Polymer Bulletin 36, 317–323 (1996)

Polymer Bulletin

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A comparative study of tetraisobutyldialuminoxane and methylaluminoxane as cocatalysts for Cp_2ZrCl_2 catalyzed ethylene polymerization

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Received: 3 October 1995/Accepted: 17 October 1995

Summary

The effect of [Al]/[Zr] mol ratio and temperature on the cocatalytic effects of tetraisobutyldialuminoxane (TIBDAO) and methylaluminoxane (MAO) for ethylene polymerization using Cp_2ZrCl_2 catalyst were studied. The decay type kinetic profile was observed for both TIBDAO and MAO cocatalyzed ethylene polymerizations. Catalytic activity and rate of polymerization were found to be low for TIBDAO cocatalyzed ethylene polymerization when compared to MAO cocatalyzed ethylene polymerization. The differences in catalytic activity and rate of polymerization for ethylene polymerization catalyzed by Cp_2ZrCl_2-TIBDAO and Cp_2ZrCl_2-MAO were discussed with respect to the structures of MAO and TIBDAO. An active species for Cp_2ZrCl_2-MAO and Cp_2ZrCl_2-TIBDAO catalyzed ethylene polymerizations was also discussed. The polyethylene was characterized by intrinsic viscosity measurements.

Introduction

The discovery of homogeneous bis(cyclopentadienyl)titanium(IV)dichloride-alkylaluminum catalyst system by Breslow and Newburg (1) for ethylene polymerization kindled considerable interest in the area of soluble catalysts for olefin polymerization (2). However, for over twenty years homogeneous catalysts did not attract wide spread interest because of the poor catalyst activity, short kinetic life time and lack of stereospecificity.

Recently aluminoxanes have received considerable attention because of implications for olefin polymerization in Ziegler-Natta catalysis (3). Aluminoxanes are prepared by controlled and partial hydrolysis of alkylaluminums. The most commonly used alkylaluminums for the synthesis of aluminoxanes are trimethylaluminum (TMA), triethylaluminum (TEA) and triisobutylaluminum (TIBA). Of the various aluminoxanes available methylaluminoxane (MAO) is more reactive in olefin polymerization. In the last 10-15 years, considerable research has been done on the synthesis and structural characterization of aluminoxanes used in α-olefin polymerization (3-5). The typical structural element is an oxygen atom joining two aluminum atoms that still bear alkyl groups. The simplest representative of aluminoxanes is μ-oxo-bisalkylaluminum or

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tetralkyldialuminoxide. Tetraalkylaluminoxanes were foud to be one of the key compounds for the stereospecific polymerization of epoxides and acetaldehyde (6-8).

Tetraisobutyldialuminoxane (TIBDAO) can be prepared by the reaction of 2 mol of TIBA with 1 mol of water in toluene. Although, TIBDAO is available commercially, very little has been reported regarding the effect of [Al]/[Zr] mol ratios and temperature on ethylene polymerization using Cp_2ZrCl_2-TIBDAO catalyst system. A catalyst activity of 175 Kg-PE/g-Zr.h.atm was reported for ethylene polymerization using $Cp_2Zr(CH_3)_2$-TIBDAO catalyst system at a [Zr] = 3.0 x 10-6 mol/L, Al/Zr = 1700, 70°C and at 8 bar ethylene pressure (9). This paper reports a study on the effect of [Al]/[Zr] mol ratio and temperature on the cocatalytic effect of TIBDAO in comparison to MAO for ethylene polymerization using Cp_2ZrCl_2 as catalyst (10).

Experimental

All manipulations involving air sensitive compounds were performed inside a Laboconco Model 50004 inert atmosphere glove box continuously purged with high purity nitrogen (<5 ppm moisture and <5 ppm oxygen), or under a positive pressure of high purity nitrogen, or using standard bench top inert atmosphere techniques.

Materials: MAO, TIBDAO (Schering-A.G., Germany) and Cp_2ZrCl_2 (Aldrich chemicals, USA) were used as received. MAO 5.5% wt Al in toluene solution (average molecular weight = 850) was found to have a methyl/aluminum ratio of 1.22:1. MAO was characterized by the methods reported earlier (4). Sulphur free toluene and benzene (Loba-AR grade, Bombay) were purified by refluxing over sodium and subsequent distillation under nitrogen prior to use. Polymerization grade ethylene was obtained from the C_2-C_3 cracker unit of Indian Petrochemical Corporation Limited at Nagothane, India (oxygen <3 ppm, moisture <4 ppm).

Polymerization: Ethylene polymerization was conducted at 70°C in a jacketed glass reaction cell connected to a one L gas buret. The desired amounts of MAO or TIBDAO were placed into 30 mL of dry toluene saturated with ethylene in the cell. The reaction was initiated by addition of toluene solution of Cp_2ZrCl_2. The temperature was maintained constant both in the reaction cell and in the gas buret by circulating water through the jacket. Consumed ethylene was measured as a function of time. The reaction was terminated by addition of acidified methanol, filtered, and dried under vacuum to a constant weight. Intrinsic viscosities of the polymers were determined at 135°C using decalin as solvent.

Results and Discussion

Ethylene polymerizations were conducted in toluene using Cp_2ZrCl_2 catalyst in combination with either TIBDAO or MAO as cocatalysts at different [Al]/[Zr] ratios and temperatures. In a typical polymerization experiment, appropriate amount of cocatalyst, followed by catalyst were injected into a constant known volume of ethylene saturated in 30 mL of toluene. Polymerizations were carried out at 70°C, [Zr] = 11.5×10^{-5}, 1.15×10^{-5} and 0.115×10^{-5} mol/L corresponding to three ratios of [Al]/[Zr] viz., 100, 1000 and 10000, at 1.15×10^{-2} mol/L of TIBDAO and the polymerizations were also conducted at temperatures 50°C and 60°C at [Zr] = 0.115×10^{-5} mol/L and [Al]/[Zr] = 10000. In case of MAO cocatalyzed ethylene polymerizations the polymerization reactions were carried out at 70°C, [Zr] = 0.028×10^{-5}, 0.055×10^{-5}, 0.087×10^{-5} and 0.111×10^{-5} mol/L corresponding to four ratios of [Al]/[Zr] viz., 344000, 172000, 109000 and 86000, at 9.51×10^{-2} mol/L of MAO (based on Al) and the polymerizations were also conducted at temperatures 50°C and 60°C at [Zr] = 0.055 x 10^{-5} mol/L and [Al]/[Zr] = 172000. The results are summarized in Table 1 and graphically plotted in Figures 1 and 2.

Compared to Cp_2ZrCl_2-MAO catalyzed ethylene polymerizations higher concentrations of Cp_2ZrCl_2 are required for Cp_2ZrCl_2-TIBDAO catalyzed ethylene polymerization to show some polymerization activity. Therefore higher concentrations of Cp_2ZrCl_2 were employed in case of Cp_2ZrCl_2-TIBDAO catalyzed ethylene polymerization. For both Cp_2ZrCl_2-TIBDAO and Cp_2ZrCl_2-MAO catalyzed ethylene polymerizations the catalyst activity and rate of polymerization Rp were found to increase with increase in [Al]/[Zr] mol ratio or with decrease in Cp_2ZrCl_2 concentration (Table 1). Activities were found to be in the range of 1 to 6 Kg-PE/g-Zr.h.atm for Cp_2ZrCl_2-TIBDAO catalyzed ethylene polymerization which is very poor when compared to Cp_2ZrCl_2-MAO catalyst system. Similarly, rate of polymerization was also found to be lower for Cp_2ZrCl_2-TIBDAO catalyst system when compared to Cp_2ZrCl_2-MAO catalyzed ethylene polymerization (Table 1). The lower catalyst activity observed for Cp_2ZrCl_2-TIBDAO catalyst system compared to Cp_2ZrCl_2-MAO catalyst system is a reflection of the differences in the structure between MAO and TIBDAO. Recently, based on spectroscopic evidences and X-ray structural studies, Mason *et al.* proposed that MAO and related aluminoxanes $(RAlO)_n$, have cluster structures similar to those found in the

Table 1. Ethylene polymerization using Cp_2ZrCl_2 as catalyst[a]

Cocatalyst	Zr. 10^5 mol/L	[Al]/[Zr]	Temp. °C	Catalyst activity[b]	Rp. 10^2 M/sec	$[\eta]^c$
TIBDAO	11.5	100	70	0.6	0.93	2.21
TIBDAO	1.115	1000	70	2.7	4.14	2.20
TIBDAO	0.115	10000	70	5.6	7.35	2.45
TIBDAO	0.115	10000	60	3.5	5.12	2.85
TIBDAO	0.115	10000	50	2.0	2.81	3.12
MAO	0.028	344000	70	763	298	2.42
MAO	0.055	172000	70	667	242	2.36
MAO	0.087	109000	70	531	251	2.21
MAO	0.111	86000	70	423	203	2.30
MAO	0.055	172000	60	512	171	2.70
MAO	0.055	172000	50	273	84	2.90

a: Toluene = 30 mL, $P_{ethylene}$ = 1 atm; b: Catalyst activity = Kg-PE/g-Zr.h.atm;
c: Intrinsic viscosity determined in decalin at 135°C (dL/g)

case of iminoalanes, where the aluminum centers are tetracoordinate (5). This is different from the structures of MAO originally proposed, i.e., a linear or cyclic chain structure consisting of alternating aluminum oxygen atoms, requiring the aluminum to have a coordination number of three. This type of cage structures proposed by Mason *et al.* appears to be uniquely responsible in contributing to the very high cocatalytic activity of MAO. Such cage structures may offer high unusual stability to the anion derived by abstraction of a methide group by MAO, by delocalizing the negative charge over a large number of adjacent atoms. Fortutiously, the Lewis acidity of the MAO also appears to be finely balanced, not too high, lest it would cause over reduction of the +4 oxidation state of zirconium (the active valence state) nor too low to inhibit the formation of the cationic zirconocene species. In comparison to MAO, TIBDAO has been shown to possess only a simple dimeric structure (9). Apparently such a structure is not ideal for producing a cocatalyst with optimum activity. A plot of rate of polymerization versus time was shown in Figures 1 and 2 for Cp_2ZrCl_2-MAO and Cp_2ZrCl_2-TIBDAO catalyzed ethylene polymerizations respectively. Similar to Cp_2ZrCl_2-MAO catalyzed ethylene polymerization the catalyst activity as well as the rate of polymerization were found to increase with increase in temperature for Cp_2ZrCl_2-TIBDAO catalyzed ethylene polymerization (Table 1).

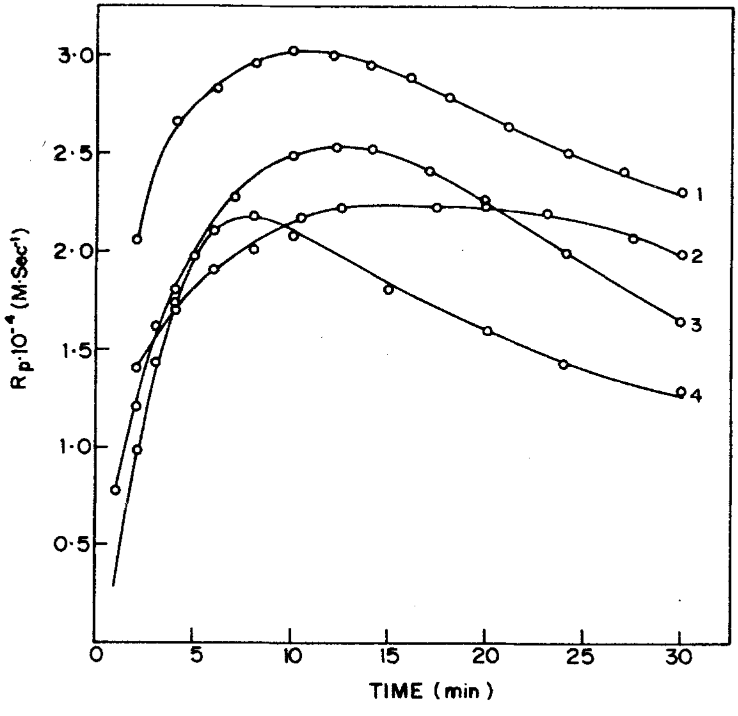

Figure 1. Polymerization of ethylene using Cp_2ZrCl_2-MAO catalyst - kinetic profile: (1) [Al]/[Zr] = 344000, [Zr] = 0.028 x 10^{-5} mol/L (2) [Al]/[Zr] = 172000, [Zr] = 0.055 x 10^{-5} mol/L (3) [Al]/[Zr] = 109000, [Zr] = 0.087 x 10^{-5} mol/L (4) [Al]/[Zr] = 86000, [Zr] = 0.111 x 10^{-5} mol/L

In both the catalyst systems the maximum rate was attained within 10 minutes of Cp_2ZrCl_2 addition. Recently, we have reported (12) that at [Al]/[Zr] mol ratio = 1000, [Zr] = 1.15 x 10^{-5} mol/L and at 70°C the ethylene polymerization was active only for about 9 min using Cp_2ZrCl_2-MAO catalyst system, where as, Cp_2ZrCl_2-TIBDAO catalyst system (in this study) is active for more than 2 h for ethylene polymerization (though activity is less) at [A]/[Zr] mol ratios of 100, 1000 and 10000. A decay type kinetic profile was observed for both the catalyst systems, though the rate of polymerization is far less for Cp_2ZrCl_2-TIBDAO catalyst system (Fig. 1 and 2). This decay type kinetics is due to the formation

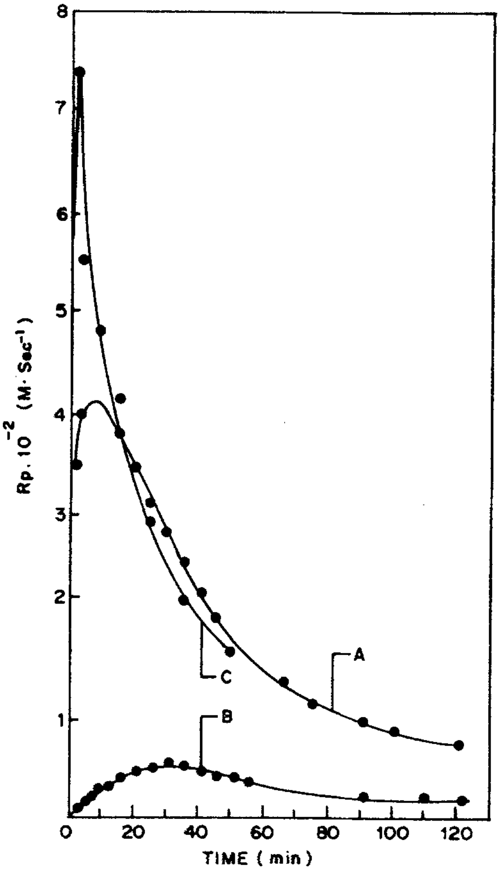

Figure 2. Polymerization of ethylene using Cp_2ZrCl_2-TIBDAO catalyst - kinetic profile: (A) [Al]/[Zr] = 100, [Zr] = 11.5 x 10^{-5} mol/L (B) [Al]/[Zr] = 1000, [Zr] = 1.115 x 10^{-5} mol/L (C) [Al]/[Zr] = 10000, [Zr] = 0.115 x 10^{-5} mol/L

of inactive species by deactivation of active Zr (IV) species. In the case of Cp_2ZrCl_2-MAO catalyst system, based on ^1H-NMR studies Kaminsky *et al.* (11), reported a deactivation process where the formation of inactive Zr-CH_2-Al structure was shown by the evolution of methane. It has been reported that in presence of excess of MAO (11) or TMA (12) (high [Al]/[Zr] mol ratio) this inactive Zr-CH_2-Al structure is converted into active Zr-CH_3 by transmetallation reaction with the loss of Al-CH_2-Al structure. Similar deactivation process must be responsible for decay type kinetics in case of Cp_2ZrCl_2-TIBDAO based catalyst system.

Higher molecular weight polyethylenes were obtained at low [Zr] for both MAO and TIBDAO cocatalyzed polymerizations (Table 1). Higher molecular weight polyethylenes were obtained at lower temperature polymerizations (Table 1). This is due to the reduced chain transfer at low temperatures. An intrinsic viscosity of 1.18 dL/g was reported earlier for polyethylene produced using Cp_2ZrCl_2-MAO catalyst system at [Al]/[Zr] = 1000, [Zr] = 1.15×10^{-5} mol/L and at 70°C (12). At the same polymerization conditions the polyethylene with intrinsic viscosity of 2.20 dL/g was obtained (entry 2 in Table 1) using Cp_2ZrCl_2-TIBDAO catalyst system. This is due to the fact that TIBA (in case of TIBDAO) is acting as a less chain transfer agent when compared to TMA (in case of MAO).

(a) (b)

Figure 3. (a) Active species for the Cp_2ZrCl_2-MAO catalyst system (b) Active species for the Cp_2ZrCl_2-TIBDAO catalyst system

An active species similar to that proposed (11) for the Cp_2ZrCl_2-MAO catalyst system appears possible in the case of Cp_2ZrCl_2-TIBDAO (Figure 3). In conclusion, the low activities and low Rp observed for Cp_2ZrCl_2-TIBDAO catalyst system may be a consequence of the simple structure of TIBDAO compared to a cage or cluster type structure of oligomeric MAO.

Acknowledgements

I am very much thankful to the Dr. S. Sivaram, National Chemical Laboratory, Pune, India, for the valuable discussions throughout my Ph.D. research work and also I am thankful to the Council of Scientific and Industrial Research, New Delhi for the grant of research fellowship.

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