

Effects of Residual and External Alkylaluminum on the Synthesis of Syndiotactic Polystyrene with Cyclopentadienyltitanium Tribenzyloxide–Methylaluminoxane Catalyst

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ABSTRACT: The effects of residual trimethylaluminum (TMA) in methylaluminoxane (MAO) and external alkylaluminum (AlR_3) on styrene syndiotactic polymerization with $\text{Cp}_2\text{Ti}(\text{OBz})_2$ as a catalyst precursor have been investigated by comparison of the polymerizations using a series of MAOs containing various amounts of residual TMA. The results indicated that the residual TMA plays a deciding role in the reduction of Ti and promotes formation of the active centers for styrene polymerization. The variations in the catalytic activity and molecular weight of the polymer caused by additions of external AlR_3 , AlMe_3 , AlEt_3 , $\text{Al}(\text{i-Bu})_3$, and AlEt_2Cl , into the catalyst systems are quite different, depending the properties of MAO used and the type of the external AlR_3 . It was found that there is an optimum range of concentration ratio of the free AlR_3 , including the residual TMA and external AlR_3 , to the total Al compounds, 25–35 mol %, for maximum catalytic activities. The catalytic activities decrease at the ratios either above or below the range. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 765–770, 1998

Key words: syndiotactic styrene polymerization; metallocene catalyst; methylaluminoxane; methyl aluminum; external alkyl aluminum

INTRODUCTION

Since Sinn and Kaminsky reported the direct synthesis of methylaluminoxane (MAO), which activates Cp_2ZrCl_2 and Cp_2ZrMe_2 to yield exceedingly active catalysts for ethylene polymerization, by controlled hydrolysis of trimethylaluminum (TMA),¹ a variety of metallocene catalyst systems for α -olefin polymerization has been reported.^{2–5} Owing to its uniqueness as a cocatalyst, MAO has been frequently used in homogeneous olefin polymerization. MAO always contains some amount of unreacted TMA that cannot be removed easily by vacuum distillation.⁵ The residual TMA can be

an important factor influencing the catalytic activity of metallocenes and molecular weight of polyolefins. It was proposed that the actual cocatalyst in metallocene–MAO systems is TMA itself, with MAO acting as a soluble carrier–activator of the catalytic species.⁶ Reddy et al.⁷ reported that addition of TMA to the Cp_2ZrCl_2 –MAO system for ethylene polymerization leads to a dramatic increase in catalyst productivity and catalyst lifetime. However, as reported by Giannetti et al.⁸ and Chien and Wang,⁹ catalytic activities decrease with increasing an $[\text{TMA}]/[\text{MAO}]$ ratio when $\text{Cp}_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ and $(\text{Ind})_2\text{ZrMe}_2$, and Cp_2ZrCl_2 were used in ethylene polymerizations.

On the other hand, monocyclopentadienyltitanium(IV) complexes are the suitable precursors of very efficient homogeneous catalysts promoting styrene syndiotactic polymerization.¹⁰ The com-

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plexes are not very stable in the presence of cocatalyst and monomer and tend to be reduced to lower oxidation states, for example, a trivalent Ti species, which is active for styrene polymerization.^{11,12} In the previous article,¹³ we have reported the styrene syndiotactic polymerization with monocyclopentadienyltitanium–MAO catalyst system and found that the residual TMA content in MAO influences the catalyst activity to a great extent.

In this work, MAOs containing various amounts of residual TMA were prepared, and the effects of the residual TMA content in MAO and addition of various alkylaluminum compounds into CpTi(OBz)₃–MAO catalyst system on Ti oxidation state and catalytic activity, as well as the molecular weight of the polystyrene, were investigated in detail.

EXPERIMENTAL

Materials

Styrene was distilled from calcium hydride under reduced pressure and stored in the darkness under nitrogen. Toluene was dried by refluxing over sodium–benzophenone and distilled just before use in nitrogen. CpTi(OBz)₃ was synthesized, as described previously.¹³ MAOs were prepared as follows. 200 mL of TMA solution (3.1M, in toluene) was added dropwise into a flask with appropriate amount of ground Al₂(SO₄)₃ · 18H₂O in toluene at 0°C. The mixture was gradually heated to 40°C and stirred for 24 h and then filtered. The filtrate was concentrated under reduced pressure to a white solid. The residual TMA contents in the MAOs prepared with initial [H₂O]/[TMA] molar ratios of 1.0, 1.3, and 1.8 are 28.0, 22.9, and 15.4%, respectively, and the corresponding MAOs are referred to MAO1, MAO2, and MAO3. By redissolving MAO2 in toluene and then vaporizing the solvent at 60°C *in vacuo*, MAO2' was obtained.

Polymerization Procedure

In a 100-mL glass flask equipped with a magnetic stirrer, 20 mL of toluene and the desired amount of MAO, AlR₃, and styrene were introduced in this order under a nitrogen atmosphere. Polymerization was initiated upon addition of the titanocene and performed at 60°C for 1 h. The polymerization was stopped, and the polymer was precip-

itated by addition of acidified alcohol. The resulting polymer was washed with alcohol and dried *in vacuo* to constant weight.

Analysis and Characterization

Residual TMA content in MAO was determined by pyridine titration.¹⁴

Oxidation state distribution of titanium species in the catalyst system was measured by redox titration¹¹ under the similar conditions as in the corresponding polymerization.

The molecular weight of the polystyrene was obtained from intrinsic viscosities measured¹⁵ at 138°C in *o*-dichlorobenzene.

RESULTS AND DISCUSSION

Polymerization with Various MAOs

Though monocyclopentadienyltitanium(IV) complexes activated with MAO have been described as the catalyst for syndiotactic polymerization of styrene in many publications, they gave little quantitative data about the properties of the cocatalyst. Certainly, there is a lack of knowledge concerning the role of residual alkylaluminum in MAO and how to influence the polymerization. With the aim of an understanding of the role played by the residual TMA in styrene polymerization, 4 MAOs containing various amounts of residual TMA were tested as cocatalysts in the polymerization with CpTi(OBz)₃ as the catalyst precursor. The results are reported in Table I. The catalytic activity increases steadily with increasing the residual TMA content from 15.4 to 28.0 mol % in MAO. It is worth noting that reducing the amount of residual TMA from 22.9 mol % (MAO2) to 17.4 mol % (MAO2') by redissolving MAO2 in toluene and then vaporizing the solvent *in vacuo* at 60°C causes a dramatic change of the catalytic activity from 31.6 kg PS per g Ti per h to 4.8 kg PS per g Ti per h, decreased by a factor of about 7. The molecular weight of the polymer decreases with a decrease in the residual TMA content. The results confirm a strong effect of the residual TMA on the styrene polymerization.

It has been reported that monocyclopentadienyltitanium(IV) complexes are not very stable in the presence of cocatalyst and tend to be reduced to lower oxidation states.^{11,12} To give a better insight into the effect of the residual TMA on the polymerization, oxidation state distributions of

Table I Styrene Polymerizations with CpTi(OBz)₃ Activated with Various MAOs

MAO No.	[H ₂ O]/[TMA] ^a	Residual TMA ^b (mol%)	Ti Valent State ^c (%)			Activity (kg PS/g Ti h)	<i>M_w</i> × 10 ⁻⁴
			Ti ⁴⁺	Ti ³⁺	Ti ²⁺		
1	1.0	28.0	12.1	83.2	4.7	32.7	9.23
2	1.3	22.9	15.4	80.9	3.7	31.6	8.51
3	1.8	15.4	75.3	23.6	1.1	5.4	3.59
2'	^d	17.4	73.7	25.7	0.6	4.8	2.73

Polymerization conditions are as follows: [Ti] = 0.209 mmol/L; [MAO]/[Ti] = 820; [St] = 4.2 mol/L; *T* = 60°C.

^a Initial molar ratio of water in the hydrated salt to TMA for preparing MAO.

^b TMA content in MAO, measured by pyridine titration.

^c Measured by redox titration.

^d MAO2' was obtained by redissolving MAO2 in toluene and then vaporizing the solvent at 60°C *in vacuo*.

the Ti species were measured by redox titration. Ti oxidation states from the reactions of the titanocene with various MAOs are shown in Table I. Large fractions of Ti are in trivalent state {[Ti³⁺] = 83.2% with MAO1, [Ti³⁺] = 80.9% with MAO2} when the titanocene reacts with MAO1 and MAO2 having higher TMA content, whereas the reactions with MAO3 and MAO2' containing less TMA give mostly Ti⁴⁺ species {[Ti⁴⁺] = 75.3% with MAO3, [Ti⁴⁺] = 73.7% with MAO2'} and less Ti³⁺ species {[Ti³⁺] = 23.6% with MAO3, [Ti³⁺] = 25.7% with MAO2'}.

The results indicate that the residual TMA content in MAO can be correlated with the valent distribution of the Ti species in the catalyst systems. It has been suggested that the active species for styrene syndiotactic polymerization are in a trivalent state.^{11,16} Higher residual TMA content in MAO (MAO1 or MAO2) favors the reduction of Ti in the catalyst system to Ti³⁺, promoting styrene polymerization more efficiently, whereas Ti in the catalyst system with MAO (MAO3 or MAO2') containing less TMA remains mostly in a tetravalent state, resulting in much lower catalytic activities for the polymerization than the former. From the above investigations, it can be concluded that the residual TMA plays a deciding role in reduction of Ti in the catalyst system and promoting formation of the active centers for the styrene polymerization.

External Alkylaluminum

Concerning the cocatalyst composition, different sets of polymerizations with CpTi(OBz)₃-MAO-AIR₃ systems were undertaken by keeping the [MAO] constant at 172 mmol/L with the aim to elucidate the effects of the type and amount of

external alkylaluminum on the catalytic activity and molecular weight of the polymer. Some differences in the dependence of these 2 parameters on the external AIR₃ concentration were found for the systems with different MAOs.

Table II shows, for CpTi(OBz)₃-MAO2-AIR₃ system in which the residual TMA content in MAO2 is 22.9 mol %, that the catalytic activity and molecular weight of the polymer decrease in general with raising the external AIR₃ concentration [AIR₃]_e, but it differs in the extent for different external AIR₃ used. For the CpTi(OBz)₃-MAO2-TMA system, the catalytic activity was reduced by 28% at [TMA]_e = 17.7 mM and reduced by 43% at [TMA]_e = 69.7 mM. It was reduced by 73% at [TEA]_e = 51 mM. There is little effect on the catalytic activity by the addition of TIBA. The catalytic activity remains unchanged at [TIBA]_e = 22 mM, and then reduces slowly with further increasing [TIBA]_e. It decreases only by 23%, even though the [TIBA]_e reaches to 149 mM. With the addition of DECA, only a trace of polymer could be recovered.

Tables III and IV show the results of styrene polymerizations with the CpTi(OBz)₃-MAO3-AIR₃ and CpTi(OBz)₃-MAO2'-AIR₃ systems, respectively, in which the MAOs originally contain less residual TMA than MAO2 (see Table I). These 2 systems behave in mutually similar features in the polymerization, but different from that shown by CpTi(OBz)₃-MAO2-AIR₃. With the addition of the external AIR₃, TMA, TIBA, or even TEA, the activities of both catalysts are enhanced remarkably. The external AIR₃ increases the activities of the catalyst systems in the following order: TIBA > TMA > TEA. By adding the appropriate amount of external TIBA, they could reach

Table II Effect of External Alkylaluminum on Styrene Polymerization with CpTi(OBz)₃-MAO2-AlR₃

[AlR ₃] _e ^a (mmol/L)	[AlR ₃] _e /[Al] _t ^b (%)	[AlR ₃] _t /[Al] _t ^c (%)	[Al] _t /[Ti]	Ti Valent State (%)			Activity (kg PS/g Ti h)	M _w × 10 ⁻⁴
				Ti ⁴⁺	Ti ³⁺	Ti ²⁺		
—	0	22.9	820	15.4	80.9	3.7	31.6	8.79
TMA, 17.7	9.3	30.1	908	—	—	—	22.7	5.44
TMA, 34.7	16.8	35.8	989	13.8	77.0	9.2	20.6	3.19
TMA, 69.7	28.8	45.1	1156	12.7	70.9	16.4	18.0	1.57
TEA, 26.3	13.3	33.1	949	—	—	—	22.0	—
TEA, 51.0	22.9	40.5	1067	—	—	—	8.4	1.52
TIBA, 22.0	11.3	31.6	928	—	—	—	31.5	9.51
TIBA, 58.5	25.4	42.5	1103	—	—	—	27.6	5.33
TIBA, 149.0	46.4	58.7	1536	—	—	—	24.2	2.24
DECA, 30.1	14.9	34.4	967	—	—	—	trace	—

Other polymerization conditions are the same as in Table I.

^a [AlR₃]_e is the concentration of external alkylaluminum; TEA, triethylaluminum; TIBA, triisobutylaluminum; DECA, diethylchloroaluminum.

^b [Al]_t is the total Al concentration.

^c [AlR₃]_t = [TMA]_r + [AlR₃]_e is the total concentration of AlR₃ compounds in the catalyst system.

the levels shown by the CpTi(OBz)₃-MAO2 and CpTi(OBz)₃-MAO1 systems, that is, over 30 kg PS per g Ti per h (see Table I).

It is worth noting that there is an optimum [AlR₃]_t/[Al]_t (mole percent ratio of total AlR₃ including the external AlR₃ and residual TMA to total Al concentration) range of 25–35 mol % for maximum catalytic activities, which decrease at the ratios either above or below it for these 2 systems, although the values of the maximum catalytic activities are varying, depending on the MAO used and on the type of external AlR₃. The optimum [AlR₃]_t/[Al]_t range is roughly the same as the contents of the residual TMA in MAO1 (28 mol %) and MAO2 (22.9 mol %). It is implied that 25–35 mol % of free AlR₃ is necessary for the titanocene/MAO catalyst to exhibit the highest activity in styrene polymerization.

As shown in Tables III and IV, the catalyst systems that originally contain mostly Ti⁴⁺ when the [AlR₃]_e = 0 give the highest [Ti³⁺] (> 70% of total Ti) at the optimum [AlR₃]_t/[Al]_t ratio. With the further increase of the ratio, [Ti³⁺] decreases slowly, and [Ti²⁺] increases.

Like the dependence of catalytic activity on the external AlR₃ concentration, molecular weights of the polymers increase to a maximum at the optimum [AlR₃]_t/[Al]_t ratio and then decrease obviously with the raising of the external AlR₃ concentrations for the CpTi(OBz)₃-MAO3-AlR₃ and CpTi(OBz)₃-MAO2'-AlR₃ systems.

These results can be interpreted as follows: free AlR₃ can alkylate and reduce the titanocenes so that the active centers form quickly. However, the excessive AlR₃ would coordinate toward the active Ti species and decompose the Ti-MAO co-

Table III Effect of External Alkylaluminum on Styrene Polymerization with CpTi(OBz)₃-MAO3-AlR₃

[AlR ₃] _e (mmol/L)	[AlR ₃] _e /[Al] _t (%)	[AlR ₃] _t /[Al] _t (%)	[Al] _t /[Ti]	Ti Valent State (%)			Activity (kg PS/g Ti h)	M _w × 10 ⁻⁴
				Ti ⁴⁺	Ti ³⁺	Ti ²⁺		
—	0	15.4	820	75.3	23.6	1.1	5.4	3.59
TMA, 34.7	16.8	29.6	989	16.4	74.4	9.2	27.1	6.88
TMA, 69.3	28.7	39.7	1155	20.2	69.3	11.5	16.7	2.42
TIBA, 34.7	16.8	29.6	989	17.2	81.3	1.5	34.1	8.93
TIBA, 69.3	28.7	39.7	1155	17.9	74.1	8.0	25.1	3.71

Polymerization conditions are the same as in Table II.

Table IV Effect of External Alkylaluminum on Styrene Polymerization with $\text{CpTi}(\text{OBz})_3\text{-MAO2}'\text{-AlR}_3$

[AlR ₃] _e (mmol/L)	[AlR ₃] _e /[Al] _t (%)	[AlR ₃] _t /[Al] _t (%)	[Al] _t /[Ti]	Ti Valent State (%)			Activity (kg PS/g Ti h)	$M_w \times 10^{-4}$
				Ti ⁴⁺	Ti ³⁺	Ti ²⁺		
—	0	17.4	820	73.7	25.7	0.6	4.8	2.73
TMA, 17.3	9.1	24.9	906	—	—	—	18.9	—
TMA, 34.6	16.7	31.2	989	29.4	67.4	3.2	22.0	5.32
TMA, 61.9	26.5	39.3	1120	—	—	—	9.9	—
TMA, 173.0	50.1	58.8	1651	12.4	55.0	32.6	7.9	1.25
TEA, 26.5	13.3	28.4	950	—	—	—	13.6	—
TIBA, 16.9	8.9	24.8	904	—	—	—	31.4	—
TIBA, 52.8	23.5	36.8	1076	12.0	85.7	2.3	32.5	7.65
TIBA, 101.0	37.0	48.0	1300	8.4	76.9	14.7	23.2	2.22

Polymerization conditions are the same as in Table II.

ordination sites that are highly active for the polymerization by a competitive equilibrium,⁹ resulting in a continued decrease in the catalytic activity with an increase in the AlR₃ concentration beyond the optimum ratio. The free AlR₃ also acts as a chain-transfer agent. An excess of the free AlR₃ will lead to decrease the molecular weight of the polymer.

Replacing MAO with Alkylaluminum

High activities of metallocene/MAO catalysts for α -olefin polymerizations usually require exceedingly larger excess of MAO.²⁻⁵ It has been found

that replacement of 90% of MAO with TMA causes only small loss of activity and molecular weight of the polyethylene for the Cp₂ZrCl₂-MAO system.⁹ An attempt at replacing the MAO with TMA by keeping the [Al]_t and [Al]_t/[Ti] constant at 172 mM and 820, respectively, was made for the styrene polymerization.

The results are given in Table V. For Cp-Ti(OBz)₃-MAO2 system, the catalytic activity is reduced by one-half at replacing 35% of MAO2 with TMA, and reduced by three-fourths when approximately 50% of MAO2 is replaced with TMA. The molecular weight of the polystyrene

Table V Effect of Replacement of MAO with External TMA on Styrene Polymerization

[MAO] (mmol/L)	[TMA] _e ^a (mmol/L)	[TMA] _e /[MAO]	[TMA] _t ^b /[Al] _t (%)	Activity (kg PS/g Ti h)	$M_w \times 10^{-4}$
MAO2					
172	0	0	22.9	31.6	8.51
142	30	0.21	36.3	20.6	—
112	60	0.54	49.8	14.6	6.79
82	90	1.1	63.2	7.6	—
62	110	1.8	72.2	7.3	0.93
0	170	—	100	trace	—
MAO2'					
172	0	0	17.4	4.8	2.73
150	22	0.15	28.0	22.4	6.33
136	36	0.26	34.7	14.8	4.90
78	94	1.26	64.9	13.5	1.31
0	172	—	100	trace	—

Polymerization conditions are as follows: [Ti] = 0.209 mmol/L; [Al]_t = 172 mmol/L, [Al]_t/[Ti] = 820; [St] = 4.2 mol/L; T = 60°C.

^a [TMA]_e is the external TMA concentration.

^b [TMA]_t = [TMA]_r + [TMA]_e is the total TMA concentration.

obviously decreases with an increase in the replaced amount of MAO2. The CpTi(OBz)₃-MAO2' catalyst gives increasing activities when MAO2' is partially replaced with TMA and exhibits a maximum activity at [TMA]_t/[Al]_t = 28 mol %. The optimum value of [TMA]_t/[Al]_t ratio is in agreement with the optimum [AlR₃]_t/[Al]_t range obtained from above investigation.

Only a trace of polymer was obtained when MAO is completely replaced with TMA. It was reported that atactic polystyrene was obtained in very low yield with a similar catalyst, CpTiCl₃-TMA.¹⁷ It indicates that certain amount of MAO is necessary for the titanocene catalyst to promote styrene syndiotactic polymerization efficiently.

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