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APPENDICES

APPENDIX A

Table A-1. Properties of catalysts at different $Al_2Et_3Cl_3$/Mg molar ratios (Ti:Mg molar ratio = 3:1).

Item	Ex.1		Ex.2		Ex.3		Ex.4		Ex.5	
EASC: Mg molar ratio	0.0625		0.125		0.25		0.5		1	
% Preactivation (Ti^{+3} :Ti total)	-		-		-		-		47.5	
Ratio (Mg:Ti:Cl)	1: 0.11 :2.30		1 : 0.09 :2.38		1: 0.07 :2.21		1 : 0.07:2.38		1: 0.39 :3.36	
%Ti (w/w)	2.0		2.9		2.6		2.4		4.8	
%Mg (w/w)	20.3		16.5		17.8		20.7		9.6	
%Cl (w/w)	65.8		65.2		65.5		68.8		38.3	
APS (μm)	9.3		10.7		8.8		7.0		13.6	
PSD	1.4		3.2		2.6		2.6		7.1	
Polymerization	H_2 feeding		H_2 feeding		H_2 feeding		H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar
Yield (kgPE/mmol Ti)	6.4	4.7	15.3	10.1	16.7	8.8	40.0	23.4	10.1	5.0
Yield (kgPE /g cat)	6.7	4.9	9.3	6.1	9.1	4.8	20.1	14.7	10.2	5.0
Melt flow properties										
$MFI_{2.16}$ (g/10 min)	0.88	8.90	0.80	10.5	0.85	12.0	1.05	10.7	1.25	10.7
MFI_5 (g/10 min)	1.62	25.7	1.50	21.1	1.63	26.2	1.98	20.8	2.72	20.7
$MFI_{21.6}$ (g/10 min)	17.2	270	15.2	202	15.4	294	11.2	206	27.5	216
MFR ($MFI_{21.6}$ / MFI_5)	10.6	10.5	10.1	9.6	9.4	11.2	8.8	9.9	10.1	10.4
APS (μm)	129	94	108	110	101	90	100	97	120	110
Bulk density (g/cm^3)	0.37	0.33	0.30	0.31	0.35	0.35	0.33	0.34	0.32	0.31

Table A-2. Properties and activities of catalysts at different Ti: Mg molar ratios ($Al_2Et_3Cl_3$: Mg molar ratio = 0.5:1 and agitation speed = 400 rpm)

Item	Ex. 6		Ex.4		Ex. 7		Ex.8	
Ti:Mg molar ratio	2		3		4		5	
Ratio(Mg:Ti:Cl)	1 : 0.04 : 2.28		1 : 0.07 : 2.38		1 : 0.09: 2.36		1 : 0.10 :3.39	
%Ti (w/w)	0.5		2.4		2.8		2.8	
%Mg (w/w)	22.6		20.7		21.8		22.4	
%Cl (w/w)	70.2		68.8		66.6		69.5	
APS (μm)	7.4		7.0		5.0		5.6	
PSD	1.8		2.6		2.5		5.8	
POLYMERIZATION	H_2 feeding		H_2 feeding		H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar
Yield (kg PE/mmol Ti)	2.6	None reacted	40.0	23.4	19.7	14.4	4.5	2.5
Yield (kg PE /g cat)	0.27	None reacted	20.1	14.7	11.5	8.4	2.6	1.5
Melt flow properties								
$MFI_{2.16}$ (g/10 min)	1.05	–	1.05	10.7	1.93	9.42	1.85	5.43
MFI_5 (g/10 min)	0.26	–	1.86	11.75	3.51	28.4	3.82	10.7
$MFI_{21.6}$ (g/10 min)	2.65	–	17.7	143	35.2	310	38.5	112
MFR($MFI_{21.6}$ / MFI_5)	10.4	–	9.5	12.1	10.0	10.9	10.1	10.5
APS (μm)	96	–	100	97	80	83	74	62
Bulk density (g/cm^3)	0.26	–	0.33	0.34	0.20	0.19	0.18	0.16

Table A-3. Properties and activities of catalysts at different numbers of titanation (Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$:Mg molar ratio = 0.5:1, and agitation speed = 400 rpm)

Item	Ex.4		Ex.9		Ex.10	
number of titanation	1		2		3	
Ratio (Mg:Ti:Cl)	1 : 0.07 : 2.38		1: 0.15: 2.57		1: 0.16 : 2.48	
%Ti (w/w)	2.4		3.3		3.4	
%Mg (w/w)	20.7		16.8		17.2	
%Cl (w/w)	68.8		65.3		63.5	
APS (μm)	7.0		10.0		10.4	
PSD	2.6		2.5		2.7	
POLYMERIZATION	H_2 feeding		H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar
Yield (kgPE/mmol Ti)	40.0	23.5	28.4	15.0	13.5	8.5
Yield (kgPE /g cat)	20.1	11.7	19.5	10.3	9.6	6.0
Melt flow properties						
$MFI_{2.16}$ (g/10 min)	1.10	19.2	1.08	14.5	1.13	15.8
MFI_5 (g/10 min)	1.86	20.8	1.9	16.8	1.85	17
$MFI_{21.6}$ (g/10 min)	17.7	206	18.6	163	17.9	168
MFR($MFI_{21.6}$ / MFI_5)	9.5	9.9	9.8	9.7	9.7	9.9
APS (μm)	100	97	130	111	120	105
Bulk density (g/cm^3)	0.32	0.34	0.31	0.30	0.32	0.30

Table A-4. Properties and activities of catalysts at different treatment time.
(Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$:Mg molar ratio = 0.5:1, agitation speed = 400 rpm, and treatment temperature = 110°C)

Item	Ex.11		Ex.4		Ex.12		Ex.13	
Treatment (h)	0		2		5		10	
Ratio (Mg:Ti:Cl)	1:0.05:2.27		1:0.07:2.38		1:0.12:2.61		1:0.12:2.54	
%Ti (w/w)	1.8		2.4		2.6		2.6	
%Mg (w/w)	19.0		20.7		19.8		25.2	
%Cl (w/w)	66.0		68.8		60.5		63.7	
APS (μm)	17.6		7.0		16.1		21.7	
PSD	2.4		2.6		2.0		2.5	
POLYMERIZATION	H_2 feeding		H_2 feeding		H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar
Yield (kgPE/mmol Ti)	7.7	6.8	40.0	23.4	18.0	10.0	16.5	8.6
Yield (kgPE /g cat)	2.9	2.5	20.1	14.7	9.8	5.4	8.6	4.4
Melt flow properties								
$MFI_{2.16}$ (g/10 min)	1.6	8.1	1.1	9.5	0.4	2.3	0.3	2
MFI_5 (g/10 min)	1.13	20.1	1.86	20.8	0.85	6.08	0.67	5.8
$MFI_{21.6}$ (g/10 min)	11.54	212.6	17.7	142.7	2.28	31.5	6.8	57.8
MFR ($MFI_{21.6}$ MFI_5)	10.2	10.6	9.5	12.1	11.3	10.4	10.1	9.9
APS (μm)	120	81	100	97	93	79	112	68
Bulk density (g/cm^3)	0.33	0.30	0.33	0.34	0.23	0.23	0.19	0.28
AB	4.8		3.1		1.3		1.3	

AB = [average CA x log[(MFI_2/MFI_2)]/|ΔCA|: where, MFI_2* = melt flow index at H_2 pressure = 3 bar, MFI_2 = melt flow index at H_2 pressure = 1 bar, CA = catalyst activity

Table A-5. Properties and activities of catalysts with ethyl benzoate (EB) addition (Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$:Mg molar ratio = 0.5:1, agitation speed = 400 rpm, treatment temperature = 110°C and treatment time = 2 h).

Item	Ex .4		Ex.14		Ex. 15		Ex. 16	
EB : Mg molar ratio	0		0.06		0.12		0.25	
Ratio (Mg:Ti:Cl)	1: 0.07: 3.32		1: 0.06: 3.58		1: 0.05: 3.50		1: 0.05 :4.96	
%Ti (w/w)	2.4		2.2		2.1		1.3	
%Mg (w/w)	20.7		19		18.6		13	
%Cl (w/w)	68.8		68		65.1		64.5	
APS (μm)	11.9		13.5		13.1		12.1	
PSD	1.7		1.6		1.8		1.7	
POLYMERIZATION	H_2 feeding		H_2 feeding		H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar
Yield (kgPE/mmol Ti)	40.0	29.4	22.5	18.5	17.7	15.0	17.5	6.5
Yield (kgPE /g cat)	20.1	14.7	11.5	9.2	9.5	8.3	4.8	1.8
Melt flow properties								
$MFI_{2.16}$ (g/10 min)	1.05	9.5	1.56	10.5	1.86	12.3	2.00	20.1
MFI_5 (g/10 min)	1.86	20.8	3.15	22.8	3.99	25.4	4.62	43.8
$MFI_{21.6}$ (g/10 min)	none	none	none	none	none	none	none	none
MFR ($MFI_{21.6}$ / MFI_5)	none	none	none	none	none	none	none	none
APS (μm)	133	108	130	100	129	105	135	97
Bulk density (g/cm^3)	0.33	0.34	0.34	0.32	0.35	0.33	0.33	0.34
AB	3.1		3.7		6.1		1.1	

AB = [average CA x log[(MFI_2/MFI_2)]/|ΔCA|: where, MFI_2* = melt flow index at H_2 pressure = 3 bar, MFI_2 = melt flow index at H_2 pressure = 1 bar, CA = catalyst activity

Table A-6. Properties and activities of catalysts with ethyl benzoate (EB) addition by varying the aging time ($Al_2Et_3Cl_3$:Mg molar ratio = 0.5:1, Ti:Mg molar ratio = 3:1, EB:Mg molar ratio = 0.12:1, treatment temperature = 110°C but aging time was varied for 2, 5, and 10 h)

Item	Ex. 15		Ex. 17		Ex. 18	
Aging time (h)	2		5		10	
Ratio (Mg:Ti:Cl)	1:0.05:3.50		1:0.07:3.60		1:0.12:3.65	
%Ti (w/w)	2.1		2.8		3.2	
%Mg (w/w)	18.6		18.0		17.6	
%Cl (w/w)	65.1		64.5		63.8	
APS (μm)	13.1		12.5		14.0	
PSD	1.8		2.0		2.3	
POLYMERIZATION	H_2 feeding		H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar	1 bar	3 bar
Yield (kgPE/mmol Ti)	17.7	15.0	25.5	22.6	29.5	25.5
Yield (kgPE /g cat)	9.5	8.3	15.0	13.2	17.3	15.0
Melt flow properties						
$MFI_{2.16}$ (g/10 min)	1.86	12.3	1.30	10.5	0.98	10.3
MFI_5 (g/10 min)	3.99	25.4	3.00	24.5	3.12	27.4
$MFI_{21.6}$ (g/10 min)	none	none	none	none	none	none
MFR ($MFI_{21.6}$ / MFI_5)	none	none	none	none	none	none
APS (μm)	129	105	133	98	135	105
Bulk density (g/cm^3)	0.35	0.33	0.33	0.32	0.35	0.33
AB	6.1		7.1		7.2	

AB = [average CA x log[(MFI_2/MFI_2)]/|ΔCA|: where, MFI_2* = melt flow index at H_2 pressure = 3 bar, MFI_2 = melt flow index at H_2 pressure =1 bar. CA = catalyst activity

Table A-7. Properties and activities of catalyst with dicyclopentyldimethoxysilane (DCPDMS) addition (Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$: Mg molar ratio = 0.5:1, and agitation speed = 400 rpm, EB:Mg molar ratio = 0.12:1, treatment temperature 110°C, treatment time = 10 h)

Item	Ex. 18		Ex.19	
DCPDMS:Mg molar ratio	0		0.25	
Ratio (Mg:Ti:Cl)	1:0.12:3.65		1:0.07:3.45	
%Ti (w/w)	3.2		2.4	
%Mg (w/w)	17.6		19.5	
%Cl (w/w)	63.8		64.8	
APS (μm)	14.0		33.5	
PSD	2.3		2.0	
POLYMERIZATION	H_2 feeding		H_2 feeding	
	1 bar	3 bar	1 bar	3 bar
Yield (kgPE/mmol Ti)	29.5	25.5	20.5	16.4
Yield (kgPE /g cat)	17.3	15.0	12.0	9.4
Melt flow properties				
$MFI_{2.16}$ (g/10 min)	0.98	10.3	2.05	51.2
MFI_5 (g/10 min)	3.12	27.4	5.10	115
$MFI_{21.6}$ (g/10 min)	none	none	none	none
MFR ($MFI_{21.6}$ / MFI_5)	none	none	none	none
APS (μm)	135	105	260	200
Bulk density (g/cm^3)	0.35	0.33	0.36	0.35
AB	7.2		5.8	

AB = [average CA x log[(MFI_2/MFI_2)]/|ΔCA|: where, MFI_2* = melt flow index at H_2 pressure = 3 bar, MFI_2 = melt flow index at H_2 pressure = 1 bar. CA = catalyst activity

APPENDIX B

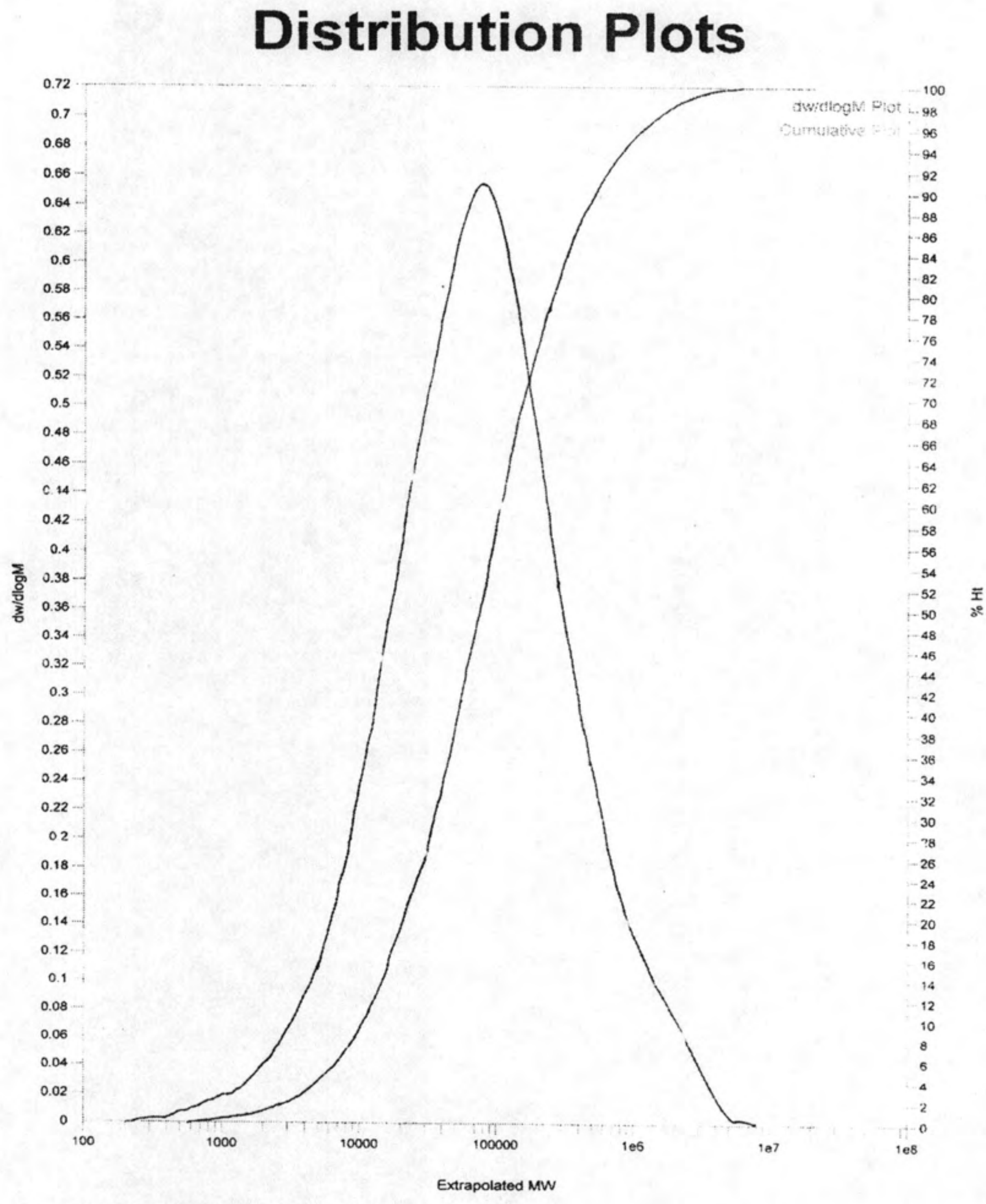

Figure B-1 GPC curve of PE obtained from the prepared catalyst.

VITA

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