2017 SPE international
Polyolefins Conference
Houston, TX

Japan Polypropylene Corporation

Feb 27th, 2017

Supported Metallocene Catalyst for Long Chain Branched Polypropylene

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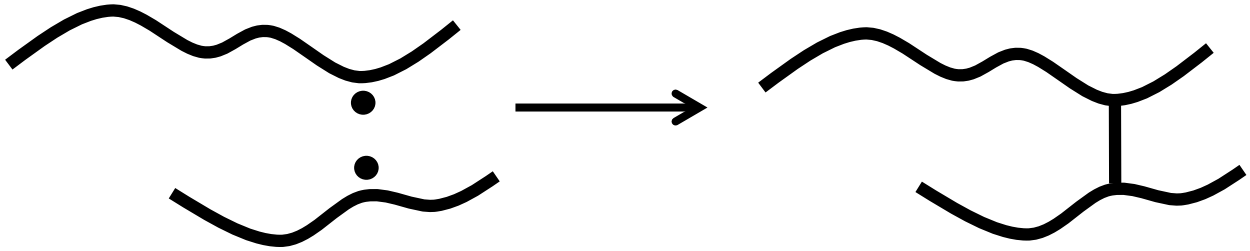
Objective of This Study

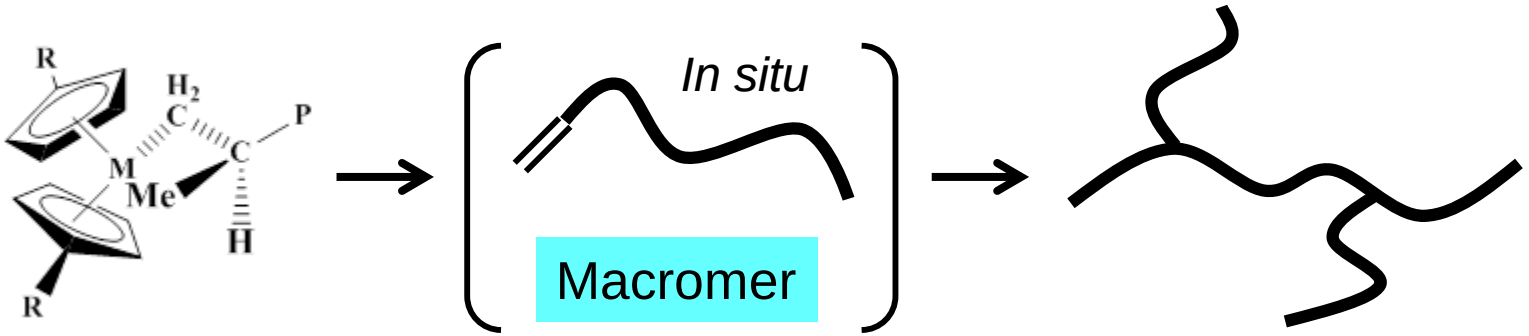
- Post reactor modification of PP to LCB-PP
  - ✓ Irradiation of electron beam
  - ✓ Reaction with peroxide and diene

Radical reaction



- Problems/concerns relating to radical reaction
  - ✓ Gel
  - ✓ Coloring

⇨ Direct synthesis from propylene

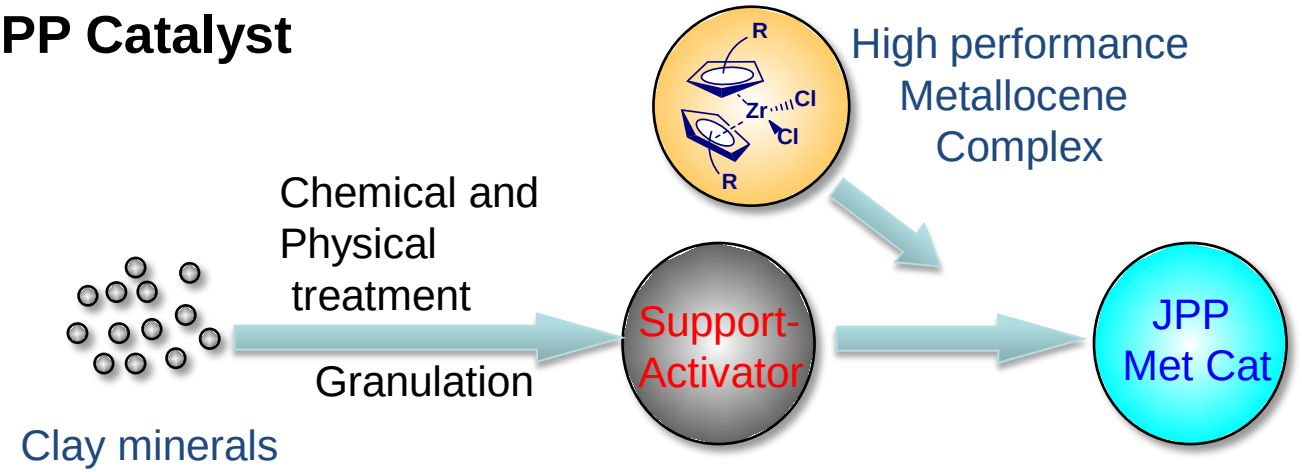


Catalyst for LCB-PP

Clay-Mineral Supported Met Catalyst

Our catalyst is very unique because we use clay minerals instead of MAO.

JPP Catalyst



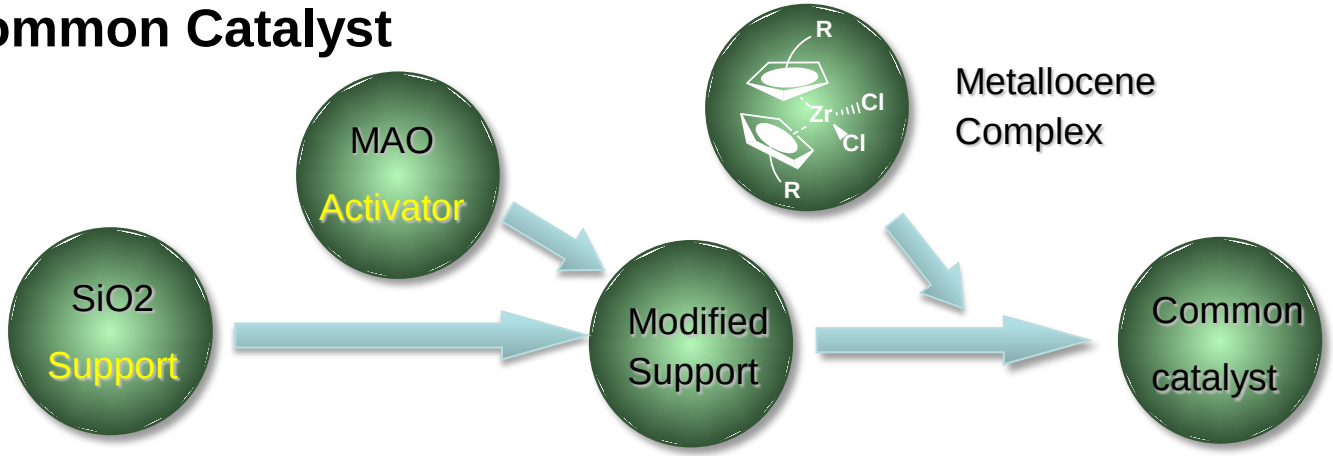
Easy handling

Non-flammable
Solid(insoluble)

Clay minerals

versus

Common Catalyst



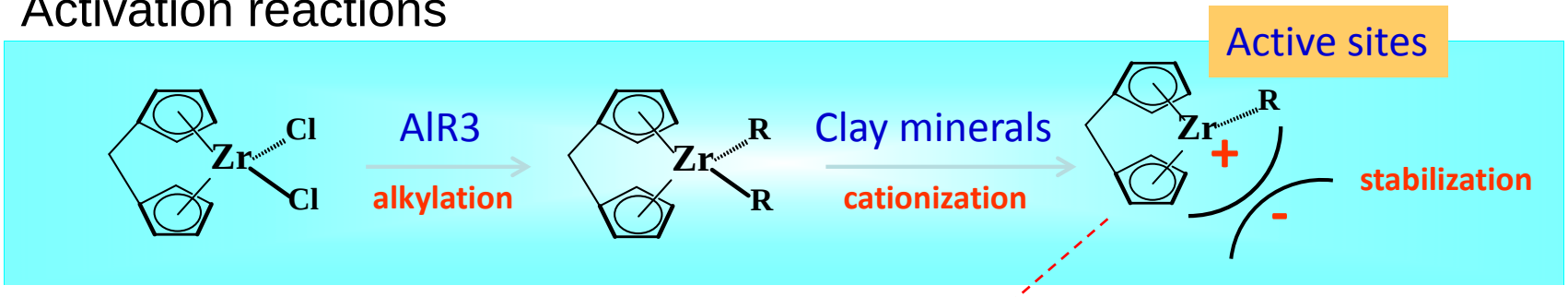
MAO

Flammable
Soluble

Difficult to handle

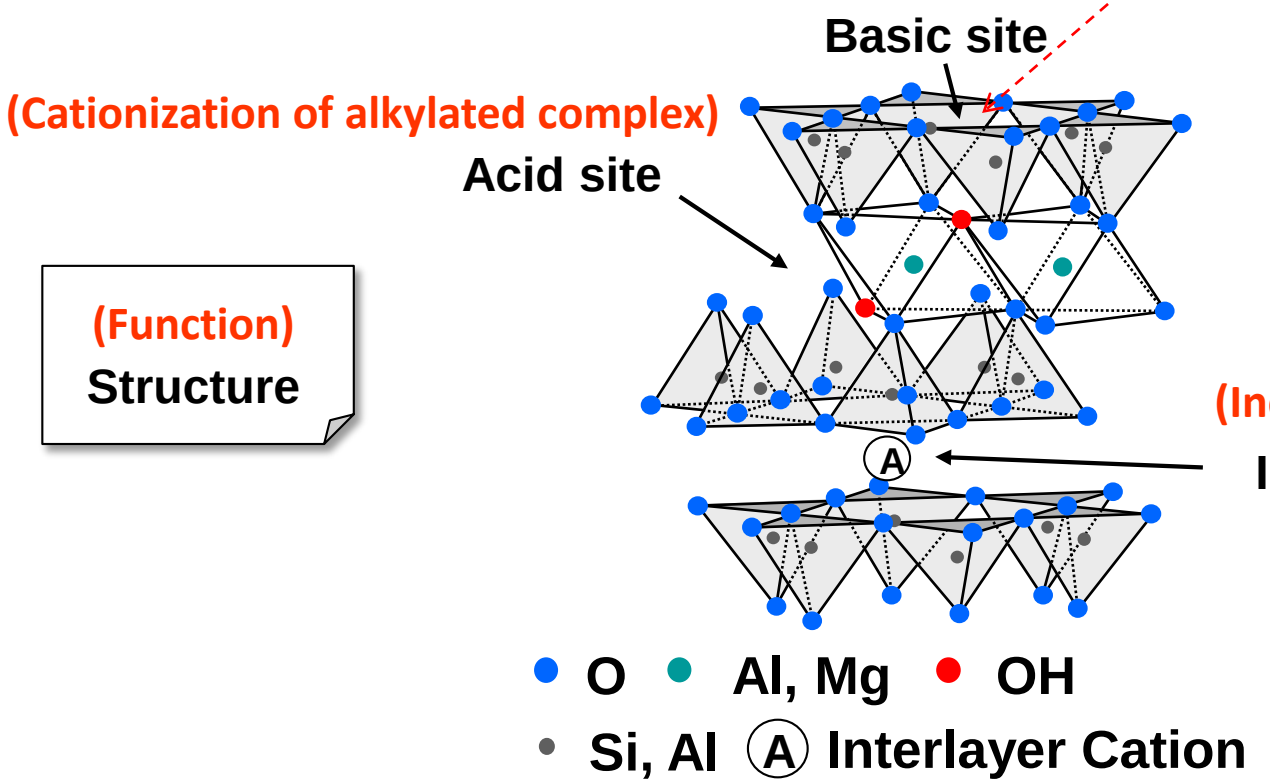
Site Architecture

Activation reactions



(Stabilization of activated complex)

Only strong acid sites can transform a complex into the active species.



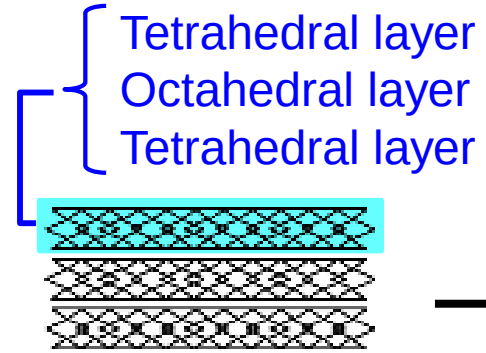
(Function)
Structure

(Increase of effective acid sites)

Interlayer cation

- **Defects of lattice (corresponding to chemical composition)**
- **Acidity**

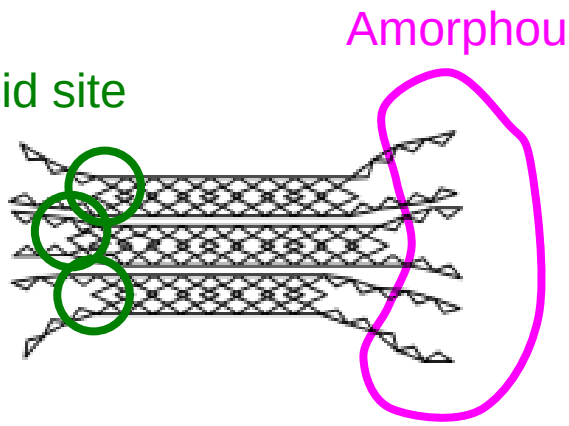
Active Site Preparation on Clay-Minerals



Montmorillonite (MMT)

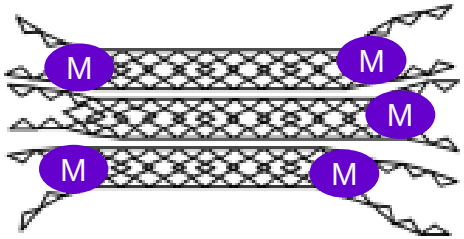
Acid treatment

(Al extraction)



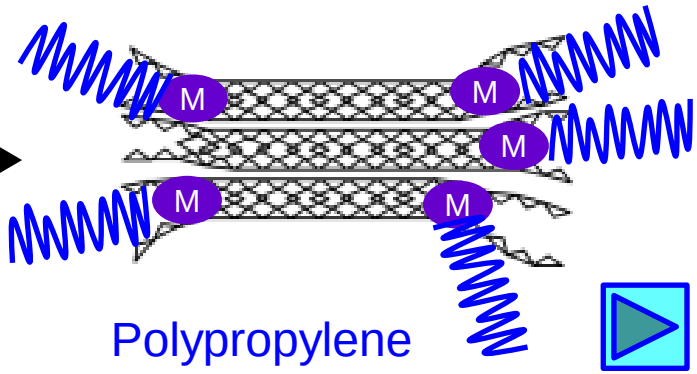
AFM

Metallocene



Activated metallocene

Propylene



Polypropylene

TEM

Active sites are concentrated on the border part.

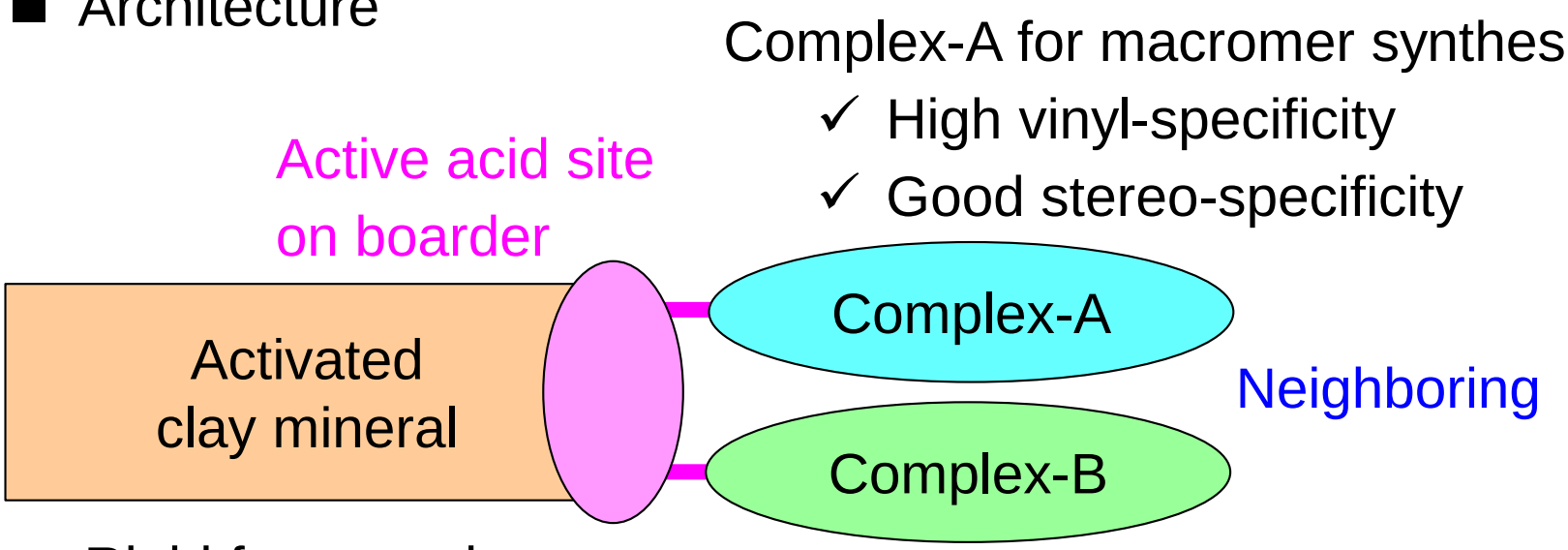
Ref) T. Tayano et al., *J. Mol. Catal. A: Chem.*, **420**, 228 (2016)

Requirements and Catalyst Architecture

- Requirements

1. Selective synthesis of active vinyl macromer
2. Effective incorporation of synthesized macromer
3. Overall MFR control for extrusion foaming application

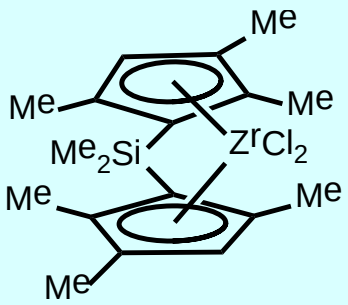
- Architecture



JPP Proprietary Metallocene Complex

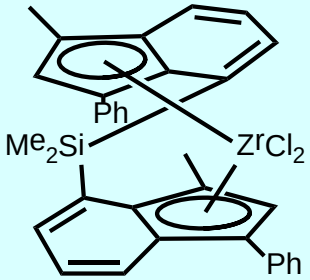
Various platform of metallocene complex

Bridged bis Cp[1)]



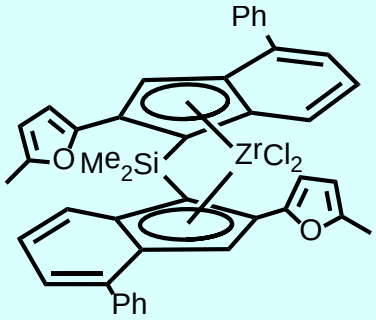
Tm=162 ºC,
Mw=134,000
(MAO, 30 ºC)

Bridged at sub-ring[2)]



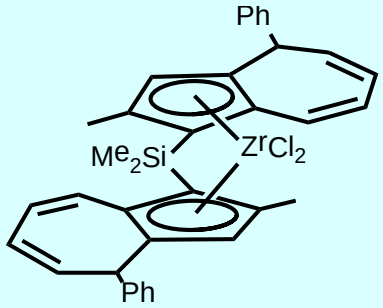
Tm=159 ºC,
Mw=61,200
(MAO, 40 ºC)

2-Furyl-indenyl[3)]



Tm= 159 ºC,
Mw= 733,000
(MAO, 30 ºC)

Bis 7memberd-ring[4)]

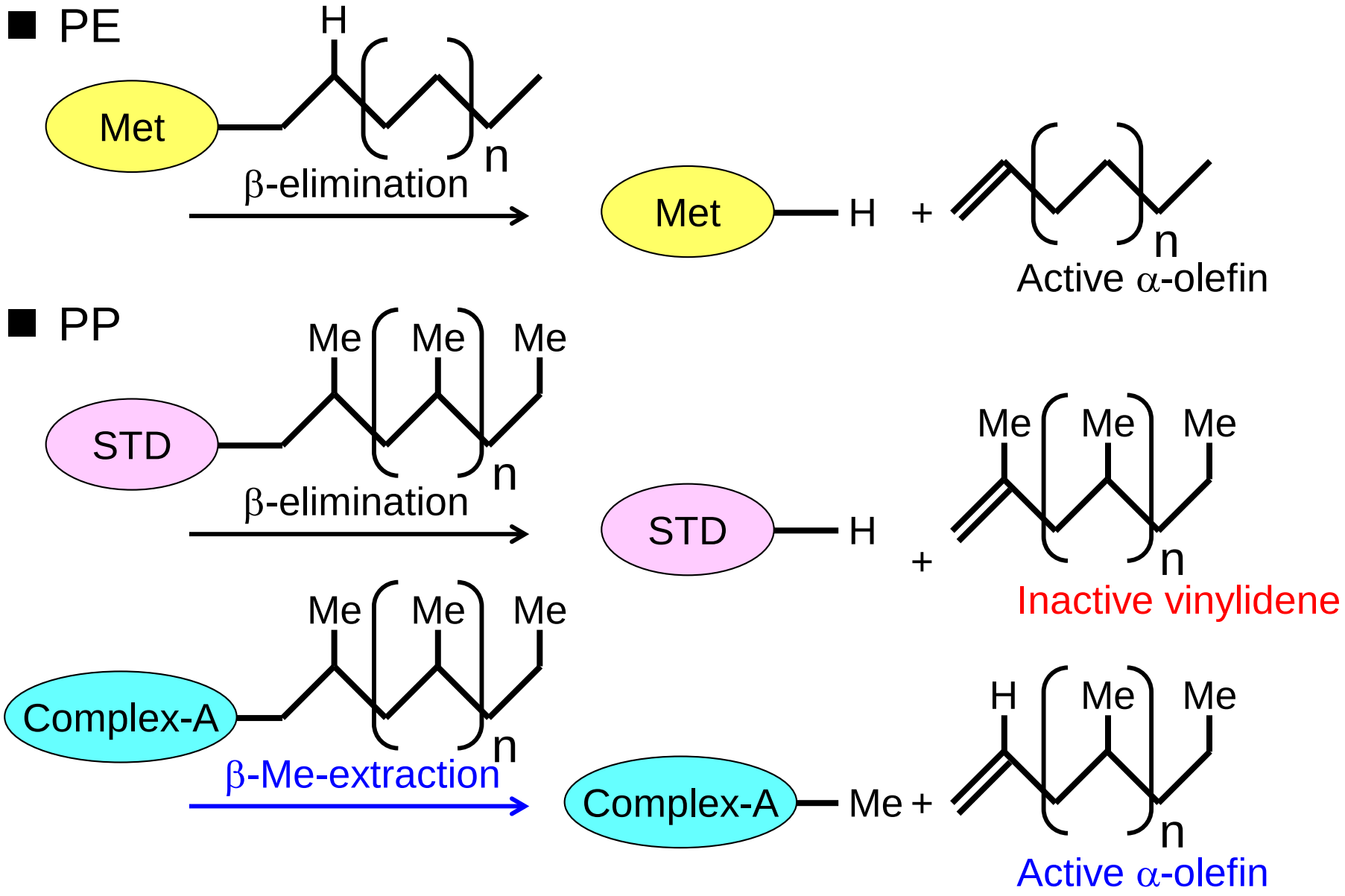


Tm=156 ºC,
Mw=166,000
(MAO, 70 ºC)

1) Mise, et al. *Chem. Lett.* **1989**, 1853.
2) Kato, et al. In *Metalorganic Catalysts for Synthesis and Polymerization;* Kaminsky, W., Ed.; **1999**; p192.
3) Ushioda, et al. In *Proceedings of Polypropylene 2002,* Zurich, **2002**.
4) Iwama, et at. *Organometallics* **2004**, *23*, 3267.

⇨ Found effective framework for macromer synthesis

Indispensable Selective β-Elimination



Microstructure of PP Obtained by Complex

- ✓ β-elimination after regular 1-2 insertion
- ✓ Unsaturated & saturated terminals relating to β-Me extraction

Complex			A-1	A-2	A-3
Stereo/Regio [mol%]	mm		97.6	98.0	97.8
	2-1		0.08	0.07	0.09
	1-3		0.18	0.16	0.18
Unsaturated terminal [unit/1,000unit]	1-Propenyl	1,2 → β-Me extraction	0.79	0.72	0.88
	Vinylidene	1,2 → β-H extraction	N.D.	N.D.	N.D.
	1-Butenyl	$\overset{2,1}{1,3}$ → β-H extraction	N.D.	N.D.	N.D.
	i-Butenyl	β-H→ Rearrangement	N.D.	N.D.	N.D.
Saturated terminal [unit/1,000unit]	*i*-Butyl	β-Me → 1,2 insertion	1.23	1.17	1.21
	n-Propyl	β-H → 1,2 insertion	N.D.	N.D.	N.D.
	n-Butyl	β-Me → 1,3 + others	N.D.	N.D.	N.D.
	Et	β-Me → 2,1 + others	N.D.	N.D.	N.D.

Note: Complex was supported on STD MMT-support and used for bulk polymerization.

Macromer Incorporation

- Catalyst preparation

  Complex-A + Complex-B + Activator

- Influence of activator

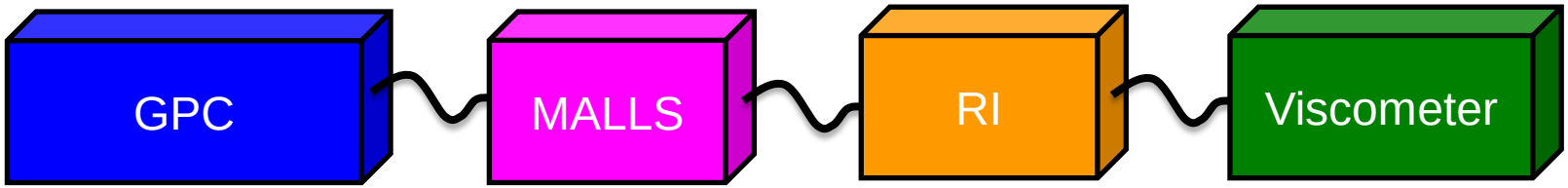
  Activated montmorillonite ⟶ LCB in high Mw chains

  MAO-SiO_2 ⟶ No LCB

- Structure control

  LCB content is controllable by complex mixing ratio.

Branching Evaluation



GPC, RI, Viscometer : Waters Alliance GPCV2000
MALLS : Wyatt Technology Dawn-E
Solvent : 1,2,4-trichlorobenzene
Temperature : 140 °C

MALLS ⟶ Absolute Mw, Turning radius

Viscometer ⟶ Intrinsic viscosity [η]

$$g' = \frac{[\eta]_{branch}}{[\eta]_{linear}}$$

at same MW

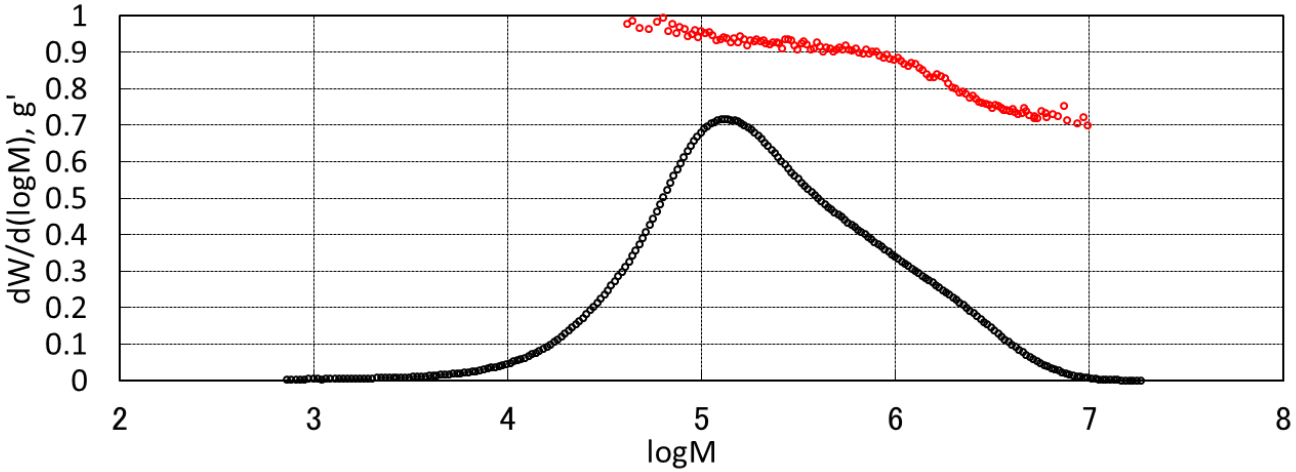
Linear ⟶ g' = 1

LCB ⟶ g' < 1

Influence of Activator

Only activated clay-mineral shows high compatibility to the LCB system.

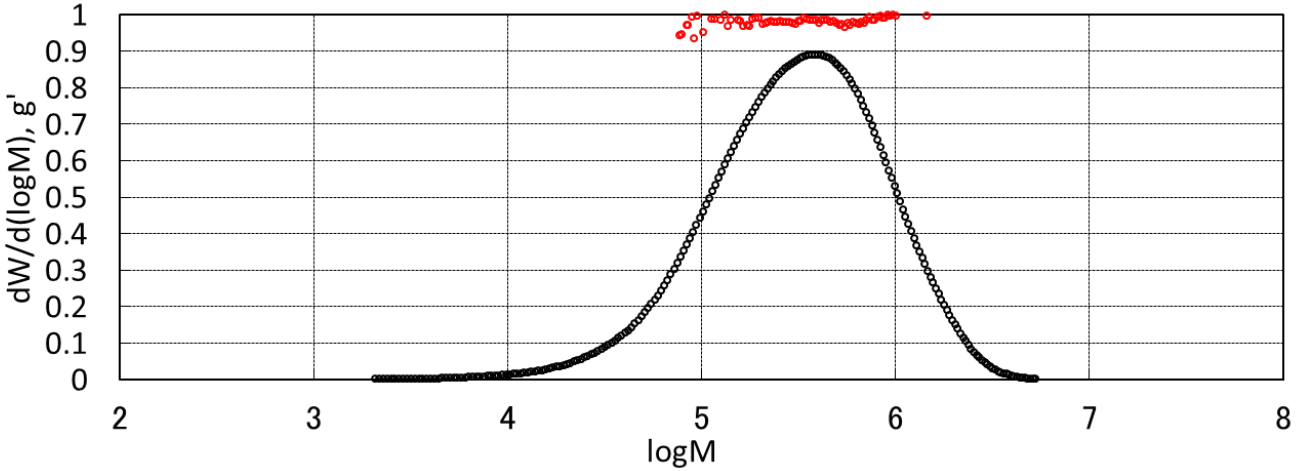
Complex-A & -B supported on activated montmorillonite



High Mw chains have LCB.

Favorable supporting state

Complex-A & -B supported on MAO-SiO_2

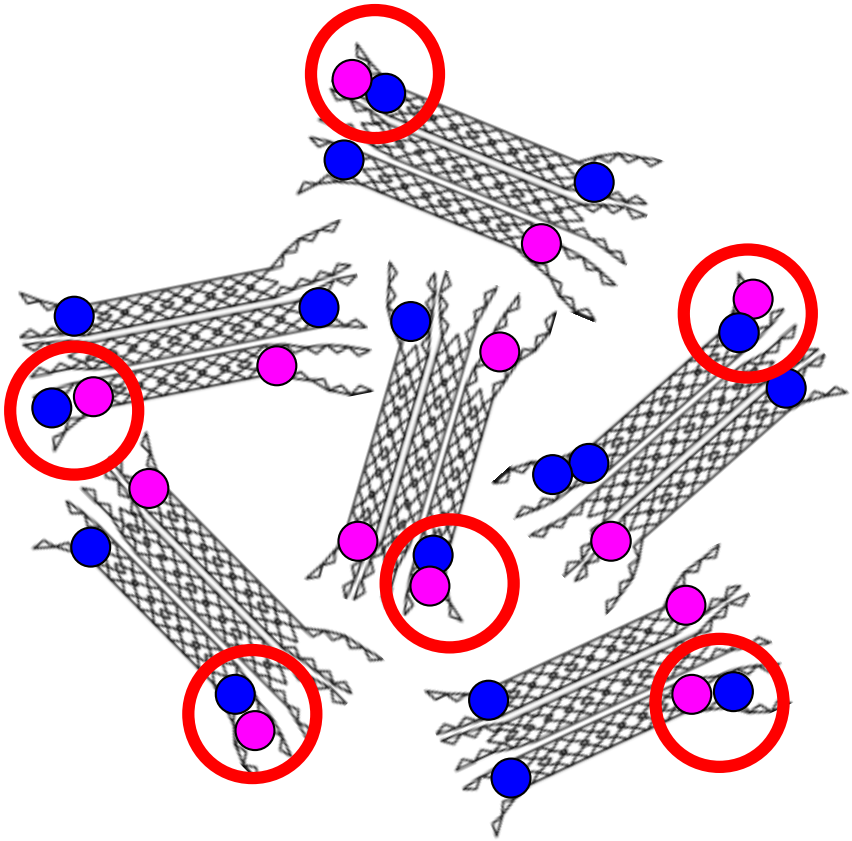


No LCB

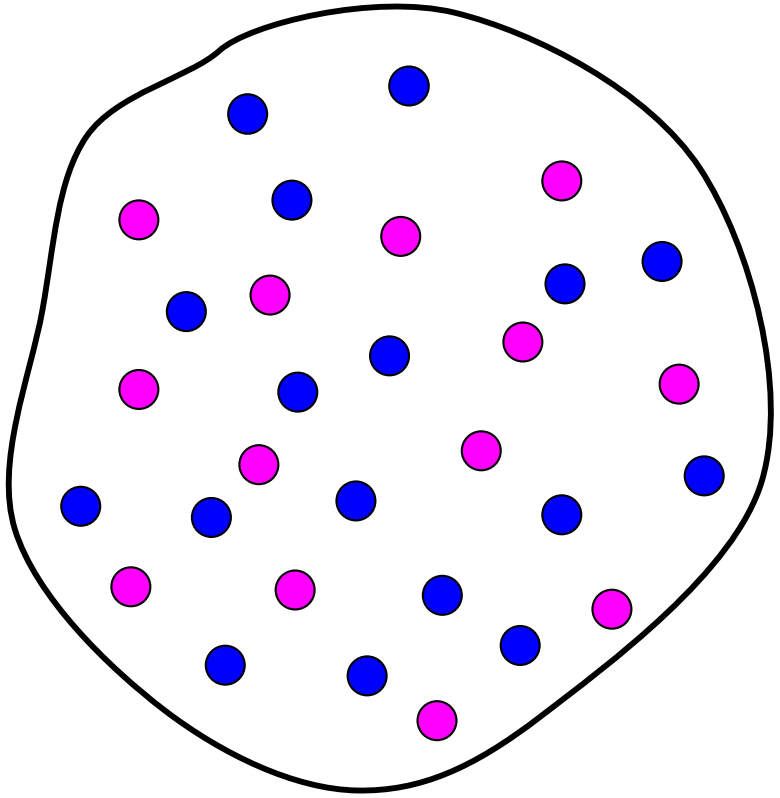
Unfavorable supporting state

Plausible Model of Supporting State

Montmorillonite



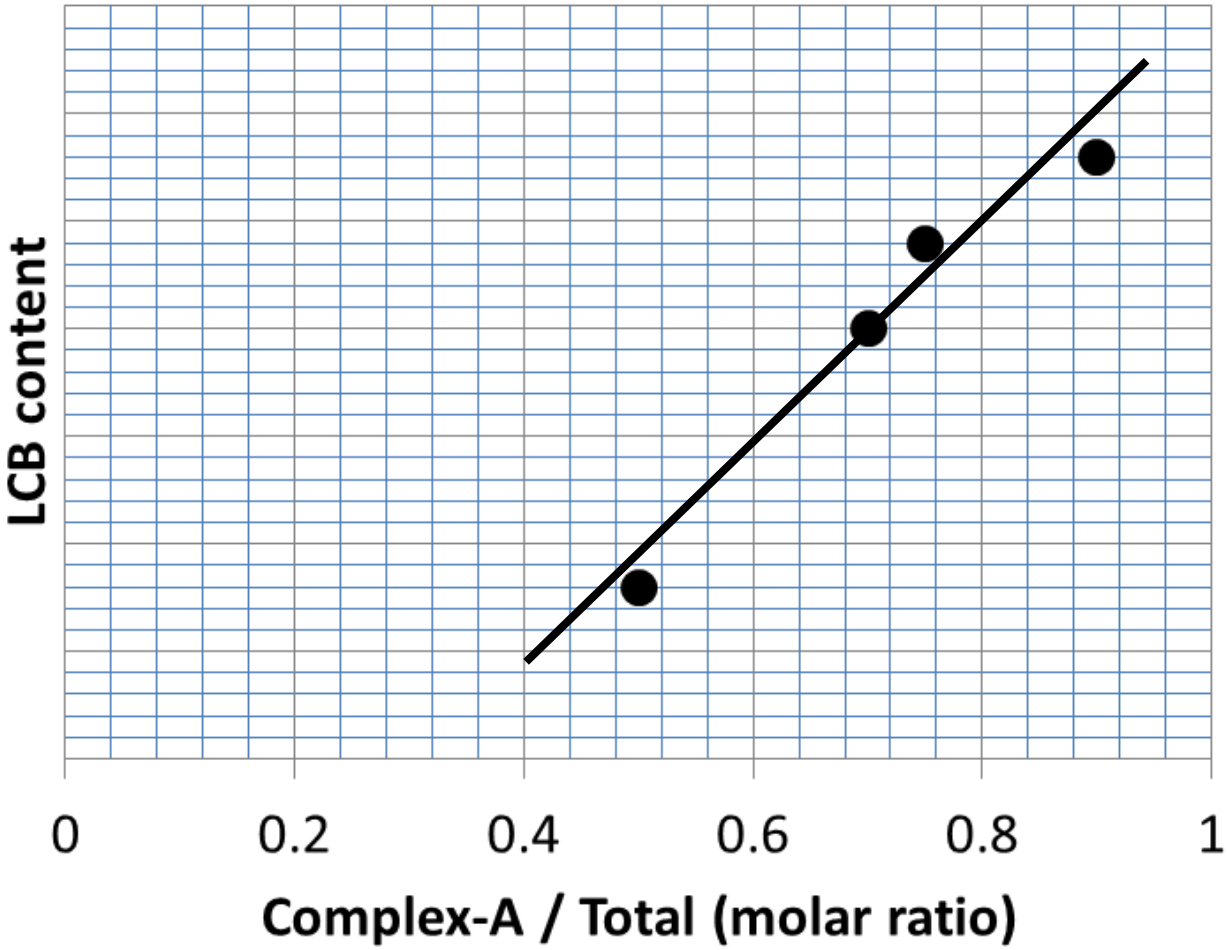
MAO-SiO_2



Complex-A Complex-B LCB site

Polymer Structure Control

LCB content is easily adjustable by preparation recipe.



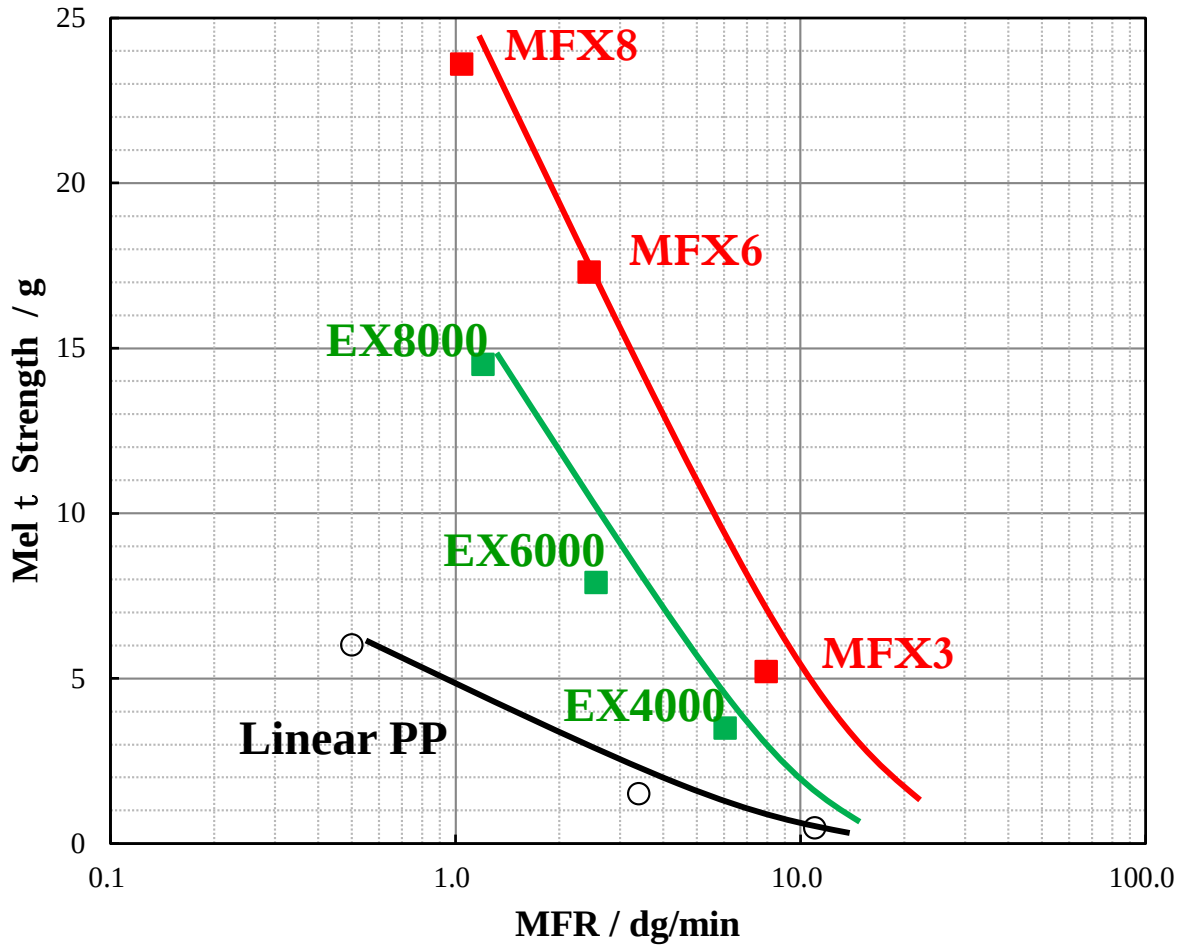
Note: LCB content was determined by ^{13}C-NMR.

Launched LCB-PP WAYMAX™

MFR	MS	MFX series			EX series		
		Grade	MFR dg/min	MS g	Grade	MFR dg/min	MS g
Low	High	**MFX8**	1	23	**EX8000**	1	15
⇕	⇕	**MFX6**	3	16	**EX6000**	3	9
High	Low	**MFX3**	9	6	**EX4000**	6	4

Note) not for specification

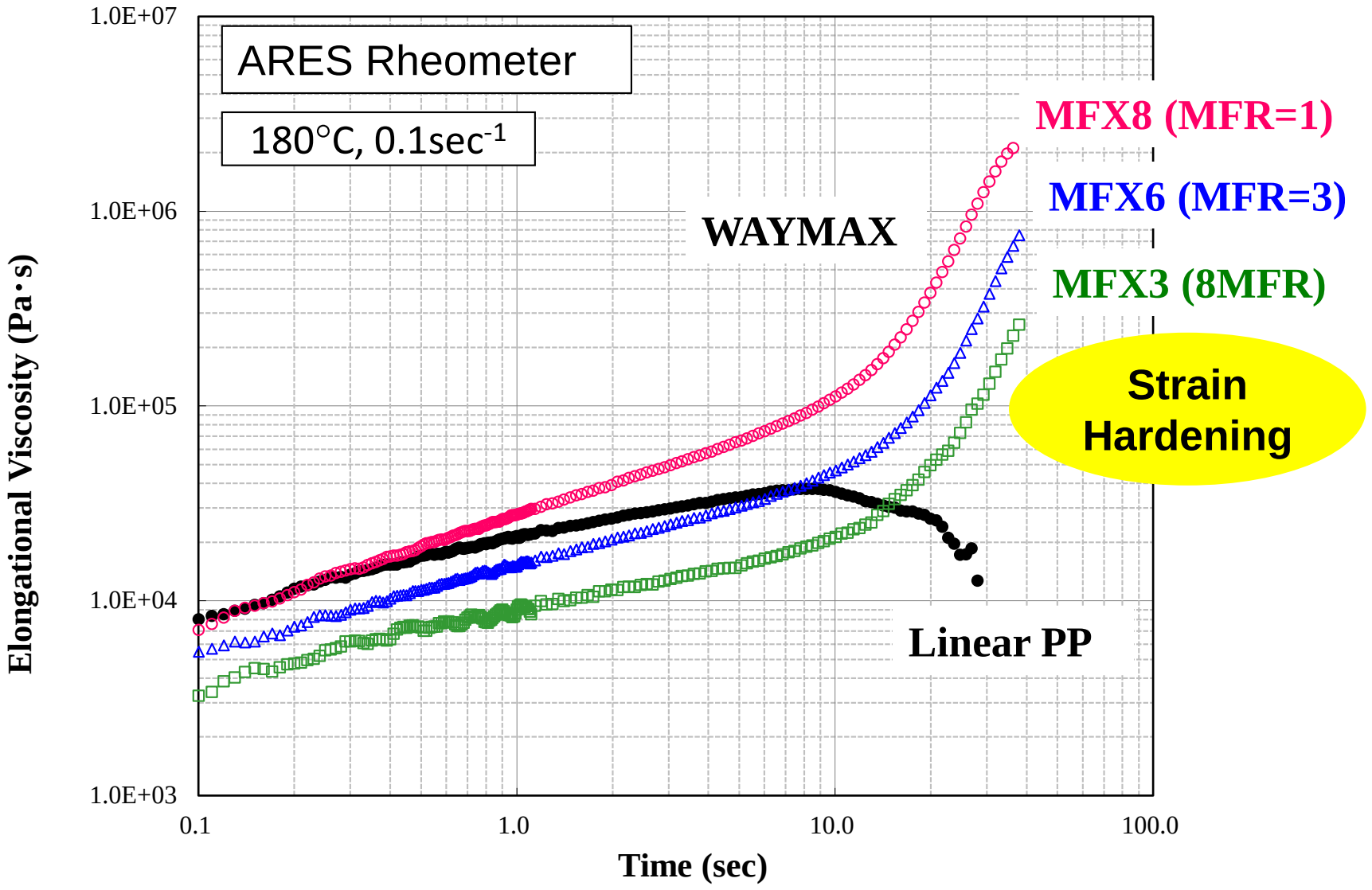
WAYMAX™ Melt Strength



MFX: High melt strength

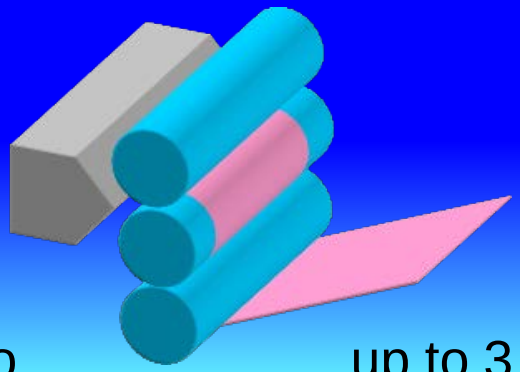
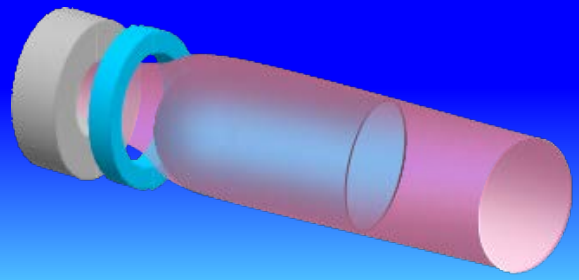
EX : Adjusted melt strength for some application

WAYMAX™ Strain Hardening

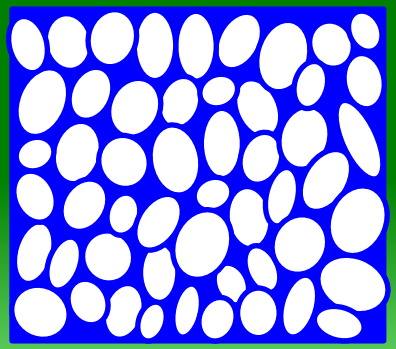
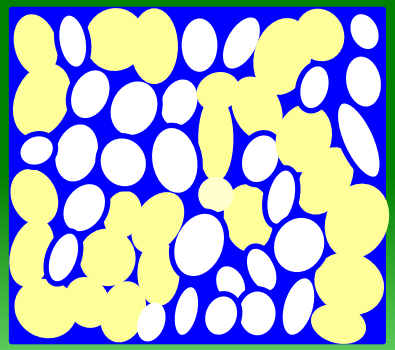


Extrusion Foaming

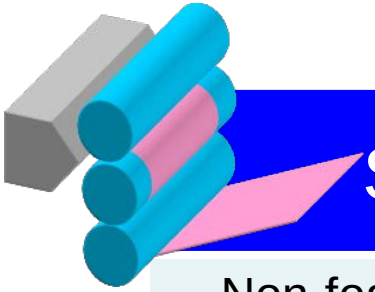
Extrusion Foaming Process

	Flat Die	Annular Die
		
Expansion ratio	up to 3	more than 5

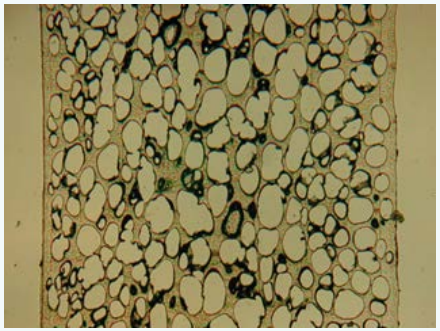
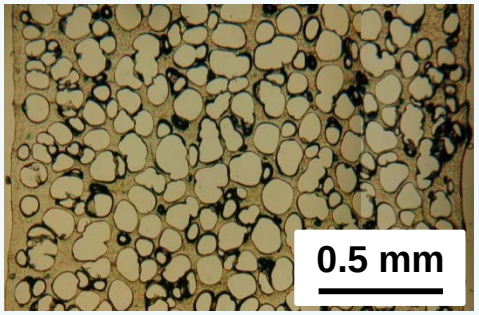
Cell structure

	Closed cell	Open cell
		
	Good thermal insulation, cushioning and thermoforming	*Good sound absorption, water absorption*

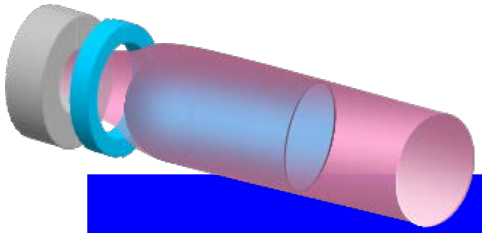
Extrusion Foaming with Flat Die



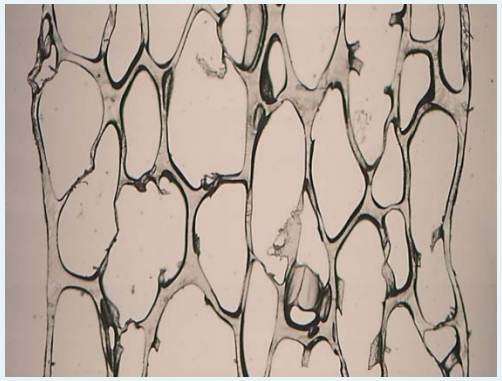
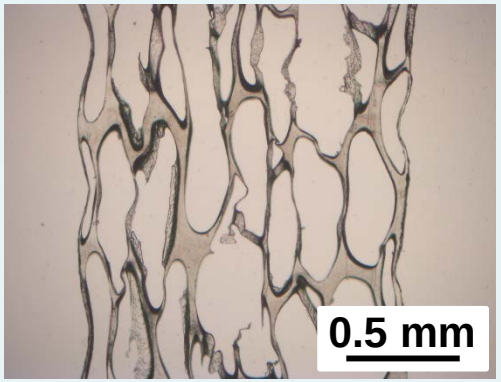
Equipment: 65mmφ single screw EXT with flat die

Sample	WAYMAX™ EX4000 (Foamed core layer: B)	
Non-foamed skin layer: A	NOVATEC™ BC3BRF	
Layer structure	A/B/A multi layered (thickness ratio: 3/96/3%)	
Blowing Agent	CO_2	
CBA	Hydrocerol CF40E-J (0.5wt%)	
Average thickness / mm	1.3	1.9
Expansion ratio / times	3.3	3.1
Closed cell cont. / vol.%	**86**	**93**
TD-ND Cross section view		

Extrusion Foaming with Annular Die



Equipment: 65mmφ single screw EXT with annular die

Sample	WAYMAX ™	
	MFX6	EX6000
Layer Structure	Single layer	
Blowing Agent	C_4H_{10}	C_4H_{10}
Average Thickness / mm	1.8	1.6
Expansion ratio / -	5.5	4.7
Closed cell cont. / vol.%	86	80
TD-ND Cross section view		

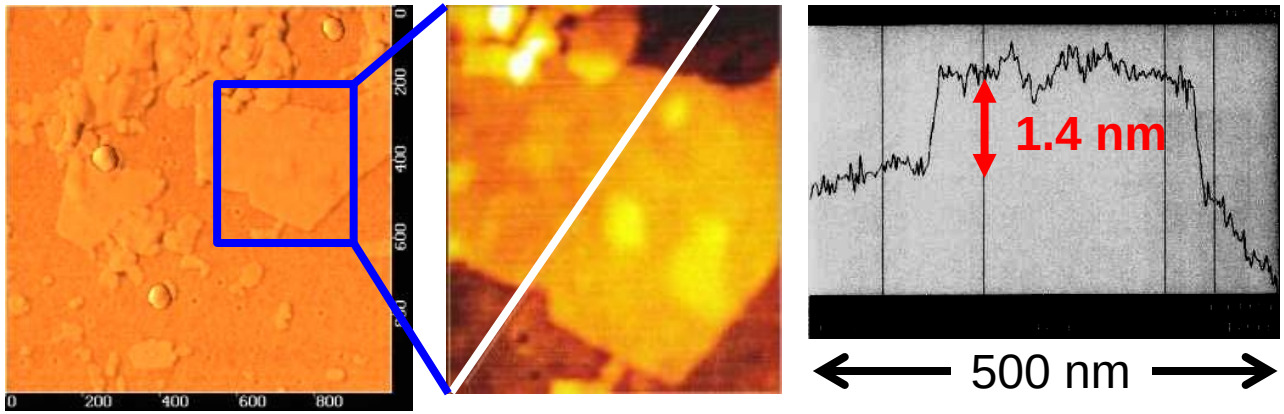
Conclusion

- Established effective catalyst system for direct synthesis of LCB-PP from propylene
- Selective β-Me extraction achieved by specific complex framework
- Clear difference of compatibility to LCB system between clay-minerals and MAO-SiO_2
- Launched LCB-PP WAYMAX™ based on the catalyst system

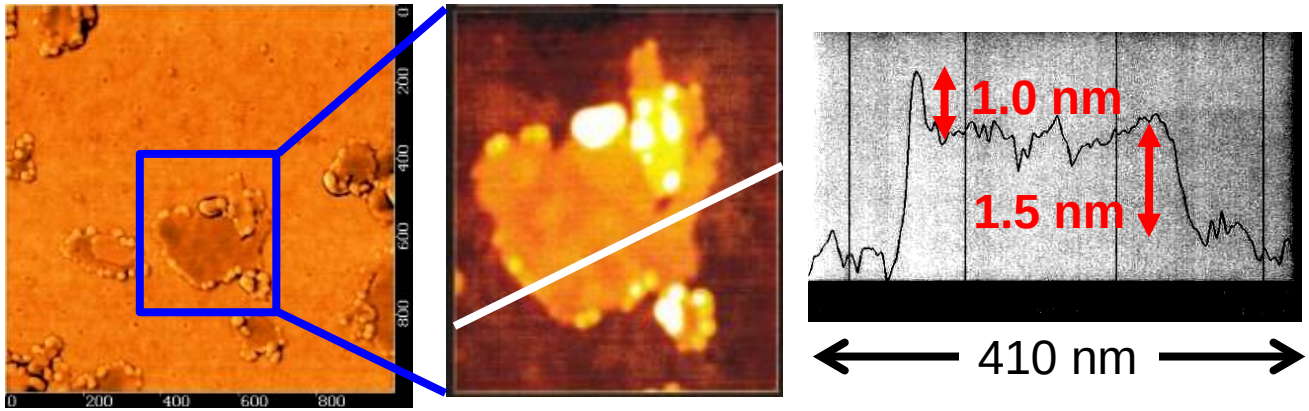
Thank you for your attention.

AFM Analysis of Acid-Treated MMT

- Raw material MMT (montmorillonite)



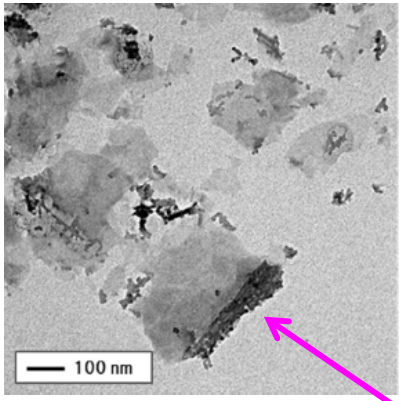
- MMT treated with sulfuric acid at 90°C 5h



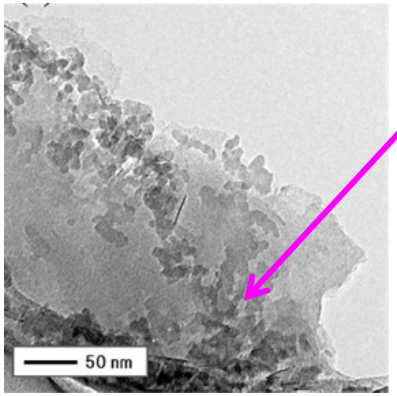
Slightly Polymerized Model Catalyst*1)

- TEM analysis
- EFTEM*2) analysis

Wide view

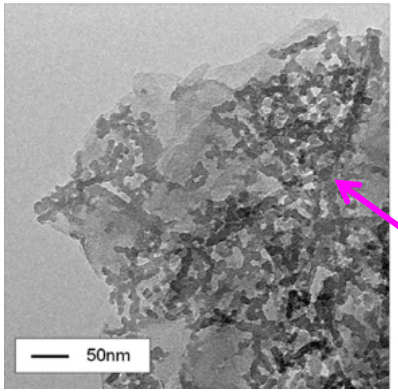


Close view

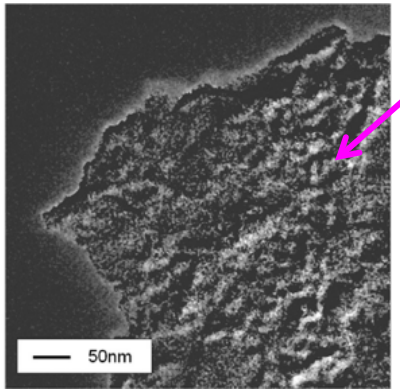


Fibril-like

Zero-loss image



Carbon map



Brighter parts are rich in carbon.

*1) Non-granulated MMT-supported metallocene catalyst was contacted with a small amount of propylene.

*2) Energy filtered transmission electron microscope