Polymer Bulletin 28, 41–45 (1992)

Polymer Bulletin

Comparison of polymerization catalyzed by the *syn* and *anti* diastereomers of [ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)]titanium dichloride and methylaluminoxane*

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Summary

Both the pure anti (**1**) and an equimolar mixture of **1** and the syn (**2**) diastereomers of *rac*-[ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)titanium dichloride have been synthesized. The polymerization behaviors of the two systems, activated by methylaluminoxane (MAO), have been compared from -20°C to +25°C. The **2**/MAO catalyst has about 30% more active species, which polymerizes propylene 20 to 50% faster depending on T_p, undergoes chain transfers less frequently, and produces PP of higher molecular weight than the **1**/MAO system.

Introduction

Kaminsky and coworkers[2] first reported the homogeneous stereoselective *ansa*-metallocene/MAO catalysts. They can polymerize propylene to either isotactic[3] or syndiotactic[4] polymers. We found that **1**/MAO is capable of producing stereoblock macromolecular chains comprised of alternating segments of stereoregular and amorphous polypropylenes[5]. Subsequent X-ray and NMR structural determinations on the analogous dimethyltitanium compound[6] provide a rational basis for the alternation of stereoselectivity during the polymerization of propylene to produce the microstructures commensurate with the thermoplastic elastomeric properties.[5,7] Now we have developed a method to synthesize an equimolar mixture of the *syn* (**2**) and *anti*-diastereomers of the title compound. The principal objective of this work is to compare the polymerization behaviors of the (**1**/**2**)/MAO with the **1**/MAO catalyst systems in order to elucidate the influence of the *syn* and *anti* placement of methyl group in the ethylidene bridge on propylene polymerization.

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*See reference 1

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Experimental

The equimolar mixture of **1** and **2** was prepared by the reaction of dilithium salt of 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane with $TiCl_4$ as it was described for the synthesis of **1**[5] except using diethylether as the solvent instead of THF. The green **1/2** solid was obtained at 72% yield. Analysis (calcd): C, 62.8% (63.02%); H, 50% (5.82%). ^1H NMR spectra (C_6D_6) of *anti* diastereomer: 1.38 (s, 3H), 1.58 (s, 3H) 1.63 (d, 3H), 1.85 (s, 3H), 1.90 (s, 3H), 4.35 (q, 1H), 5.34 (d, 1H) 6.7-7.50 (m, 5H). ^1H NMR spectra (C_6D_6) of *syn* diastereomer: 1.37 (s, 3H), 1.61 (s, 3H) 1.80 (d, 3H), 1.86 (s, 3H), 1.92 (s, 3H), 4.27 (q, 1H), 5.02 (d, 1H) 6.7-7.50 (m, 5H). Polymerization,[8] quenching with tritiated methanol,[9] polymer work up, and radioassay were as given previously. The viscosity average molecular weight was calculated from $[\eta]$ measured in decalin at 135°C according to $\log[\eta] = 0.8 \log M_v - 4$.[10]

RESULTS AND DISCUSSION

Propylene polymerization catalyzed by an equimolar mixture of diastereomers **1** and **2** were carried out at 25°, 0° and -20°C and quenched at different times of polymerization (t_p) using [Ti] = 27 μM and [Al]/[Ti] = 2000. Similar experiments were performed with the **1**/MAO catalyst. Table 1 contains the results of polymerization activity (**A**) in g PP (mol Ti • mol C_3H_6 • h)$^{-1}$ and M_v. One can calculate the value of $\mathbf{A_2}$ for the **2**/MAO catalyst from values of $\mathbf{A_1}$ and $\mathbf{A_{1/2}}$ for the **1**/MAO and the (**1/2**)/MAO systems, respectively, using $(\mathbf{A_2}) = 2(\mathbf{A_{1/2}} - 0.5\,\mathbf{A_1})$. Comparison of columns 2 and 8 in Table I showed that $\mathbf{A_2}$ is greater than $\mathbf{A_1}$ by 2.8 and 5 fold respectively, at T_p of 25 and -20°C. The M_v of PP obtained in a 60 min. batch polymerization at -20°C have about the same M_v by either catalyst. It is 2.4 times greater for the mixed diastereomer catalyst than the **1**/MAO at T_p = 0°C but the difference is only 1.6 times at T_p = 25°C

Isotopic labeling was used to estimate the active species concentration, $[C^*]_o$. The specific radioactivity of tritium labeled polypropylene was converted to concentration of metal-polymer-bonds, [MPB] = [Ti-P] + [Al-P]. The intercept at Y = 0 of the [MPB] versus Y plot is the $[C^*]_o$. The values of $[C^*]_o$ thus obtained are found to be 5.2%, 5.1% and 4.4% of Ti at 25°, 0° and -20°C, respectively. These values are only slightly greater than the 4.5%, 4.25% and 3.8% of Ti for $[C^*]_o$ in the **1**/MAO systems found earlier at these temperatures. Both sets of values are given in Table II. With the

Table I **Propylene polymerization catalyzed by 1/MAO and (1/2)/MAO**

T_p (°C)	1/MAO			(1/2)/MAO			2/MAO
	$\mathbf{A}^a$ x10^{-5}	M_vx10^{-5}		**A** x10^{-5}	M_vx 10^{-5}		$(\mathbf{A})^c$ x10^{-5}
		10 min.^{b}	60 min.		10 min.	60 min.	
-20	2.2	2.9	4.6	6.7	2.2	4.5	$(11)^c$
0	1.5	0.5	1.4	2.4	1.2	2.5	$(5)^c$
25	1.2	0.6	0.7	2.1	1.0	1.1	$(3.3)^c$

^{a}Activity in g PP (mol Ti • mol C_3H_6 • hr)$^{-1}$; $^b t_p$; ^{c}calculated value.

Table II **Kinetic parameters for propylene polymerization**

	k_p (Msec)$^{-1}$			k_{tr}^A x 10^3 (sec)$^{-1}$			[C*] % of Ti		
Catalyst	**1**	**1 / 2**	$(\mathbf{2})^a$	**1**	**1 / 2**	$(\mathbf{2})^a$	**1**	**1 / 2**	$(\mathbf{2})^a$
-20°C	360	420	$(460)^a$	4	3	$(2)^a$	3.8	4.4	$(5)^a$
0°C	240	310	$(360)^a$	9	7	$(6)^a$	4.3	5.1	$(6)^a$
25°C	210	230	$(250)^a$	15	8	$(3)^a$	4.5	5.2	$(6)^a$

^{a}Calculated values.

knowledge of $[C^*]_o$, we can readily calculate the rate constant of propagation from $k_p = R_{p,m}$ $([C^*]_o\,[C_3H_6])^{-1}$. The rate constant of chain transfer to MAO (k_{tr}^A) was obtained from the slope of the [MPB] versus Y plot by $[MPB]_t = [MPB]_o + Yk_{tr}^A\,(k_p\,[C_3H_6])^{-1}$. The rate parameters, summarized in Table II, for the **1**/MAO and (**1**/**2**)/MAO catalysts may be used to estimate the rate constants for the **2**/MAO catalyst by the relationships,

$$k_{i,2} = \frac{k_{i,1/2}\,([C^*]_1 + [C^*]_2) - k_{i,1}\,[C^*]_1}{[C^*]_2}$$

where k_i is either k_p or k_{tr}. Thus we were able to estimate the values of the rate constants for **2**/MAO, given in Table II in parenthesis, even though we do not have a synthetic method for the synthesis of pure syn isomer. The rate constants are not greatly different from the values for the **1**/MAO system. Comparison of the **2**/MAO versus the **1**/MAO catalyst showed that the former contains about 30% more $[C^*]_0$, which polymerizes propylene 20 to 50% faster depending on T_p, but smaller $k^A{}_{tr}$ value than the latter. These kinetic parameter differences can account for the higher **A** and M_v seen in Table I for the (**1**/**2**)/MAO than the **1**/MAO catalyst.

The other noteworthy observation is that the k_p values actually increased with the decrease of T_p. We have found similar variation for the aluminum-free cationic metallocene alkyl catalyst: $[Et(Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$.[11] It is suggested that the catalytic species here is also a cation.

Acknowledgments

G. H. LL. acknowledges the ministerio de Educaciòn y Ciencia (Spain) for a posdoctoral fellowship.

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Accepted January 10, 1992 K