

Correlation between configuration/conformation of zirconocenes on the stereoselectivity of the propylene polymerization reaction

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Received: 25 April 1995/Revised version: 23 May 1995/Accepted: 5 June 1995

Summary

The catalytic performance (activity and polymer properties) of metallocenes with different symmetries in combination with methylaluminoxane (MAO) in the polymerization of propylene has been investigated at different temperatures, under standardized reaction conditions. The zirconocene *rac*-ethylene bis(η^5 -1-indenyl) zirconium (IV) dichloride, with C_2 symmetry, produces isotactic polypropylene and isopropylidene(η^5 -cyclopentadienyl) (η^5 -9-fluorenyl) zirconium (IV) dichloride, with C_s symmetry, syndiotactic polypropylene. The degree of the tacticity of these polymers increases with decreasing polymerization temperature. Only atactic polypropylene was formed with the unbridged zirconocenes bis(η^5 -cyclopentadienyl) zirconium (IV) dichloride and bis(η^5 -indenyl) zirconium (IV) dichloride at any temperature investigated (10–60°C).

Introduction

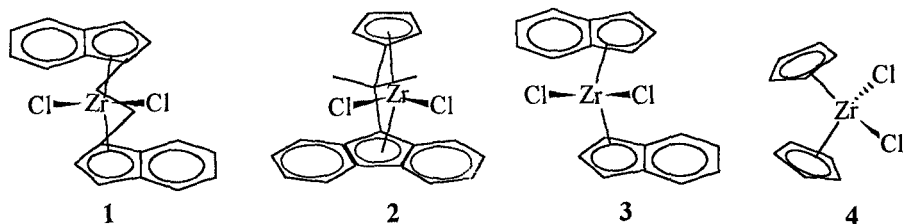
A new and large family of group 4 metallocenes has been developed in the last two decades. These organometallic complexes in combination with methylaluminoxane (MAO) are able to polymerize stereoselectively α -olefins [1]. It is now well established that even slight modifications of the substituents of the cyclopentadienyl ligand causes significant changes in the activities and selectivities as well as on the tacticity of the polyolefins produced by these polymerization reactions [1]. The stereoselectivity of these polymerizations is mainly attributed to the geometry and stereorigidity of the organometallic catalytic precursors[2]. For example, *rac*-ethylene bis(η^5 -1-indenyl) titanium (IV) dichloride, with C_2 symmetry, yields isotactic polyolefins [3], but with the *meso*-ethylene bis(η^5 -1-indenyl) titanium (IV) dichloride only atactic polyolefins were produced [3a]. Syndiotactic polymers are formed if isopropylidene(η^5 -cyclopentadienyl) (η^5 -9-fluorenyl) zirconium (IV) dichloride, with C_s symmetry, dichloride is used as a catalytic precursor [3b, 4]. The unbridged complex bis(η^5 -1-methylfluorenyl) zirconium (IV) dichloride produces polypropylene with high degrees of isotacticity. This behavior can be attributed to the conformations of C_2 symmetry assigned to this zirconocene [5].

Although there is a tremendous amount of work dealing with the influence of the metallocene geometry on the stereoselectivity of α -olefin polymerizations, only isolated results have been reported and they do not allow a straightforward comparative study. In this work the catalytic performance (activity and polymer properties) of metallocenes with different symmetries in combination with MAO is evaluated for the polymerization of propylene at different temperatures and under standardized reaction conditions [3c].

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Results and discussion

The complexes 1-4 chosen for this study are shown in Scheme 1.



Scheme 1. Catalyst precursors 1-4.

The catalyst activity and the polypropylene properties obtained with the catalyst precursors 1 and 2 are summarized in Table 1.

Entry	Temp. (°C)	Activity gPP/molZr.h.bar		Yield (g)		[η] in dL/g		M_v		I.I. %	
		1	2	1	2	1	2	1	2	mmmm	rrrr
1	10	33	340	0,20	3,4		1,21		112600		89
2	20	930	571	4,6	5,7	0,39	1,04	27300	93300	88	84
3	30	3870	1000	19,4	9,9	0,30	0,54	19000	41100		76
4	40	7200	720	36,0	7,2	0,24	0,55	15000	42000	79	
5	50	5950	290	29,8	2,9	0,18	0,23	10500	14100	76	65
6	60	5630		28,2		0,11		5600		74	

Table 1. Catalytic activity and polypropylene properties obtained with catalyst precursors 1 and 2. Polymerization conditions i) $[1] = 33 \cdot 10^{-6}$ mol/L ($5 \cdot 10^{-6}$ mol), Al/Zr= 1440, 120min, in 250mL of toluene; ii) $[2] = 66 \cdot 10^{-6}$ mol/L ($10 \cdot 10^{-6}$ mol), Al/Zr= 750, 120min, toluene= 150 mL.

It is important to note that only low molecular-weight polypropylene has been obtained from any polymerization reaction conditions used with the catalytic precursors 3 and 4. Moreover, the catalyst activities were very low even when high concentrations of MAO, catalysts 3 and 4 or very long reaction times were used. The polypropylene obtained with both unbridged metallocenes were typical atactic as indicated by the analysis of their ^{13}C NMR spectra.

It is obvious from Table 1 that both, the yield in polypropylene and the catalytic activity for metallocene 1 increase with the temperature of the polymerization up to 40°C and then decrease for higher temperature values. This behavior is probably due to the decomposition or deactivation of the active catalyst species and/or to lowering monomer concentrations in the medium with the increasing of the polymerization temperature since these reactions were carried out in a non-pressurized reactor. The very low yield in polypropylene at low polymerization temperatures can be related to low reaction rates of propylene coordination and the monomer insertion into the Zr-C bond (chain growth reaction). Similar results have been obtained with the catalyst precursor 2, however, the activity starts to decrease at 30°C.

It is also apparent from Table 1 that the viscosity and molecular weight of the polymers obtained by complexes **1** and **2** decrease with the increase of the polymerization temperature. The remarkable difference between the polypropylenes obtained with catalyst precursors **1** and **2** is that the viscosity and M_v are always higher for the syndiospecific one at any temperature. The lower molecular weight polymers produced at higher polymerization temperatures can be related to an increase in chain termination reaction rates, probably via β -elimination processes, as suggested by the presence of the characteristic resonances of vinylidene carbons in the ^{13}C NMR spectra of these polymers.

The microstructure analysis of the polypropylenes obtained by the catalyst **1** and **2**, by ^{13}C NMR clearly indicates an isotactic and syndiotactic stereoregularity, respectively. For both catalytic systems the polymer stereoregularity increases with declining polymerization temperature. The production of only atactic polypropylene with the catalyst precursors **3** and **4**, even at low polymerization temperatures, suggests that these zirconocenes do not possess a preferred conformation that is able to induce stereoselectivity.

Although, it is necessary to investigate in more details the fluxionality, in solution, of the model zirconocenes **1-4** (assuming that stereoselectivity is mainly due to the geometry of the catalyst precursor), the results obtained here suggest that even the so-called stereorigid metallocenes **1** and **2** contain a certain degree of fluxionality.

Experimental

General

All operations were realized in inert atmosphere. Polymerization grade propylene has been obtained from PPH and dried through molecular sieve (4Å) columns. MAO (5.5% Al in toluene) was used as received from Schering SA. The toluene was dried by refluxing over metallic sodium and distilled under argon atmosphere. The catalyst precursors: **1** [6], **2** [3b,4,7], **3** [8] and **4** [9] were prepared according to the literature procedures.

Polymerizations

The polymerizations were carried out in a 2-liter glass reactor (Büchi) with toluene as solvent. The MAO and the required amount of catalyst were mixed in a Schlenk tube and after 15 min they were transferred by syringe under positive pressure of propylene into the reactor at the reaction temperature. After the desired time the polymerization was quenched by the addition of a 1% HCl/methanol solution. The polymer was recovered by filtration and vacuum dried at 70°C until constant weight has been achieved.

Polymer Characterization

Carbon 13 Nuclear Magnetic Resonance (^{13}C NMR, 50.309 MHz) measurements were performed at 90°C with an acquisition time of 1.4 s, pulse width of 68° and pulse delay of 3s on a VARIAN XL-200 Spectrometer. The samples were dissolved in orthodichlorobenzene. Benzene- d_6 (30 % v/v) was used as an internal lock. [3a,4,7,10].

Acknowledgments

Financial support by PPH and FINEP-PADCT is greatfull acknowledged. One of us (M. R. M.) expresses his appreciation of a fellowship from the CAPES.

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