

Synthesis and Characterization of Polybutadiene with Monotitanocene/Methylaluminumoxane Catalyst

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ABSTRACT: Butadiene was polymerized using a monotitanocene complex of η^5 -pentamethylcyclopentadienyltribenzyloxy titanium [$\text{Cp}^*\text{Ti}(\text{OBz})_3$] in the presence of four types of modified methylaluminumoxanes (mMAO), which contained different amounts of residual trimethylaluminum (TMA). The titanium oxidation states in $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{mMAO}$ and $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{mMAO}/\text{triisobutylaluminum}$ (TIBA) catalytic systems were determined by redox titration method. The effects of various oxidation states of titanium active species on butadiene polymerization were investigated. It was found that Ti(III) active species is more effective for preparing polybutadiene with high molecular weight. The addition of TIBA to the $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{mMAO}$

system could reduce a greater number of Ti(IV) complexes to Ti(III) species and lead to significant increases of polymerization activity and molecular weight of polymer, whereas the polybutadiene microstructure was only slightly changed. On the basis of microstructure and property characterization by FTIR, ^{13}C -NMR, DSC, and WAXD, all resultant polymers were proved to be amorphous polybutadiene with mixed 1,2; *cis*-1,4; and *trans*-1,4 structures. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2494–2500, 2004

Key words: metallocene catalysts; methylaluminumoxane; butadiene polymerization; microstructure; amorphous

INTRODUCTION

It has been well established that monotitanocene, activated by methylaluminumoxane (MAO), can effectively catalyze styrene polymerization to afford syndiotactic polystyrene.^{1–7} Recently, a great deal of interest in monotitanocene/MAO catalysts for other olefin polymerization has been generated by their ability to produce polyolefin with specific molecular structure and a narrow molecular weight distribution. In the presence of these catalysts, branched polyethylene could be prepared by ethylene homopolymerization.^{8–11} Interestingly, it has been found that monotitanocene catalysts promoted propene and butene-1 homopolymerizations to provide atactic polypropene^{12–15} and multi-stereoblock polybutene-1.^{16,17}

Over the last decade, several studies have been reported in the literature that monotitanocene/MAO catalyst, especially $\text{CpTiCl}_3/\text{MAO}$ catalyst ($\text{Cp} = \eta^5$ -cyclopentadienyl), was also able to polymerize conjugated diolefins.^{18–30} The main factor that determined polymer structure was monomer structure. Ricci et al.³¹ found that by using $\text{CpTiCl}_3/\text{MAO}$ as catalyst for the polymerization of (*Z*)-pentadiene, (*E*)-2-meth-

ylpentadiene and 2,3-dimethylbutadiene gave polymers with *cis*-1,4 configuration, for 4-methylpentadiene polymerization yielded 1,2-syndiotactic polymer, whereas for butadiene and (*E*)-pentadiene polymerization produced polymers with a mixture of 1,2; *cis*-1,4; and *trans*-1,4 structures. Kaminsky et al.³² reported that the polybutadienes produced half-sandwich complexes and MAO had nearly identical microstructures of about 80% 1,4-*cis*, 1% 1,4-*trans*, and 19% 1,2-linked units.

Analysis of titanium oxidation states revealed three kinds of active species, including alkylated Ti(IV), Ti(III), and Ti(II) complexes in the monotitanocene/MAO catalyst systems. Some evidence has confirmed that Ti(III) active species was more favorable for syndiospecific polymerization of styrene^{2,3,6,33–35} and polymerization of conjugated diolefins,^{20,25,29} whereas Ti(IV) active species was more favorable for polymerization of α -olefin, such as ethylene,^{10,11} propene,^{12–15} and butene-1.^{16,17} Additionally, the distribution of titanium oxidation state of active species depended on the content of trialkylaluminum in MAO.

With MAO as cocatalyst, the reported monotitanocene complexes for polymerization of conjugated diolefins were almost all η^5 -cyclopentadienyl titanium complexes. To explore the influence of substituted η^5 -cyclopentadienyl ligand on the polymerization of conjugated diolefins, η^5 -pentamethylcyclopentadienyltribenzyloxy titanium [$\text{Cp}^*\text{Ti}(\text{OBz})_3$] was used for butadiene polymerization in this study. At the same

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TABLE I
Butadiene Polymerization with Cp*Ti(OBz)₃ Activated by Various mMAOs^a

Run	Sample	Ti oxidation state (mol %)			Activity (kg P/mol Ti h ⁻¹)	M _w (×10 ⁻⁴)	Structure (mol %)		
		Ti(II)	Ti(III)	Ti(IV)			<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
1	mMAO1	0.3	13.8	85.9	11.7	—	—	—	—
2	mMAO2	4.3	58.5	37.2	26.5	28.2	63.0	11.9	25.1
3	mMAO3	12.3	73.6	14.1	38.8	30.3	62.7	12.6	24.7
4	mMAO4	26.5	70.8	2.7	31.6	32.6	61.8	10.2	28.0

^a Polymerization conditions: [Ti] = 1.0 × 10⁻³ mol/L, Al_{mMAO}/Ti = 400 (mol/mol), P_{Bd} = 0.13 MPa, T_p = 60°C, t_p = 60 min.

time, the effect of titanium oxidation state of active species was investigated. In addition, under the adopted conditions by which the amount of MAO is reduced, we tested the addition of triisobutylaluminum (TIBA) into the Cp*Ti(OBz)₃/MAO catalyst system. The microstructure and property of the resulting polymer were also characterized by GPC, ¹³C-NMR, FTIR, DSC, and WAXD.

EXPERIMENTAL

Materials

Polymerization-grade butadiene was further purified through triisobutylaluminum (TIBA, 2.0M in heptane) before feeding to the reactor. Toluene was refluxed over metallic sodium for 24 h and distilled under nitrogen atmosphere before use. η⁵-Pentamethylcyclopentadienyltribenzoyloxy titanium [Cp*Ti(OBz)₃] was synthesized as described in the literature.³ A yellow liquid product (yield 89%) was obtained. ANAL. calcd for C₃₁H₃₆O₃Ti: C, 73.81%; H, 7.14%. Found: C, 73.26%; H, 7.02%. Modified methylaluminoxane (mMAO) was prepared, first, by the controlled reaction of trimethylaluminum (TMA) with H₂O from Al₂(SO₄)₃·18H₂O dispersed in toluene for several hours, then filtration, and finally evaporation under vacuum. The contents of TMA retained in mMAO were determined by ¹H-NMR.³⁶ Four types of mMAO solid (i.e., mMAO1, mMAO2, mMAO3, and mMAO4 containing 16.2, 20.0, 22.5, and 26.1 wt % of TMA,

respectively) were obtained by regulating the molar ratio of H₂O and TMA.

Polymerization

The butadiene polymerization runs were carried out in 250-mL glass flasks, equipped with a magnetic stirrer, under an extrapure-grade nitrogen atmosphere using Schlenk line techniques. The mMAO, toluene, TIBA (required), and butadiene were introduced sequentially into the reactors. Polymerization began after the injection of Cp*Ti(OBz)₃ and maintaining constant temperature and pressure. The polymerization was terminated after 1 h by the addition of 10 wt % HCl in ethanol. The oxidation states of titanium in different Cp*Ti(OBz)₃/mMAO/TIBA catalytic systems were determined by the K₂Cr₂O₇ redox titration method, as described in a previous study,³⁷ and sodium diphenylaminesulfonate was used as the indicator. The polymers were washed with ethanol and dried in vacuum at 50°C to constant weight.

Characterization

Gel-permeation chromatography (GPC) of polymers was performed on a Waters 150C ALC/GPC apparatus (Waters Chromatography Division/Millipore, Milford, MA), using standard polystyrene as reference and chloroform as solvent at 40°C. ¹³C-NMR spectra were recorded at 40°C in chloroform using an INOVA

TABLE II
Influences of Temperature on Butadiene Polymerization with Cp*Ti(OBz)₃/mMAO3 Catalyst^a

Run	Temperature (°C)	Activity (kg P/mol Ti h ⁻¹)	M _w (×10 ⁻⁴)	Structure (mol %)		
				<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
5	40	12.5	21.3	65.0	18.2	16.8
3	60	38.8	30.3	62.7	12.6	24.7
6	80	34.1	38.4	60.3	13.7	26.0
7	100	16.9	39.8	55.8	16.3	28.9

^a Polymerization conditions: [Ti] = 1.0 × 10⁻³ mol/L, Al_{mMAO3}/Ti = 400 (mol/mol), P_{Bd} = 0.13 MPa, t_p = 60 min.

TABLE III
Influences of Al/Ti Molar Ratio on Butadiene Polymerization with Cp*Ti(OBz)₃/mMAO₃ Catalyst^a

Run	Al _{mMAO₃} /Ti (mol/mol)	Activity (kg P/mol Ti h ⁻¹)	M _w (×10 ⁻⁴)	Structure (mol %)		
				<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
8	100	4.8	—	—	—	—
9	200	17.2	26.9	64.0	12.8	23.2
10	300	32.7	29.0	63.5	12.2	24.3
3	400	38.8	30.3	62.7	12.6	24.7
11	500	30.3	31.6	62.5	12.9	24.6

^a Polymerization conditions: [Ti] = 1.0 × 10⁻³ mol/L, P_{Bd} = 0.13 MPa, T_p = 60°C, t_p = 60 min.

500MHz spectrometer (Varian Associates, Palo Alto, CA). The quantitative analysis of *cis*, *trans*, and 1,2 unit content was mainly determined by infrared spectra analysis with a Nicolet 205 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI), and their corresponding absorbances at about 968, 911, and 733 cm⁻¹ were adopted for the determination. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin–Elmer DCS-7 system (Perkin Elmer Cetus Instruments, Norwalk, CT) at 10°C/min. A D/MAX-3AX diffractometer (Rigaku, Corp., Tokyo, Japan) was used to obtain patterns by using a Ni-filtered Cu–K_α X-ray beam.

RESULTS AND DISCUSSION

Butadiene polymerization

As shown in Table I, by the combination of monotitanocene complex of η⁵-pentamethylcyclopentadienyl-tribenzyloxy titanium [Cp*Ti(OBz)₃] with four modified methylaluminumoxanes (mMAOs) for butadiene polymerization, the higher the TMA content in mMAO is, the more Ti(IV) complexes were reduced to Ti(III) and Ti(II) states. The catalytic activity was increased with increasing content of Ti(III) complexes. When the percentage of Ti(III) complexes reached 73.6 wt %, the catalytic activity was as much as 38.8 kg P/mol Ti h⁻¹. It was notable that an overdose of TMA content gave rise to a greater number of Ti(III) complexes to be reduced sequentially to Ti(II), so the catalytic activity was decreased. In addition, the molecular weight of

the obtained polymer was also increased with increasing molar ratio of Ti(III) to Ti(IV). Therefore, it is rather straightforward to conclude that Ti(III) active species is more effective for preparing polybutadiene with high molecular weight. By ¹³C-NMR characterization, the proportion of *cis*-1,4, *trans*-1,4, and 1,2 structures in all polybutadienes produced by different mMAOs were similar.

Data for the butadiene polymerization, at various temperatures, are presented in Table II. At lower polymerization temperatures, the Cp*Ti(OBz)₃/mMAO₃ catalyst exhibited an obvious increase in activity with increasing temperature, up to a maximum catalytic activity of 38.8 kg P/mol Ti h⁻¹ at 60°C. Further increasing the polymerization temperature would lead to a decrease in catalytic activity because a greater number of Ti(III) complexes could be reduced to Ti(II) species, which proved to be disadvantageous for preparing polybutadiene; at the same time, the solubility of butadiene was also decreased with increasing temperature. In addition, one can find that the catalyst imparted a high molecular weight, even at polymerization temperatures as high as 100°C. Much more likely, there are more Ti(III) active species in this catalyst system at higher temperature. It is noteworthy that the 1,2 structure was increased with the increase of polymerization temperature.

In view of the fact that mMAO promotes Ti(IV) monotitanocene complexes to become Ti(III) active species for butadiene polymerization and other functions of mMAO, such as scavenging trace impurities

TABLE IV
Butadiene Polymerization with Cp*Ti(OBz)₃/mMAO₃ Catalyst in the Presence of TIBA^a

Run	Al _{mMAO₃} /Ti (mol/mol)	Al _{TIBA} /Ti (mol/mol)	Activity (kg P/mol Ti h ⁻¹)	M _w (×10 ⁻⁴)	Structure (mol %)		
					<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
12	400	50	47.9	34.2	61.3	11.4	27.3
13	400	100	55.0	39.6	61.3	8.8	29.9
14	400	150	43.6	42.2	60.2	10.5	29.3
15	400	200	35.8	46.5	59.8	9.9	30.3
16	200	100	33.7	28.3	60.9	11.3	27.8
17	100	100	16.5	27.2	61.0	11.4	27.6

^a Polymerization conditions: [Ti] = 1.0 × 10⁻³ mol/L, P_{Bd} = 0.13 MPa, T_p = 60°C, t_p = 60 min.

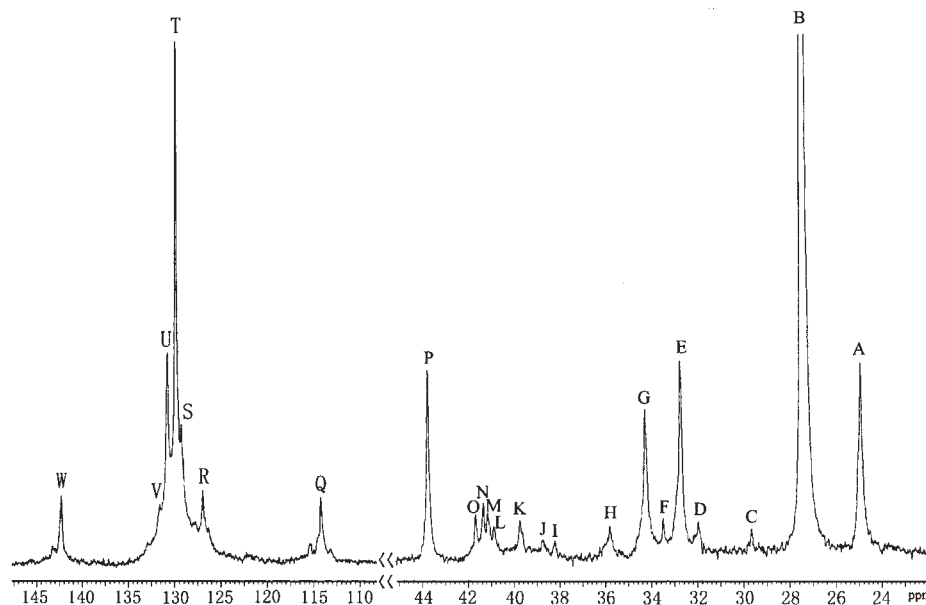


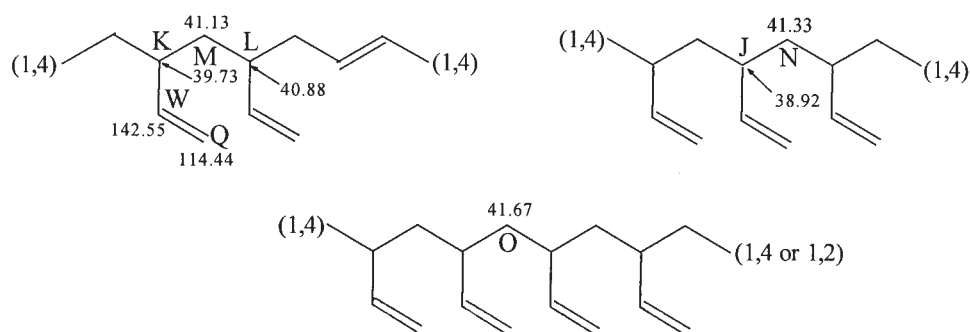
Figure 1 ^{13}C -NMR spectrum of polybutadiene obtained from Run 3.

present in the solvent and monomer, a large excess of mMAO is necessary. As shown in Table III, with mMAO3 as cocatalyst to activate $\text{Cp}^*\text{Ti}(\text{OBz})_3$, the butadiene polymerizations were examined in different Al/Ti molar ratios. The catalytic activity increased with increasing Al/Ti molar ratio, but the highest activity was around 400. At lower Al/Ti ratios, a sharp decline of activity was observed, and a minimum

value of Al/Ti (~ 100 mol/mol) was required, given that the mMAO is necessary for the reaction of mMAO with $\text{Cp}^*\text{Ti}(\text{OBz})_3$, to produce alkylated Ti(III) active species for butadiene polymerization. In contrast, some of the Ti(III) active species would be reduced to Ti(II) at very high Al/Ti molar ratios, which resulted in a decrease of polymerization activity. Additionally, the Al/Ti molar ratios did not distinctly affect poly-

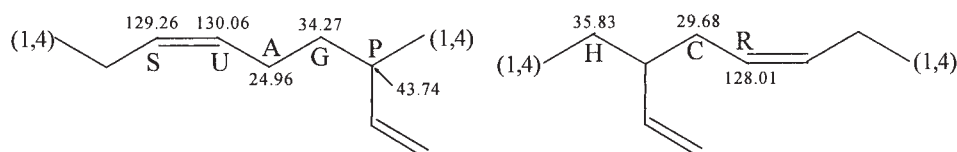
TABLE V
Assignment of ^{13}C -NMR Spectrum of Polybutadiene

Peak	Sequence assignment and carbon type	Chemical shift (ppm)		Peak intensity
		Observed	Calculated	
A	(T)CCV*C(T), $\text{CH}_2(\text{R})$	24.96	25.0	2.69
B	CCT, $\text{CH}_2(\text{R}$ and L)	27.40	27.4	12.45
C	(T)CV*C, $\text{CH}_2(\text{L})$	29.68	30.5	1.00
D	CTT, CH_2 , $\text{CH}_2(\text{L})$	31.97	32.0	2.38
E	TTT, CH_2	32.74	32.9	1.02
F	TV*C(T), CH_2	33.50	33.3	2.72
G	CV*C(T), CH_2	34.27	34.6	0.86
H	(T)CV*C, CH_2	35.83	35.3	0.81
I	(T)CV*I, $\text{CH}_2(\text{L})$	38.21	38.6	0.44
J	(T)CVVVC(T), CH	38.92	38.8	0.42
K	(T)CV*VT, CH	39.73	39.3	1.05
L	(T)CVV*T, CH	40.88	40.5	0.31
M	(T)CV*VCT, CH_2	41.13	41.0	0.46
N	V*VC(T), CH_2	41.33	41.2	0.52
O	VV*VV, CH_2	41.67	41.7	0.48
P	CV*C(T), CH	43.74	43.5	2.51
Q	V, $=\text{CH}_2(\text{pendant})$	114.44	114.3	1.42
R	V*CC(T), $=\text{CH}(\text{L})$	128.01	127.9	1.38
S	(T)CCV*, $=\text{C}(\text{L})$	129.26	129.5	1.66
T	CCC, $=\text{CH}$	129.57	129.4	9.93
U	(T)CCV*, $=\text{C}(\text{R})$	130.06	130.0	1.98
V	TTT, $=\text{CH}$	130.48	130.2	1.32
W	V, $=\text{CH}(\text{pendant})$	142.55	142.5	1.36



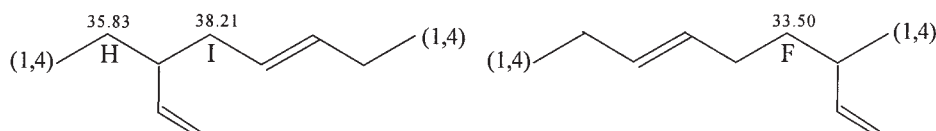
The chemical shifts of secondary carbon A and tertiary carbon P at 24.96 and 43.74 ppm were assigned to the isolated 1,2-unit on the right-hand side of the *cis*-1,4 unit.

It is of interest that a resonance at 29.68 ppm for secondary carbon C, assigned to the isolated 1,2-unit on the left-hand side of the *cis*-1,4 unit, was observed.



The sequences with an isolated 1,2-unit neighboring on the right- or left-hand side of a *trans*-1,4 unit were

also assigned by the resonances at 38.21 and 33.50 ppm of secondary carbons I and F.



The wide-angle X-ray diffractogram for the polybutadiene, obtained from Run 3, does not display a crystalline reflection in the range $2\theta = 4\text{--}40^\circ$ (Fig. 2), whereas DSC measurement also did not show the melting temperature. The results implied that the resultant polymer was amorphous.

which is attributed to an increase of Ti(III) active species, whereas the microstructure is scarcely influenced. On the basis of microstructure and property characterization by FTIR, ^{13}C -NMR, DSC, and WAXD, all resultant polymers were proved to be amorphous polybutadiene with mixed 1,2; *cis*-1,4; and *trans*-1,4 structures.

CONCLUSION

The monotitanocene catalyst, composed of η^5 -pentamethylcyclopentadienyltribenzyloxy titanium [$\text{Cp}^*\text{Ti}(\text{OBz})_3$] and modified methylaluminoxane (mMAO), for butadiene polymerization represents higher catalytic activity. The residual TMA in mMAO could reduce Ti(IV) complexes to Ti(III) and Ti(II) ones. Ti(III) active species was proved to be more effective for butadiene polymerization and could provide polybutadiene with higher molecular weight. The catalytic activity, molecular weight, and microstructure depend on polymerization conditions including temperature and Al/Ti molar ratio. Addition of triisobutylaluminum (TIBA) to the catalyst system leads to reduction of mMAO dosage and enhances catalytic activity and polybutadiene molecular weight,

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