A Kinetic Study of Novel Bimetallic Titanocene Catalyst for Syndiospecific Styrene Polymerization

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ABSTRACT: A kinetic study of a syndiospecific polymerization was performed with two kinds of catalysts: $Cp*Ti(O(C_6H_4)CMe_2(C_6H_4)O)TiCp*$ [bimetallic system] and $Cp*Ti(OMe)_3$ [monometallic system]. The purpose of this study was to determine the reasons behind the high activity of a bimetallic catalyst system. The active site structures of the two kinds of catalysts appears to be similar to the cationic Ti [III] species having η^5-pentamethylcyclopentadienyl ligand, while the rate of the activation process of the bimetallic catalyst was found to be higher than that of the monometallic catalyst. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 297–301, 2007

Key words: syndiotactic; kinetics (polym.); polystyrene; metallocene catalysts

INTRODUCTION

Ishihara et al.[1,2] first investigated the syndiospecific polymerization of styrene by organotitanium compounds with methylaluminoxane (MAO) as a cocatalyst. The catalytic activity decreased in the order $CpTiCl_3$ (Cp = η^5-cyclopentadienyl) $\sim Cp*TiCl_3$ (Cp* = η^5-pentamethylcyclopentadienyl) > $CpTiCl_2H \sim Ti(OEt)_4 > Ti(OMe)_4 > TiBr_4$. A great deal of research has been carried out in the field of homogeneous catalysts leading to the production of syndiotactic polystyrene (sPS) as one of the most promising engineering plastics.[3] Many catalytic systems for sPS can be classified into two groups:[4,5] (1) complexes with a Cp-type ligand,[6–8] and (2) complexes without a Cp-type ligand.[9–11] The former complexes show higher activity and structural similarity, with a three-legged piano-stool half-sandwich; each has a cyclopentadienyl (Cp), pentamethylcyclopentadienyl (Cp*), and indenyl (Ind) ligand. Mainly investigated have been the electronic and steric effects on the activities of catalysts as well as the structures of polymers. The change of substituents on the Cp-type ligands has been regarded as a more important factor for more active catalysts, and much less attention has been paid to the change of monodentate ligands i.e., the ancillary ligand.

The binuclear catalytic system[12] and titanatranes[13–15] have also drawn considerable interest. Recently, the bimetallic titanium catalytic system bridged with the bispenol group, $Cp*Ti(O(C_6H_4)CMe_2(C_6H_4)O)$-

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$TiCp*$ has been investigated.[16] This bimetallic catalyst shows fairly good activity toward sPS polymerization compared with the conventional monometallic catalyst $Cp*Ti(OMe)_3$.

In the present study, kinetic parameters at the initial state of sPS polymerization have been evaluated to determine the reason for the high activity of the bimetallic catalyst system $Cp*Ti(O(C_6H_4)CMe_2(C_6H_4)O) TiCp*$.

EXPERIMENTAL

Materials and the preparation of $Cp*Ti(O(C_6H_4)CMe_2(C_6H_4)O)TiCp*$

Nitrogen was purified by removing traces of residual oxygen and moisture with columns packed with an oxygen scavenger (Fisher RIDOX, Pittsburgh, PA) and the molecular sieve 5A (Aldrich, Milwaukee, WI), respectively. Styrene (Junsei Chemical, Tokyo, Japan) was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. The purified styrene was stored under nitrogen at $-25°C$. Toluene (J.T. Baker, Phillipsburg, NJ) was purified by drying after refluxing through a distillation column over sodium metal under dry nitrogen. $Cp*TiCl_3$ (Strem, Tully Town, PA), $Cp*Ti(OMe)_3$ (Strem) and modified methylaluminoxane (MMAO-3A: Tosoh Akzo, Tokyo, Japan) were used as received without further purification. The bimetallic catalyst, $Cp*Ti(O(C_6H_4)CMe_2(C_6H_4)O)TiCp*$ was prepared according to the procedures in a previous article.[16] All operations were carried out under a dry nitrogen atmosphere using a glove-box and Schlenk line technique.

TABLE I
The Results of the Short-Time Polymerization at a Low Polymerization Temperature (30°C)

Catalyst	Time (s)	Yield (g)	Activity (Kg PS/[Ti] h)	M_n (g/mol)	MWD	T_m (°C)
Monometallic[a]	1	Trace	–	–	–	–
Monometallic[a]	3	0.05	5000	25,400	7.08	268.9
Monometallic[a]	5	0.21	12,600	34,100	8.61	269.9
Monometallic[a]	10	0.44	13,200	45,000	8.51	271.3
Bimetallic[b]	1	0.08	24,000	17,723	9.40	270.7
Bimetallic[b]	3	0.15	15,000	20,784	10.20	268.9
Bimetallic[b]	5	0.28	16,800	28,414	12.80	271.7
Bimetallic[b]	10	0.71	21,300	46,680	10.00	272.3

Polymerization conditions: Styrene = 50 cc, Ti = 1.2×10^{-5} mol, MAO = 1.2×10^{-3} mol, Al/Ti = 100, Temperature = 30°C.
[a] Monometallic type catalyst: Cp*Ti(OMe)$_3$.
[b] Bimetallic type catalyst: Cp*Ti(O(C6H4) CMe2(C6H4)O)TiCp*.

Polymerization procedures and polymer characterization

Styrene polymerizations were carried out in a 250 mL Schlenk flask with magnetic stirring. Toluene was distilled from a sodium potassium alloy under a dried nitrogen atmosphere just before use. The polymerizations were carried out as follows: toluene, styrene, MMAO (Akzo, 3A type), and the titanium compound were injected into a 250 mL Schlenk flask with magnetic stirring in that order at the desired temperature. After the desired reaction time had passed, the reaction was terminated following the addition of 100 mL of 10% HCl in methanol. The resulting precipitated polymer was washed three times with 50 mL portions of methanol and dried in vacuum at 70°C for 12 h. The polymer was extracted through refluxing with 2-butanone for 12 h to determine the sPS portion. The differential thermal analysis was carried out with a calorimeter (Dupont Instruments, Thermal Analyst 2000, Raleigh, NC) under a nitrogen atmosphere at a heating rate of 10°C/min. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (Waters 150CV) at 145°C with 1, 3, 5-trichlorobenzene as a solvent.

RESULTS AND DISCUSSION

There have been several studies to evaluate the kinetic parameters associated with olefin polymerization. Keii et al.[17] and Soga et al.[18] used an interesting experimental scheme, termed stopped-flow polymerization (SFP), to evaluate the kinetic parameters at the initial polymerization state. The active site concentration and the kinetic parameters of the catalyst could be obtained at the initial state of ethylene and propylene homopolymerization. In the present study, short-time polymerization (STP), meaning that the polymeriza-

tion time is at the extreme initial stage (typically below 10 s) was performed during the syndiospecific styrene polymerization. It is feasible to postulate that both the active sites and the monomer concentration are nearly constant at the initial state during the polymerization. Therefore, the initial styrene polymerization yield (Y) can be expressed as follows:

$$Y = k_p \cdot [\text{St}][\text{C}^*]t \tag{1}$$

where k_p is the propagation rate constant, [St] is the initial styrene concentration and [C*] is the initial active titanium. In general, the molecular weight (M_n) can be expressed as

$$M_o/M_n = k_{tr}/(k_p M_n) + 1/(k_p[\text{St}]t) \tag{2}$$

Where M_n is the number averaged molecular weight, M_o is the molecular weight of monomer, and k_{tr} is the chain transfer rate constant. The propagation rate constant must be much higher than the chain transfer rate constant at the initial stage ($k_p \gg k_{tr}$). Therefore, eq. (2) can be simplified as eq. (3).

$$k_p = M_n/(M_o[\text{St}]t) \tag{3}$$

Here, the active site concentration can be simply calculated by eq. (4), when eq. (3) is applied to eq. (1).

$$[\text{C}^*] = Y/M_n \tag{4}$$

A large amount of MAO was required to achieve a high yield of sPS production (typically Al/Ti $\gg$ 100). Also necessary is an adequate polymerization temperature (typically >50°C). However, it is difficult to analyze kinetic parameters at the initial stage, as both the

TABLE II
The Results of the Short-Time Polymerization at a High Polymerization Temperature (70°C)

Catalyst	Time (s)	Yield (g)	Activity (Kg PS/[Ti] h)	M_n (g/mol)	MWD	T_m (°C)
Monometallic[a]	1	0.11	16,500	25,300	7.24	270.2
Monometallic[a]	3	0.12	6000	39,100	6.62	271.0
Monometallic[a]	5	0.29	8700	49,400	6.25	272.4
Monometallic[a]	10	0.57	8550	10,6200	3.37	270.9
Bimetallic[b]	1	0.19	57,000	31,600	8.60	269.8
Bimetallic[b]	3	0.22	22,000	41,500	9.97	270.4
Bimetallic[b]	5	0.27	16,200	57,800	9.81	270.4
Bimetallic[b]	10	0.55	16,500	11,3900	5.15	273.4
Monometallic[c]	1800	2.11	1055	24,6500	2.14	275.5
Bimetallic[c]	1800	3.10	1550	23,5100	2.09	274.9

[a] Monometallic type catalyst: Cp*Ti(OMe)$_3$; Polymerization conditions: Styrene = 50 cc, Ti = 2.4×10^{-5} mol, MAO = 1.2×10^{-3} mol, Al/Ti = 50, Temperature = 70°C.
[b] Bimetallic type catalyst: Cp*Ti(O(C$_6$H$_4$)CMe$_2$(C$_6$H$_4$)O)TiCp*; Polymerization conditions: Styrene = 50 cc, Ti = 1.2×10^{-5} mol, MAO = 6.0×10^{-4} mol, Al/Ti = 50, Temperature = 70°C.
[c] Polymerization conditions: Styrene = 5 cc, Toluene = 80 cc, Ti = 4.0×10^{-6} mol, MAO = 1.0×10^{-4} mol, Al/Ti = 250, Temperature = 70°C.

activation rate of the titanocene complex by the MAO and the propagation rate are exceedingly fast. Therefore, it is necessary to select two extreme polymeriza- tion conditions that can reduce the activation rate and the propagation rate. The first is a low polymerization temperature (30°C) and the second is a low Al/Ti
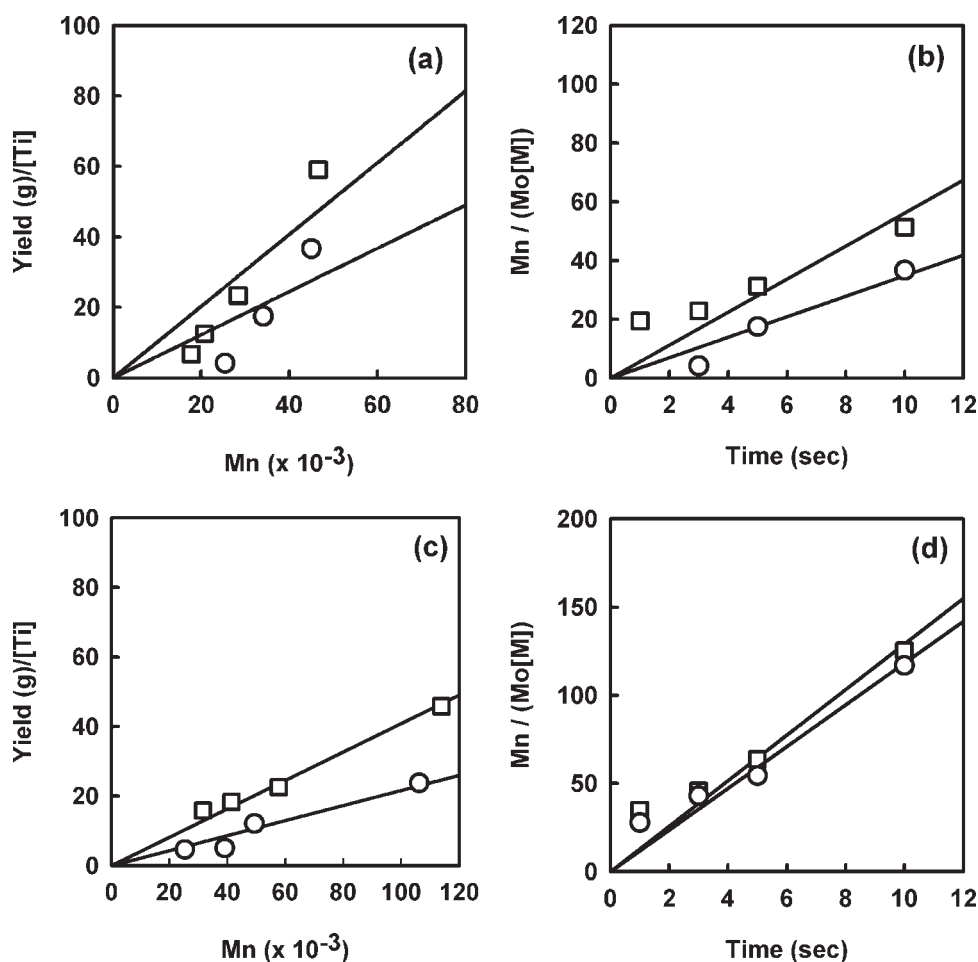

Figure 1 The results of the kinetic parameters from the STP with different types of catalysts. Polymerization conditions of (a) and (b); polymerization temperature = 30°C, Al/Ti = 100. Polymerization conditions of (c) and (d): polymerization temperature = 70°C, Al/Ti = 50.

TABLE III
List of Calculated Kinetic Parameters with Different Types of Catalysts by STP

Temperature (°C)	Al/Ti ratio	Bimetallic catalyst		Monometallic catalyst	
		k_p (L/(mol s))	[C*]/[Ti] (10^3)	k_p (L/(mol s))	[C*]/[Ti] (10^3)
30	100	5.61	1.01	3.48	0.61
70	50	12.90	0.41	11.83	0.22

Monometallic type catalyst: Cp*Ti(OMe)$_3$; Bimetallic type catalyst: Cp*Ti(O(C$_6$H$_4$)CMe$_2$(C$_6$H$_4$)O)TiCp*.

mole ratio ($\sim$ 50). Table I shows that the results of the syndiospecific styrene polymerization at the low temperature of 30°C. The activity of the styrene polymerization using the bimetallic catalyst is higher than that using a monometallic catalyst under all of the short-time polymerization conditions (<10 s). The molecular weight (M_n) of the produced sPS monotonically increases with polymerization time for both of the cases. Surprisingly, molecular weight distribution (MWD) of the produced sPS are very broad (MWD = 7–12) due to various kinds of growing polymeric chain at the initial state. In general, typical MWD of sPS produced by half metallocene catalyst is around 2.0. Considering the broad MWD of sPS, it can be confirmed that the propagation rate constant is much higher than the chain transfer rate constant ($k_p \gg k_{tr}$).

Table II shows that the results of syndiospecific styrene polymerization at the low Al/Ti mole ratio of 50. The activity of styrene polymerization using a bimetallic catalyst is also higher than if using a monometallic catalyst under a polymerization conditions (<10 s). In this low Al/Ti mole ratio, the molecular weight (M_n) of the produced sPS also increases with the polymerization time and MWD also very broad (MWD = 3–10). A long-time polymerization (LTP) was performed to compare the catalytic behaviors with the STP. The activity of the LTP is almost one order of magnitude lower than that of the STP. This phenomenon could be explained by two kinds of aspect. One is that a monomer concentration of the LTP is much lower than that of STP, and the other reason seems to be that the deactivation process of the activated Ti(III) complex can be incorporated into the LTP. MWD of sPS produced by LTP is around 2.0 as expected.

Figure 1 shows the plot evaluating the kinetic parameters of k_p and [C*] under a low polymerization temperature and Al/Ti mole ratio. The linear regression shows fairly good fitting results although some experimental points deviate at the extreme initial time ($\sim$ 1 s). It is possible to obtain the kinetic parameters of k_p and [C*] from the slope of the regression lines at the low polymerization temperature and Al/Ti mole ratio, respectively. The calculated kinetic results are summarized in Table III. The active site concentration [C*] of the bimetallic catalyst is much higher than that

of the monometallic catalyst. However, the difference of the k_p values are not extreme if compared to [C*] for the relatively low Al/Ti mole ratio (50). In general, the kp value is strongly correlated with the structure of the active site, while the [C*] value is related with the activation process of the titanocene catalyst by the MAO.

For the aforementioned reasons, the active site of two types of catalysts appears to be similar to the cationic Ti [III] species having the η^5-pentamethylcyclopentadienyl ligand, as reported Zambeli et al.,[19–20] despite the fact that the titanocene precursors are completely different structures. The reason for high relative activity of the bimetallic catalyst may result from an efficiency of an active site formation via an activation process between the titanocene precursor and the MAO. In other words, the bimetallic catalyst formed the cationic Ti [III] species comparatively easily through the reaction of the MAO when compared with the monometallic system. In particular, the propagation rate constant (k_p) of the two kinds of catalysts is approximately the same as the low Al/Ti mole ratio condition (Al/Ti = 50). This means that the activation process of the titanocene precursor appears to be main factor determining the catalytic activity under a low Al/Ti condition. The active site concentration, [C*] resulting from the bimetallic system is two times higher than that of the monometallic system. It is postulated that bimetallic system is more susceptible to the reduction reaction of MAO.

CONCLUSIONS

The kinetic parameters at the initial state of sPS polymerization were evaluated to determine the reason for the higher activity of the bimetallic catalyst system of Cp*Ti(O(C$_6$H$_4$)CMe$_2$(C$_6$H$_4$)O)TiCp*. The active site concentration of the bimetallic catalyst was found to be much higher than that of the monometallic catalyst, while the propagation rate constants of the two kinds of catalysts are similar. This shows that the active sites for sPS seem to be equivalent, i.e., for the cationic Ti [III] species. The reason for the high activity of bimet-

allic catalyst may stem from an efficiency of the active site formation with MAO.

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