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APPENDICES

APPENDIX A

DETERMINATION OF KINETIC PARAMETERS

Determination of the kinetic parameters is one of the useful methods to elucidate how the polymerization proceeds on the active sites formed by reaction between catalyst and cocatalyst. Several methods, for example, the radio tagging technique with ^{14}CO [44,221,222], the inhibition method with CO, CO_2 or SO_2 [223], the tritiated alcohol quenching method [224-226] and measurements of the allene concentration consumed, have been proposed to obtain accurate kinetic parameters in olefin polymerization using Ziegler catalysts. Among them, the stopped-flow method seems to be the most reliable and useful due to its excellent features.

Here, the example of kinetic parameter calculation of entry 2 (methanol) in Chapter VI is shown.

Based on Natta equation [3].

$$\overline{M}_n = M_0 \cdot \frac{k_p \cdot [M] \cdot t}{1 + k_{tr} \cdot t} \qquad (1),$$

$$Y = k_p \cdot [M] \cdot [C^*] \cdot t \qquad (2),$$

Combining Equations 1 and 2 we obtain

$$\frac{1}{\overline{P}_n} = \frac{M_0}{\overline{M}_n} = \frac{k_{tr}}{k_p \cdot [M]} + \frac{1}{k_p \cdot [M]} \cdot \frac{1}{t} \qquad (3),$$

where

$\overline{M}_n$	=	number-average molecular weight of the polymer (GPC result)
M_o	=	molecular weight of the monomer (43 g/mol)
[M]	=	monomer concentration (0.6 mol/L at 30°C in *n*-heptane)
t	=	polymerization time (experimental result)
k_{tr}	=	transfer rate constant
k_p	=	propagation rate constant
Y	=	polymer yield (experimental result)

The experimental data are tabulated in the following columns 1, 2 and 3.

t (s)	Yield (g-PP/mol-Ti)	$\overline{M}_n$	$1/\overline{P}_n = M_0/\overline{M}_n$	$1/t$
0.1044	32.2280	12,130	0.0310	9.58
0.1579	52.0145	17,604	0.0192	6.33
0.1901	77.8656	19,515	0.0128	5.26

Since the polymer yield is proportion to polymerization time up to ca. 0.2 s. Therefore, a plot of $1/\overline{P}_n$ versus $1/t$ should be linear (Equation 3).

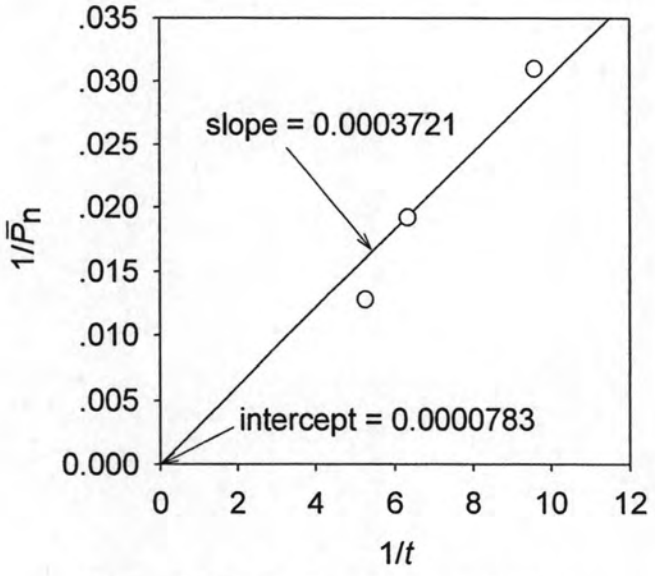

Figure A.1 Time dependency of $1/\overline{P}_n$.

From the tangent and the intercept of the plot of $1/\overline{P}_n$ vs $1/t$, k_p and k_{tr} were obtained from Equation 3.

$$k_p = \frac{1}{\text{slope} \cdot [\text{M}]} = \frac{1}{(0.000372) \cdot (0.6)} = 4{,}479.33$$

$$k_{tr} = \text{intercept} \cdot k_p \cdot [\text{M}] = (0.0000783) \cdot (4{,}479.33) \cdot (0.6) = 0.21$$

When this value of k_p was substituted, [C*] can be calculated in Equation (2).

t (s)	Yield (g-PP/mol-Ti)	[C*]=Y/(k_p·[M]·t)
0.1044	32.2280	32.2280/(4,479.33×0.6×0.1044) = 0.244
0.1579	52.0145	52.0145/(4,479.33×0.6×0.1579) = 0.260
0.1901	77.8656	77.8656/(4,479.33×0.6×0.1901) = 0.324

The average of the number of active centers was

$$[C^*]_{ave.} = ((0.244)+(0.260)+(0.324))/3 = 0.28$$

This calculation led to the final conclusion of kinetic parameter value as follows:

k_p = 4,500 L/mol·s

[C*] = 0.28 mol%

APPENDIX B

^{13}C NMR SPECTRA OF POLYPROPYLENE

Table B.1 Assignments of the methyl and methylene resonances in ^{13}C NMR spectrum of polypropylene [145]

peak no.	δ (ppm)[a]	assignment
	Methyl Resonances	
1	22.0–21.7	*mmmm*
2	21.7–21.4	*mmmr*
3	21.4–21.2	*rmmr*
4	21.2–21.0	*mmrr*
5	21.0–20.7	*mmrm + rmrr*
6	20.7–20.5	*rmrm*
7	20.5–20.0	*rrrm + rrrr*
8	20.0–19.7	*mrrm*
	Methylene Resonances	
1	47.75–47.60	*mrmrm*
2	47.60–47.42	*mrmrr*
3	47.42–47.28	*rrmrr + mrrrm*
4	47.28–47.02	*mrrrr*
5	47.02–46.85	*rmmrm + rrrrr*
6	46.85–46.58	*rmmrr + mmmrm + mmmrr*
7	46.58–46.40	*rmrrm*

[a]Downfield of TMS.

APPENDIX C

IR AND RAMAN SPECTRA OF ZIEGLER-NATTA CATALYST

Table C.1 Characteristic IR and Raman vibrations of the Ziegler-Natta catalyst sample [227].

Vibration	Type of vibration	Region (cm^{-1})	
		IR	Raman
$C–H_{Ar}$	Stretching	3070	3080
CH_2/CH_3	Stretching	2800-3000	2800-3000
C=O	Stretching	1684	1685
$C=C_{Ar}$	Stretching	–	1592
CH_2/CH_3	Deformation vibration	1454	1449
CH_3	Symmetric deformation vibration	1392	1395
C–O–C	Asymmetric stretching	1308	1302
C–O–C	Symmetric stretching	1156	1156
$C–H_{Ar}$	In plane deformation vibration	–	1140
O–C=O	Asymmetric stretching	1082	–
$C–H_{Ar}$	In plane deformation vibration	–	1052
O–C=O	Symmetric stretching	934	–
C–H	Out of plane deformation vibration	736	647
M–O (Mg–O or Ti–O)	Stretching	460	–
Titanium compound	Stretching	–	419
M–O (Mg–O or Ti–O)	Stretching	350	350
M–O (Mg–O or Ti–O)	Stretching	314	303
Ti–Cl	Stretching	375	–
Ti–Cl	Stretching	365	–
Ti–Cl	Stretching	382	–
Mg–Cl	Stretching	233	238
Mg–Cl	Stretching	242	–

APPENDIX D

ZINC OXIDE INFLUENCE ON POLYMERIZATIONS AND POLYMER CHARACTERISTICS

Table D.1 Characterization of polypropylene obtained by catalysts with different ZnO content[a]

Zn/Ti mole ratio	Yield (g)	Activity (kg polymer/mol Ti h)	I.I.[b]	T_m (°C)[c]	X_c[c]
0	2.2390	355	87.3	155.3	25.2
2	2.3436	372	85.5	151.3	26.8
4	2.5011	397	80.0	156.5	27.3
6	2.7709	440	77.3	152.4	29.0
8	2.8916	459	75.2	157.3	27.9
10	2.5493	405	74.8	152.7	27.2
14	1.9646	312	74.3	152.7	29.9
20	1.9051	302	74.3	155.7	28.9

[a]Polymerization conditions: catalyst weight: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 167, Propylene pressure: 60 psi, solvent: hexane (30 ml), temperature: 60°C, time: 60 min.
[b]I.I. of the insoluble boiling heptane polymer fraction.
[c]Obtained from DSC.

LIST OF PUBLICATIONS

Articles

This dissertation is based on the following publications (I-III), hereafter referred to by the corresponding Praserthdam numerals. Some new material is presented.

I. K. Tangjituabun, B. Jongsomjit, P. Praserthdam, The role of CaO in the Ziegler-Natta catalyst for propylene polymerization, Catalysis Letters, 109 (2006) 147-152.

II. K. Tangjituabun, S.Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, B. Jongsomjit, P. Praserthdam, Effects of various poisoning compounds on the activity and stereospecificity of heterogeneous Ziegler-Natta catalyst, Science and Technology of Advanced Materials, accepted 2008.

III. K. Tangjituabun, S.Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, B. Jongsomjit, P. Praserthdam, Poisoning of active sites on Ziegler-Natta catalyst for propylene polymerization, Chinese Journal of Polymer Science, accepted 2008.

IV. K. Tangjituabun, B. Jongsomjit, P. Praserthdam, Effect of SiO_2-supported aluminoxanes as coactivators on the catalytic properties of Ziegler-Natta catalyst for propylene polymerization, submitted 2008.

Conference contributions

A. Poster: K. Tangjituabun, S.Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, Poisoning of active sites on Ziegler-Natta catalyst for the study of stereospecificity distribution, International Workshop on Heterogeneous Ziegler-Natta Catalysts 2007, Ishikawa, March 18-20, 2007.

B. Poster: S.Y. Kim, K. Tangjituabun, Y. Hiraoka, T. Taniike, M. Terano, Effects of various external donors on the stereoselectivity of $MgCl_2$-supported propylene polymerization catalysts, 56th Polymer Yearly Meeting, Kyoto, May 29-31, 2007.

C. Poster: P. Praserthdam, K. Tangjituabun, S.Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, B. Jongsomjit, Study of the deactivating impact on Ziegler-Natta catalyst by poisoning materials, Advances in Polyolefins 2007, California, September 23-26, 2007.

D. Poster: K. Tangjituabun, B. Jongsomjit, P. Praserthdam, Effect of CaO on propylene polymerization with recrystallized $MgCl_2$ supported Ziegler-Natta catalyst, Advances in Polyolefins 2007, California, September 23-26, 2007.

E. Poster: K. Tangjituabun, S.Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, P. Praserthdam, Investigation on stereospecificity distribution of poisoned active species for propylene polymerization catalyst, 1st International Symposium on Ultimate Stability of Nano-structured Polymers and Composites 2007, Ishikawa, October 11-13, 2007.

F. Oral: K. Tangjituabun, S.Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, P. Praserthdam, Effect of poisoning materials on active site destruction in propylene polymerization with Ziegler-Natta catalyst, Asian Polyolefin Workshop 2007, Hangzhou, November 1-3, 2007.

VITA

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