Homogeneous Ethylene Polymerization Using Zirconocene Aluminohydride Complexes

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- Results and Discussion
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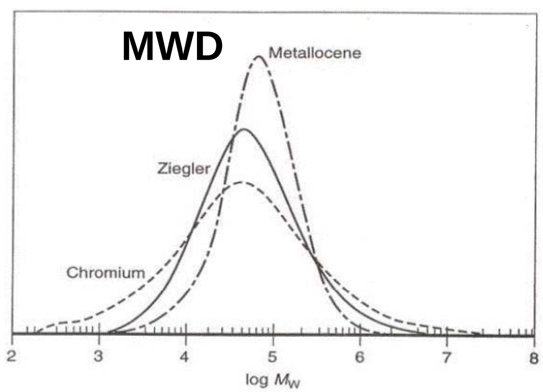
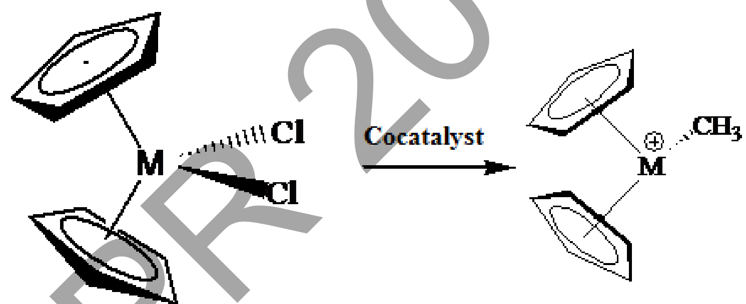
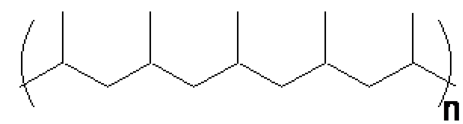
Introduction

- Metallocene catalysts produce polymers with special molecular architectures
- Controlled microstructures
- Broad variety of materials (Elastomers, Plastomers, LLDPE, HDPE)



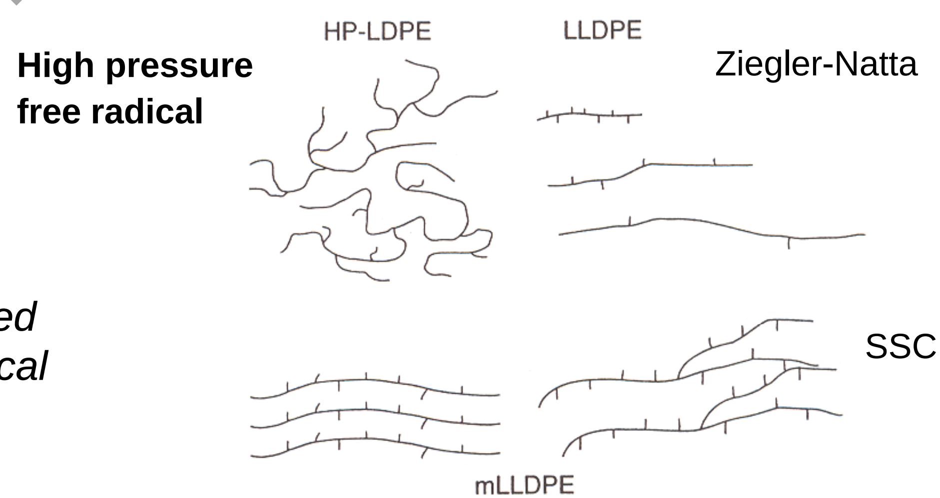




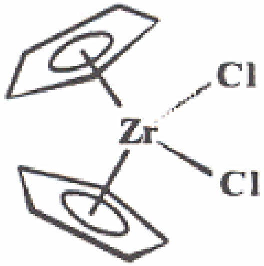
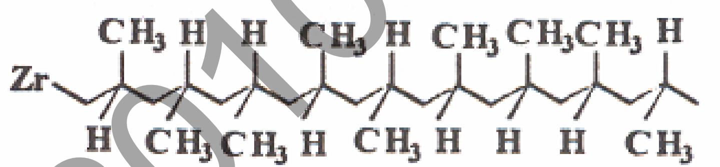
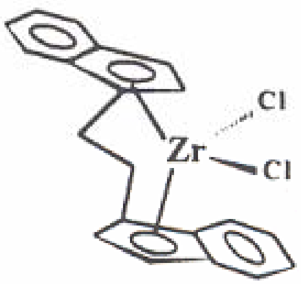
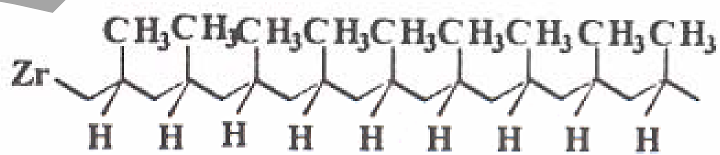
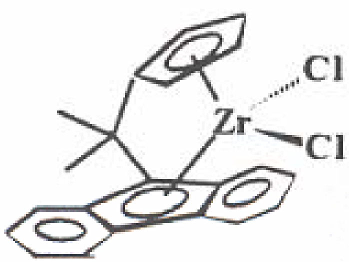
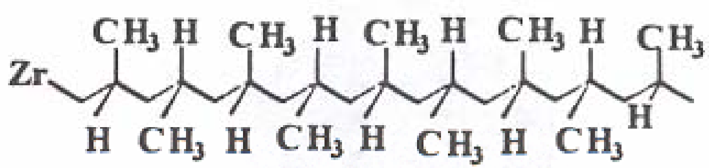
iPP

Stereoregularity control

Polymers with improved physical and mechanical properties

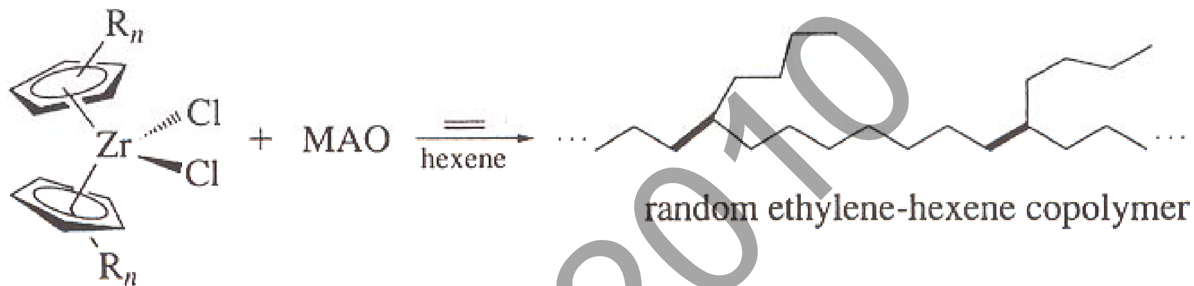


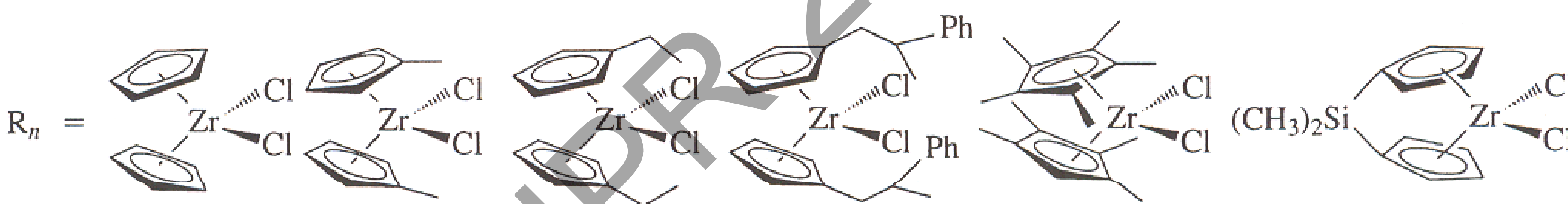
Catalyst Symmetry and Microstructure of the Polymers Produced

Metallocene	Symmetry	Microstructure	
	C_{2v}		a-PP
	C_2		i-PP
	Cs		s-PP

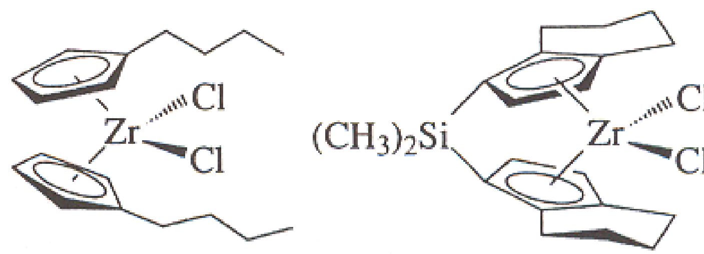
Metallocenes containing simpler ligands

Ethylene Polymerization and copolymerization





1 2 3 4 5

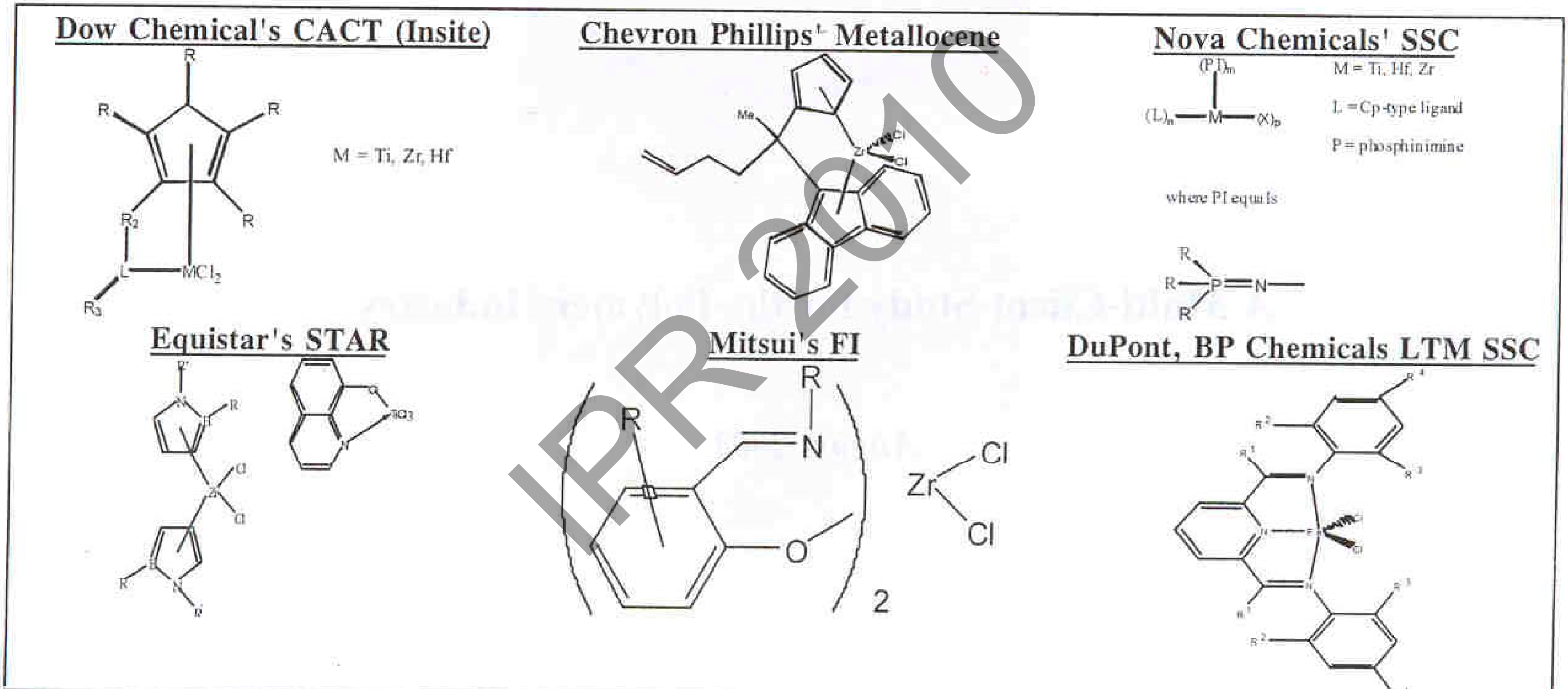


6 7

Basell

End-use application of LLDPE in films

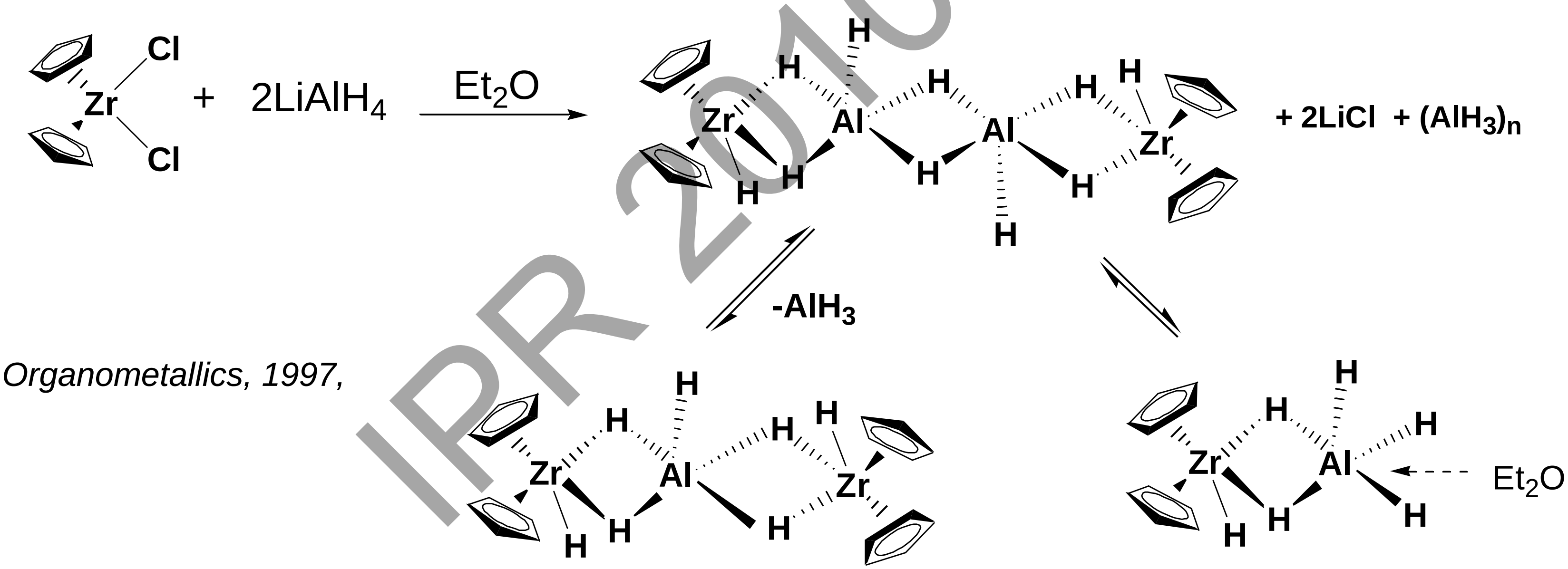
Some Comercial SSC



Source: TCGR's The Metallocene & Single-Site Catalyst Monitor

Zirconocene aluminohydride complexes

(Modification of the typical metallocenes)



Raston, et. al. *Organometallics, 1997, 16, 3252*

Main species in solid state

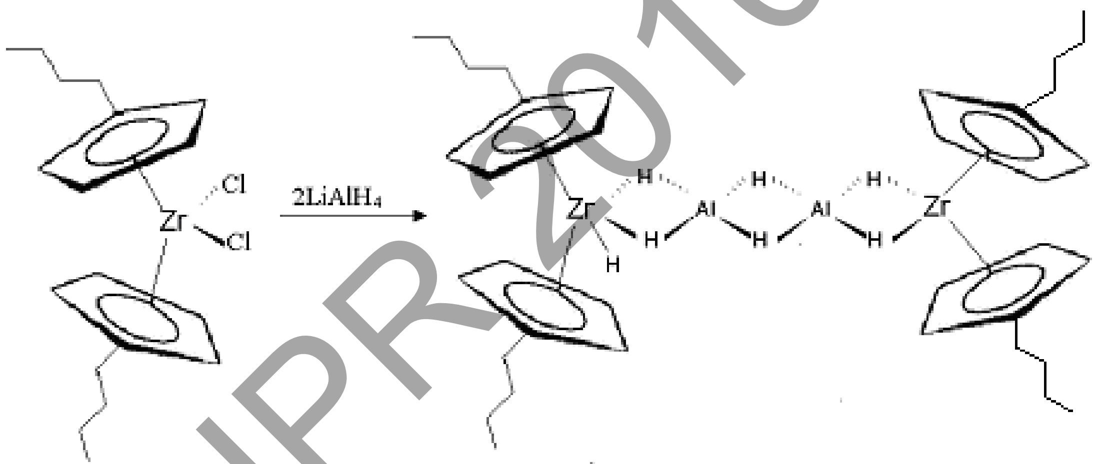
Fluxional behavior in solution

Stephan, et. al. *Organometallics, 1998, 17, 763*

Zirconocene aluminohydride complexes

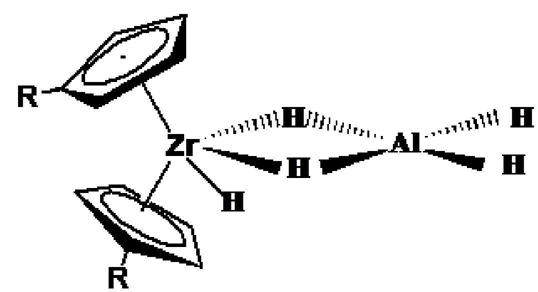
(Modification of the typical metallocenes)

- Catalytic systems for propylene and ethylene polymerizations



nBu-Cp_2ZrCl_2
Commercial catalyst

High activities at mild polymerization conditions (50^oC and 42 psi ethylene) in homogeneous phase but high concentrations of MAO
Al/Zr = 20,000 – 40,000



R= nBu, SiMe3, Me5

Goals

- Study the kinetic behaviour of zirconocene aluminohydrides derived from nBu-Cp_2ZrCl_2 for the homogeneous polymerization of ethylene at low MAO concentrations
- Compare the polymerization kinetic data with that for the corresponding classical metallocene activated under the same polymerization conditions

Experimental

- Homogeneous Ethylene Polymerization

Polymerization conditions

- **500 mL semibatch reactor**
- **Hexane**
- **T = 60ºC**
- **$P_{C2=}$ 65 psi**
- **500 rpm**
- **t = 30 min**
- **[Cat] = 10^{-7} M**

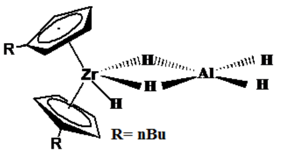
PE characterization

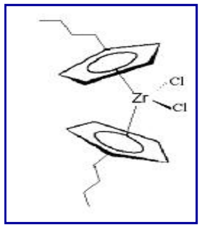
GPC (GPC, Polymer Char) 140ºC 1,2,4-trichlorobenzene using three linear columns, calibrated with polystyrene standars 1mL/min

DSC TA Instruments DSC 2920

Results and Discussion

Ethylene Polymerization using **$nBuCp_2ZrH_3AlH_2$** and **$nBuCp_2ZrCl_2$** Activated with MAO





Exp	[Cat] 10^{-6} M	MAO (gr)	(Al/Zr)	A KgPE/molZr h	Mn	Mw	Mw/ Mn
1	1.23	0.5	700	2,200	44,685	174,350	3.9
1’	1.23	0.5	700	4,530	38,851	206,440	5.3
2	1.23	1	1,400	6,140	75,312	316,863	4.2
2’	1.23	1	1,400	6,323	43,131	140,447	3.2
3	1.23	1.7	2,400	7,840	81,246	316788	3.9
3’	1.23	1.7	2,400	6,800	116,392	342,338	2.9
4	1.23	2.5	3,500	8,400	84,000	310,650	3.7
4’	1.23	2.5	3,500	6,300	118,858	357163	3.0
5	1.23	3.4	4,700	8,600	90,743	320,409	3.5
5’	1.23	3.4	4,700	6,100	63,505	257332	4.0
6	1.23	5.1	7,100	8,400	58,618	290,804	4.9
6’	1.23	5.1	7,100	5,400	83,116	298,055	3.5
7	1.23	6.8	9,500	8,700	54,748	311,715	5.6
7’	1.23	6.8	9,500	5,900	72,362	285,438	3.9

T = 60°C, 150 mL hexane, P_{C2}= 65 psig, 500 rpm, t = 0.5 h

$nBuCp_2ZrH_3AlH_2$ (Exp. 1-7) and $nBuCp_2ZrCl_2$ (Exp. 1’ – 7’)

DSC

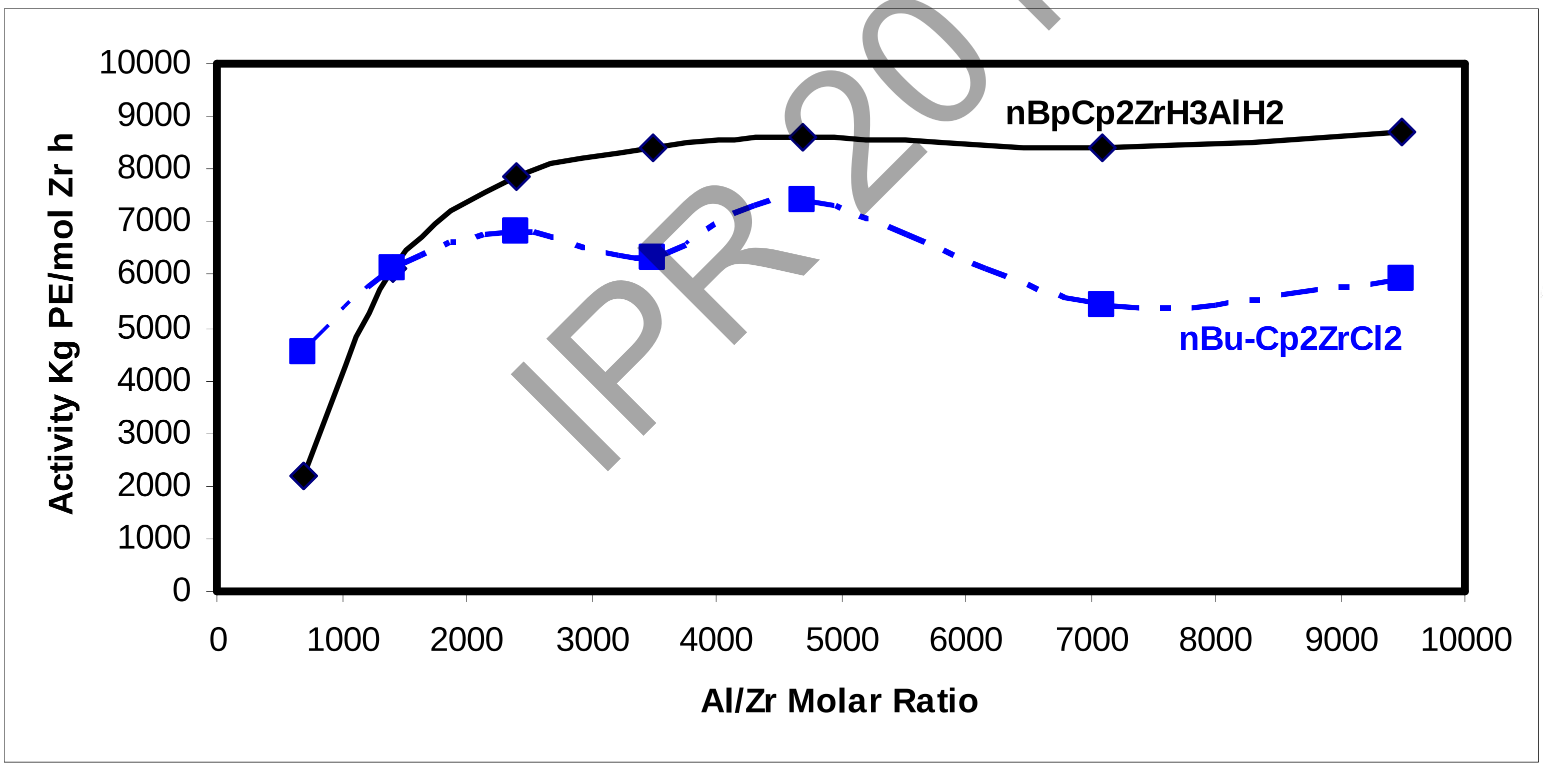
Tm=134°C

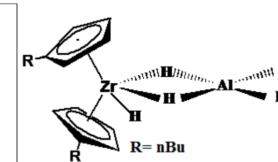
Tc= 119°C

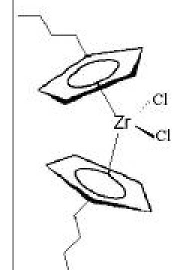
13% - 30 % higher activity for the aluminohydride system

Effect of Al/Zr ratio on Polymerization Activity

Effect of Al/Zr ratio on the activity of ethylene polymerization with zirconocene aluminohydride (nBu-Cp2ZrH3AlH2/MAO) and zirconocene dichloride (nBu-Cp2ZrCl2/MAO).

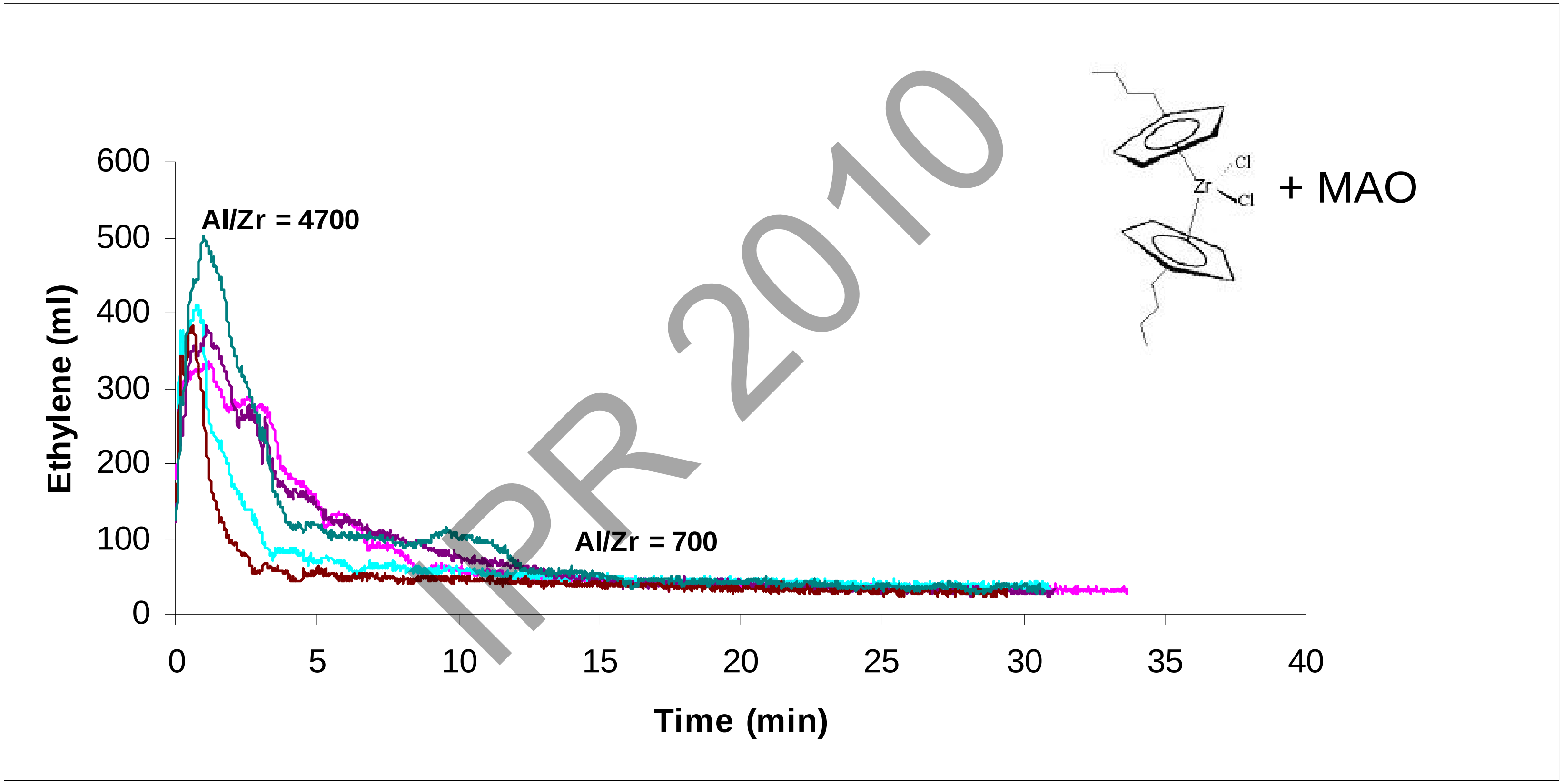






Kinetic Behaviour

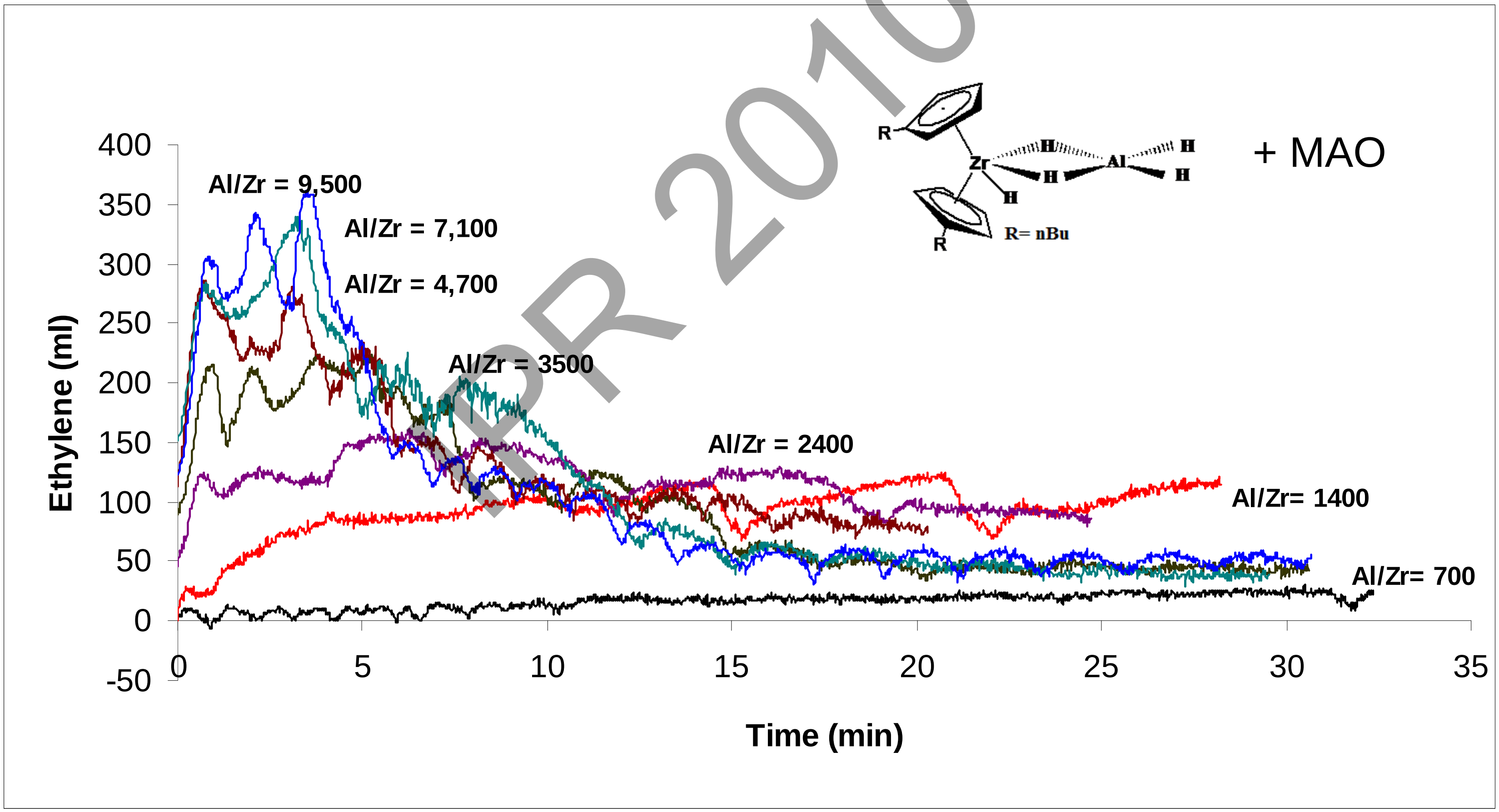
Classical Metallocene with Different Al/Zr Ratios



Kinetic Behaviour

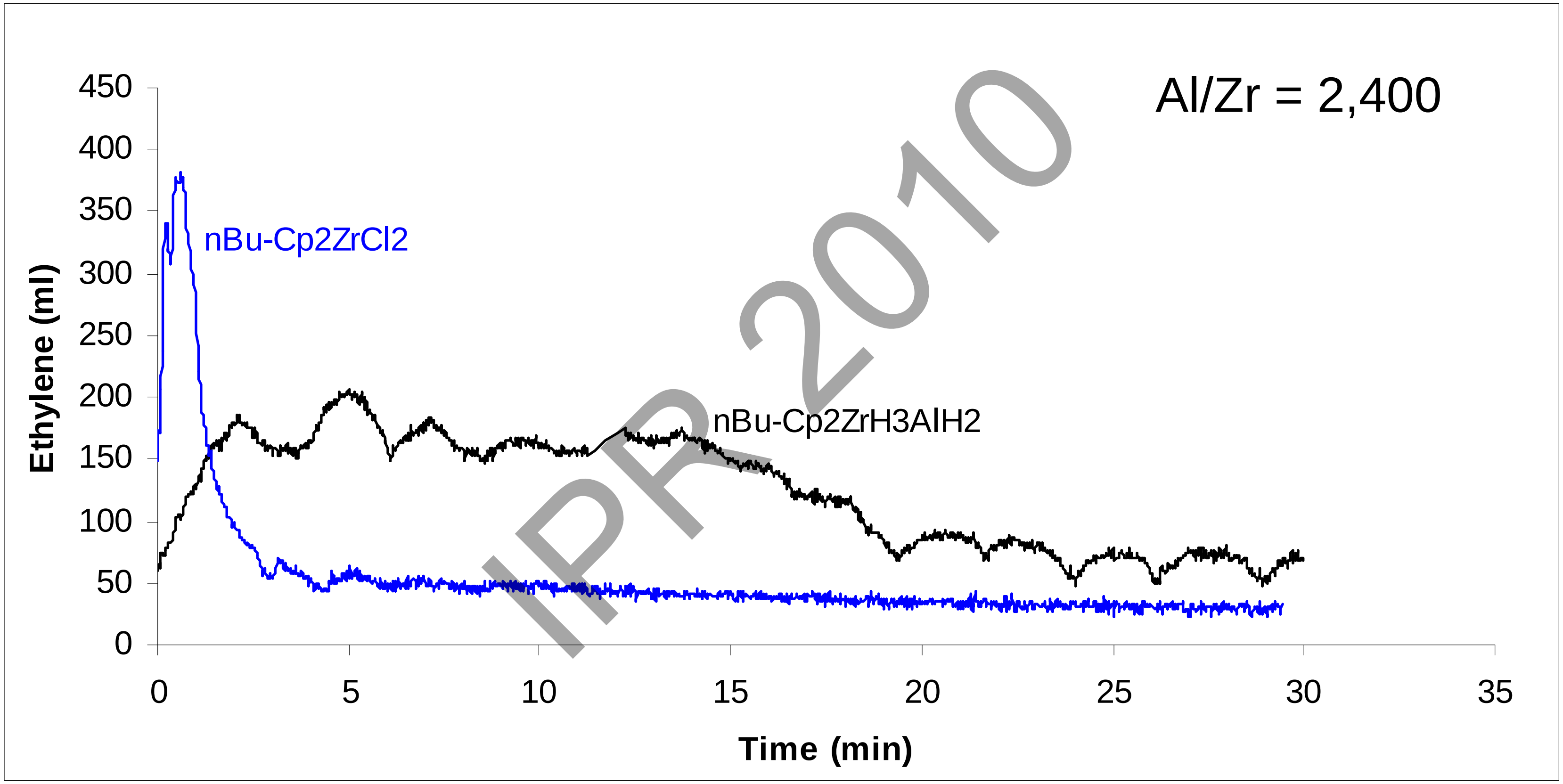
Zirconocene Aluminohydride with Different Al/Zr Ratios

Ethylene consumption with nBu-$Cp_2ZrH_3AlH_2$, activated with different Al/Zr ratios.



Comparison of Polymerization Kinetics

(Classical x Zirconocene Alumnohydride)



Conclusions

- **The activity of nBu-$Cp_2ZrH_3AlH_2$ was approximately 30% higher than that obtained for the classical zirconocene (nBu-Cp_2ZrCl_2) under the same polymerization conditions.**

- **The ethylene consumption rate was also more stable with the aluminohydride zirconocene catalyst. However, the MWDs for the polyethylenes obtained with this catalyst were broader than those made with the classical metallocene (PDI 3.9-4.2 versus 2.8 – 3.0).**

- **The MWD broadening was attributed to the fluxional nature of the zirconocene aluminohydride complexes in solution.**

- **The aluminohydride zirconocenes could be potencially applied at higher levels of polymerizations. (scaled up).**

Aknowledgments

- Department of Chemical Engineering, University of Waterloo (Prof. João Soares research group)
- CONACYT México