

## REFERENCES

- Akimoto, A. and Yano, A. (1999). New Catalyst Concept for the polymerization of Ethylene with Metallocenes. Metaloorganic Catalysts for Synthesis and Polymerization, 180-181.
- Chien, J. C. W. (1988) and Wang, B.(1988). Metallocene -Methylaluminumoxane Catalysts for Olefin Polymerization. I. Trimethylaluminum as Coactivator. Journal of Polymer Science: Part A: Polymer Chemistry, 26, 3089-3102.
- Chu, K., Soares, J. B. P., and Penlidis, A. (2000) Polymerization Mechanism for In Situ Supported Metallocene Catalysts. Journal of Polymer Science: Part A: Polymer Chemistry, 38, 462-468.
- Daniel, J. (2000) Metallocenes : New Technology in Catalytic Polymerization. <http://www.chee.iit.edu>.
- Eskelinen, M., and Seppala, J.V. (1995). Effect of polymerization Temperature on the Polymerization of Ethylene with Dicyclopentadienyl Zirconocene Dichloride/ Methylaluminumoxane Catalyst. Journal of Europe Polymer, 32, 331-335.
- Haddin, D., and Marks, T.J. (1988). Surface Chemistry and Catalyst, Direct NMR Spectroscopic Observation of Surface Alkylation and Ethylene Insertion/Polymerization on  $MgCl_2$ . J. Am.Chem. Soc., 110(5)
- Hamielec, A.E., and Soarse, J.B.P. (1997). Polymerization Reaction Engineering-Metallocene Catalyst. Progress in Polymer Science, 21, 651-706.
- Janiak, C., Rieger, B., Voelkel, R., and Braun, H.(1993). Polymeric Aluminoxane: A Possible Cocatalytic Support Materail for Ziegler-Natta-Type Metallocene Catalysts. Journal of Polymer Science: Part A: Polymer Chemistry, 31, 2959-2968.

- Janimak, J.J., and Stevens, G.C. (2000). Comparative Crystallization and Exploratory Microstructure Studied of novel Polyethylene with Tailored Molecular Characteristics. Polymer, 41, 4233- 4248.
- Jordan, R.F., Bajgur, C.S., Willett, R., and Scotto, B. (1986). J. Am. Chem. Soc. 108, 7410.
- Kim, I., and Choi, C. (1999). The Effect if  $AlR_3$  on Propylene Polymerization by  $rac\text{-}(EBI)Zr(NMe_2)_2AlR_3/[CPh_3][B(C_6F_5)_4]$  Catalyst. Journal of Polymer Science: Part A: Polymer Chemistry, 37, 1523-1539.
- Kolodka, E., Wang, W.J., Charpentier, P.A., Zhu, S., and Hamilelec, A.E., (2000). Long-Chain Branching in Slurry Polymerization of Ethylene with Zirconocene Dichloride / modified methylaluminooane. Polymer, 41, 3985-3991.
- Liu, S., Yu, G., and Huang B. (1997). Polymerization of Ethylene by Zirconocene- $B(C_6F_5)_3$  Catalysts with Aluminum Compounds. Journal of Applied Polymer Science, 66, 1715-1720.
- Marks, T.J., and Chen, Y. (1997). Organo-Lewis Acid Acid as Cocatalyst for Cationic Homogeneous Ziegler-Natta Olefin.US5856256.
- Marks, T.J., Yang, X., and Stern, C.L. (1991). J. Am. Chem. Soc., 113, 3623.
- Naga, N., Shiono, T., and Ikeda, T.(1999). Profiles of Ethylene Polymerization with Zirconocene-Trialkylaluminum/Borane Compound. Journal of Molecular Catalyst A : Chemical, 150, 155-162.
- Petitjean, L., Pattou, D., and Ruiz-Lopez, M.F. (1999). Theoretical Study of the Mechansims of Ethylene Polymerization with Metallocene-Type Catalysts. J. Phys. Chem. B, 103, 27-35.
- Reddy, S.S., and Sivaram, S. (1995). Homogeneous metallocene-MAO Catlyst Systems for Ethylene Polymerization. Process in Polymer Science. 20, 309-367.
- Rieger, B., and Janiak, C. (1994). Concentration Effects of Methylaluminoxane, Zirconocene dichloride and Trimethylaluminum

- in ethylene Polymerization. Die Angwandte Makromolekulare Chemie. 215, 35-57.
- Siedle, A.R., Lamana, W.M., Newmark, R.A., and Schroepfer, J.N. (1998). Mechanism of Olefin Polymerization by a Soluble Zirconocene Catalyst. Journal of Molecular Catalyst A: Chemical, 128, 257-271.
- Sin, H., and Kaminsky, W. (1980). Avd. Organomet. Chem., 18,99
- Sin, H., Kaminsky, W. (1994). Zirconocene Catalysts for Olefin polymerization. Catalyst Today, 20, 257-271.
- Soares, J. B. P., Kim, J. D., and Rempel, G. L. (1997). Analysis and Control of The Molecular Weight and Chemical Composition Distribution of Polyolefins Made with Metallocene and Ziegler Natta Catalyst. Ind. Eng. Chem. Res., 36(4), 1144-1150.
- Starck, P., Lehmus, P., and Seppala, J.V. (2000). Thermal Characterization of Ethylene Polymers Prepared with Metallocene Catalysts. Polymer Engineering and Science, 39(8) 1444-1455.
- Yang, X., Stern, C.L., and Marks, T.J. (1990). "Cation-like" Homogeneous Olefin Polymerization Catalyst Based upon Zirconocene Alkyl and  $B(C_6F_5)_3$ . J. Am. Chem. Soc., 113,3623-3625.
- Yang, X., Stern, C.L., and Marks, T.J. (1994). Cationic ZirconoceneOlefin Polymerization Catalyst Based on the Organo-Lewis Acid  $B(C_6F_5)_3$  A Synthetic, Structural, Solution Dynamic, and Polymerization Catalytic Study. J. Am. Chem. Soc., 116, 10015-10031.
- Zambelli, A. and Longo, A. (1989) Macromolecules, 22, 2186-2189.

## APPENDIX

**Table A1** Ethylene consumption using different zirconium concentrations at Al/Zr = 100, P<sub>ET</sub> = 2 bar, reaction time = 1 hr, T = 20°C.

Time (min)	Ethylene consumption (ml/min) from mass flow meter		
	[Zr] = 10 $\mu$ mol	[Zr] = 8 $\mu$ mol	[Zr] = 5 $\mu$ mol
0	0	0	0
1	1300	1023	1365
2	859	709	740
3	622	859	1373
4	1100	924	834
5	806	310	557
6	467	203	413
7	276	124	276
8	230	229	200
9	183	656	180
10	165	390	150
11	150	270	61
12	144	225	56
13	141	170	75
14	130	140	66
15	125	115	68
16	110	106	53
17	118	71	24
18	103	63	8
19	100	70	15
20	99	65	12

Time (min)	Ethylene consumption (ml/min) from mass flow meter		
	[Zr] = 10 $\mu$ mol	[Zr] = 8 $\mu$ mol	[Zr] = 5 $\mu$ mol
21	96	62	5
22	100	58	7
23	86	54	6
24	90	52	7
25	87	49	5
26	81	45	6
27	76	44	6
28	79	42	7
29	110	40	4
30	98	39	7
31	91	38	11
32	90	36	7
33	81	36	7
34	79	46	6
35	75	54	8
36	62	45	4
37	51	51	2
38	64	48	4
39	59	44	3
40	55	42	6

Time (min)	Ethylene consumption (ml/min) from mass flow meter		
	[Zr] = 10 $\mu$ mol	[Zr] = 8 $\mu$ mol	[Zr] = 5 $\mu$ mol
41	53	41	4
42	55	38	6
43	46	34	8
44	54	34	8
45	49	30	7
46	43	34	5
47	32	28	9
48	36	22	7
49	38	26	7
50	36	30	11
51	29	29	9
52	25	34	8
53	30	26	6
54	28	30	4
55	16	24	6
56	19	26	6
57	21	34	4
58	20	34	3
59	24	28	3
60	29	26	3
Yield (g)	7.66	7.46	6.03

**Table A2** Ethylene consumption using different Al/Zr ratios at  $[Zr] = 5 \mu\text{mol}$   
 $P_{\text{ET}} = 1.0 \text{ bar}$ , reaction time = 1 hr,  $T = 20^\circ\text{C}$ .

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
0	0	0	0	0	0	0
1	0	789	600	658	280	110
2	0	740	610	640	790	81
3	0	709	600	600	700	70
4	0	700	512	585	600	65
5	0	567	480	456	330	60
6	0	539	400	356	300	56
7	0	346	380	320	294	55
8	0	185	350	300	286	54
9	0	188	313	258	244	50
10	0	150	278	231	246	50
11	0	128	242	210	236	50
12	0	120	200	200	233	49
13	0	122	186	200	194	49
14	0	100	150	201	190	49
15	0	95	142	205	164	48
16	0	80	130	221	164	48
17	0	69	125	200	150	49
18	0	63	120	185	154	49
19	0	63	120	163	150	48
20	0	65	110	150	146	47

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
21	0	65	90	100	100	47
22	0	55	85	50	30	47
23	0	50	80	40	13	47
24	0	47	76	10	13	47
25	0	50	55	9	16	46
26	0	42	40	9	15	46
27	0	46	32	8	16	48
28	0	49	21	7	15	49
29	0	51	20	8	16	47
30	0	44	9	9	11	47
31	0	38	9	5	13	47
32	0	35	9	4	12	45
33	0	33	9	6	14	45
34	0	32	9	3	13	45
35	0	30	9	2	12	46
36	0	30	8	1	12	45
37	0	28	8	1	12	41
38	0	32	8	2	12	40
39	0	31	8	3	13	40
40	0	29	7	4	13	40



Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
41	0	30	6	5	10	40
42	0	30	5	6	9	40
43	0	31	5	2	9	36
44	0	27	5	2	10	39
45	0	26	5	2	10	36
46	0	24	5	1	15	37
47	0	22	5	1	15	35
48	0	22	1	1	5	34
49	0	22	1	1	5	33
50	0	21	1	1	3	32
51	0	22	1	1	3	30
52	0	22	1	0	6	31
53	0	21	2	0	6	32
54	0	22	2	0	3	30
55	0	22	2	0	2	30
56	0	22	2	0	0	30
57	0	25	2	0	0	30
58	0	22	1	0	0	30
59	0	20	1	0	0	32
60	0	20	1	0	0	31
Yield (g)	0	5.50	9.20	6.90	6.20	1.90

**Table A3** Ethylene consumption using different Al/Zr ratio at  $[Zr] = 5 \mu\text{mol}$   
 $P_{ET} = 0.5 \text{ bar}$ , reaction time = 1 hr,  $T = 30^\circ\text{C}$ .

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
0	0	0	0	0	0	0
1	0	870	1148	1061	645	0
2	0	682	1100	950	776	0
3	0	650	1000	900	654	0
4	0	593	950	850	467	0
5	0	411	750	725	276	0
6	0	365	600	70	200	0
7	0	276	521	671	190	0
8	0	250	500	505	178	0
9	0	180	421	439	150	0
10	0	173	356	345	143	0
11	0	164	219	328	140	0
12	0	150	190	299	123	0
13	0	149	176	291	130	0
14	0	100	165	273	116	0
15	0	99	152	229	112	0
16	0	60	147	210	117	0
17	0	50	135	199	112	0
18	0	50	125	210	110	0
19	0	50	108	227	109	0
20	0	50	100	207	105	0

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
21	0	50	96	200	100	0
22	0	50	89	159	98	0
23	0	41	95	143	95	0
24	0	40	82	118	91	0
25	0	10	79	110	91	0
26	0	4	86	100	91	0
27	0	4	80	89	90	0
28	0	4	73	85	90	0
29	0	1	64	52	89	0
30	0	1	60	45	95	0
31	0	1	57	43	82	0
32	0	1	46	41	80	0
33	0	1	45	40	80	0
34	0	1	43	38	79	0
35	0	1	43	31	79	0
36	0	1	40	23	50	0
37	0	1	40	21	50	0
38	0	1	43	20	50	0
39	0	1	41	20	41	0
40	0	1	41	17	41	0

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
41	0	0	35	8	39	0
42	0	0	37	7	35	0
43	0	0	34	6	31	0
44	0	0	32	6	30	0
45	0	0	31	3	30	0
46	0	0	29	1	25	0
47	0	0	25	1	20	0
48	0	0	20	1	19	0
49	0	0	15	1	15	0
50	0	0	14	0	14	0
51	0	0	14	0	10	0
52	0	0	12	0	10	0
53	0	0	12	0	9	0
54	0	0	10	0	4	0
55	0	0	10	0	4	0
56	0	0	10	0	3	0
57	0	0	9	0	2	0
58	0	0	9	0	1	0
59	0	0	5	0	1	0
60	0	0	4	0	1	0
Yield (g)	0	4.10	8.00	5.30	2.80	0

**Table A4** Ethylene consumption using different Al/Zr ratios at  $[Zr] = 5 \mu\text{mol}$   
 $P_{\text{ET}} = 0.5 \text{ bar}$ , reaction time = 1 hr,  $T = 40^\circ\text{C}$ .

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
0	0	0	0	0	0	0
1	0	230	650	486	200	0
2	0	210	500	327	187	0
3	0	204	420	276	135	0
4	0	200	313	250	133	0
5	0	148	276	225	128	0
6	0	145	242	210	120	0
7	0	136	220	200	120	0
8	0	120	182	198	11	0
9	0	111	164	185	103	0
10	0	108	150	175	99	0
11	0	108	139	150	98	0
12	0	106	121	149	95	0
13	0	106	116	138	90	0
14	0	99	115	130	89	0
15	0	97	110	113	75	0
16	0	96	90	120	72	0
17	0	95	82	100	60	0
18	0	82	80	80	64	0
19	0	80	71	97	60	0
20	0	70	65	82	55	0

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
21	0	58	55	80	40	0
22	0	52	50	71	32	0
23	0	47	44	65	32	0
24	0	42	41	55	32	0
25	0	30	40	50	25	0
26	0	20	33	44	21	0
27	0	21	31	41	20	0
28	0	20	28	40	19	0
29	0	19	25	33	19	0
30	0	15	21	31	18	0
31	0	13	22	28	17	0
32	0	10	20	25	17	0
33	0	10	18	20	15	0
34	0	10	16	15	6	0
35	0	8	15	15	6	0
36	0	8	15	15	6	0
37	0	8	15	15	5	0
38	0	8	15	12	5	0
39	0	2	14	12	4	0
40	0	1	12	12	3	0

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
41	0	1	10	10	2	0
42	0	1	10	9	1	0
43	0	0	9	9	1	0
44	0	0	0	5	1	0
45	0	0	0	6	1	0
46	0	0	0	2	1	0
47	0	0	0	2	0	0
48	0	0	0	2	0	0
49	0	0	0	2	0	0
50	0	0	0	2	0	0
51	0	0	0	1	0	0
52	0	0	0	1	0	0
53	0	0	0	1	0	0
54	0	0	0	0	0	0
55	0	0	0	0	0	0
56	0	0	0	0	0	0
57	0	0	0	0	0	0
58	0	0	0	0	0	0
59	0	0	0	0	0	0
60	0	0	0	0	0	0
Yield (g)	0	2.0	6.00	4.75	1.30	0

**Table A5** Ethylene consumption using different Al/Zr ratios at  $[Zr] = 5 \mu\text{mol}$   
 $P_{\text{ET}} = 0.5 \text{ bar}$ , reaction time = 1 hr,  $T = 50^\circ\text{C}$ .

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
0	0	0	0	0	0	0
1	0	188	359	607	545	0
2	0	88	523	494	500	0
3	0	48	300	422	450	0
4	0	44	278	399	323	0
5	0	27	235	325	120	0
6	0	27	240	304	100	0
7	0	23	203	148	90	0
8	0	23	190	103	85	0
9	0	22	189	82	78	0
10	0	21	150	62	71	0
11	0	20	145	69	65	0
12	0	21	143	61	50	0
13	0	20	142	58	54	0
14	0	29	147	55	53	0
15	0	15	120	49	51	0
16	0	14	118	50	51	0
17	0	10	115	39	50	0
18	0	9	112	59	45	0
19	0	5	113	55	44	0
20	0	2	111	52	44	0



Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
21	0	1	105	50	21	0
22	0	0	104	50	20	0
23	0	0	105	50	20	0
24	0	0	101	49	20	0
25	0	0	100	49	20	0
26	0	0	118	50	19	0
27	0	0	86	55	19	0
28	0	0	79	60	18	0
29	0	0	54	50	15	0
30	0	0	51	49	13	0
31	0	0	40	48	12	0
32	0	0	37	47	12	0
33	0	0	43	47	12	0
34	0	0	40	45	12	0
35	0	0	35	40	11	0
36	0	0	28	41	10	0
37	0	0	28	30	10	0
38	0	0	28	25	10	0
39	0	0	27	21	10	0
40	0	0	25	3	10	0

Time (min)	Ethylene consumption (mL/min) from mass flow meter					
	Al/Zr = 0	Al/Zr=160	Al/Zr=200	Al/Zr=220	Al/Zr=260	Al/Zr=300
41	0	0	22	3	5	0
42	0	0	20	2	5	0
43	0	0	21	0	5	0
44	0	0	22	0	5	0
45	0	0	21	0	5	0
46	0	0	18	0	5	0
47	0	0	21	0	2	0
48	0	0	20	0	1	0
49	0	0	23	0	1	0
50	0	0	21	0	1	0
51	0	0	22	0	1	0
52	0	0	21	0	1	0
53	0	0	18	0	1	0
54	0	0	17	0	0	0
55	0	0	16	0	0	0
56	0	0	14	0	0	0
57	0	0	11	0	0	0
58	0	0	10	0	0	0
59	0	0	8	0	0	0
60	0	0	3	0	0	0
Yield (g)	0	0.70	5.20	4.75	3.10	0

**Table A6** Ethylene consumption using different ethylene pressures at Al/Zr = 220, reaction time = 1 h, T = 30°C.

Time (min)	Ethylene consumption (ml/min) from mass flow meter		
	P <sub>ET</sub> = 0.5 bar	P <sub>ET</sub> = 1.0 bar	P <sub>ET</sub> = 2.0 bar
0	0	0	0
1	1148	1150	1365
2	1100	928	1135
3	917	756	834
4	850	747	557
5	418	591	413
6	300	336	276
7	312	255	200
8	300	189	180
9	297	65	150
10	249	64	61
11	219	41	56
12	190	40	75
13	176	35	66
14	165	30	62
15	152	29	53
16	147	29	24
17	135	29	8
18	125	28	15
19	108	26	12
20	100	26	7

Time (min)	Ethylene consumption (ml/min) from mass flow meter		
	$P_{ET} = 0.5$ bar	$P_{ET} = 1.0$ bar	$P_{ET} = 2.0$ bar
21	96	25	6
22	89	30	5
23	95	30	6
24	82	30	6
25	79	32	6
26	86	32	5
27	80	34	5
28	73	36	5
29	64	35	5
30	60	34	6
31	57	34	6
32	46	25	6
33	45	21	4
34	43	15	4
35	43	15	4
36	40	14	4
37	40	12	3
38	43	7	2
39	41	4	2
40	41	4	2

Time (min)	Ethylene consumption (ml/min) from mass flow meter		
	$P_{ET} = 0.5$ bar	$P_{ET} = 1.0$ bar	$P_{ET} = 2.0$ bar
41	35	4	2
42	37	4	4
43	34	0	4
44	32	0	4
45	31	0	3
46	29	0	0
47	25	0	0
48	20	0	0
49	15	0	0
50	14	0	0
51	14	0	0
52	12	0	0
53	12	0	0
54	10	0	0
55	10	0	0
56	10	0	0
57	9	0	0
58	9	0	0
59	5	0	0
60	4	0	0
Yield (g)	12.92	9.50	7.50

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