low Al_{MAO}/Ti ratio of 50, and the kinetics of polymerization was stable during the reaction process.

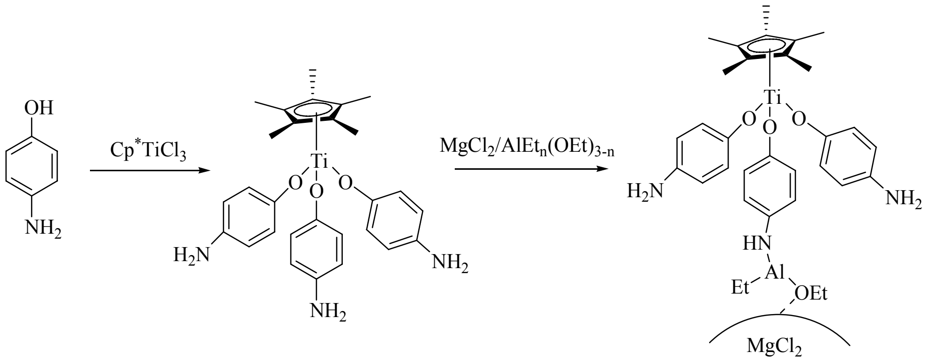
Introduction

The use of titanium complex/methylaluminoxane catalyst system in the first preparation of syndiotactic polystyrene (sPS) by Ishihara and his colleagues has impelled an active search for new types of sPS catalysts [1]. After that, extensive research has been embarked on it [2-10].The catalytic activities for styrene polymerization increased in this order, $TiBr_4<TiCl_4<Ti(OMe)_4\sim CpTiCl_2H<Cp^*TiCl_3\sim CpTiCl_3$ (Cp = cyclopentadienyl, Cp^* = η^5–pentamethylcyclopentadienyl), and half-titanocene catalysts exhibited good stereo control in the syndiospecific polymerization of styrene. Campbell and Chien [11] found that the catalyst $CpTiCl_3$ was converted into $CpTi(OMe)_3$, $CpTi(OEt)_3$ and $CpTi(OBu)_3$, their catalytic activity and polymerization behaviors showed considerable changes. In our previous study [12, 13], any change of substituents R in the $Cp^*Ti(OR)_3$ catalytic systems could result in dramatically difference in catalytic activity and

polymerization performance. The presence of a phenyl ring ligand moiety in R could stabilize the active species and give the higher activity.

These homogeneous catalysts, however, require a large amount of expensive MAO which limits the application of the above catalysts to industrial processes. Several attempts have been made in order to reduce Al_{MAO}/Ti or to use other cocatalysts instead of MAO. One approach is immobilization of these catalysts on a porous solid such as SiO_2, Al_2O_3, $MgCl_2$ and polymer. Supported half-titanocene catalysts for syndiospecific polymerization of styrene on these supports have been widely investigated by both academic and industrial sectors [14-19].So far, three methods have been developed for half-titanocene supported catalysts. The first method involves direct immobilization of the catalyst on the support surface, which usually significantly suppresses the catalytic activity of the catalyst and changes the catalyst structure and the microstructure of the resultant polymer [14]. The second method, commonly used, is the immobilization of the catalyst on the support pretreated with MAO or alkylaluminium compounds. It is thought that the catalyst and the MAO or alkylaluminium compounds on the support are bound by loose ionic interactions. This fairly weak bond has given rise to the assumption that the catalyst can float on the surface of the support [15-17]. The third method involves the covalent bonding of the catalyst to the carrier by one of its ligands, which is commonly used in the ethylene polymerization [20], however, has few reports in the syndiospecific polymerization of styrene.

In this article, a half-titanocene catalyst of $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ covalently anchored on the $MgCl_2/AlEt_n(OEt)_{3-n}$ support, by reaction of the functional groups, has been studied (Scheme 1). Styrene polymerizations were carried out with half-titanocene–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalysts and corresponding homogeneous catalysts in the presence of various cocatalysts. The surface morphology and internal porous structure of the supported catalysts were investigated by SEM, XRD. The influences of the structure of the supported catalyst, polymerization conditions on the catalytic activity and the properties of syndiotactic polystyrene were discussed.



Scheme 1. Synthesis of $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3\text{–}MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst

Experimental

Materials

Toluene was refluxed over metallic sodium for 24 h and distilled under nitrogen atmosphere before use. Styrene was purified by stirring over CaH_2 for about 24 h and then distilled under reduced pressure over CaH_2 and was finally stored under nitrogen atmosphere. Trimethylaluminium (TMA), $AlEt_3$, diethylaluminium chloride ($AlEt_2Cl$) and triisobutylaluminium (TIBA) from Ethyl Company were taken as 300 g/L solution in *n*-heptane, respectively. MAO was prepared by the controlled hydrolysis reaction of TMA with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene. Cp^*TiCl_3 was prepared according to the literature [10]. $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ was synthesized by the reaction of Cp^*TiCl_3 with *p*-amino phenol in the presence of NEt_3 at 75 °C for 5 h. A yellow powder (yield 40 %) was obtained and identified. $C_{28}H_{33}O_3N_3Ti$ (507):Calc. C 66.27, N 8.28, H 6.51. Found C 66.05, N 8.17, H 6.79.

Preparation of $MgCl_2/AlEt_n(OEt)_{3-n}$ support

The $MgCl_2$/2.92EtOH adduct was prepared according to the literature [21] using the recrystallization method. $MgCl_2/AlEt_n(OEt)_{3-n}$ support was prepared by the addition of $AlEt_3$ to a slurry of the $MgCl_2$/2.92EtOH adduct in heptane at 0 °C, and then the mixture was kept at ambient temperature for 24 h with occasional agitation. The resultant support was washed three times with heptane, and finally dried by evaporation under vacuum.

Catalyst Immobilization

A toluene solution of $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ (or Cp^*TiCl_3) was added to the slurry of $MgCl_2/AlEt_n(OEt)_{3-n}$ support in toluene at 50 °C. After reaction for 4 h, the slurry was filtered through a fritted disk. The resultant solids were washed several times with toluene until the liquid phase was colorless. The solid catalysts were dried by evaporation under vacuum and then stored in nitrogen atmosphere. ICP-AES analysis of supported catalysts $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3\text{–}MgCl_2/AlEt_n(OEt)_{3-n}$ (wt %): Ti (0.13), Al (5.49), Mg (11.89), $Cp^*TiCl_3\text{–}MgCl_2/AlEt_n(OEt)_{3-n}$ (wt %): Ti (0.15), Al (5.83), Mg (12.70).

Polymerization of Styrene

Polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in 100 mL glass reactor equipped with a magnetic stirrer. The MAO, toluene, styrene, TIBA, and the supported catalysts (or homogeneous catalysts) were introduced in that order into the reactor. After selected reaction time, the polymerization was terminated by the addition of 10 wt % HCl in ethanol. The polymers were washed with ethanol and dried in vacuum at 80 °C to constant weight. The syndiotactic index (SI) of polystyrene was determined as the weight percentage of the insoluble fraction after the obtained polymer was extracted for 12 h with boiling butanone.

Characterization

ICP-AES measurement for determining the loading of Mg, Al, and Ti in supported catalysts was performed on IRIS Advantage (HR) spectrometer. Powder X-ray diffraction (XRD) patterns of the supports and supported catalysts were obtained with Bruker D8 Advance Diffractometer instrument equipped with a source using a Cu anode, operating at 40 kV and 40 mA for Cu kα radiation. The dried sample was covered with collodion to avoid contact with air and moisture. BET (Brunauer–Emmett–Teller) surface area, pore volume, and average pore size of the support were determined by nitrogen physisorption using an ASAP 2010 surface area and pore size analyzer.

^{13}CNMR spectra of polystyrene (PS) were carried out on INOVA 500MHz spectrometer at 120 °C in *o*-dichlorobenzene /*o*-dichlorobenzene-*d*6 solution (or at room temperature in chloroform-*d* solution). Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system, data reported were gathered for the second melt with a heating and cooling scan of 10 °C/min. Molecular weight (M_w) and molecular weight distribution (M_w/M_n) of polymers were determined by GPC (gel permeation chromatography, Waters 150-CV) in 1, 2, 4-trichlorobenzene at 135 °C, and the data were analyzed using polystyrene calibration curves.

Results and Discussion

In our investigation, the recrystallized $MgCl_2$ in the formation of the $MgCl_2$/2.92EtOH adduct was modified by $AlEt_3$ to prepare $MgCl_2/AlEt_n(OEt)_{3-n}$ support. Organoaluminium compound, through the alkoxy bridges between aluminium and magnesium and the coordination of chloride to aluminium, was firmly retained on the $MgCl_2/AlEt_n(OEt)_{3-n}$ support [22]. Such organoaluminium compound was very important, providing for the immobilizing sites of $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ complex as shown in Scheme 1. In this study, the Ti content in the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst was 0.13 % (w/w).

Anhydrous $MgCl_2$ has a cubic close packing structure which gives a strong XRD pattern at 2θ = 15°, 35°, 50°. The XRD patterns of $MgCl_2$-based supports vary depending on their composition and preparation methods [23, 24]. As shown in Figure 1, $MgCl_2$/EtOH adduct, $MgCl_2/AlEt_n(OEt)_{3-n}$ support and the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst were tested by XRD. Compared with the XRD pattern of $MgCl_2$/EtOH adduct, the diffraction peaks at $2\theta < 10^\circ$ of the $MgCl_2/AlEt_n(OEt)_{3-n}$ support disappears, which reveals that the crystal aggregates of $MgCl_2$/EtOH adduct have been destroyed to some extent through the treatment of $AlEt_3$. The irregular structure, high porosity and small primary crystallite size would be beneficial for effective immobilization of $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$. The similarity of the XRD patterns before and after catalyst immobilization indicates that little change of the $MgCl_2$ skeleton takes place during the process of supporting the catalyst precursors.

The $MgCl_2/AlEt_n(OEt)_{3-n}$ supports were porous secondary particles, formed by loosely aggregated primary $MgCl_2$ particles. The SEM photograph in Figure 2 showed that particles of the supported catalyst were irregular in shape with roof surface and filled with pores, which were useful for the dispersion of the active species. The results of nitrogen physisorption measurements demonstrate that the BET surface area, pore volume, and average pore diameter of the $MgCl_2/AlEt_n(OEt)_{3-n}$ support were about 15 m^2/g, 0.035 ml/g, and 7.7 nm, respectively. The surface morphology and internal porous structure of the supported catalysts will influence the catalyst performance for styrene polymerization and the structure of resultant polymers.

Some studies have reported that $MgCl_2/AlR_n(OR')_{3-n}$ supported metallocene catalysts can directly catalyze ethylene coordination polymerization without any cocatalysts or in the presence of various organoaluminium compounds, such as $AlEt_3$, $AlEt_2Cl$ and TIBA [25, 26], taking into account the possibility that the cationic active species may be generated *via* alkyl abstraction by Lewis acid sites on the support. As for the

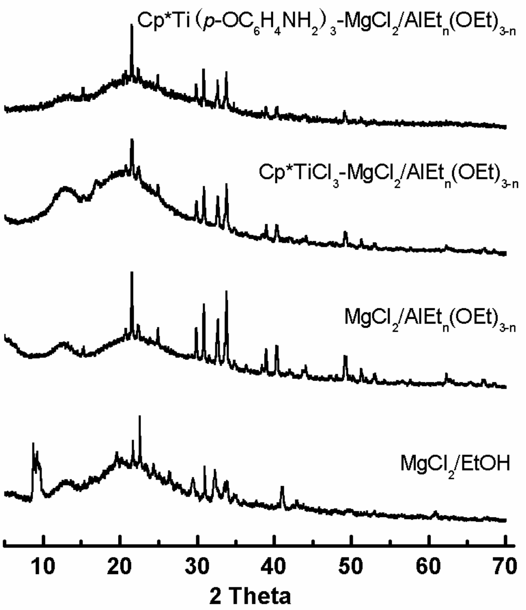


Figure 1. XRD patterns of $MgCl_2$/EtOH adduct, $MgCl_2/AlEt_n(OEt)_{3-n}$ support, $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ and Cp^*TiCl_3–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalysts

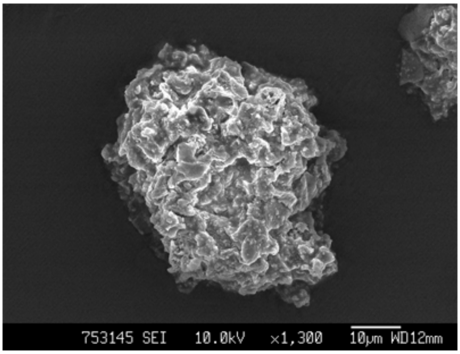


Figure 2. SEM image of $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst

$Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst, the effect of cocatalysts ($AlEt_2Cl$, TIBA, MAO) on styrene polymerization under the condition of temperature 70 °C was investigated in this paper. On basis of our experimental results, we found that MAO was an efficient cocatalyst for styrene polymerization, giving syndiotactic polystyrene confirmed by ^{13}C NMR spectrum as shown in Figure 3. Under the adopted conditions, preliminary tests performed with $AlEt_2Cl$ as cocatalyst to promote $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst for styrene polymerization indicated the production of atactic polystyrene (aPS) and no sPS (Figure 3). The obtained polymers were completely soluble in THF, MEK and acetone. It should be noted that TIBA as cocatalyst can hardly catalyze styrene polymerization, but the external addition of TIBA to $Cp^{*}Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2$/ $AlEt_n(OEt)_{3\text{-}n}$–MAO catalyst system causes an increase in activity for styrene syndiospecific polymerization, compared with the system without TIBA.

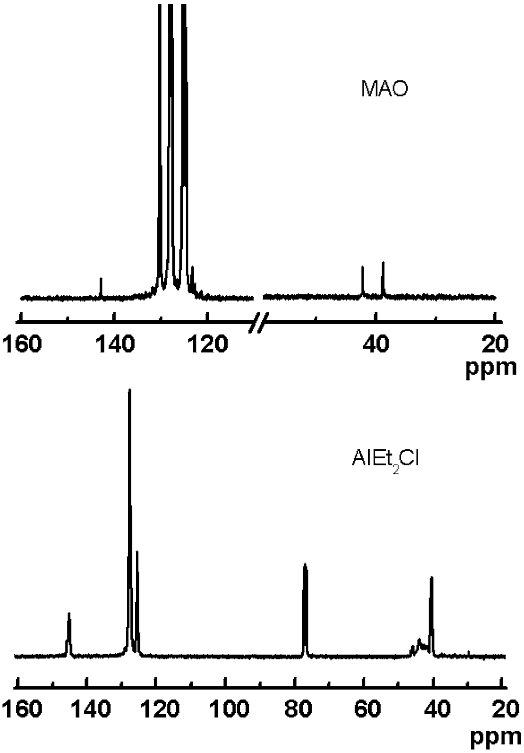


Figure 3. ^{13}C NMR profiles of polystyrenes with $Cp^{*}Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3\text{-}n}$ supported catalyst activated by MAO (120 °C in *o*-dichlorobenzene /*o*-dichlorobenzene-*d*6 solution) and $AlEt_2Cl$ (room temperature in chloroform-*d* solution)

To confirm the immobilized $Cp^{*}Ti(p\text{-}OC_6H_4NH_2)_3$ catalyst not to be removed from $MgCl_2/AlEt_n(OEt)_{3\text{-}n}$ support into toluene when activated by MAO, the following experiment was designed. In a flame-dried Schlenk-type apparatus, the $Cp^{*}Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3\text{-}n}$ supported catalyst and MAO were added in 30 mL toluene under nitrogen atmosphere. After vigorously stirring at 70 °C for 1h, the mixture was filtered under nitrogen atomosphere. The solid and the liquid were used to catalyze styrene polymerization in the usual procedure, respectively. After polymerization for 1h, the solid-catalyzed styrene polymerization displayed very high activity, while for the liquid only a trace of product. Therefore, it may be concluded from the result that the prepared supported catalyst was anchored on the support by covalent bond.

Polymerizations of styrene with $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst activated by MAO and TIBA were performed in toluene. In order to assess the significance of the catalytic activity, we also carried out the styrene polymerization experiments by using Cp^*TiCl_3–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst and their corresponding homogeneous catalysts under the same polymerization conditions. The polymerization data, summarized in Table 1, reveal that the order of activity of the four catalysts is $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$– $MgCl_2/AlEt_n(OEt)_{3-n}$ > Cp^*TiCl_3 > $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ > Cp^*TiCl_3–$MgCl_2/AlEt_n(OEt)_{3-n}$, especially at low Al_{MAO}/Ti ratios, such as $Al_{MAO}/Ti = 50$. These results implied that the covalent bonding of the catalyst $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ to the $MgCl_2/AlEt_n(OEt)_{3-n}$ support was more effective than Cp^*TiCl_3 directly anchoring on the support.

Table 1. Results of styrene polymerization with half-titanocene catalysts in the presence of MAO and TIBA [a]

Catalyst	Al_{MAO}/Ti	Activity [b]	Yield %	sPS [c] %	M_w [d] ($\times 10^{-5}$)	M_w/M_n [d]	T_m [e] (°C)
$Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$	450	3.2	97.8	95.1	2.6	2.3	271
	300	2.4	73.1	94.0	/	/	272
	150	1.5	46.9	93.8	3.6	2.5	271
	100	1.1	34.6	90.9	3.9	2.2	271
	50	0.8	25.2	89.7	4.5	2.1	271
Cp^*TiCl_3–$MgCl_2/AlEt_n(OEt)_{3-n}$	450	1.4	43.4	87.3	4.0	2.3	271
	150	0.4	11.6	74.1	/	/	/
	50	trace	trace	/	/	/	/
$Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$	450	1.8	97.6	95.7	1.5	2.5	269
	150	0.8	25.6	84.0	2.5	2.2	270
	50	0.3	8.3	55.3	/	/	/
Cp^*TiCl_3	450	3.1	94.4	96.3	1.6	2.6	272
	50	0.6	18.8	88.7	/	/	270

[a] Polymerization conditions: $[Ti] = 2.1 \times 10^{-4}$ mol/L, [styrene] = 6.2 mol/L, polymerization temperature = 70 °C, polymerization time = 1 h, $Al_{TIBA}/Ti = 150$ (mol/mol);

[b] Activity $\times 10^6$ gPS/molTi·h;

[c] sPS% (g of polymer insoluble in boiling 2-butanone)/(g of total polymer)×100%;

[d] Determined by GPC;

[e] Determined by DSC.

Another highly influential factor on the activity of these supported catalysts is the Al_{MAO}/Ti molar ratio. The catalytic activity and the syndiotacticity drastically decreased with decreasing Al_{MAO}/Ti molar ratio in the homogeneous $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ which is consistent with the previous report [10]. However, the catalytic activity and the syndiotacticity of the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst are less sensitive to Al_{MAO}/Ti molar ratio. It is noteworthy that the resultant supported catalyst showed fairly good catalytic activity and yielded syndiotactic polystyrene with the syndiotacticity of 89.7 % at a relatively low Al_{MAO}/Ti ratio of 50 (Table 1) indicating the stabilization of the active sites by internal porous structure of the support. For industrial uses, the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst system appear to be viable, as they require a less amount of expensive cocatalyst MAO. The melting point of syndiotactic polystyrene was almost unchanged in our experimented Al_{MAO}/Ti mole ratio conditions.

The results of kinetic profiles of styrene polymerization over the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst and the homogeneous $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ catalyst in the presence of MAO and TIBA are shown in Figure 4. The activity of the immobilized catalyst remained higher than that of the homogeneous counterpart throughout the whole polymerization. This result can be attributed to the steric hindrance of the support around the active species, preventing the aggregation of active species in $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst.

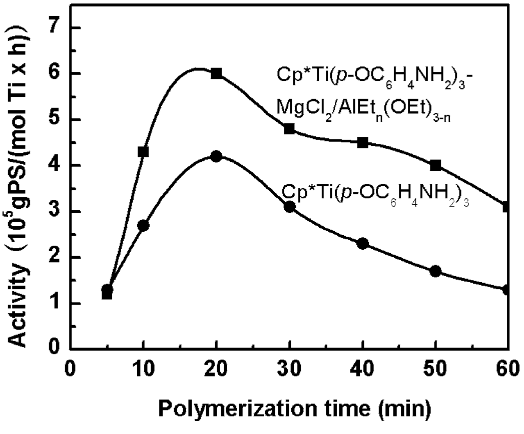


Figure 4. Kinetic profiles of styrene polymerization with $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ and $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ activated by MAO and TIBA as cocatalysts, polymerization temperature= 50 °C, $[Ti]= 1.0 \times 10^{-4}$ mol/L, Al_{MAO}/Ti= 150(mol/mol), Al_{TIBA}/Ti= 150(mol/mol)

As shown in Figure 5, the molecular weight distribution of syndiotactic polystyrene obtained with the present supported catalysts was about 2.2, indicating single-site nature of the $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst. Compared with the corresponding homogeneous catalyst, the polystyrene prepared with the supported catalyst displayed much higher molecular weight. The increase of molecular weight indicates that the active species anchored on confined space of $MgCl_2/AlEt_n(OEt)_{3-n}$ pores effectively inhibit the chain-transferring reaction, especially β-H elimination during polymerization.

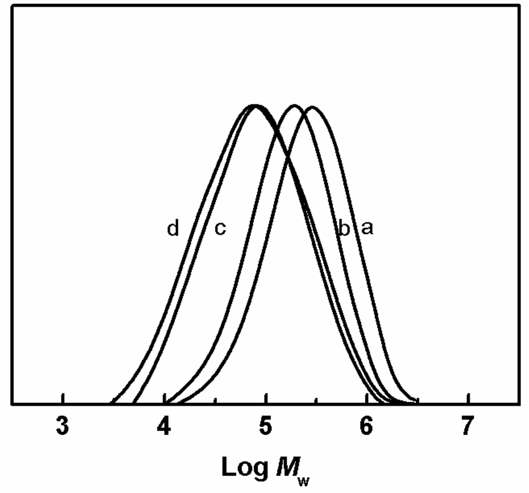


Figure 5. GPC profiles of sPS with Cp^*TiCl_3–$MgCl_2/AlEt_n(OEt)_{3-n}$ (a) and $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ (b) supported catalysts, Cp^*TiCl_3 (c) and $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ (d) homogeneous catalysts ([Ti] = 2.1×10^{-4} mol/L, styrene = 6.2 mol/L, polymerization temperature = 70 °C, polymerization time = 1 h, Al_{MAO}/Ti =450 (mol/mol), Al_{TIBA}/Ti = 150 (mol/mol))

Conclusions

In this report, a highly active half-titanocene supported catalyst for syndiospecific polymerization of styrene has been studied. By reaction of the functional amino groups in $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$ catalyst with $MgCl_2/AlEt_n(OEt)_{3-n}$, the resultant half-titanocene was covalently anchored on the support. The $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$–$MgCl_2/AlEt_n(OEt)_{3-n}$ supported catalyst could be used to polymerize styrene with fairly high activity, stable reaction kinetics and provide enhanced properties of syndiotactic polystyrene. Compared with the corresponding homogeneous $Cp^*Ti(p\text{-}OC_6H_4NH_2)_3$/MAO catalyst, the present supported catalyst exhibited much higher catalytic activity for styrene polymerization at a relatively low (~50) Al_{MAO}/Ti molar ratio, indicating the stabilization of the active species in terms of the internal porous structure of the support. Moreover, the molecular weight distribution of syndiotactic polystyrene obtained with the supported catalyst was about 2.2, indicating retention of single-site catalyst characteristics after immobilization.

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