

Synthesis of Syndiotactic Polystyrene with Novel Titanocene Catalysts Activated by Modified Methylaluminoxane

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Abstract: Novel highly active η^5 -pentamethylcyclopentadienyltribenzyloxy titanium catalyst activated by modified methylaluminoxane (m-MAO) was prepared for styrene syndiospecific polymerization. The influences of the contents of trimethylaluminum (TMA) in m-MAO and external addition of tri-isobutylaluminum (TIBA) on the distribution of the oxidation states of titanium were investigated in detail. The Ti (III) is in favour of styrene syndiospecific polymerization in higher catalytic activity.

Keywords: Metallocene; syndiotactic polystyrene; methylaluminoxane.

The synthesis of syndiotactic polystyrene (sPS) has attracted much interest for its properties and applications. Half-sandwich titanocene and methylaluminoxane (MAO) catalysts have been found to be the favour precursors to catalyze syndiospecific polymerization of styrene¹⁻¹⁰. MAO as cocatalysts always contains some amount of free trimethylaluminum (TMA) both in a form coordinated to MAO and as free TMA¹¹. However, the roles of the TMA coexisting in MAO are still unclear. In this paper, several modified methylaluminoxanes (m-MAO) which contained different percentage contents of TMA were compared as the cocatalyst to activate the η^5 -pentamethylcyclopentadienyl tribenzyloxytitanium[CpTi* (OBz)₃] for styrene syndiospecific polymerization. The results show that the contents of TMA coexisted in m-MAO influence the distribution of oxidation states of the titanium in the polymerization systems, and Ti (III) is in favour of styrene syndiospecific polymerization in higher catalytic activity. At the same time the influences of external addition of tri-isobutylaluminum (TIBA) to the catalytic systems on styrene syndiospecific polymerization were also investigated.

Experimental

Toluene was refluxed over metallic sodium for 24h and distilled under nitrogen atmosphere before use. Styrene was purified by distillation under reduced pressure over CaH₂ and was finally stored under nitrogen atmosphere.

$\text{Cp}^*\text{Ti}(\text{OBz})_3$ was prepared by the reaction of pentamethylcyclopentadienyl trichloride titanium (Cp^*TiCl_3) with benzyl alcohol in the presence of the absorbent of HCl (such as $\text{N}(\text{Et})_3$), and yellow liquid product (yield 89%) was obtained. Anal. Calcd for $\text{C}_{31}\text{H}_{36}\text{O}_6\text{Ti}$: C: 73.81, H: 7.14; Found: C: 73.26, H: 7.02.

Modified methylaluminoxanes (m-MAO) were prepared by the carefully controlled reaction of trimethylaluminum (TMA) with H_2O from $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dispersed in toluene for several hours, then filtration, and finally evaporation under vacuum. The content of TMA coexisted in m-MAO was determined by pyridine titration method. Phenazine used as indicator and benzene as solvent. Five species of m-MAO solid, i.e., m-MAO1, m-MAO2, m-MAO3, m-MAO4 and m-MAO5 containing 28.6wt%, 26.1wt%, 24.3wt%, 22.8wt% and 20.4wt% of TMA were respectively obtained by regulating the molar ratio of H_2O and TMA.

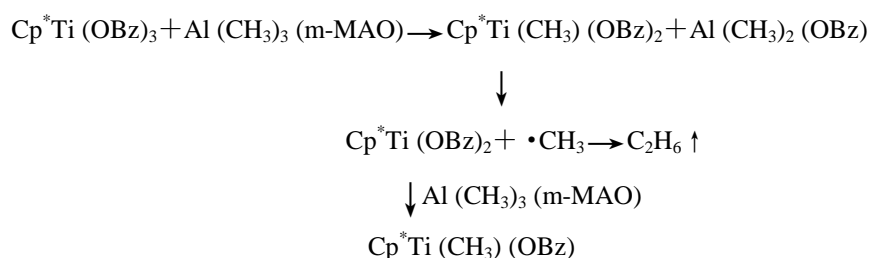
The polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in 100mL glass flasks provided with a magnetic stirrer. The m-MAO, toluene, TIBA (needed) and $\text{Cp}^*\text{Ti}(\text{OBz})_3$ were introduced respectively into the reactor, and the mixed reactants were stirred at 40°C for 10min. When the temperature was quickly warmed to 90°C , styrene was introduced. The polymerizations were terminated after 1h by the addition of 10wt% HCl in ethanol. The polymers were washed with ethanol and dried in vacuum to constant weight at 80°C . The syndiotactic index (S.I.) of polystyrene was determined as the weight percent of the insoluble fraction after the polymer obtained was extracted for 12h with boiling 2-butanone.

The oxidation states of titanium in different polymerization systems catalyzed by $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{m-MAO}$ catalysts were determined by redox titration method of $\text{K}_2\text{Cr}_2\text{O}_7$ under an extra-pure-grade nitrogen atmosphere.

The viscosity-average molecular weight (M_v) of sPS was calculated from $[\eta]$ measured in *o*-dichlorobenzene at 135°C . The melting temperature (T_m) of sPS was determined by differential scanning calorimetry (DSC) analysis with a Perkin-Elmer DCS-7 system at $10^\circ\text{C}/\text{min}$.

Results and Discussion

The results of the styrene syndiospecific polymerization with $\text{Cp}^*\text{Ti}(\text{OBz})_3$ activated by different modified methylaluminoxanes (m-MAO) are given in **Table 1**. By use of the $\text{Cp}^*\text{Ti}(\text{OBz})_3$ catalyst, from run 5 to run 2, the higher the molar percentage contents of TMA coexisted in m-MAO, the more Ti (IV) were reduced to Ti (III) and Ti (II). The activity of the catalyst was increased with increasing of the content of Ti (III). In run 2, the Ti (III) approached 83.3mol%, the activity of the catalyst was up to $8.6 \times 10^4 \text{gPS/gTi.h}$. TMA is not only a strong reducing agent but also a good chain transfer agent. Therefore the excess TMA in m-MAO, such as m-MAO1, results in a decrease of catalytic activity and the molecular weight of sPS. The process of reduction of $\text{Cp}^*\text{Ti}(\text{OBz})_3$ by TMA in m-MAO is shown in **Scheme 1**.

Scheme 1.

Table 1. Styrene Syndiospecific Polymerization with $\text{Cp}^*\text{Ti}(\text{OBz})_3$ and Different m-MAO Catalyst Systems

Run NO.	m-MAO Sample	Ti oxidation states (mol%)			Activity $\times 10^{-4}$ (gPs/gTi.h)	S.I. (wt)	T _m (°C)	M _v $\times 10^{-4}$
		Ti (II)	Ti (III)	Ti (IV)				
1	m-MAO1	12.8	81.1	6.1	8.1	96.3	268.8	2.3
2	m-MAO2	3.6	83.3	13.1	8.6	97.5	270.6	3.1
3	m-MAO3	2.0	70.1	27.9	5.7	96.3	271.3	3.6
4	m-MAO4	0.8	61.2	38.0	4.3	96.6	270.5	3.8
5	m-MAO5	0.2	46.6	53.2	2.1	95.8	269.9	3.5

Polymerization conditions: [Ti]= 1.04×10^{-4} mol/L, [Al]= 8.34×10^{-2} mol/L, Al/Ti=800 (mol/mol), [Styrene]=4.34 mol/L, Temperature 90°C, Time 1 h

Table 2. Influences of External Addition of TIBA on Styrene Syndiospecific Polymerization with $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{m-MAO5}$ Catalyst Systems

Run NO.	Al (m-MAO5) /Ti (mol/mol)	Al (TIBA) /Ti (mol/mol)	Ti oxidation states (mol%)			Activity $\times 10^{-4}$ (gPs/gTi.h)	S.I. (wt%)	T _m (°C)	M _v $\times 10^{-4}$
			Ti (II)	Ti (III)	Ti (IV)				
11	800	0	0.2	46.6	53.2	2.1	95.8	269.9	3.5
12	0	400	78.2	21.6	0.2	trace	—	—	—
13	800	200	11.5	76.8	11.7	8.6	96.6	269.1	3.3
14	600	200	4.7	73.9	21.4	8.3	96.8	269.9	3.5
15	400	200	3.6	72.2	24.2	7.8	96.5	268.9	3.2
16	200	200	2.5	51.9	45.6	4.1	96.6	268.5	3.0
17	400	400	31.6	67.3	1.1	4.8	93.2	267.7	2.1

Polymerization conditions: [Ti]= 1.04×10^{-4} mol/L, [Styrene]=4.34 mol/L, Temperature 90°C, Time 1 h

The external additions of tri-isobutylaluminum (TIBA) to the $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{m-MAO5}$ catalyst system cause to increase the mol% of Ti (III), and promote the styrene syndiospecific polymerization with higher catalytic activity as shown in **Table 2**. When m-MAO5 was only replaced by TIBA as cocatalyst in run 12, the catalyst of $\text{Cp}^*\text{Ti}(\text{OBz})_3$ could not catalyze the syndiospecific polymerization of styrene. The activity in run 13 is four-folds higher than that in run 11 with nearly the same order

of syndiotactic index, while the molecular weight of sPS in run 13 is slightly smaller than that in run 11. The external additions of TIBA into the catalyst system may also reduce the dosage of m-MAO5 to get good results of syndiospecific polymerization of styrene as compared run 13 with run 14, or elsewhere in **Table 2**. However the polymerization result in run 17 is worse than that of run 15, owing to the overdose of TIBA added that cause the drastic decrease in mol% of Ti (III) complexes and the obvious chain transferring effect of TIBA.

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