第８４回応用化学科セミナー
（第１４回愛媛地区触媒講演会共催）
２００５年1月１８日

ポリオレフィン工業が果たした技術革新と未来へ向けての新たなる挑戦

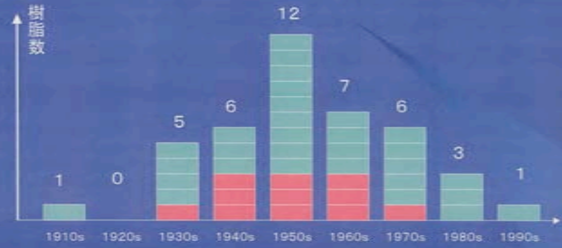
三井化学・触媒研究所・シニアリサーチフェロー
柏　典夫

2005.1.18
第14回愛媛地区
触媒講演会

ポリオレフィン工業が果たした技術革新と未来へ向けての新たなる挑戦

柏 典夫
（三井化学）

国内主要樹脂の発展史



国内の樹脂生産(販売)量1t／yを越えた時期、現在の生産(販売)量

国内生産量
≧30万t／y
＜30万t／y

国内主要樹脂の発展史

国内の樹脂生産(販売)量1t／yを越えた時期	現在の生産(販売)量 ≧30万t／y(赤字)、＜30万t／y(白地) の国内主要樹脂
1910s	フェノール樹脂
1930s	酢ビ、アルキド、メタクリル、セルロースフィルム、尿素ホルムアルデヒド
1940s	ポリスチレン、同共重合体、塩ビ、ナイロン、メラミンホルムアルデヒド、セルロースアセテート
1950s	HDPE、ABS、LDPE、PVA、ポリエステルフィルム、シリコーン、セルロースエーテル、SBラテックス、不飽和ポリエステル、ポリウレタン、フッ素化ポリマー、エポキシ
1960s	PET、PC、PP、塩素化ポリオレフィン、SAN、ポリアセタール、PVB
1970s	LLDPE、アクリレート、ポリアクリルアミド、熱可塑性ポリエステル、PPE、石油樹脂
1980s	液晶ポリマー、PPS、ポリアミド
1990s	生分解性ポリマー

1955 Mitsui Petrochemical obtained Patent Licence from Ziegler

Catalyst Innovations in Polyolefin Industry at Mitsui Chemicals

HDPE HI-ZEX®

Commercialization in Japan
1958

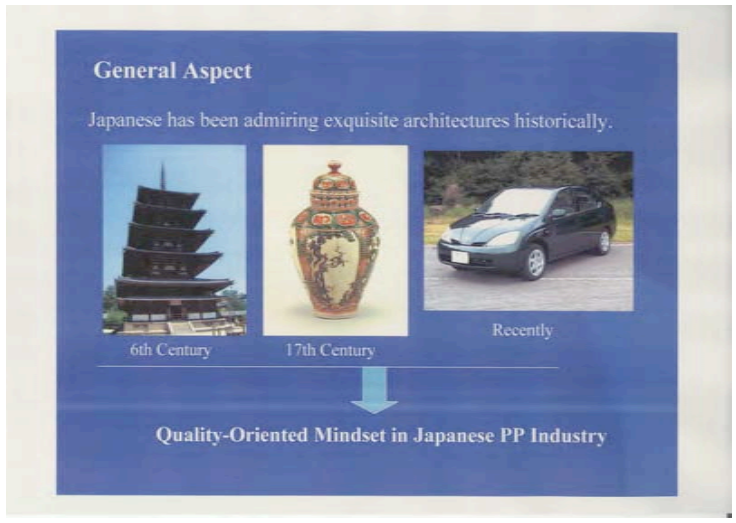
Initial major application of "HI-ZEX®"

Ziegler-Natta Catalyst (1953)

1960 1970 1980

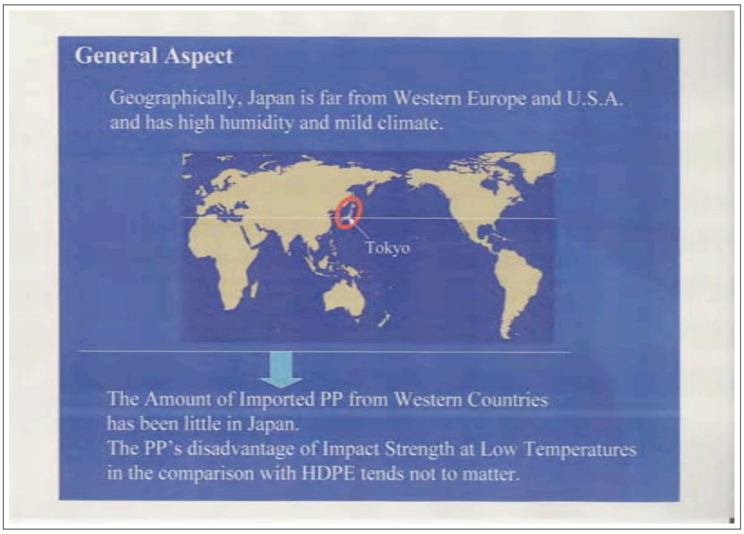
The Uniqueness of PP Growth and Development in Japan

- General Aspect
- Historical Observation of the Early Stage
- Historical Observation of the Late Stage


General Aspect
Japanese has been admiring exquisite architectures historically.
6th Century
17th Century
Recently
Quality-Oriented Mindset in Japanese PP Industry

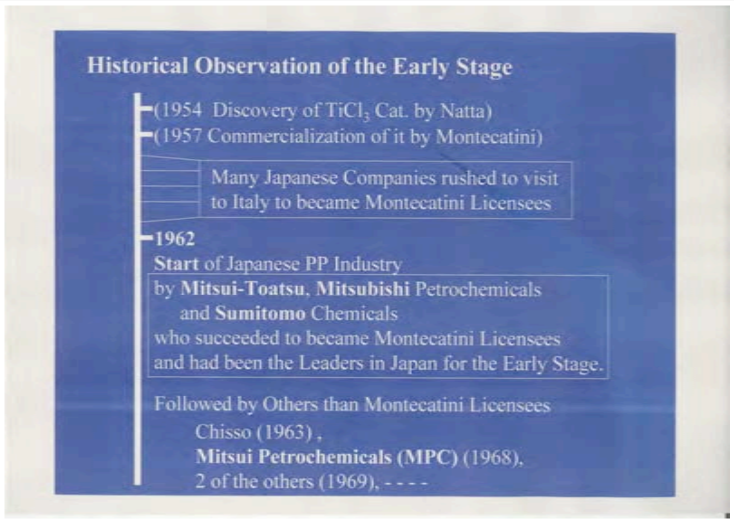

General Aspect
Japanese has adopted the latest technologies mainly from foreign countries and modified them into Japanese style.
By 9th Century
From China
Since 19th Century
From Western Countries
Influences on Developmental Policies
in Japanese PP Industry

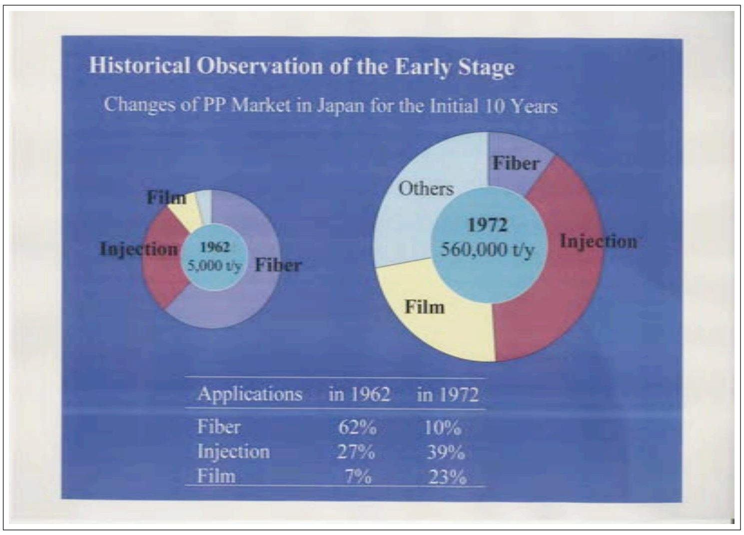

General Aspect
“Keiretsu” worked.
The Three Major Group: Mitsui, Mitsubishi, Sumitomo
The Three Influential Group: Fuyoh, Sanwa, Ichikan
Mitsui (19th Century)
Mitsui (17th Century)
Unique Relation between Makers and Customers
in Japanese PP Industry

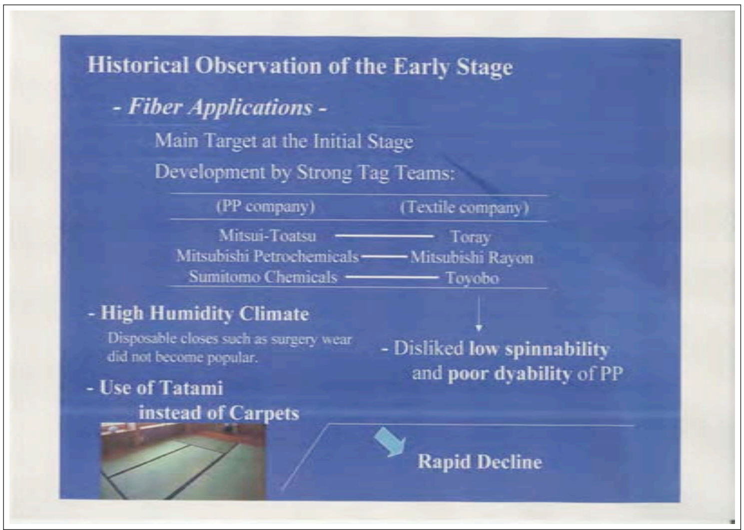

General Aspect
Geographically, Japan is far from Western Europe and U.S.A.
and has high humidity and mild climate.
Tokyo
The Amount of Imported PP from Western Countries
has been little in Japan.
The PP’s disadvantage of Impact Strength at Low Temperatures
in the comparison with HDPE tends not to matter.

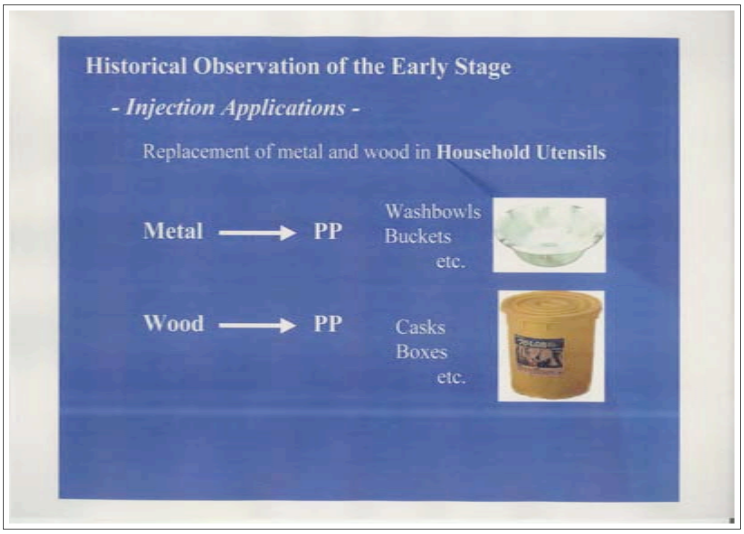

General Aspect
The Start of Japanese PP Industry corresponded with
the Beginning of the Miraculous Economic Growth in Japan
and No Nations competed with Japan Economically at that time
in Asia.
Japanese Ministry of International Trade and Industry (MITI)
carried out the Protective and Exclusive Policies.
Ineffective Business System in Japanese PP Industry
was tolerated.
Many Small Players survived in Japanese PP Industry
with Specific Relation with PP Users.

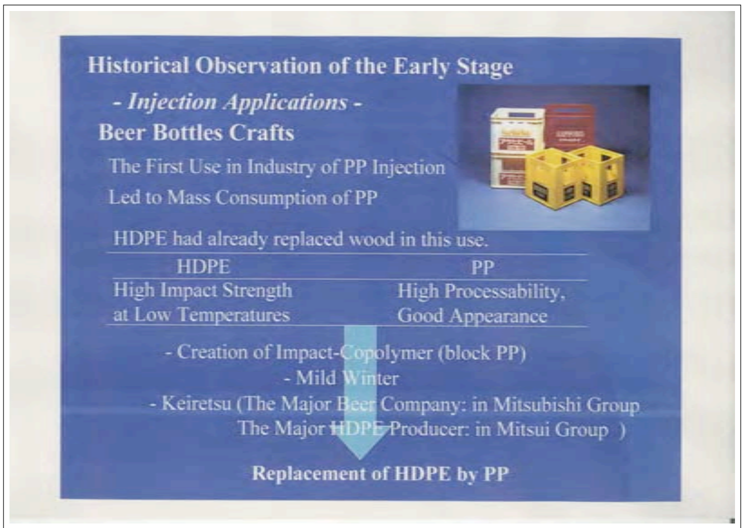

General Aspect
Summary
- Quality-Oriented Mindset
- Adoption of the Latest Technologies
- Keiretsu
- Far from Western Countries
- High Humidity and Mild Climate
- PP Growth linked with Growth of Japanese Economy
- Little Competition in Asia
- Protective and Exclusive Policies by MITI

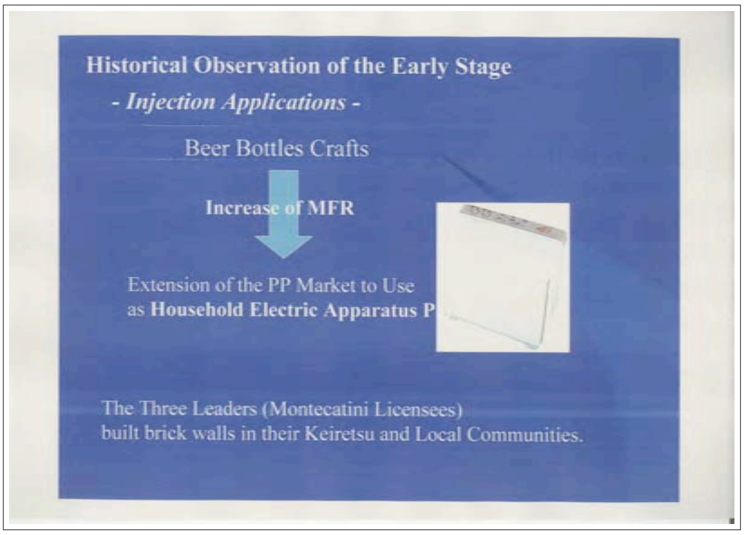

Historical Observation of the Early Stage
(1954 Discovery of TiCl3 Cat. by Natta)
(1957 Commercialization of it by Montecatini)
Many Japanese Companies rushed to visit
to Italy to became Montecatini Licensees
1962
Start of Japanese PP Industry
by Mitsui-Toatsu, Mitsubishi Petrochemicals
and Sumitomo Chemicals
who succeeded to became Montecatini Licensees
and had been the Leaders in Japan for the Early Stage.
Followed by Others than Montecatini Licensees
Chisso (1963),
Mitsui Petrochemicals (MPC) (1968),
2 of the others (1969), - - - -

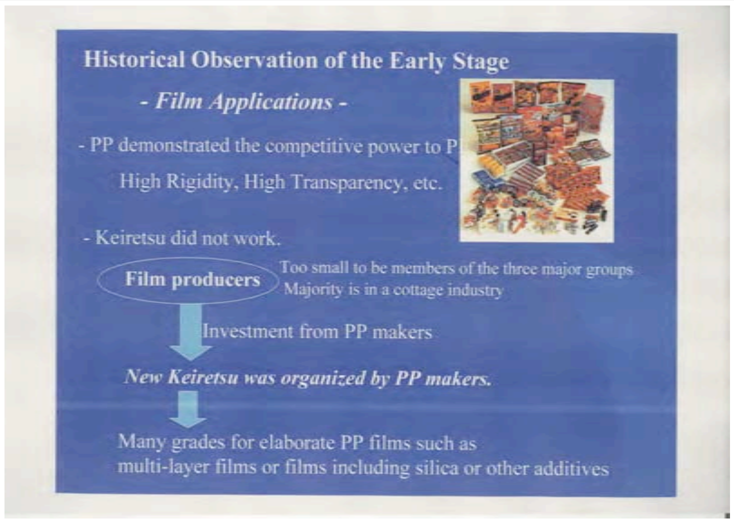

Historical Observation of the Early Stage
Changes of PP Market in Japan for the Initial 10 Years
Film
Injection
1962
5,000 t/y
Fiber
Fiber
Others
1972
560,000 t/y
Injection
Film
Applications in 1962 in 1972
Fiber 62% 10%
Injection 27% 39%
Film 7% 23%

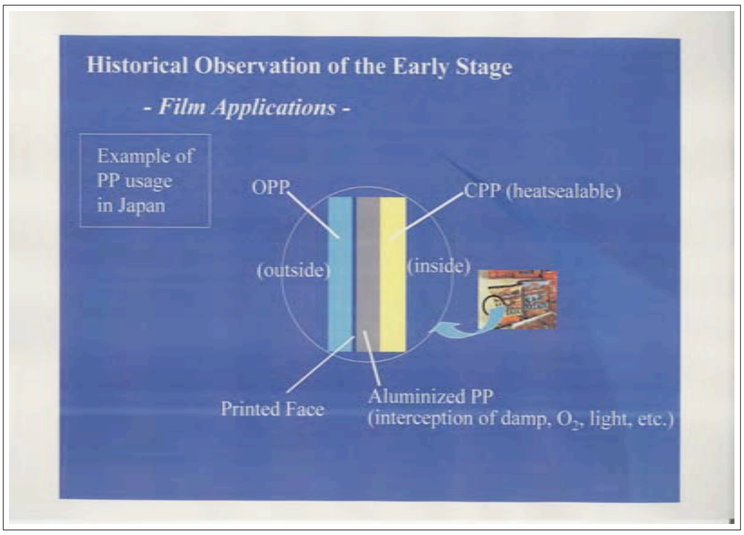

Historical Observation of the Early Stage
- Fiber Applications -
Main Target at the Initial Stage
Development by Strong Tag Teams:
(PP company) (Textile company)
Mitsui-Toatsu — Toray
Mitsubishi Petrochemicals — Mitsubishi Rayon
Sumitomo Chemicals — Toyobo
- High Humidity Climate
Disposable closes such as surgery wear did not become popular.
- Use of Tatami
instead of Carpets
- Disliked low spinnability
and poor dyability of PP
Rapid Decline

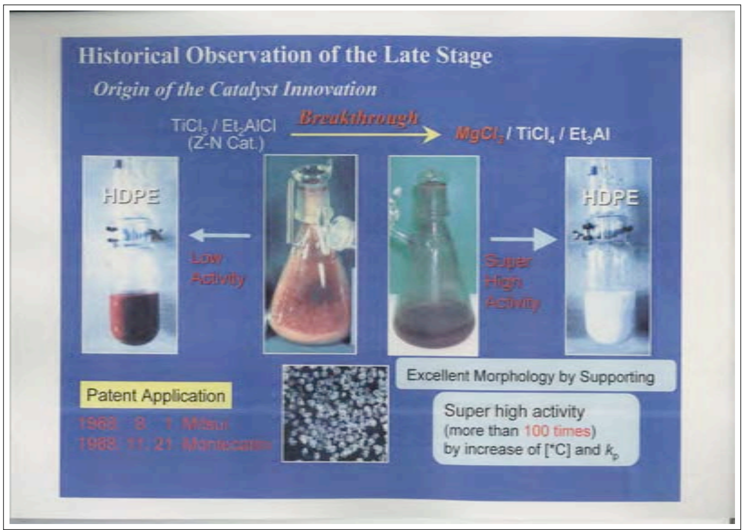

Historical Observation of the Early Stage
- Injection Applications -
Replacement of metal and wood in Household Utensils
Metal → PP
Washbowls
Buckets
etc.
Wood → PP
Casks
Boxes
etc.

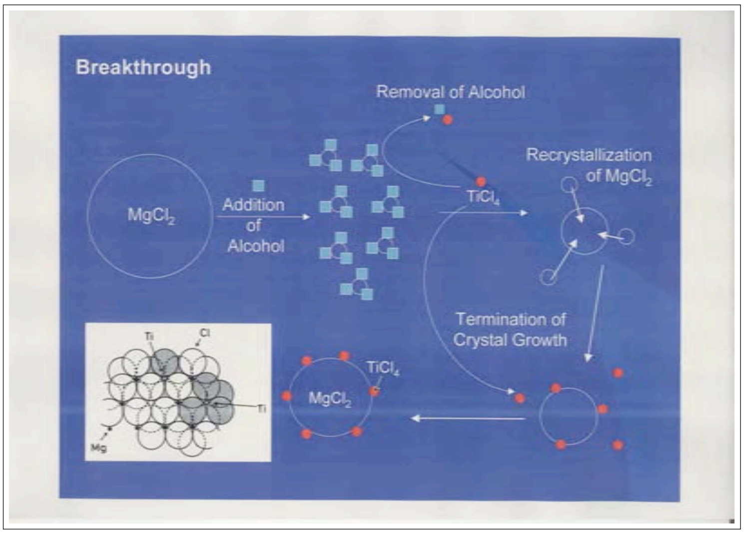

Historical Observation of the Early Stage
- Injection Applications -
Beer Bottles Crafts
The First Use in Industry of PP Injection
Led to Mass Consumption of PP
HDPE had already replaced wood in this use.
HDPE PP
High Impact Strength at Low Temperatures
High Processability, Good Appearance
- Creation of Impact-Copolymer (block PP)
- Mild Winter
- Keiretsu (The Major Beer Company: in Mitsubishi Group
The Major HDPE Producer: in Mitsui Group)
Replacement of HDPE by PP

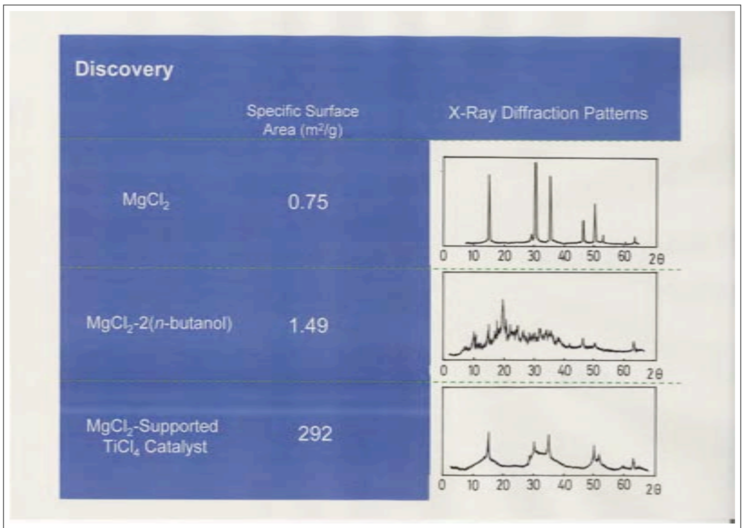

Historical Observation of the Early Stage
- Injection Applications -
Beer Bottles Crafts
Increase of MFR
Extension of the PP Market to Use
as Household Electric Apparatus P
The Three Leaders (Montecatini Licensees)
built brick walls in their Keiretsu and Local Communities.

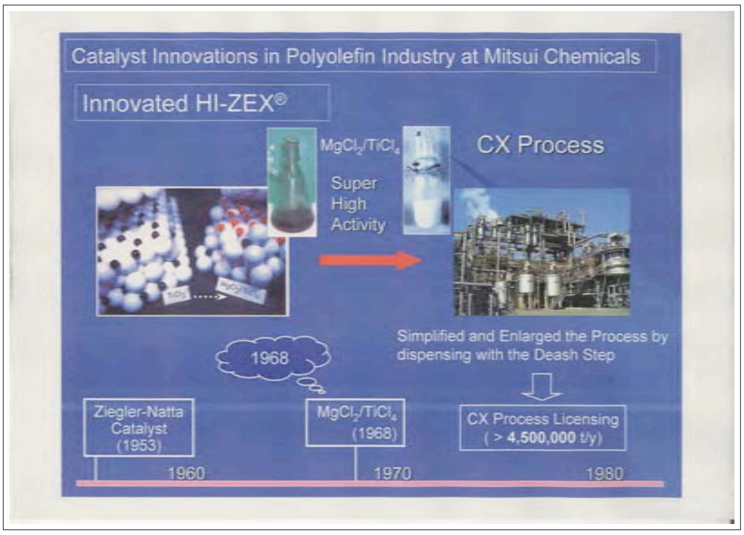

Historical Observation of the Early Stage
- Film Applications -
- PP demonstrated the competitive power to P
High Rigidity, High Transparency, etc.
- Keiretsu did not work.
Film producers
Too small to be members of the three major groups
Majority is in a cottage industry
Investment from PP makers
New Keiretsu was organized by PP makers.
Many grades for elaborate PP films such as
multi-layer films or films including silica or other additives

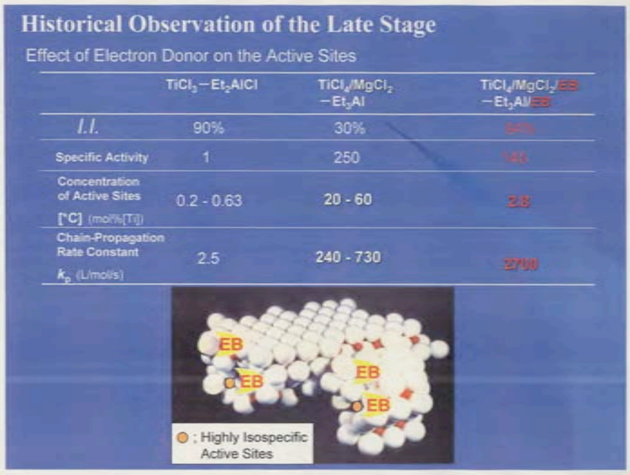

Historical Observation of the Early Stage
- Film Applications -
Example of
PP usage
in Japan
OPP
CPP (heatsealable)
(outside)
(inside)
Printed Face
Aluminized PP
(interception of damp, O2, light, etc.)

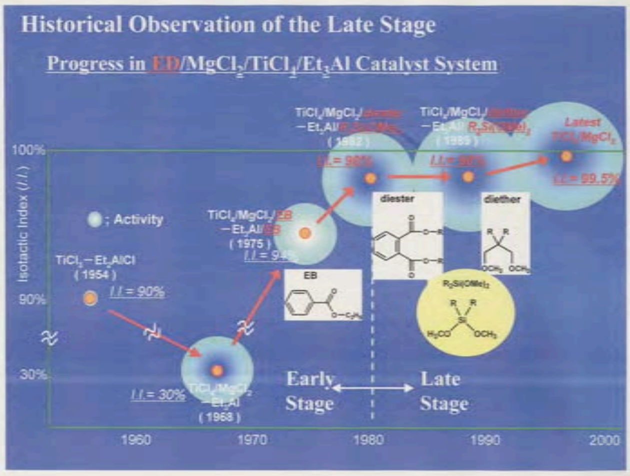

Historical Observation of the Late Stage
Origin of the Catalyst Innovation
TiCl3 / Et2AlCl
(Z-N Cat.)
Breakthrough
MgCl2 / TiCl4 / Et3Al
HDPE
HDPE
Patent Application
Excellent Morphology by Supporting
Super high activity
(more than 100 times)
by increase of [*C] and kp

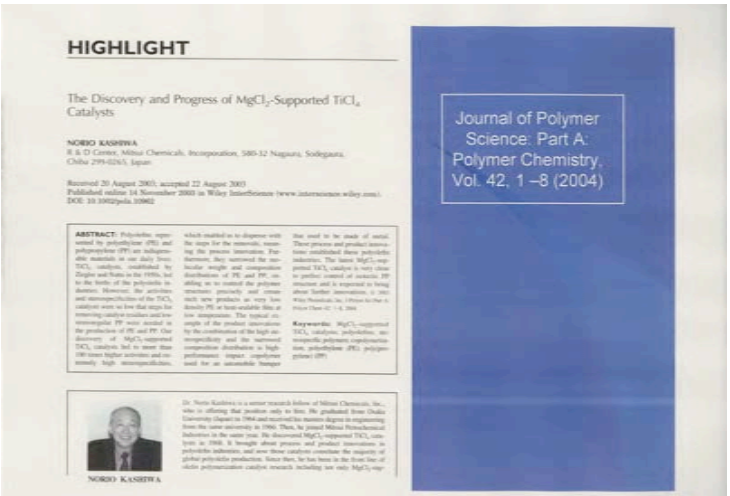

Breakthrough
Removal of Alcohol
Recrystallization
of MgCl2
MgCl2
Addition
of
Alcohol
TiCl4
Termination of
Crystal Growth
TiCl4
MgCl2

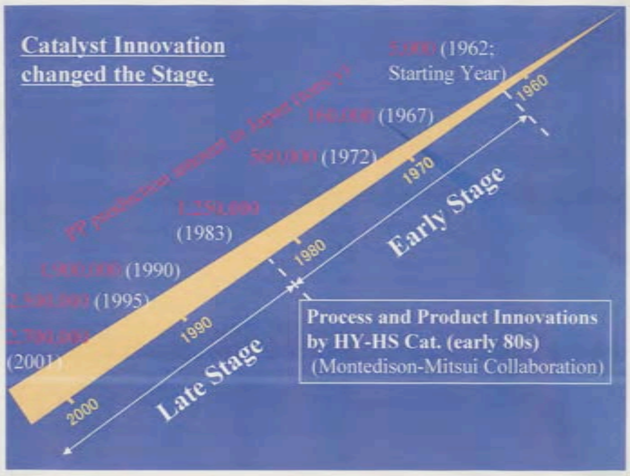

Discovery
Specific Surface
Area (m²/g)
X-Ray Diffraction Patterns
MgCl2
0.75
MgCl2-2(n-butanol)
1.49
MgCl2-Supported
TiCl4 Catalyst
292


Catalyst Innovations in Polyolefin Industry at Mitsui Chemicals
Innovated HI-ZEX®
MgCl2/TiCl4
Super
High
Activity
CX Process
Simplified and Enlarged the Process by
dispensing with the Deash Step
1968
Ziegler-Natta
Catalyst
(1953)
MgCl2/TiCl4
(1968)
CX Process Licensing
(> 4,500,000 t/y)
1960
1970
1980


Historical Observation of the Late Stage
Effect of Electron Donor on the Active Sites
TiCl3−Et2AlCl
TiCl4/MgCl2 −Et3Al
TiCl4/MgCl2/EB −Et3Al/EB
I.I.
90%
30%
Specific Activity
1
250
Concentration of Active Sites [*C] (mol%[Ti])
0.2 - 0.63
20 - 60
2.8
Chain-Propagation Rate Constant kp (L/mol/s)
2.5
240 - 730
2700
EB
EB
EB
EB
; Highly Isospecific Active Sites

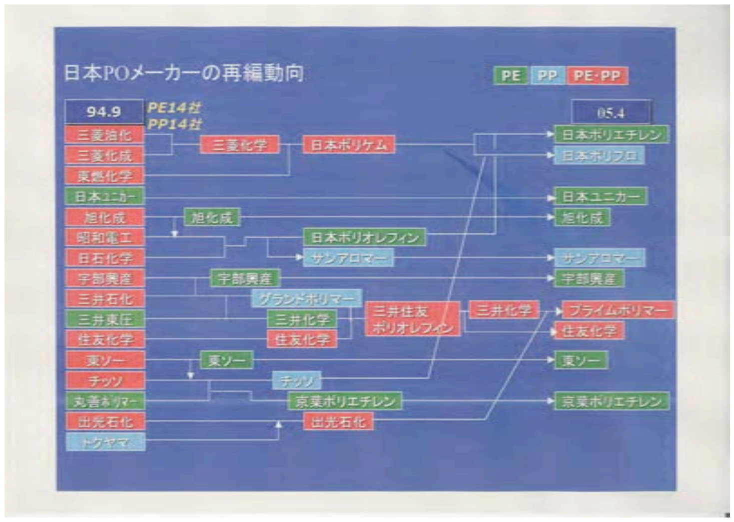

Historical Observation of the Late Stage
Progress in ED/MgCl2/TiCl4/Et3Al Catalyst System
Isotactic Index (I.I.)
100%
90%
30%
; Activity
TiCl3−Et2AlCl (1954)
I.I. = 90%
I.I. = 30%
TiCl4/MgCl2 −Et3Al (1968)
TiCl4/MgCl2/EB −Et3Al/EB (1975)
EB
TiCl4/MgCl2/ −Et3Al/ (1982)
TiCl4/MgCl2/ −Et3Al/ (1985)
diester
diether
Latest TiCl4/MgCl2
I.I. = 99.5%
Early Stage
Late Stage
1960
1970
1980
1990
2000

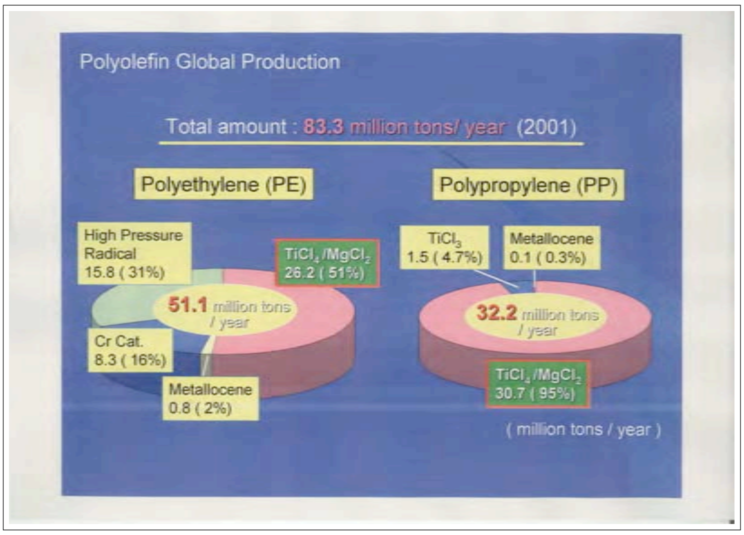

HIGHLIGHT
The Discovery and Progress of MgCl2-Supported TiCl4 Catalysts
NORIO KASHIWA
Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 42, 1−8 (2004)

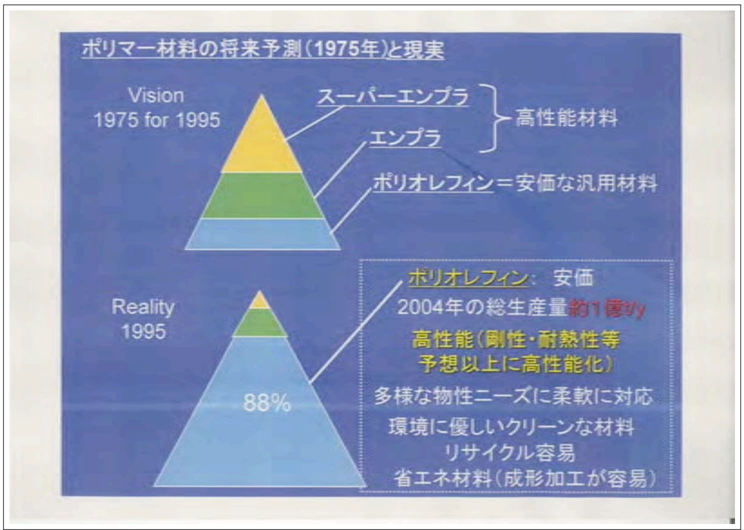

Catalyst Innovation changed the Stage.
(1962: Starting Year)
(1967)
(1972)
(1983)
(1990)
(1995)
(2001)
1960
1970
1980
1990
2000
Early Stage
Late Stage
Process and Product Innovations by HY-HS Cat. (early 80s)
(Montedison-Mitsui Collaboration)


Mitsui Chemicals is changing.
New loop-type PP plant was constructed in Japan (2003).
300,000 t/y


Japan is changing.
- Quality-Oriented Mindset
- Adoption of the Latest Technologies
- Keiretsu
Main PP users changed to global companies.
- Far from Western Countries
- High Humidity and Mild Climate
- PP Growth linked with Growth of Japanese Economy
Japanese Economy is in recession.
- Little Competition in Asia
Asian business is very Competitive.
- Protective and Exclusive Policies by MITI
MITI changed the policies.
14 PP makers for 2.2 million t/y (1994)
→ 4 PP makers for 2.7 million t/y (2005)

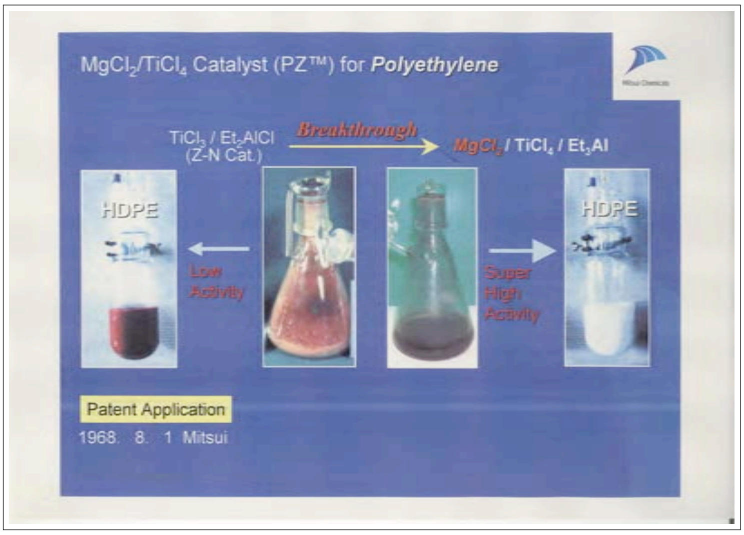

日本POメーカーの再編動向
PE
PP
PE·PP
94.9
PE14社
PP14社
05.4
三菱油化
三菱化成
東燃化学
日本ユニカー
旭化成
昭和電工
日石化学
宇部興産
三井石化
三井東圧
住友化学
東ソー
チッソ
丸善ポリマー
出光石化
トクヤマ
三菱化学
日本ポリケム
旭化成
日本ポリオレフィン
サンアロマー
宇部興産
グランドポリマー
三井化学
住友化学
三井住友ポリオレフィン
東ソー
チッソ
京葉ポリエチレン
出光石化
日本ポリエチレン
日本ポリプロ
日本ユニカー
旭化成
サンアロマー
宇部興産
プライムポリマー
住友化学
東ソー
京葉ポリエチレン


Polyolefin Global Production
Total amount : 83.3 million tons/ year (2001)
Polyethylene (PE)
Polypropylene (PP)
High Pressure Radical 15.8 (31%)
TiCl4 /MgCl2 26.2 (51%)
51.1 million tons / year
Cr Cat. 8.3 (16%)
Metallocene 0.8 (2%)
TiCl3 1.5 (4.7%)
Metallocene 0.1 (0.3%)
32.2 million tons / year
TiCl4 /MgCl2 30.7 (95%)
(million tons / year)

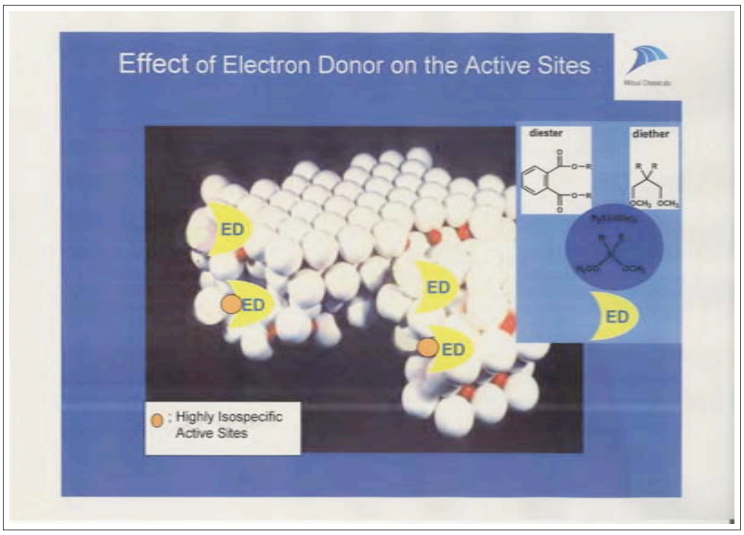

ポリマー材料の将来予測（1975年）と現実
Vision 1975 for 1995
スーパーエンプラ
エンプラ
高性能材料
ポリオレフィン＝安価な汎用材料
Reality 1995
88%
ポリオレフィン：安価
2004年の総生産量約1億t/y
高性能（剛性・耐熱性等予想以上に高性能化）
多様な物性ニーズに柔軟に対応
環境に優しいクリーンな材料
リサイクル容易
省エネ材料（成形加工が容易）

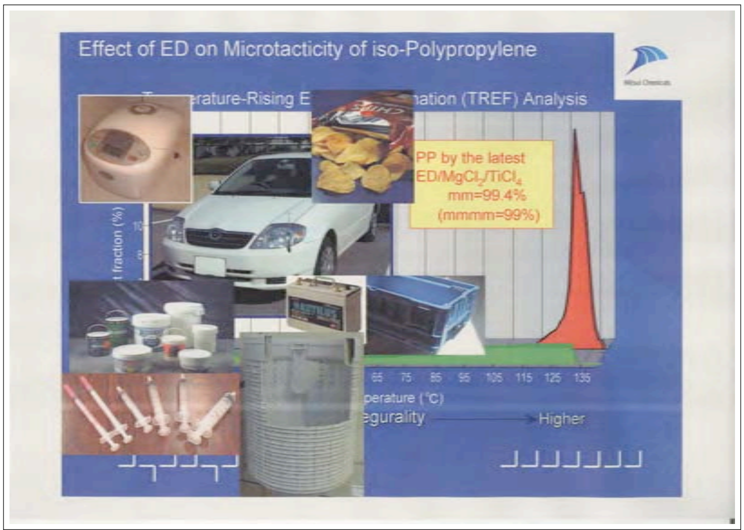

ポリオレフィンの誕生
1933 エチレン高圧ラジカル重合の発見（ICI） LDPE
1953 遷移金属触媒重合（エチレン重合）の発見（Ziegler）
HDPE
LLDPE／エラストマーの前身
1954 遷移金属触媒重合（プロピレン重合）の発見（Natta）
Iso-PP
Ata-PP
Syn-PP
1968 MgCl2担持型TiCl4触媒によるBreakthrough
（三井化学）
1980 メタロセン触媒によるBreakthrough
(Kaminsky)
分布が狭くなった
（分子量、組成、立体規則性）

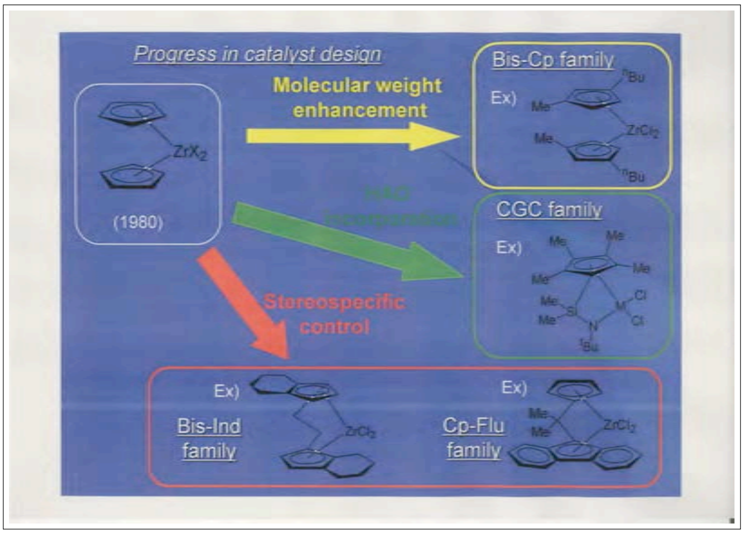

Process & Product Innovations in Polyolefin industries
Discovery by Ziegler
Commercialization of PE
Catalyst Innovations
Process & Product Innovations
HDPE
LLDPE
PP
LLDPE
Elastomer

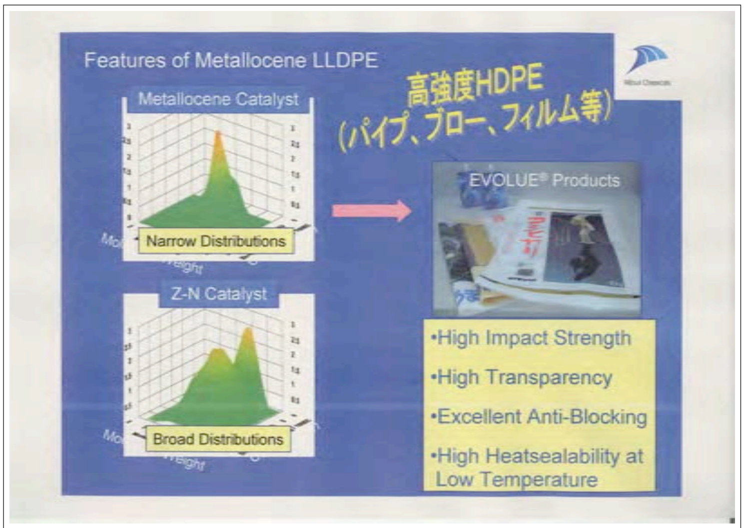

MgCl2/TiCl4 Catalyst (PZ™) for Polyethylene
TiCl3 / Et2AlCl (Z-N Cat.)
Breakthrough
MgCl2 / TiCl4 / Et3Al
HDPE
Low Activity
Super High Activity
HDPE
Patent Application
1968. 8. 1 Mitsui

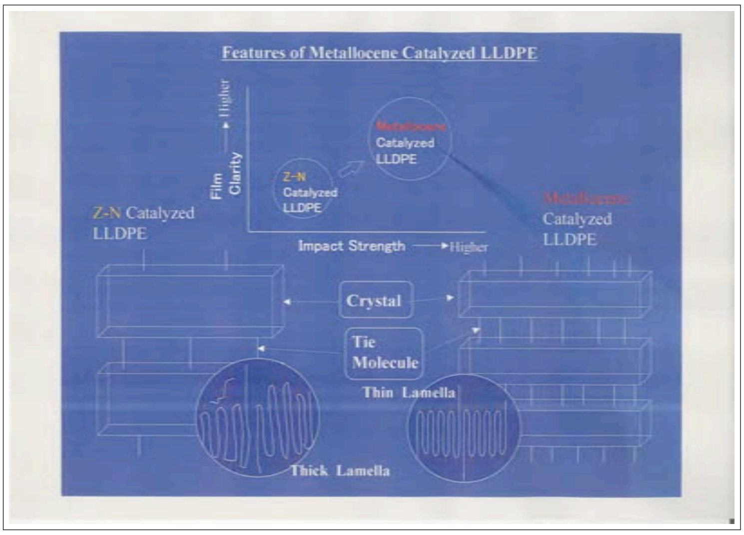

PE Product Innovation By $MgCl_2$-Supported $TiCl_4$ Catalysts
Purified Active Site Nature
Narrowed Molecular Weight and Composition Distributions
HI-ZEX® 7000F (HDPE)
HI-ZEX® Other Grades
NEO-ZEX® (LLDPE)
ULT-ZEX®

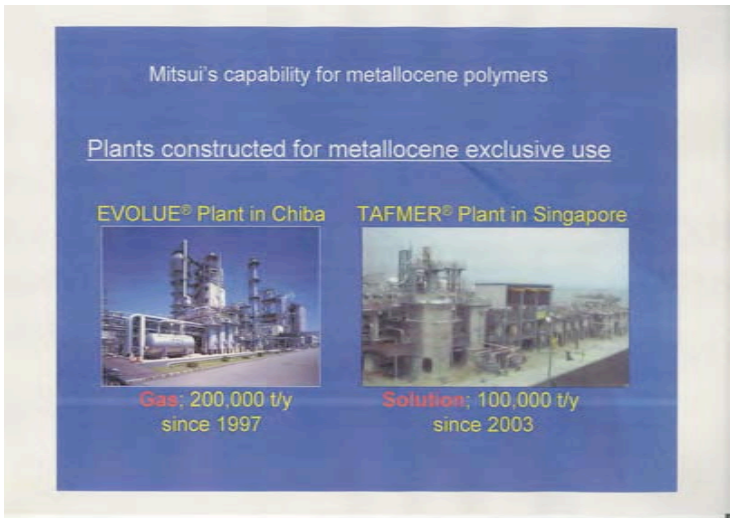

Effect of Electron Donor on the Active Sites
diester
diether
ED
ED
ED
ED
ED
: Highly Isospecific Active Sites

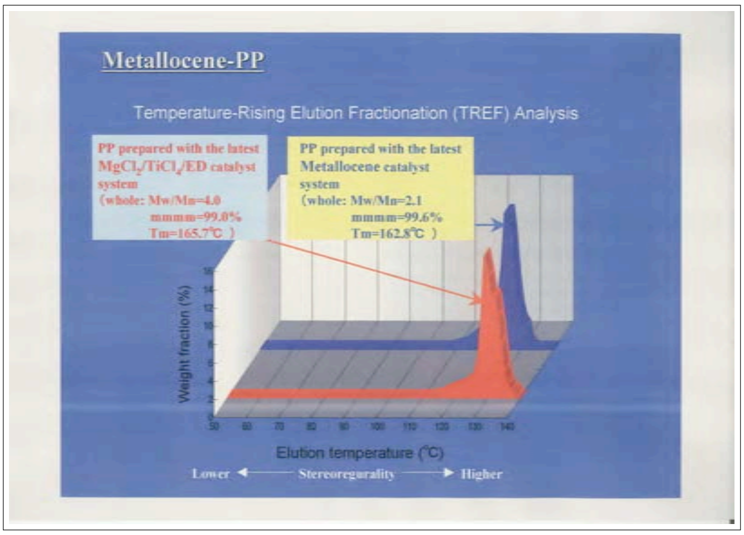

Effect of ED on Microtacticity of iso-Polypropylene
PP by the latest ED/$MgCl_2$/$TiCl_4$
mm=99.4%
(mmmm=99%)
65 75 85 95 105 115 125 135
Higher


Progress in catalyst design
Molecular weight enhancement
ZrX_2
(1980)
Bis-Cp family
Ex)
$ZrCl_2$
CGC family
Ex)
Stereospecific control
Ex)
Bis-Ind family
$ZrCl_2$
Ex)
Cp-Flu family
$ZrCl_2$

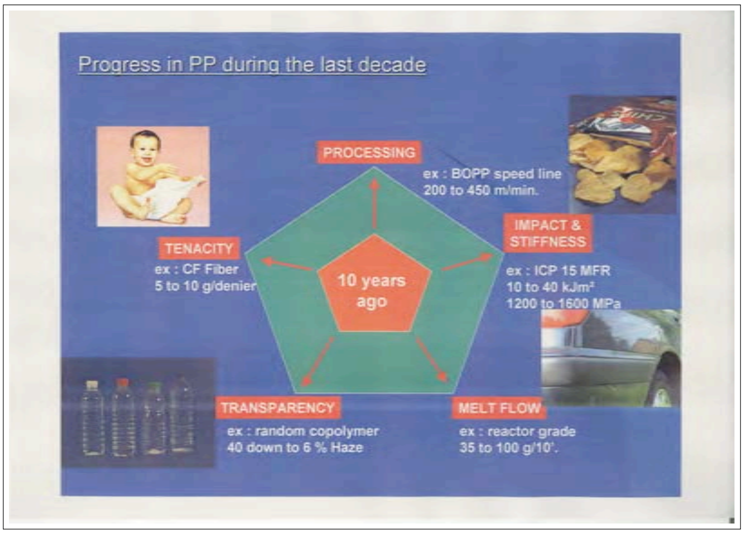

Features of Metallocene LLDPE
高強度HDPE
(パイプ、ブロー、フィルム等)
Metallocene Catalyst
Narrow Distributions
Z-N Catalyst
Broad Distributions
EVOLUE® Products
•High Impact Strength
•High Transparency
•Excellent Anti-Blocking
•High Heatsealability at Low Temperature

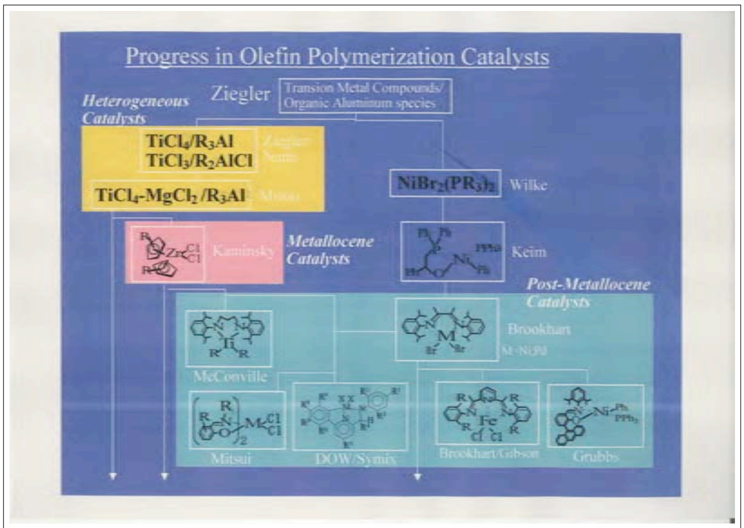

Features of Metallocene Catalyzed LLDPE
Film Clarity
Higher
Z-N Catalyzed LLDPE
Catalyzed LLDPE
Impact Strength
Higher
Z-N Catalyzed LLDPE
Catalyzed LLDPE
Crystal
Tie Molecule
Thin Lamella
Thick Lamella

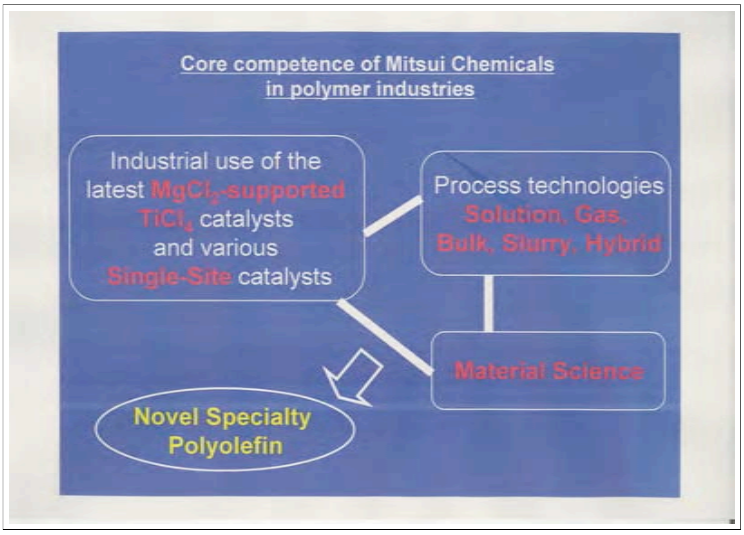

Mitsui's capability for metallocene polymers
Plants constructed for metallocene exclusive use
EVOLUE® Plant in Chiba
TAFMER® Plant in Singapore
Gas; 200,000 t/y
since 1997
Solution; 100,000 t/y
since 2003

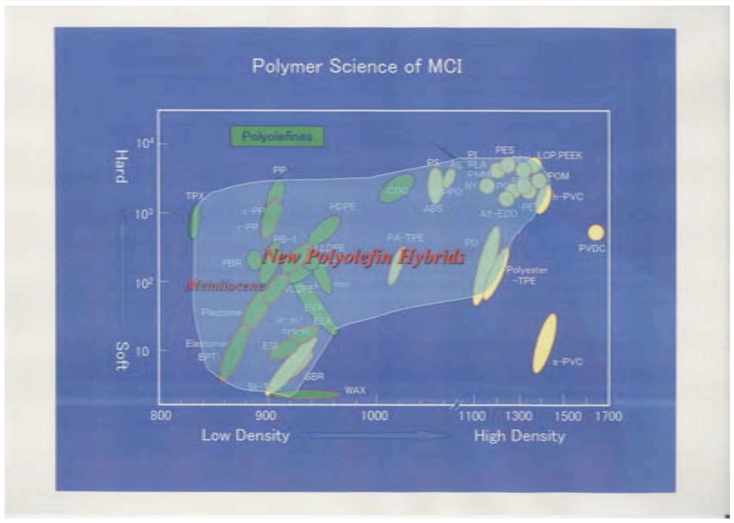

Metallocene-PP
Temperature-Rising Elution Fractionation (TREF) Analysis
PP prepared with the latest MgCl2/TiCl4/ED catalyst system (whole: Mw/Mn=4.0 mmmm=99.0% Tm=165.7℃)
PP prepared with the latest Metallocene catalyst system (whole: Mw/Mn=2.1 mmmm=99.6% Tm=162.8℃)
Weight fraction (%)
Elution temperature (℃)
Lower
Stereoregurality
Higher

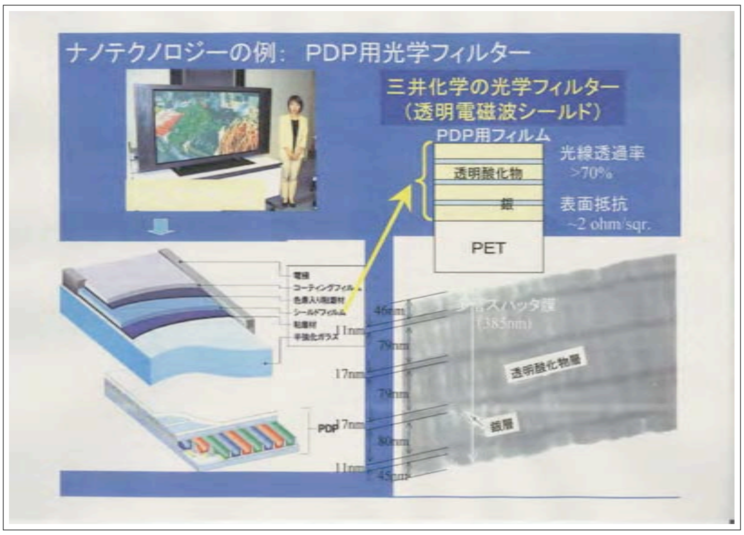

従来r-PP
メタロセンr-PP
分子量分布
組成分布
立体規則性分布
狭い

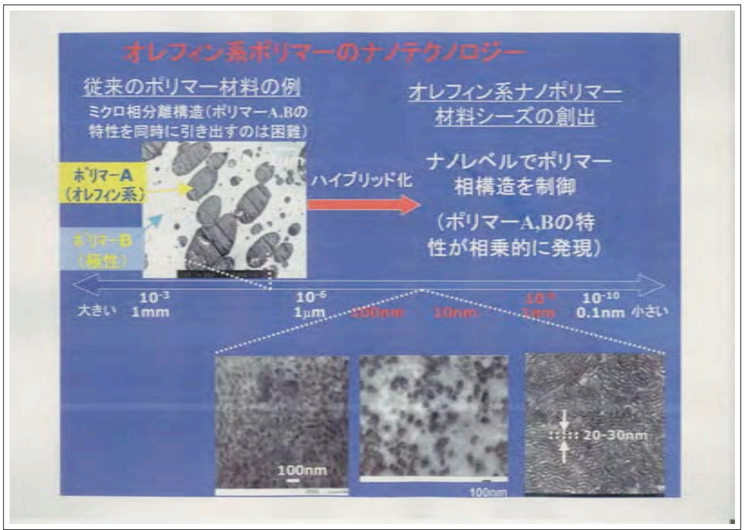

Progress in PP during the last decade
PROCESSING
ex : BOPP speed line 200 to 450 m/min.
IMPACT & STIFFNESS
ex : ICP 15 MFR 10 to 40 kJm² 1200 to 1600 MPa
TENACITY
ex : CF Fiber 5 to 10 g/denier
10 years ago
TRANSPARENCY
ex : random copolymer 40 down to 6 % Haze
MELT FLOW
ex : reactor grade 35 to 100 g/10'.

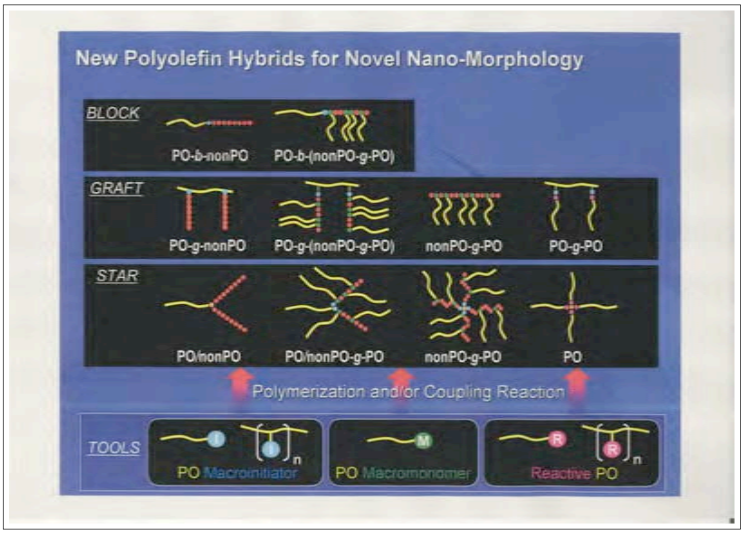

Progress in Olefin Polymerization Catalysts
Heterogeneous Catalysts
Ziegler
Transion Metal Compounds/ Organic Aluminum species
TiCl4/R3Al
TiCl3/R2AlCl
Ziegler Natta
TiCl4-MgCl2/R3Al
Mitsui
NiBr2(PR3)2
Wilke
Kaminsky
Metallocene Catalysts
Keim
Post-Metallocene Catalysts
Brookhart
McConville
Mitsui
DOW/Symix
Brookhart/Gibson
Grubbs

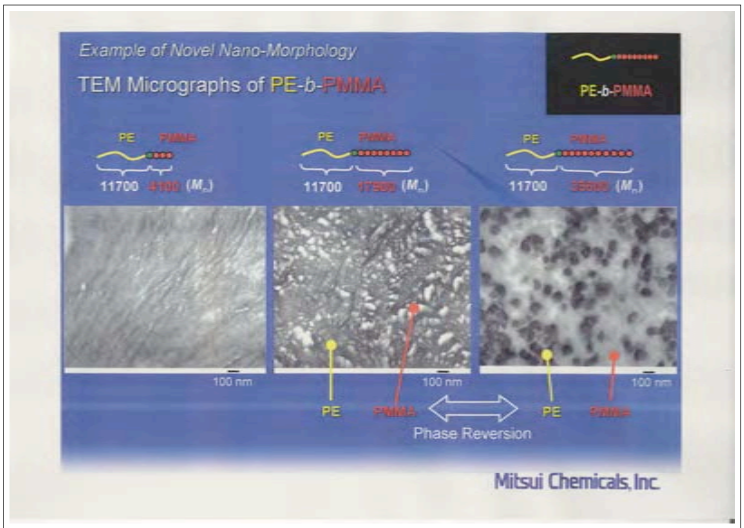

Core competence of Mitsui Chemicals in polymer industries
Industrial use of the latest MgCl2-supported TiCl4 catalysts and various Single-Site catalysts
Process technologies
Solution, Gas, Bulk, Slurry, Hybrid
Material Science
Novel Specialty Polyolefin

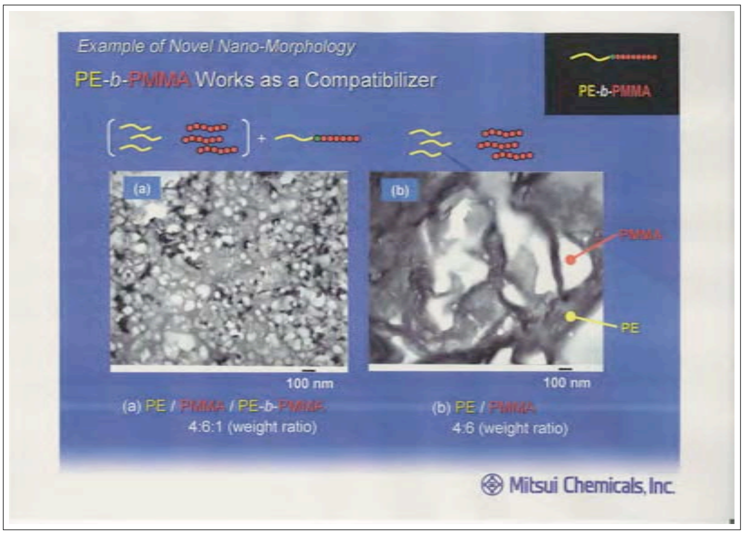

Polymer Science of MCI
Polyolefines
New Polyolefin Hybrids
Hard
Soft
Low Density
High Density
PVDC
s-PVC

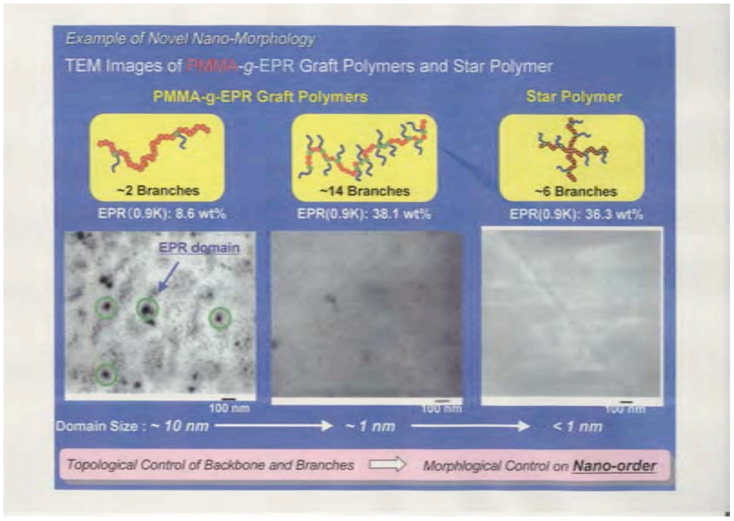

ナノテクノロジーの例：PDP用光学フィルター
三井化学の光学フィルター
（透明電磁波シールド）
PDP用フィルム
透明酸化物
銀
PET
光線透過率
>70%
表面抵抗
~2 ohm/sqr.
透明酸化物層
銀層

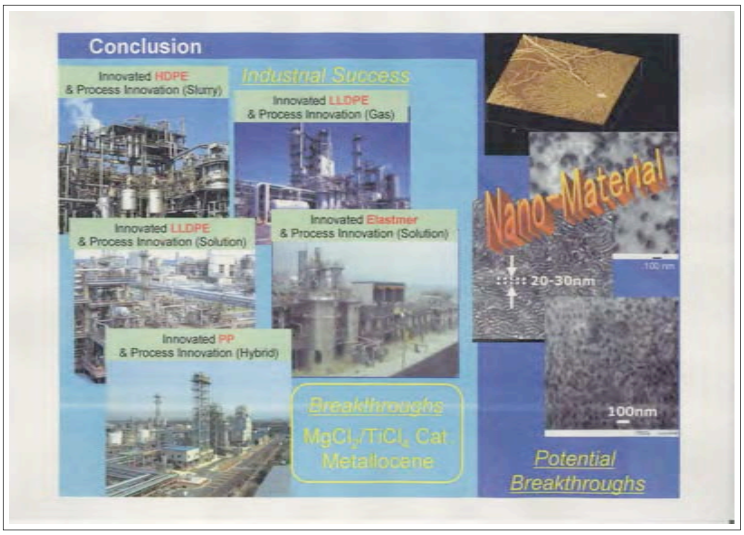

オレフィン系ポリマーのナノテクノロジー
従来のポリマー材料の例
ミクロ相分離構造（ポリマーA,Bの特性を同時に引き出すのは困難）
オレフィン系ナノポリマー材料シーズの創出
ポリマーA（オレフィン系）
ポリマーB（極性）
ハイブリッド化
ナノレベルでポリマー相構造を制御
（ポリマーA,Bの特性が相乗的に発現）
大きい 10-3 1mm
10-6 1μm
100nm
10nm
10-10 0.1nm 小さい
100nm
20-30nm


New Polyolefin Hybrids for Novel Nano-Morphology
BLOCK
PO-b-nonPO
PO-b-(nonPO-g-PO)
GRAFT
PO-g-nonPO
PO-g-(nonPO-g-PO)
nonPO-g-PO
PO-g-PO
STAR
PO/nonPO
PO/nonPO-g-PO
nonPO-g-PO
PO
Polymerization and/or Coupling Reaction
TOOLS
PO Macroinitiator
PO Macromonomer
Reactive PO


Example of Novel Nano-Morphology
TEM Micrographs of PE-b-PMMA
PE-b-PMMA
PE
PMMA
11700
100 nm
Phase Reversion
Mitsui Chemicals, Inc.


Example of Novel Nano-Morphology
PE-b-PMMA Works as a Compatibilizer
PE-b-PMMA
(a)
(b)
PMMA
PE
100 nm
(a) PE / PMMA / PE-b-PMMA
4:6:1 (weight ratio)
(b) PE / PMMA
4:6 (weight ratio)
Mitsui Chemicals, Inc.


Example of Novel Nano-Morphology
TEM Images of PMMA-g-EPR Graft Polymers and Star Polymer
PMMA-g-EPR Graft Polymers
Star Polymer
~2 Branches
EPR(0.9K): 8.6 wt%
~14 Branches
EPR(0.9K): 38.1 wt%
~6 Branches
EPR(0.9K): 36.3 wt%
EPR domain
100 nm
Domain Size : ~ 10 nm → ~ 1 nm → < 1 nm
Topological Control of Backbone and Branches ⇨ Morphlogical Control on Nano-order


Conclusion
Industrial Success
Innovated HDPE & Process Innovation (Slurry)
Innovated LLDPE & Process Innovation (Gas)
Innovated LLDPE & Process Innovation (Solution)
Innovated Elastmer & Process Innovation (Solution)
Innovated PP & Process Innovation (Hybrid)
Breakthroughs
MgCl2/TiCl4 Cat.
Metallocene
Nano-Material
20-30nm
100nm
Potential Breakthroughs