

# VALUE CREATION IN POLYOLEFINS: OPPORTUNITIES FOR INNOVATION



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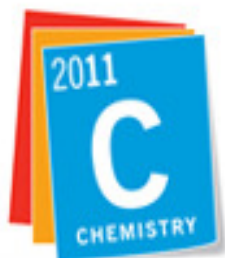
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**June 29, 2011**



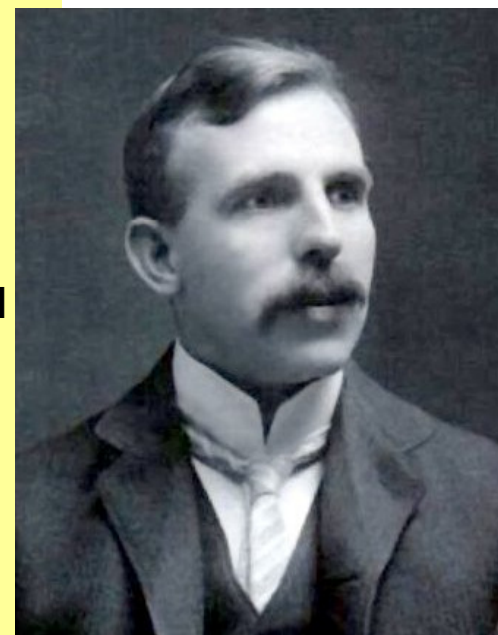
# International Year of **CHEMISTRY** 2011



**Madame Curie, Nobel Prize in Chemistry, 1911**

- Celebrate the achievements of chemistry
- Improve public understanding of chemistry
- Champion the role of chemistry in addressing the critical challenges of our society
  - Food and nutrition
  - Clean water
  - Sustainable energy
  - Climate change
- Broader outreach and engagement
- Get younger people more interested in chemistry

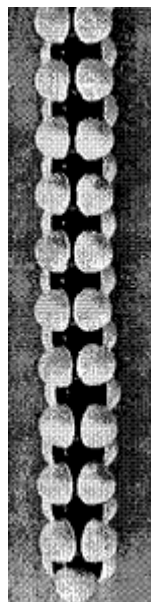
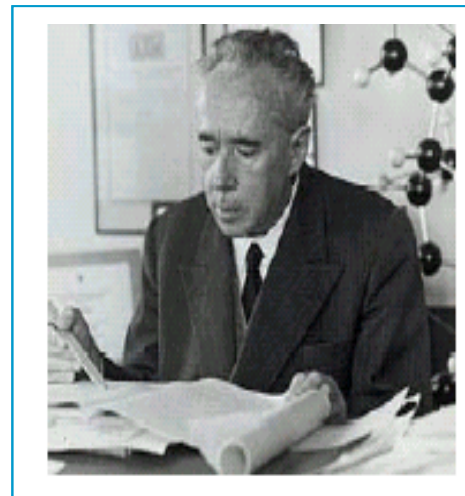
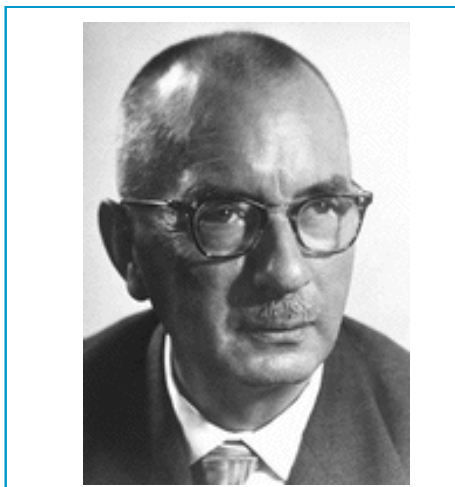
***Poly(olefin)s, along with other synthetic polymers are considered as some of the most significant contributions of chemistry to mankind***



**Ernest Rutherford, The Structure of the Atom. 1911**



# FIFTY FIVE YEARS OF METAL CATALYZED OLEFIN POLYMERIZATION



## CRYSTALLINE HIGH POLYMERS OF $\alpha$ -OLEFINS Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained<sup>1</sup> by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

**G.Natta**  
**JACS 77, 1708, 1955**  
**( March 20, 1955 )**

## ***POLYMER GROWTH IN INDIA***

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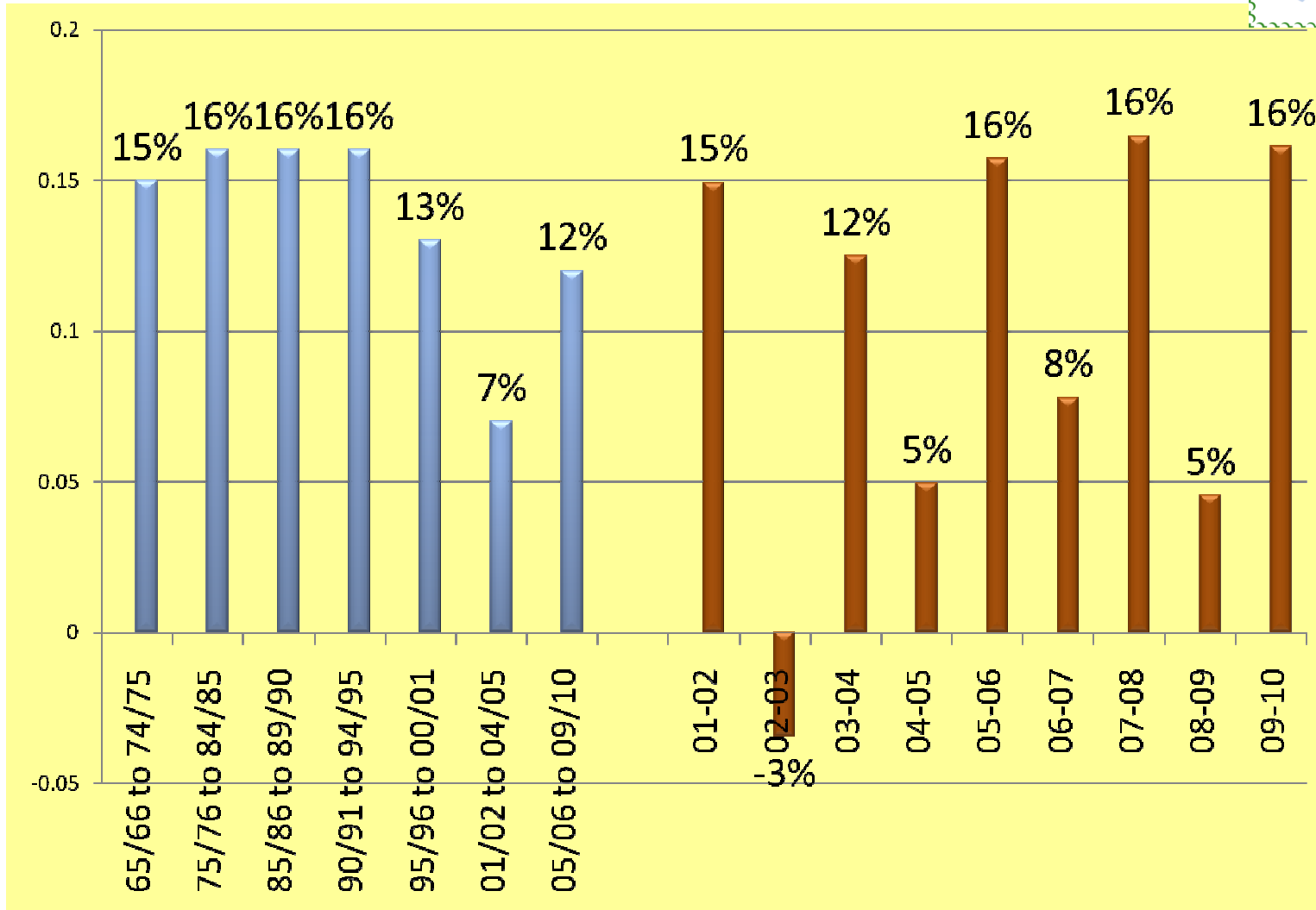
- **Rapid growth in polymer consumption in the initial 3 decades 1970s, 1980s and 1990s**
- **Growing at rates 2 - 2.5 times the GDP growth rate**
- **Other petrochemicals, especially, LAB, Phthalic Anhydride (PAN) , EO and VAM also picked up in 1980s and 1990s.**
- **Synthetic Elastomers continue to show strong demand growth from mid 90s**
- **Demand growth is supply driven and not import dependant.**
  - **RIL's Hazira PP plant (350 kta capacity at the startup) started commercial production in 1997 at the time when Indian PP demand was below 100 kta.**
  - **Within a short span of 2-3 years, Indian demand picked up and the entire production was absorbed.**



## **VALUE ADDITION TO NAPHTHA**

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Crude to Naphtha	→ 25%
Crude to Gasoline	→ 35%
Crude to C3/PX	→ 150%
Crude to Polymers	→ 150-200%
Crude to End products	→ 250-300%



**Indian Demand → Trebling every decade**

Source: Industry Estimates

## PE GROWTH DRIVERS



Sector		08-09 Apr-Dec	09-10 Apr-Dec	Growth
LDPE	General Purpose	48	73	52%
LDPE	Heavy Duty	29	38	30%
LDPE	Liquid Packaging	36	41	16%
LDPE	Extrusion Coating	47	51	10%
LDPE	Injection Moulding	14	16	18%
LDPE	W&C	12	12	2%
LDPE	Adhesive Lamination	14	15	2%
LDPE	Others	11	16	45%
<b>Total LDPE</b>		<b>210</b>	<b>262</b>	<b>25%</b>

Sector		08-09 Apr-Dec	09-10 Apr-Dec	Growth
LLDPE	LL Butene	362	403	11%
LLDPE	LL Octene	72	88	22%
LLDPE	Rotomoulding	59	75	28%
LLDPE	Extrusion Coating	51	56	10%
LLDPE	High Flow	59	61	3%
LLDPE	Waste / Others	3	11	224%
<b>Total LLDPE</b>		<b>607</b>	<b>695</b>	<b>14%</b>

Sector		08-09 Apr-Dec	09-10 Apr-Dec	Growth
<b>HDPE</b>	<b>Raffia</b>	154	158	2%
HDPE	MF	21	32	53%
HDPE	Blow Moulding	170	186	9%
HDPE	MBM	36	59	64%
HDPE	LBM	28	38	35%
<b>HDPE</b>	<b>HD Film</b>	36	58	61%
<b>HDPE</b>	<b>HM Film</b>	162	167	3%
HDPE	Pipe	73	75	2%
<b>HDPE</b>	<b>HM Pipe</b>	52	50	-4%
HDPE	Pipe Coating	26	21	-20%
<b>HDPE</b>	<b>Inj. Moulding (High)</b>	65	77	18%
HDPE	Inj. Moulding (Low)	35	39	10%
HDPE	IM (UV)	8	7	-6%
HDPE	Insulation	9	5	-46%
HDPE	Sheathing	0	2	688%
HDPE	Waste / Others	14	19	43%
<b>Total HDPE</b>		<b>891</b>	<b>992</b>	<b>11%</b>

## PP & PVC GROWTH DRIVERS



Sector		08-09 Apr-Dec	09-10 Apr-Dec	Growth
PP	Raffia/Lam	453	544	20%
PP	IM	230	318	38%
PP	TQ/ CPP	129	152	18%
PP	ICP	205	255	24%
PP	BOPP	127	161	27%
PP	F&F	57	102	80%
PP	RCP	50	61	22%
PP	EXT	29	50	74%
<b>Total PP</b>		<b>1279</b>	<b>1642</b>	<b>28%</b>

Sector		08-09 Apr-Dec	09-10 Apr-Dec	Growth
PVC	Pipe & Fittings	688	949	38%
PVC	Calendered Products	75	91	21%
PVC	Films	48	64	33%
PVC	Sheets	15	17	15%
PVC	Wires & Cables	82	95	16%
PVC	Footwear	20	32	62%
PVC	Profiles	31	35	13%
PVC	Blow Moulding	2	3	47%
PVC	Misc	13	13	6%
<b>Total PVC</b>		<b>973</b>	<b>1300</b>	<b>34%</b>

## **CAPACITY ADDITIONS CONTINUES FOR POLYMERS**



(Capacities in -000-mt)	Additional Capacity		
	2009	2010	2011
Iran	---	500	---
Kuwait	744	---	---
Qatar	---	1,300	---
SaudiArabia	2,642	1,858	2,525
UAE	---	1,400	---
India	---	1,010	---
China	832	4,778	815
Singapore	---	800	1,000
Thailand	---	1,900	---
Debottlenecks/Closures	(2,024)	(608)	---
<b>World</b>	<b>2,194</b>	<b>12,939</b>	<b>4,340</b>

Source: CMAI, Jan. 2009

- **Feed availability issues continue in Middle East → Shortage of Ethane**
- **China: New projects under start-up (ZRCC, Tainjin, Panjin, Dushanzi PC and Fujian)**
- **Global operating rates to remain under pressure**

## ***FUTURE DEMAND SUPPLY SCENARIO: INDIA***



	Demand		Demand CARG	Capacity	Required Capacity
	2008	2015	2015/2008	2010	2015
(kT)					
<b>Polymer</b>	<b>5707</b>	<b>13370</b>	<b>12.9%</b>	<b>8318</b>	<b>5052</b>
LDPE	263	650	13.8%	205	445
LLDPE	980	2164	12.0%	1970	194
HDPE	1040	2305	12.0%	660	1645
PP	1827	4328	13.1%	3545	783
PVC	1408	3472	13.8%	1486	1986
PS	188	452	13.4%	452	0
<b>Chemicals</b>	<b>967</b>	<b>1906</b>	<b>10.2%</b>	<b>965</b>	<b>941</b>
LAB	422	750	8.6%	449	301
EO	122	210	8.1%	117	93
n-Butanol	41	91	12.1%	14	77
VAM	83	185	12.1%	45	140
Isopropanol	24	60	14.3%	0	60
PAN	223	480	11.6%	271	209
Oxo-Alcohol	12	30	14.0%	28	2
2EH	40	100	14.0%	41	59
<b>Rubber</b>	<b>416</b>	<b>923</b>	<b>12.0%</b>	<b>135</b>	<b>788</b>
PBR	108	240	12.1%	50	190
SBR	135	300	12.0%	62	238
NBR	26	58.5	12.0%	13	46
EVA	128	283	12.0%		283
EPDM	18	41	12.3%	10	31

***India will need additional capacities for a long time to come***



## **NEW CAPACITIES IN INDIA**

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- ONGC Petro Additions ,Dahej Gujarat, Rs 12240 Crores (2012)
- Mangalore Refinery, Mangalore, Karnataka, Rs12000 Crores (??)
- IOC, Panipat, Haryana, Rs 14439 crores (2009)
- IOC, Paradeep, Orissa (??)
- GAIL, Lapetkata, Assam, Rs 5460 crores (2012)
- HMEL, Vishakapatnam, Andhra Pradesh (??)
- HMEL, Bhatinda, Punjab, Rs 18900 Crores including refinery (??)
- Haldia Exp, Haldia, WB, Rs 800 crores (Nov 09)(??)
- GMR, Kakinada, Andhra Pradesh, Rs 40000 crore (PCPIR) (??)
- Essar,Vadinar ,Gujarat, ~ Rs 25000 crores (On hold)
- Reliance, Jamnagar, Gujarat ~ Rs 40500 crores (??)

## TOP 5 CHEMICAL COMPANIES : STRATEGIES ADOPTED



- **Exxon Mobil and Shell (mainly basics)**
  - Delayed capital investment
  - Focus on costs
  - Integration benefit
  - Focus of R&D → alternate energy
- **BASF**
  - Focus on specialty
  - Cost control project NEXT
  - Ciba acquisition integration
- **Dow Chemicals**
  - Focus on specialty
  - Rohm & Haas acquisition
  - Capacity rationalization
  - Commodity Polyolefin put on sale

### **Key down cycle strategies**

**Survive**

**Focus on cost**

**Consolidate**

**Integration benefits**

**Move to specialty**

**Unusual down cycle in 2008-09: Recession → lower demand**

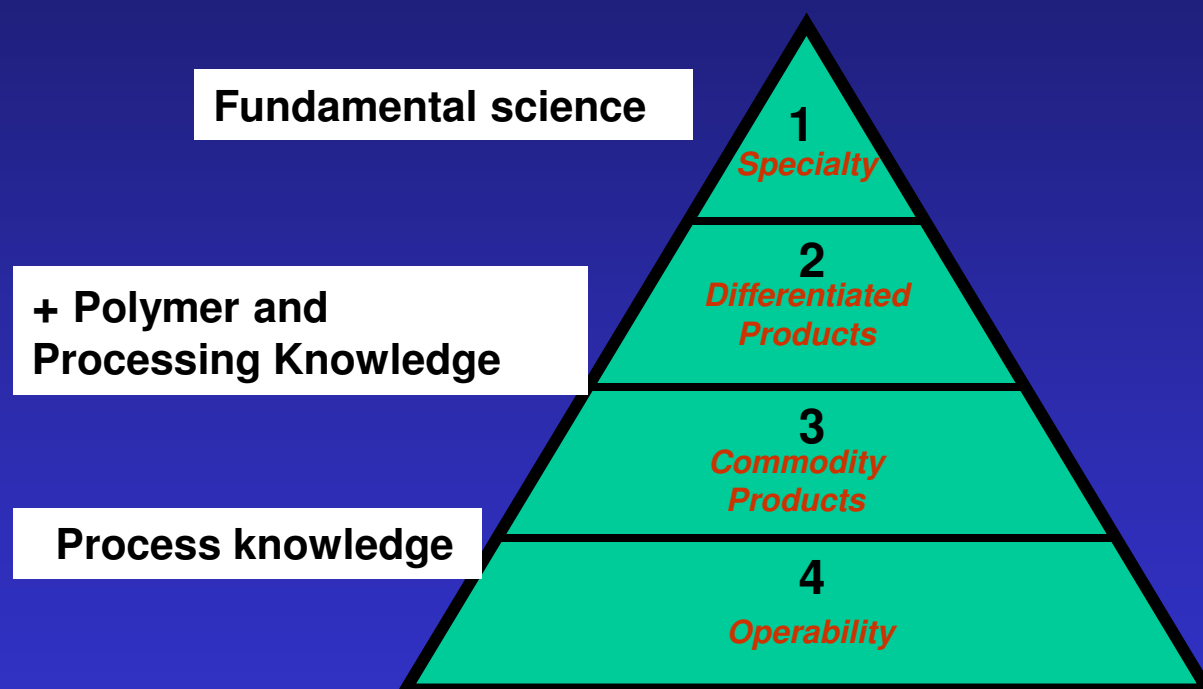
## **PRODUCT DIFFERENTIATION : DEFINITION**

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- **Commodities** : Very large volume products that are sold by a large number of suppliers to a large number of customers with less product differentiation and price as the major criteria
- **Differentiated Commodities**: Very large volume products that are sold by selected suppliers to large number of customers by differentiating products based on performance and price (EVA-high VA, mLLDPE, mPP, uhmwPE, impact PP)
- **Large Volume Specialties** : Medium volume products that are sold based on technology, performance and meeting end use requirements as the major criteria
- **Specialties** : Small volume products supplied by limited suppliers with high margins and high barrier to entry based on technology  
( Ionomers, TPO, TPV, EVOH, PE/PP foam, syndio PP, polybutene-1, poly 4- methylpentene-1)

# TECHNOLOGY PYRAMID FOR POLYOLEFIN PRODUCERS





## **TIER 4 AND TIER 1 PP PRODUCERS : FEATURES**

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- **Tier 4**
  - Large capacities with limited grade offerings
  - Access to low cost feed-stocks
  - Serves emerging markets
  - Technology Licensed
- **Tier 1**
  - Advanced PP producer
  - often suffers from a disadvantaged feedstock position
  - Serving mature and competitive markets
  - Strong R&D, self reliant for technology
  - Operating philosophy : high operating margins, niche products



# **VALUE CREATION IN POLYOLEFINS**

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- **Catalysts**
  - **Mg-Ti Catalysts**
  - **Metallocenes**
  - **Post Metallocenes**
- **Processes**
- **Products**



## ***Mg-Ti CATALYSTS : PE***

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- Emulsion process for catalyst preparation (Borealis, 2004) having low surface area , spherical particle shape and narrow particle size, reduced porosity, high bulk density and intra-particle homogeneity. PE with superior properties and low fines are produced.
- BCE/BCS catalysts (SINOPEC) for slurry (loop) and gas phase processes.



## ***Mg-Ti CATALYSTS: PP***

- **Workhorse catalysts are based on phthalate esters as internal donors and alkoxysilanes as external donors**
- **New internal donors to avoid using phthalates; 1,3-diethers (BASELL, 1989), succinates (BASELL, 2003), 1,3-diol esters (SINOPEC, 2002), Advanced Donors (Dow, Consista D 7000, 2010)**
- **External donors**
  - **Dialkyl dialkoxy silane (alkyl = cyclopentyl, isopropyl, isobutyl, methylcyclohexyl) (BASELL)**
  - **Aminosilanes (BASELL, TOHO, 2006) – high isotacticity with broad molecular weight distribution**
  - **Calixarene (EQUISTAR, 2004)**



## ***ADVANCED DONOR SYSTEMS***

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- **Judicious combination of internal/external donor to control**
  - **Molecular weight distribution (narrow/broad)**
  - **Hydrogen response (low/high)**
  - **Catalyst activity**
  - **Isotacticity index**
- **Combination of two external donors can be used to produce PP with broad polydispersity**
- **Combinatorial and computational chemistry approach for the discovery of new donors**

## **EVOLUTION OF DONORS**

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<b>Year of commercial introduction</b>	<b>Internal donor (Di)</b>	<b>External donor</b>
<b>1978<sup>a</sup></b>	<b>Ethyl benzoate (EB)</b>	<b>Methyl-p-toluate (MPT)</b>
<b>1985<sup>b</sup></b>	<b>Ethyl benzoate (EB)</b>	<b>p-Ethoxy ethylbenzoate (DEEB)</b>
<b>1985<sup>c</sup></b>	<b>Di-isobutyl phthalate (DIB)</b>	<b>Alkoxy silanes phenyl triethoxy silane (PES) Diphenyl dimethoxy silane (DPMS)</b>
<b>1998<sup>d</sup></b>	<b>1,3-diethers</b>	<b>None</b>

<sup>a</sup>Ger Pat 2,643,143 (1977) : Montedison-Mitsui

<sup>b</sup>US Pat 4,414,132 and 4,393,182 (1979) : Shell

<sup>c</sup>Europ Pat 45,977 (1982) : Montedison

<sup>d</sup>US Pat 4,971,937 (1990) : Himont

## STRUCTURE-ACTIVITY RELATIONSHIP IN ALKOXY SILANE DONORS

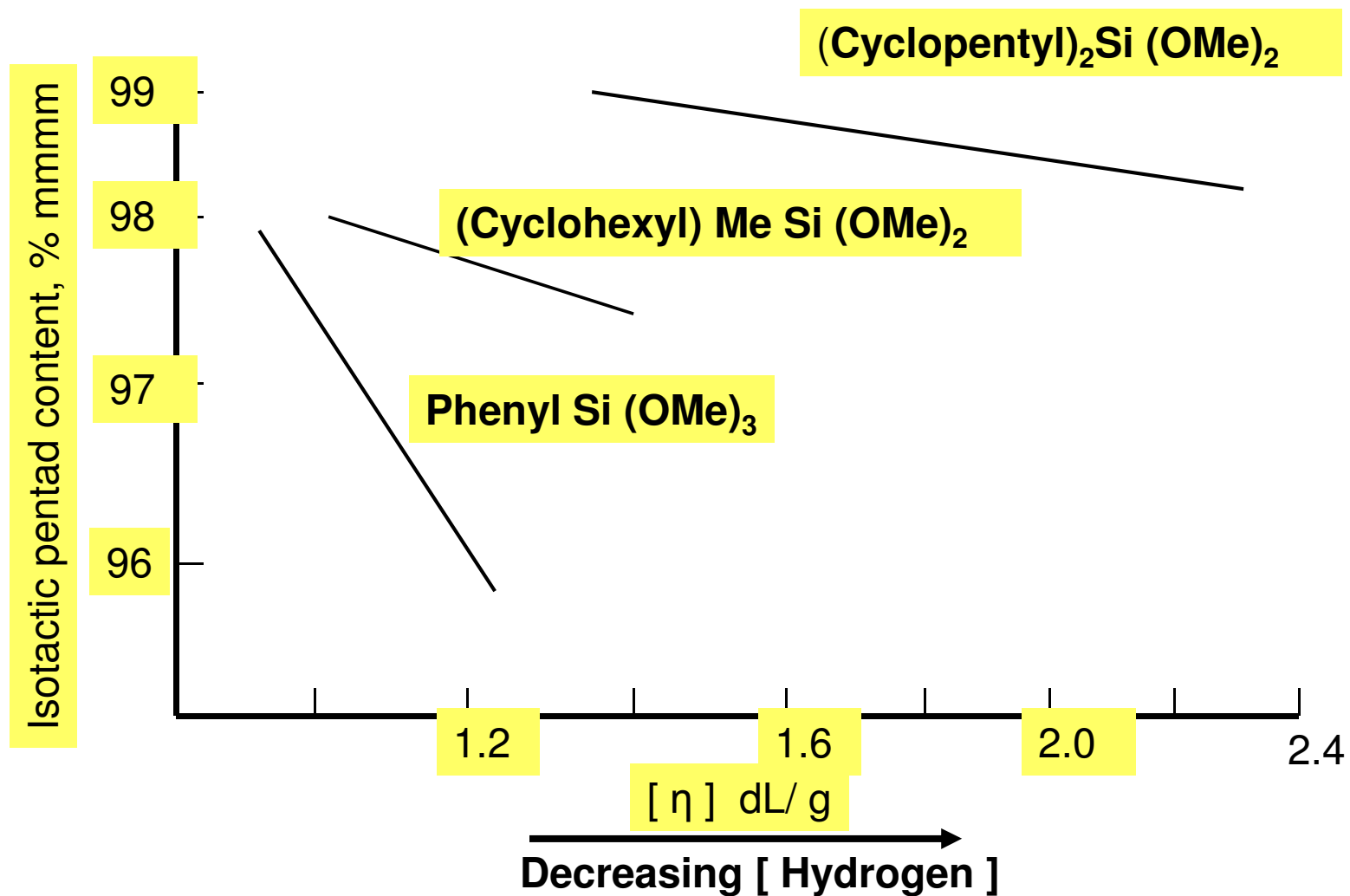
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### **General structure $R_nSi(OR^1)_{4-n}$**

- Two or three alkoxy groups essential ( $n = 1$  or  $2$ )
- Bulky alkyl group needed for high Isotacticity Index  $R = Me < Bu < C_6H_5 < iPr < cycloalkyl$
- Mw increases with increasing steric bulkiness of R  
 $Me < nBu < C_6H_5 < iPr < cycloalkyl$
- Q (Mw/Mn) broadens with increasing steric bulk of R
- $H_2$  increases catalyst productivity and causes further broadening of molecular weight distribution

**RELATIONSHIP BETWEEN PP MOLECULAR WEIGHT AND  
CATALYST STEREOSPECIFICITY :  
EFFECT OF EXTERNAL DONOR AND HYDROGEN**



## COMMERCIAL Mg-TI CATALYST SUPPLIERS FOR PP

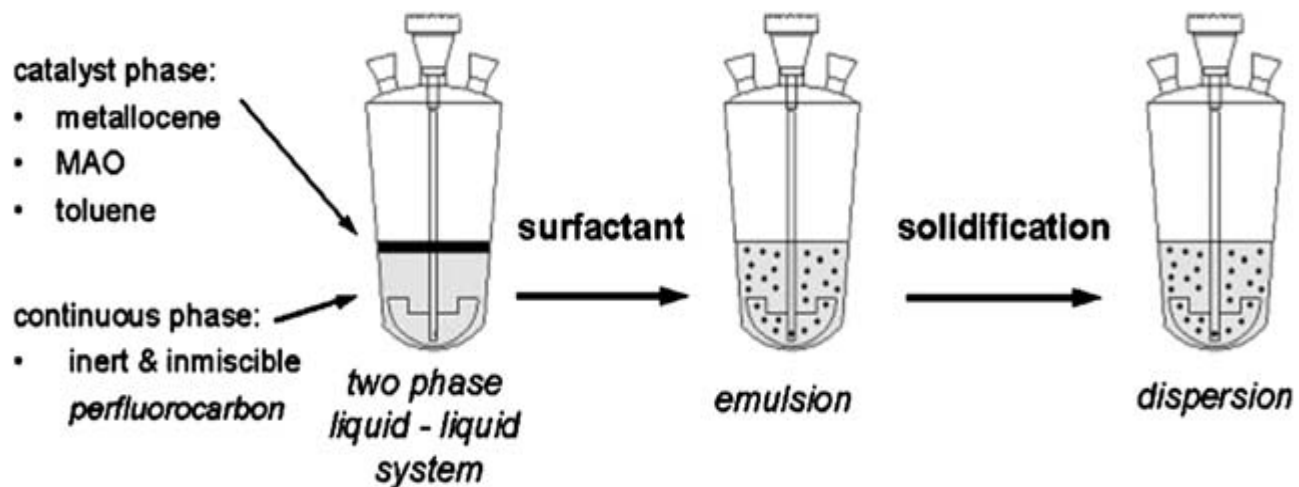


<i>Supplier</i>	<i>Catalyst</i>	<i>Process</i>
Lyondell Basell	GF 2A, Avant	Spheripol Loop and Slurry
Dow	SHAC 100, 200, 300	Unipol Gas phase
Toho	THC	Loop
Englehard	LYNX	Loop, gas phase and slurry
Chisso/Toho	THC	Loop, Slurry and gas phase
Mitsui	TK	Loop, Slurry and gas phase
Sinopec	DQ, N	Hypol. Spheripol, slurry
Xiang Yang Chemicals	CS	Spheripol, gas phase, slurry
Yan Hua High Tech	YS, HDC	Spheripol, gas phase, slurry
Sud Chemie	C-Max 120 /125 (spherical) C-Max 320/325/330 C-Max 220 (Granular)	Spheripol Gas phase Hypol

## ***METALLOCENE CATALYSTS: PE***

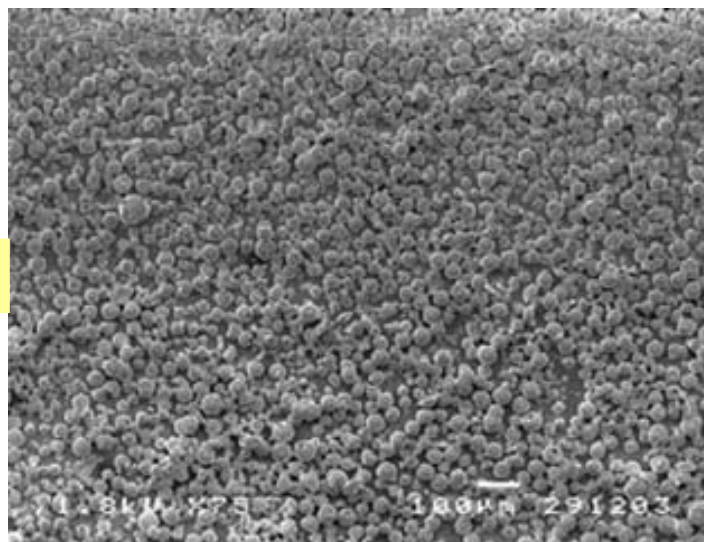
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- **ActivCat (Albermale, 2008) : 200% increase in activity over conventional silica supported catalyst**
- **MgCl<sub>2</sub> + SiO<sub>2</sub> supported metallocenes (Sinopec)**
- **SiO<sub>2</sub> + clay (IOLA, Grace)**
- **Emulsion – based SSC with improved activity and compact morphology (Borealis)**
- **Bimodal HDPE (Univation – PRODIGY BMC -200, 300) in single reactor/gas phase, having a combination of metallocene – post metallocene catalysts for high and low molecular weights PE ( PE 100, film and blow molding)**

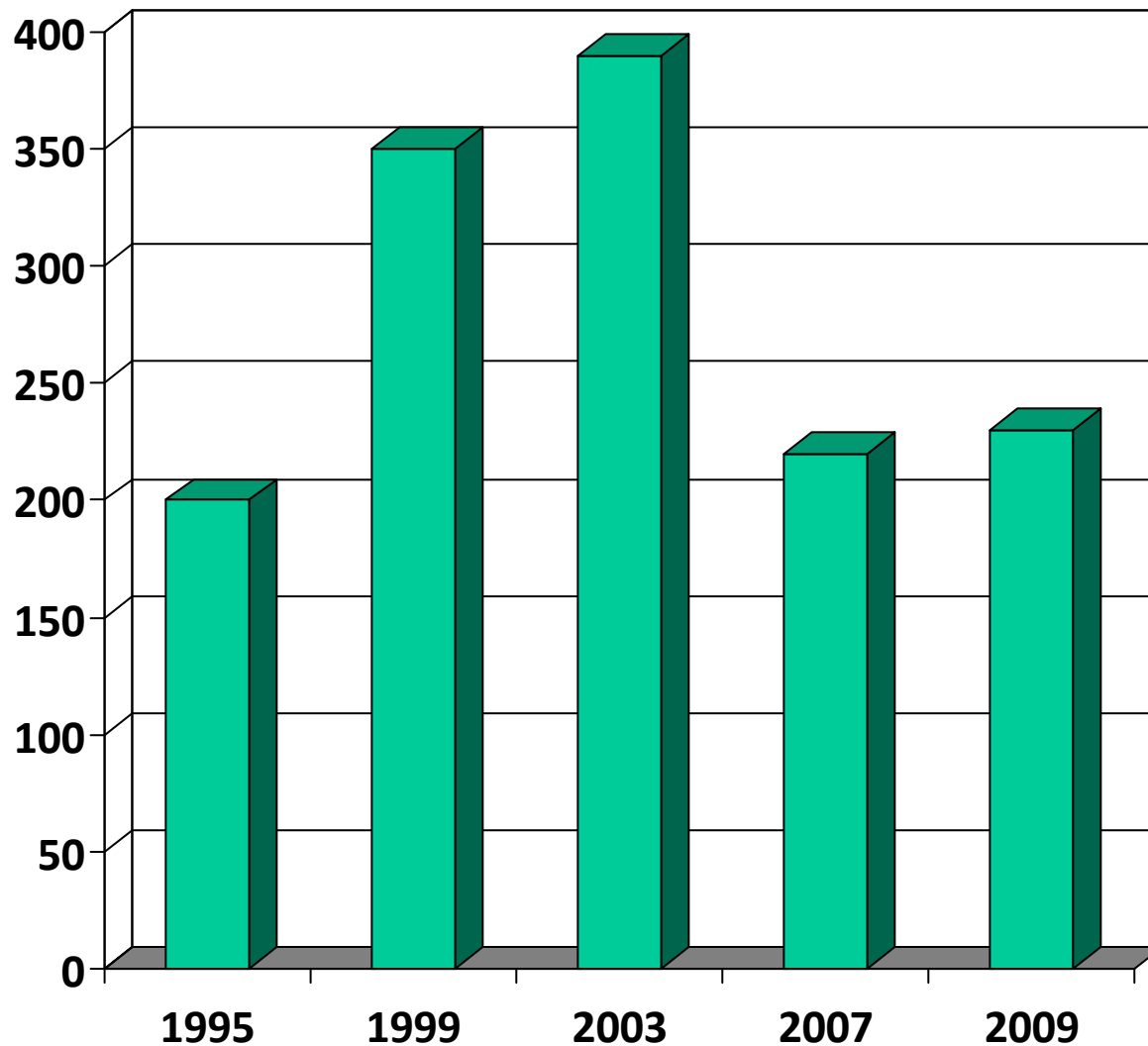


## Emulsion Process for the Preparation of Metallocene Catalysts (Borealis)

### SEM of SSC by emulsion Process



## **PATENTING TRENDS IN METALLOCENE BASED PROCESSES**



*Between 1991-2008, about 9,000 patents have been issued on metallocene poly(olefin)s*

■ Patents Issued

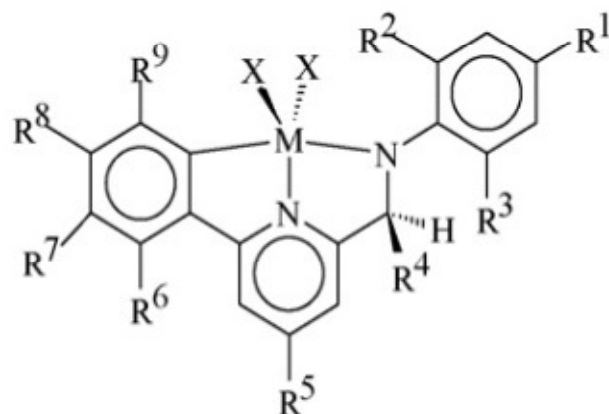
***Patent activity in the metallocene is on the decline; Many early patents issued in the nineties are on the verge of expiry***



## POST METALLOCENE CATALYSTS : PE contd....

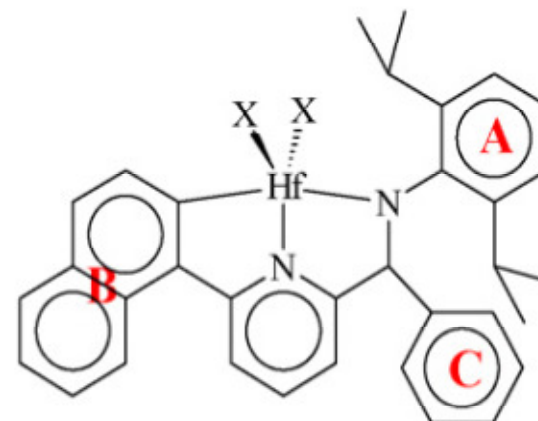
- **VERSIFY** – Dow plastomers based on propylene – ethylene copolymer using pyridylamine – based catalysts, possessing narrow mwd, a broad and unique CD and unique regio errors

### Pyridyl Amine Catalyst



M = Zr, Hf  
X = Cl, CH<sub>3</sub>, NR<sub>2</sub>

Structure 1



(DIP-NAP-Ph) HfX<sub>2</sub>

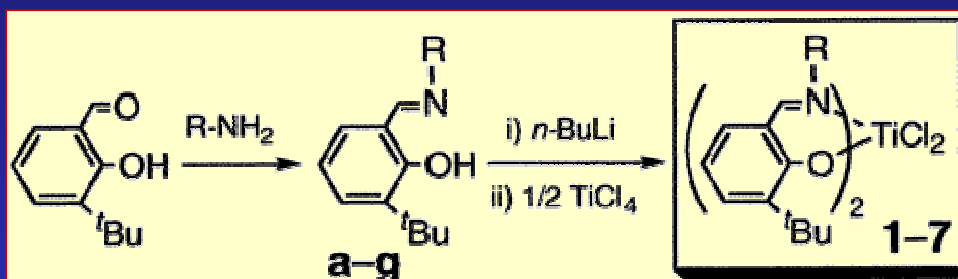
**A B C**

- Active with a wide variety of cocatalysts
- MAO, MMAO, Lewis acids & Bronsted acids

## POST METALLOCENE CATALYSTS



- FI catalysts (MITSUI, 1998) show high activity for ethylene polymerization. Depending on metal and co-catalyst, PP with high syndiotacticity or high molecular weight atactic PP on isotactic PP can be produced



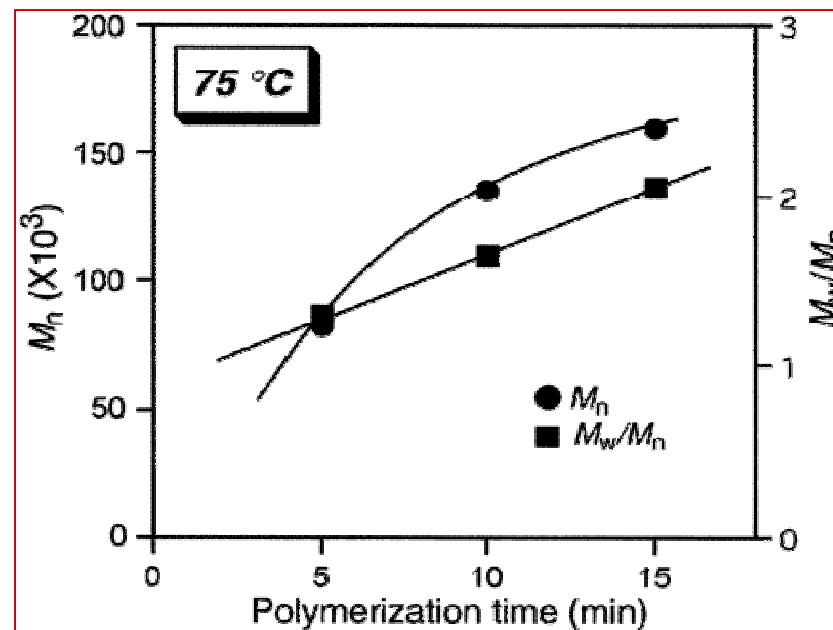
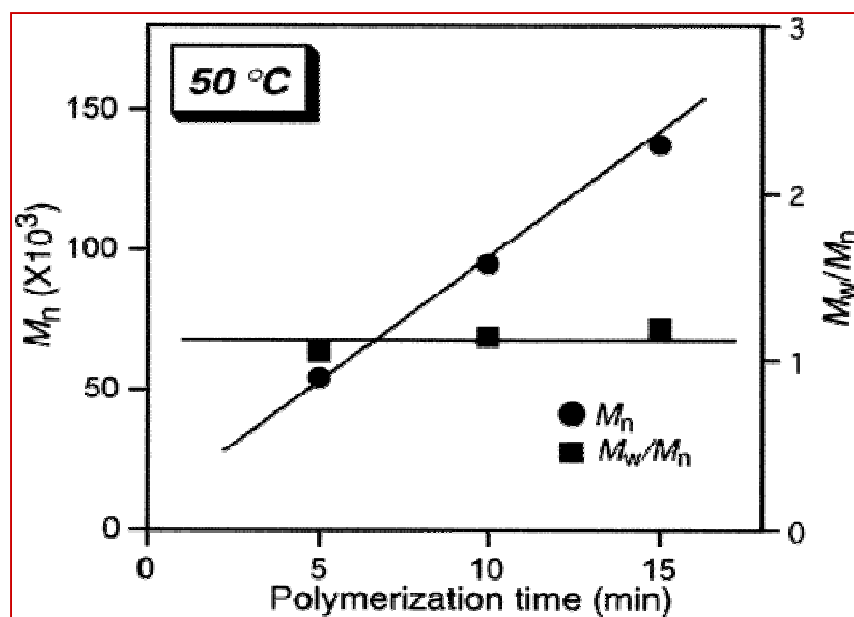
R:				
ligand	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>
complex	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
R:				
ligand	<b>e</b>	<b>f</b>	<b>g</b>	
complex	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>



## POLYMERIZATION OF ETHYLENE USING COMPLEX 1/ MAO

MAO : 1.25 mmol, Catalyst : 0.5  $\mu$ mol, T: 25°C, Ethylene : 1 atm, Toluene :250 ml, Time : 1 min

Complex 1 shows features of a living polymerization behavior even at 50°C; note the high dilution conditions and short reaction times !



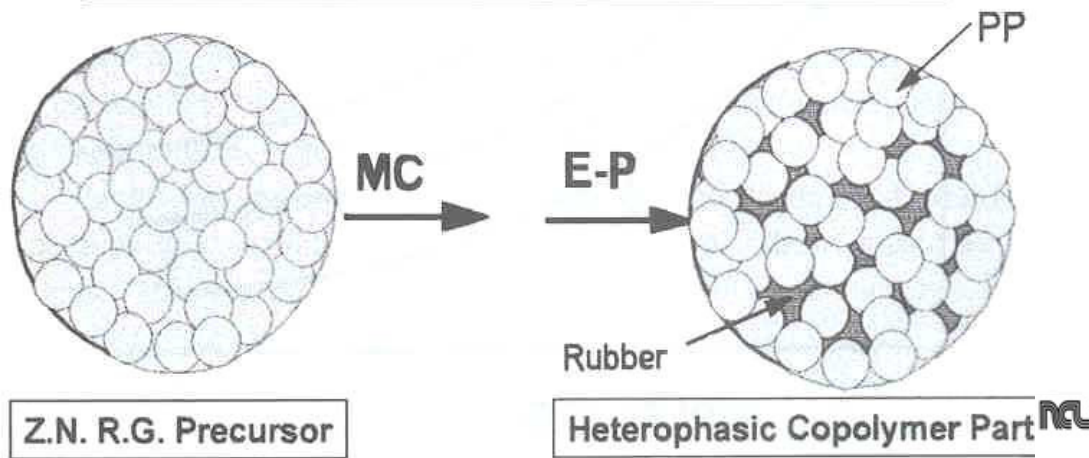
Catalyst	Yield,g	TOF ( per min)	Mn	Mw/Mn
1/ MAO	0.283	20,200	412,000	1.13
Cp <sub>2</sub> ZrCl <sub>2</sub> /MAO	0.258	18,400	157,000	1.73

# PROCESSES : PE/PP

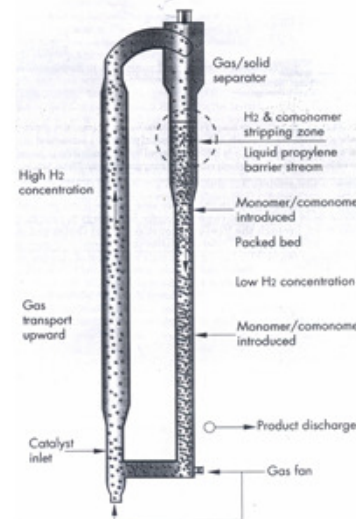


- Large single line capacities ( > 500 ktpa)

## Mixed Catalysis Reactor Granule

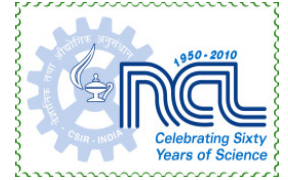


## BASELL'S NEW MZCR REACTOR FOR BIMODAL OR COPOLYMER PP



The multi-zone circulating reactor is a new concept for making PP, replacing a series of separate reactors with a single reactor loop that creates different gas-phase polymerization conditions in the two sides by means of a liquid barrier

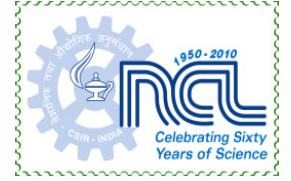
## **METALLOCENE POLYOLEFINS : PROGRESS AND PROSPECTS FOR COMMODITIES**



- Success with LLDPE, HDPE promising, PP disappointing
- Significant market failures : Ethylene-styrene (Dow) and ethylene-carbon monoxide (polyketones, Shell)
- 5 million tons of metallocene LLDPE was consumed in 2009, about 25% of global LLDPE markets
- With the advent of new processing equipment, processability is not as much of an issue as it was when these resins first appeared in the market
- Syndio- and iso-PP introduced in 1994-95. Early difficulties (oriented PP and continuous filament-fiber, limitations in achieving high mw, poor impact copolymer grades) have been resolved. About 1.4 million tons of metallocene PP were consumed in 2009 (< 3% of total PP market)
- Cyclic olefin copolymers (COC, Mitsui-Ticona) and syndiotactic polystyrene (Dow-Idemitsu) are growing, but slowly. Global capacity less than 35,000 tpa. Market development began in 1990 based on pilot plants and commercial plants were built in

***Metallocene polyolefins : Painfully slow growth, struggling to find its unique identity***

## **METALLOCENE POLYOLEFINS - SPECIALTIES**



- Ethylene plastomers and elastomers (VERSIFY-Dow)
- Poly(norbornene)s for microelectronics
- Polyethylene waxes for inks, coatings, adhesives etc.
- Propylene rich EP copolymers – specialty elastomers
- Propylene plastomers
- Olefin copolymers for additives in petroleum products (drag reducers, VI improvers)
- PP with long chain branching

***Small markets, high value and profitable***

## SYNDIOTACTIC POLYPROPYLENE



	iPP( Mg-Ti)	s-PP ( metallocene)
MI g/min	-	5.3
Mw/Mn	8	2.6
<i>mmmm</i> , %	98.6	8.6
<i>rrrr</i> ,%	1.4	91.4
Crystallinity, %	55	21
Density, g/cc	0.91	0.87
Tm	163	125
Flex Modulus, MPa	1170	380
Notched Izod, J/m	25	775
Haze, %	Opaque	20

## COMMERCIAL SINGLE SITE CATALYST BASED PRODUCT AND APPLICATIONS



SSC-based products	Applications / markets
LLDPE	Cast and blown film (often multilayer), extrusion coating, shrink film
HDPE and MDPE (0.935 to 0.960 g/ml)	Rotomolding, injection molding, blow molding, film
VLDPE	Heat-seal layers in packaging films, specialty soft films
ULDPE	PP modification, ETP modification, geomembranes
Ethylene- $\alpha$ -olefin plastomers (0.880 – 0.910 g/ml)	PP modification, controlled permeability packaging films
Ethylene elastomers (ethylene-octene, ethylene-butene)	TPOs and TPVs, particularly for automotive markets
EPDM and very high Mooney EPDM	All traditional EPDM markets

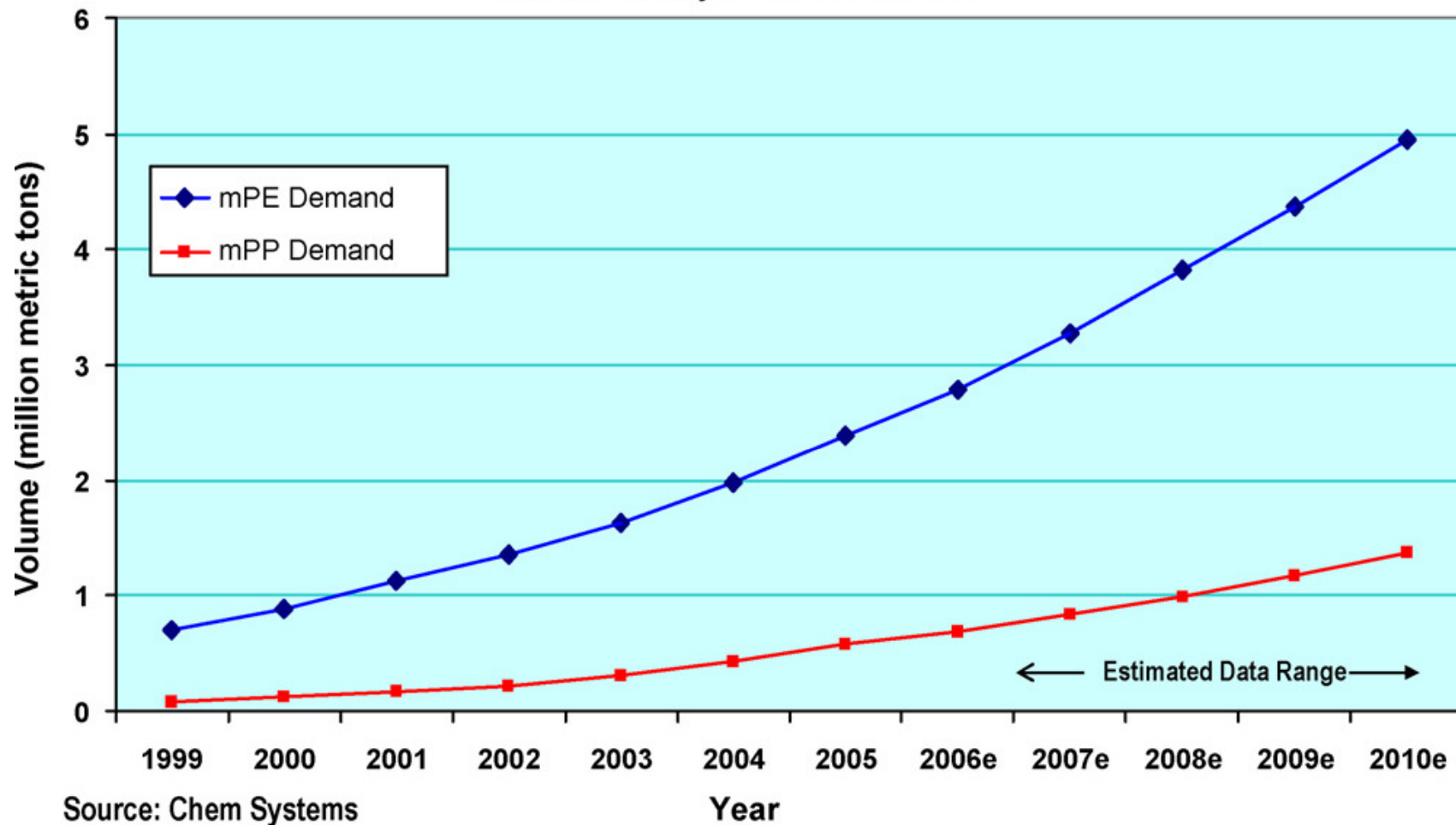
## COMMERCIAL SINGLE SITE CATALYST BASED PRODUCT AND APPLICATIONS



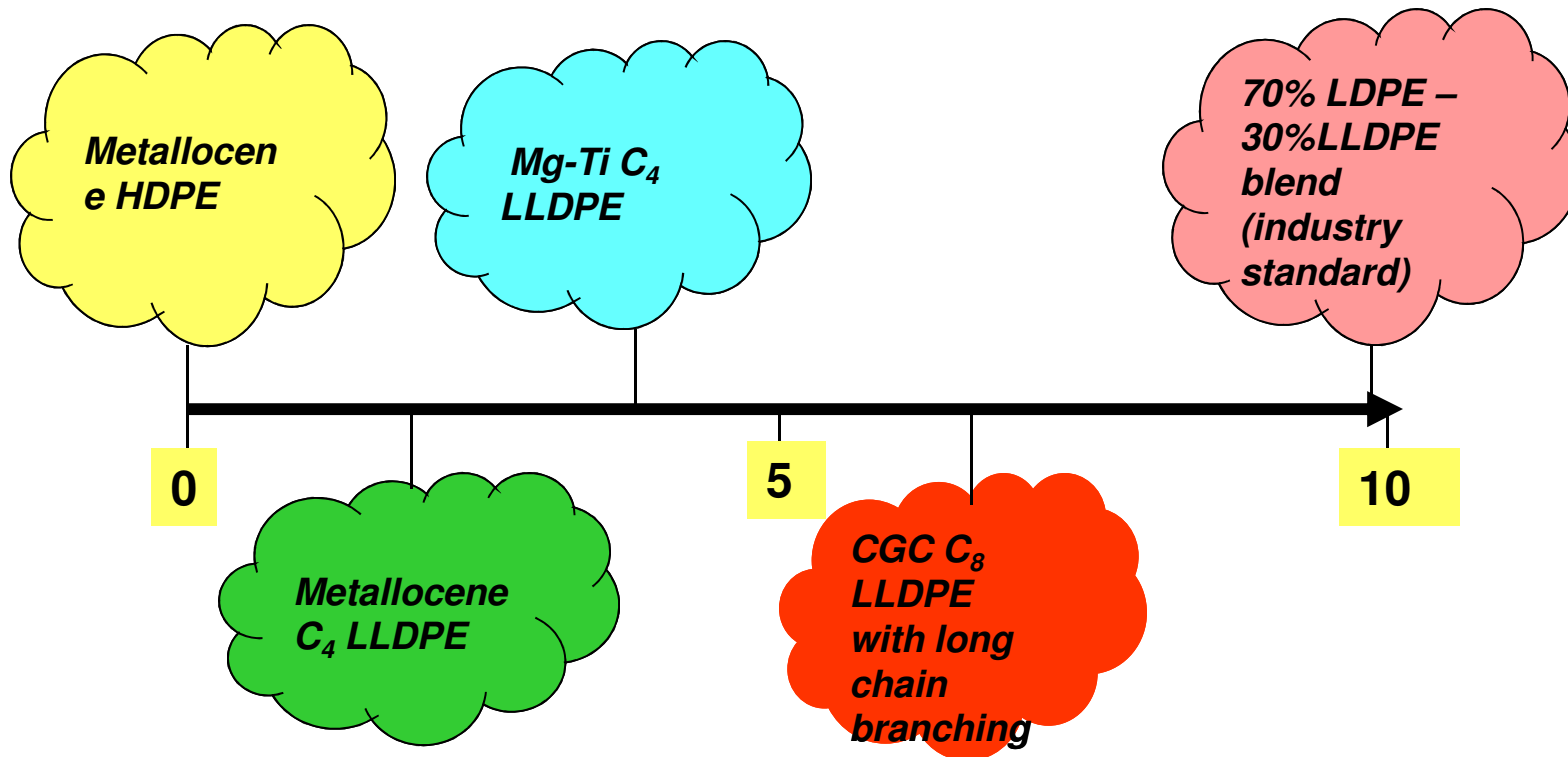
SSC-based products	Applications / markets
Propylene elastomers and plastomers	Elastic cast films, elastic fibers and fabrics, soft touch non-tacky films and moldings, heat-seal layers, polymer modification
Liquid E/P copolymers	Viscosity improvers
PP and PE waxes	Dispersion aids, lubricants, inks, polishes
Isotactic PP homo-, random- and impact-copolymers	Injection molding, non-woven fabrics, fibers, films, automotive interiors
Syndiotactic PP copolymers	Shrink films for labels, injection moldings, adhesives, sheet extrusion
Syndiotactic polystyrene	Engineering plastic competing with nylons, PBT, acetals, PPS and other ETPs
Cyclic olefin copolymers [ethylene with norbornene or tetracyclododecene (TCD)]	Barrier packaging film and sheet, optical media



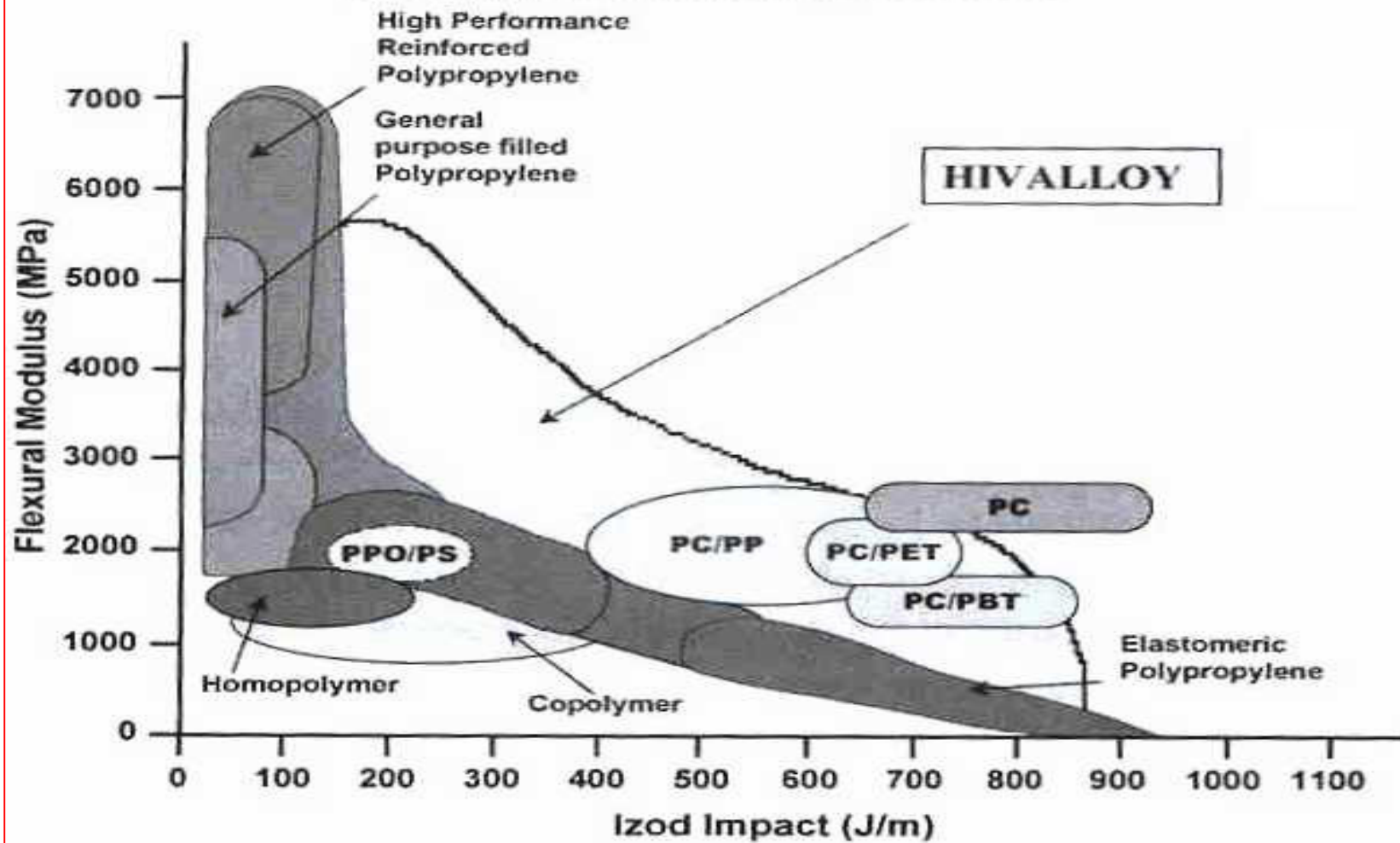
### Metallocene Polyolefins Market Growth



# PROCESSABILITY SCALE



# STIFFNESS-IMPACT CONTOUR MAP ENGINEERING PLASTICS



## **PRODUCTS, PREFERRED PROCESSES AND CATALYSTS**



<b>Product</b>	<b>Gas phase</b>	<b>Slurry phase in light hydrocarbon</b>	<b>Solution phase</b>
<b><i>i</i> - PP</b>	<b>Mg-Ti/ Supported metallocene</b>	<b>Mg-Ti/Supported metallocene</b>	<b>----</b>
<b>Syndio- PP</b>	<b>----</b>	<b>Supported metallocene</b>	<b>----</b>
<b>PP Copolymers</b>	<b>Mg-Ti/ Supported metallocene</b>	<b>Mg-Ti/Supported metallocene</b>	<b>----</b>
<b>Elastomeric PP</b>	<b>Supported metallocene</b>	<b>----</b>	<b>----</b>
<b>HDPE/MDPE</b>	<b>Mg-Ti/ Supported metallocene</b>	<b>Mg-Ti/Supported metallocene</b>	<b>Al-Ti/Metallocene</b>
<b>LLDPE</b>	<b>Mg-Ti/ Supported metallocene</b>	<b>Mg-Ti/Supported metallocene</b>	<b>Al -Ti/Metallocene</b>
<b>VLDPE</b>	<b>?</b>	<b>----</b>	<b>Metallocene</b>
<b>EPDM</b>	<b>Supported metallocene (?)</b>	<b>----</b>	<b>Metallocene</b>

## OLEFIN BLOCK POLYMERS



- Stereoblock copolymers of  $\alpha$ -olefins can be made using the principles of “living “ olefin polymerization
- They comprise of a block of isotactic poly  $\alpha$ - olefin and a block of amorphous polyolefin (either atactic or random copolymer of  $\alpha$ -olefin with ethylene)
- Using the principle of degenerative chain transfer involving a rapidly equilibrating active and dormant chain end, a catalytic route to olefin block copolymers was demonstrated.
- However from a material property point of view a polypropylene rigid block is not interesting in view of its high  $T_g$
- The question is whether one can make a block copolymer with hard and soft segments consisting of ethylene copolymers at high temperatures and in a catalytic fashion ?

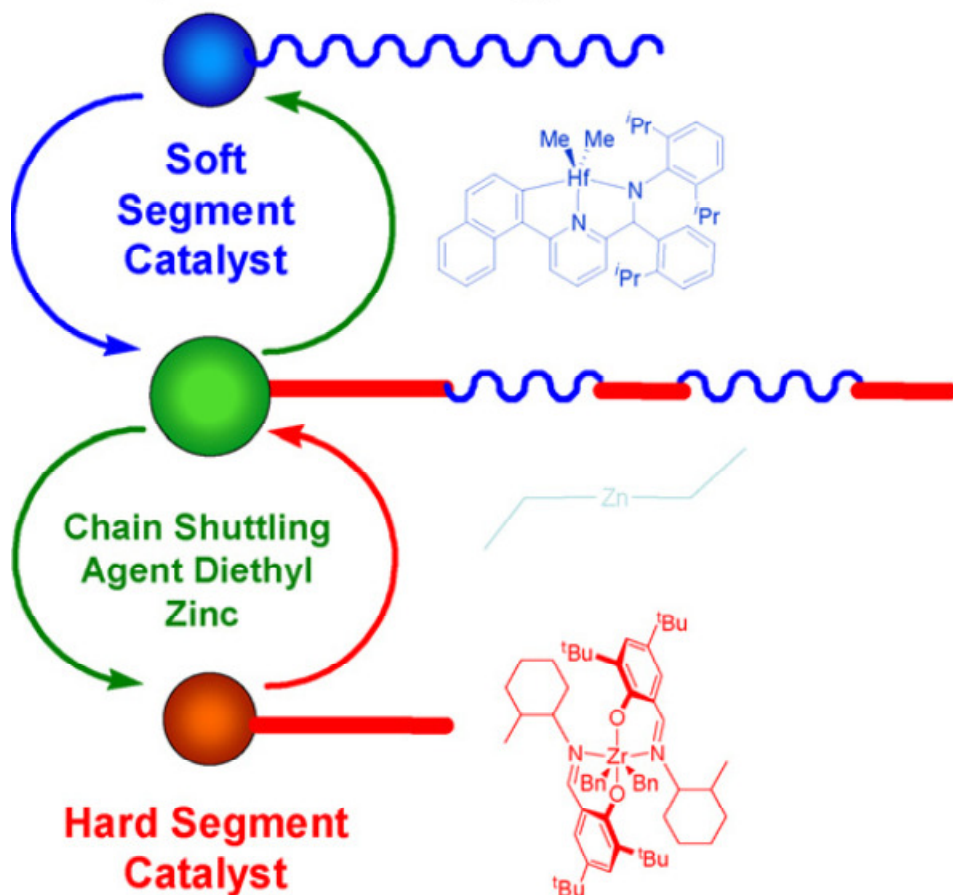
## ***REVERSIBLE CHAIN TRANSFER WITH A DUAL FUNCTIONAL CATALYSIS***



- Combining creatively dual functional catalysts with a reversible transfer process an ethylene based block copolymers has been recently prepared which works at high temperatures
- Polyethylene with low comonomer content are semicrystalline (hard segments) with  $T_m = 135^\circ\text{C}$ , whereas polyethylene with high levels of comonomer content are amorphous (soft segments) with  $T_g < -40^\circ\text{C}$
- This requires two catalyst system which work in parallel in a common reaction environment, one producing the hard segment and the other, the soft segment
- However, if such a process is to lead to a block structure, then each of the growing chain ends must undergo facile transfer of their chain ends. In the absence of such an event, one will end up with a physical mixture of a hard and soft segment polymers
- This requires an appropriate chain transfer agent

**CHAIN SHUTTLING CATALYST, SINGLE REACTOR – DUAL CATALYST  
APPROACH TO MAKE OLEFIN BLOCK COPOLYMERS (ETHYLENE – OCTENE-1,  
INFUSE,DOW)**

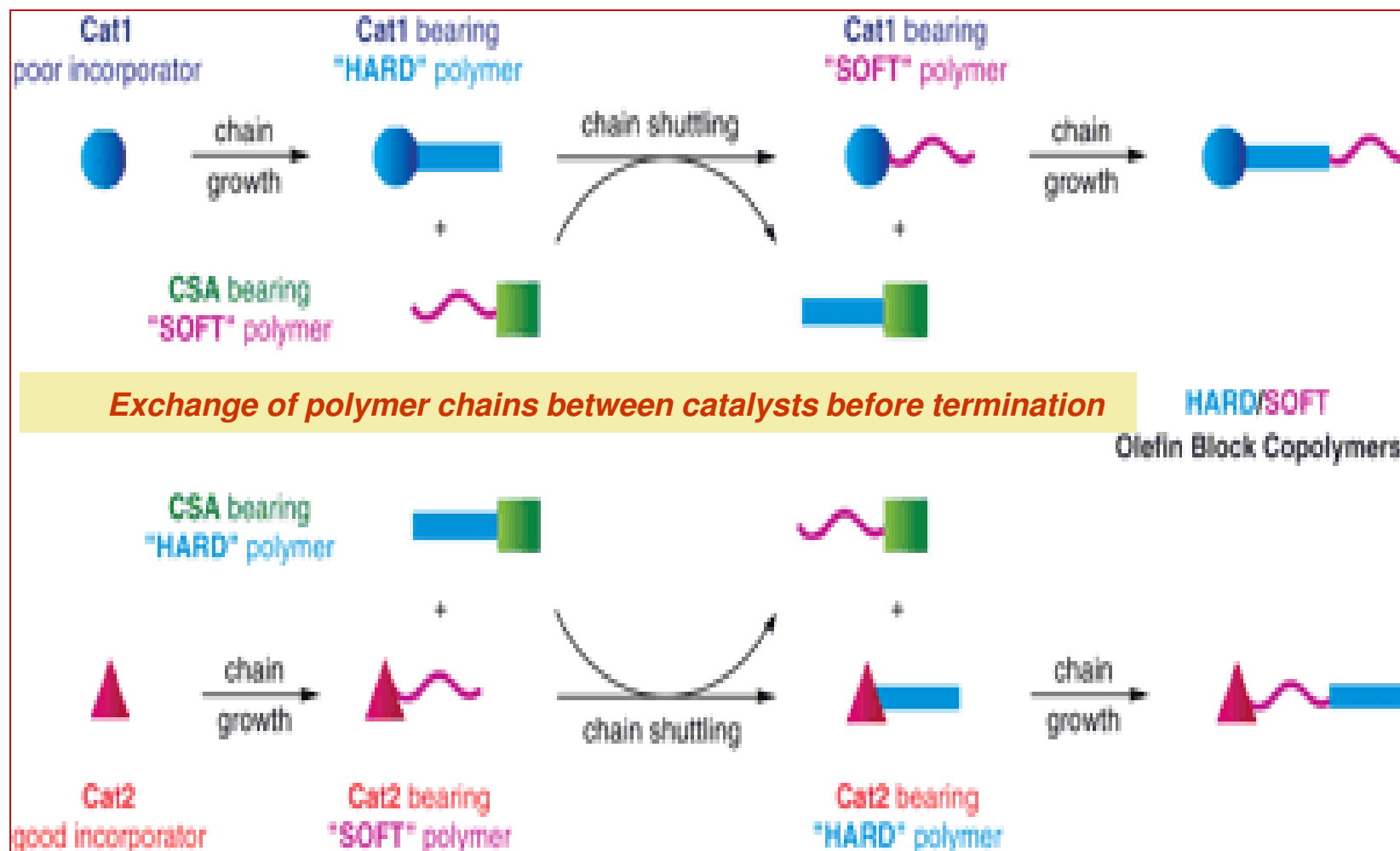
**Catalytic Block Technology**



**Dow Chain Shuttling System**

- Coupled, reversible chain transfer between 2 different catalysts in one reactor
- High catalyst efficiency
- Excellent control of average block lengths
- Excellent control of number of blocks per chain
- Compatible with a wide variety of low cost monomers (octene, butene, etc.)
- Made in Dow's solution process

## CHAIN TRANSFER OR SHUTTLING POLYMERIZATION

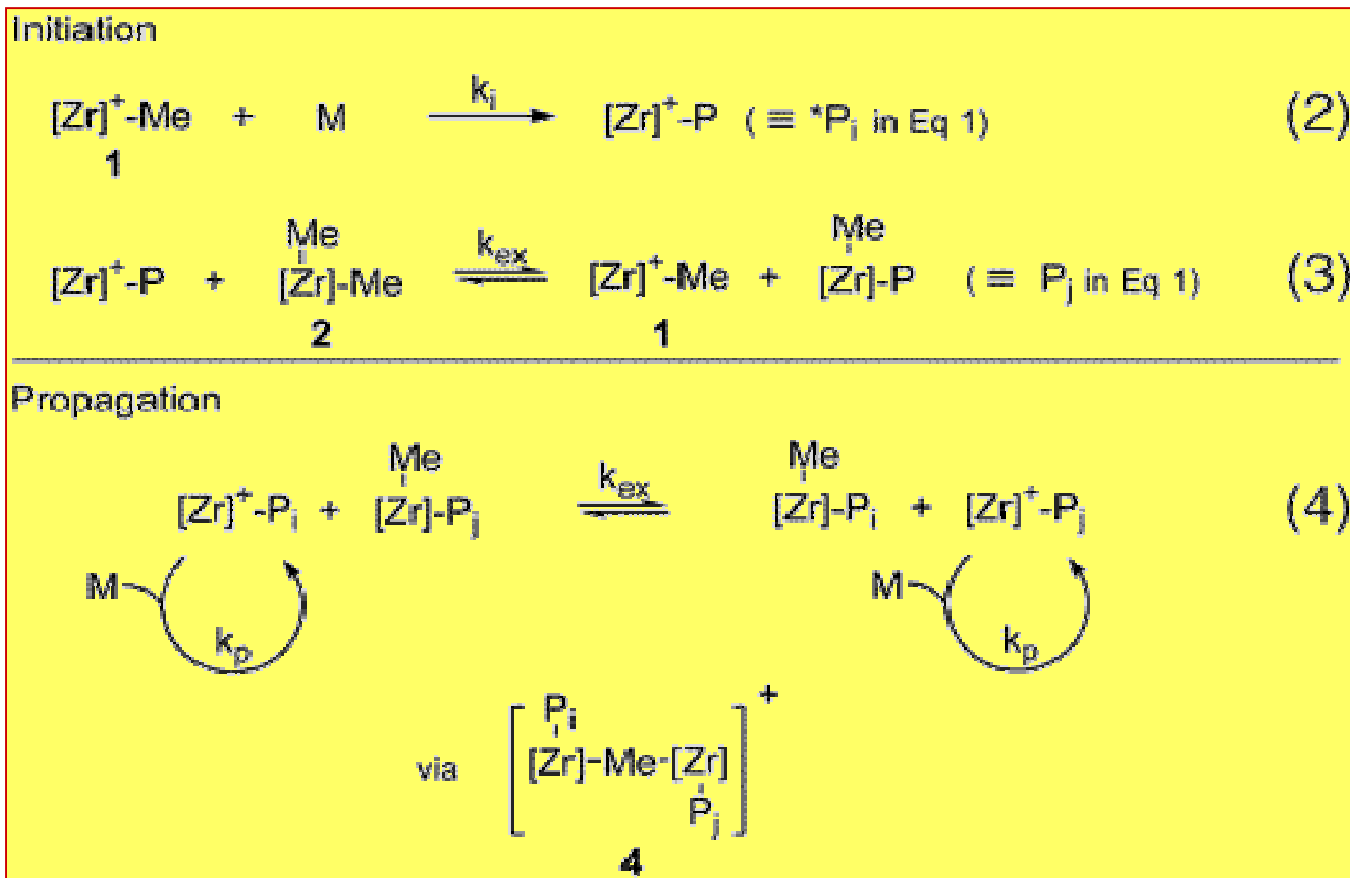


## CHAIN TRANSFER OR SHUTTLING POLYMERIZATION



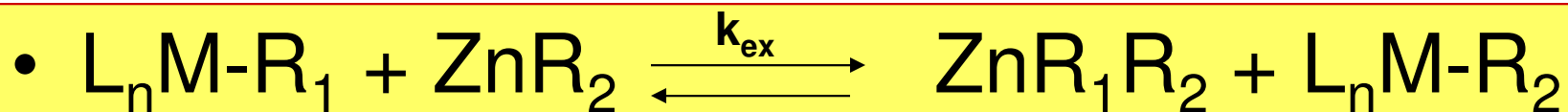
- The chain begins growing on Catalyst 1 as a hard polymer
- The growing chain transfers to the chain transfer agent where it stays for a period as a dormant chain
- The dormant chain may then return to another molecule of the same catalyst and lengthen the hard segment or it may migrate to a molecule of catalyst 2, from which subsequent chain growth results forming a polymer chain with both hard and soft segments
- This process may be repeated any number of times during the lifetime of the chain before termination
- This results in a multi-block copolymer with a most probable distribution of block lengths and number of blocks per chain
- This microstructure is different from those obtained by living polymerization techniques which have a Poisson distribution of block lengths and precise number of blocks
- Unlike Living polymerization, the above mentioned polymerization is truly catalytic
- Fast rate of chain transfer is mandatory for the synthesis of homogeneous copolymers
- The overall composition can be controlled by the relative amount of catalyst 1 and 2. The average length of the blocks, which is a function of the relative rates of chain growth and transfer, can be controlled by adjusting the ratio of concentrations of chain transfer agent and monomer

## REVERSIBLE DEACTIVATION BY DEGENERATIVE TRANSFER



When  $k_i, k_{ex} \gg k_p$ , instantaneous consumption of 1 and 2 will occur to produce a 1:1 mixture of  $[\text{Zr}]^+-\text{P}_i$  (active) and  $\text{Me}-[\text{Zr}]-\text{P}_j$  (inactive) species, both of which can engage in chain growth via degenerative transfer.

## DIETHYL ZINC AS THE PREFERRED CHAIN TRANSFER AGENT



If  $K_{ex} < k_p$  chain transfer dominates

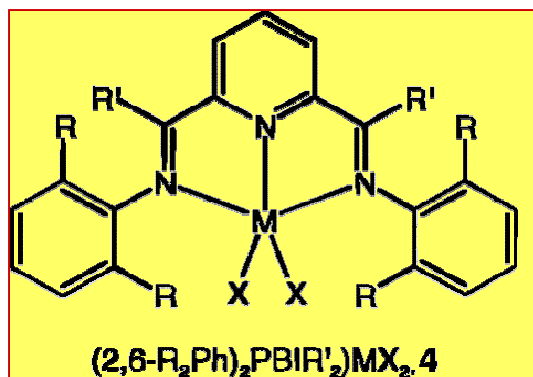
If  $K_{ex} \gg k_p$  catalysed chain growth

- Transition metal catalysts undergo facile transfer to metal alkyls (aluminum alkyl, zinc alkyl)
- If chain transfer to aluminum or zinc is the **sole** chain transfer event and the exchange of the growing polymer chains between the transition metal and the aluminum or zinc is very fast and **reversible**, the polymer chains will appear to be growing on the aluminum or zinc centers. This can be described as the transition metal catalysed chain growth reaction on aluminum or zinc
- Such a chain growth reaction will lead to a Poisson distribution of molecular weights, as opposed to the Schultz Flory distributions of products observed when  $\beta$ -hydrogen transfer accompanies propagation

## DIETHYL ZINC AS THE PREFERRED CHAIN TRANSFER AGENT

- Diethyl zinc fulfills many of the criteria needed for accomplishing these conditions
- The bond energies and polarities of the Zn-C bond is very similar to many transition metal- carbon bonds

*Toluene, 5  $\mu$ mol of catalyst, 100 equiv of MAO, 25°C, 1 atm*



**R = Ethyl, M = Fe**

Diethyl Zinc, equiv	Activity	Mn	Mw/Mn	Vinyl chain ends	Saturated chain ends
0	1204	1000	20	0.20	2,7
500	1404	700	1.1	0.23	38.7

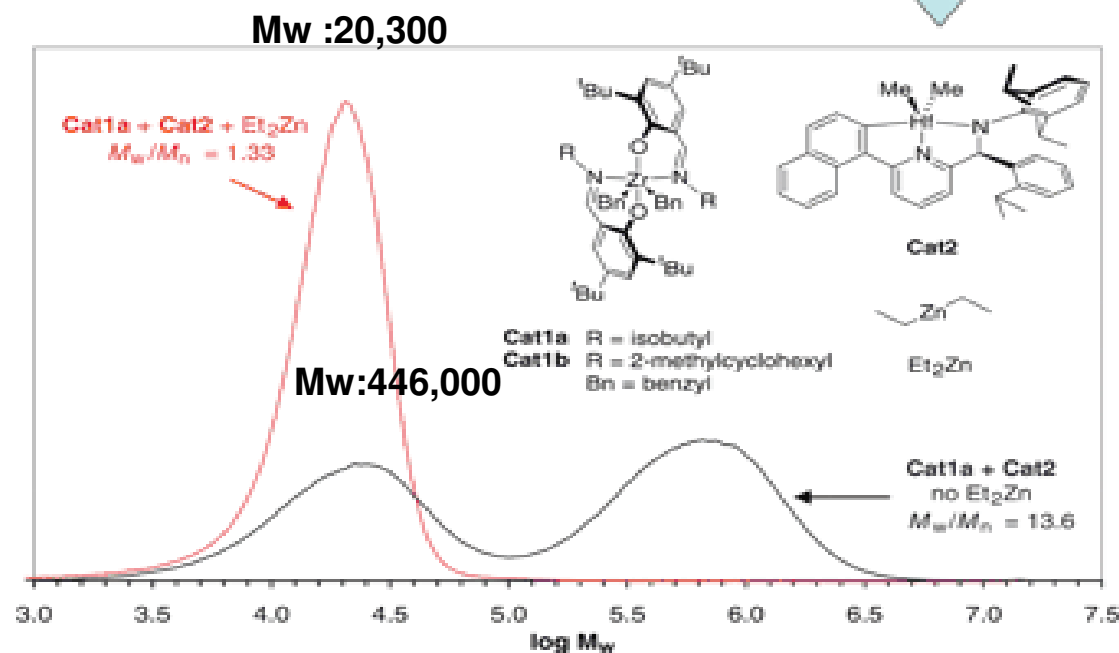
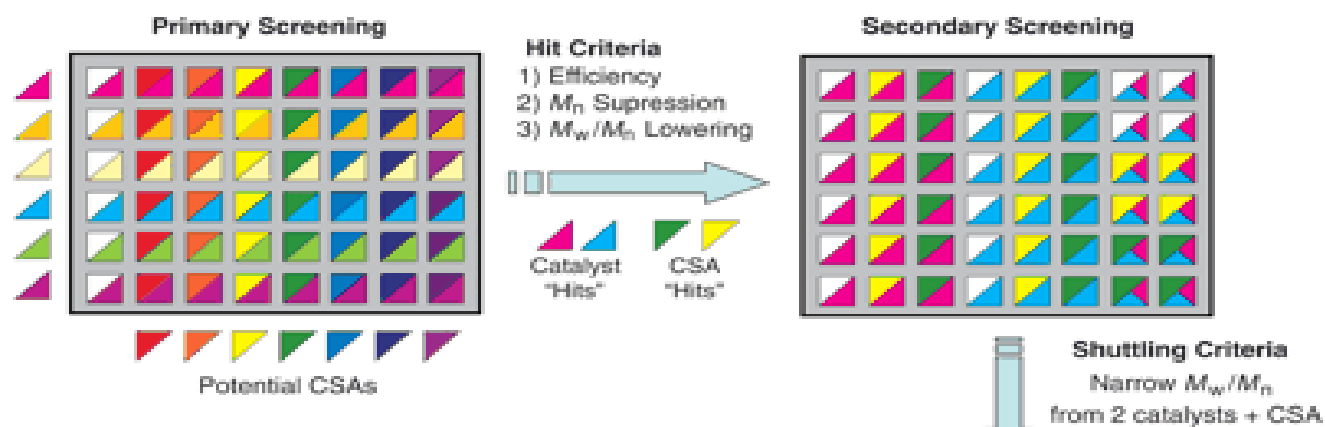
- The above reaction is an iron catalyzed chain growth reaction on zinc, which after hydrolysis yields linear alkanes
- However this behavior is not applicable to all polymerization catalysts. Hafnium phenoxyimine and Fe(II) pyridyl imine complexes exhibit this characteristic

*JACS 127,9913 (2005)*

# HIGH THROUGHPUT COMBINATORIAL METHODS FOR THE IDENTIFICATION OF CATALYST 1 AND 2 AND CHAIN TRANSFER AGENT

➤ 1600 individual composition of catalysts and chain transfer agents were screened in about three weeks

➤ Reduction in  $M_n$  accompanied by a narrowing of polydispersity was used as the diagnostic for efficient chain transfer

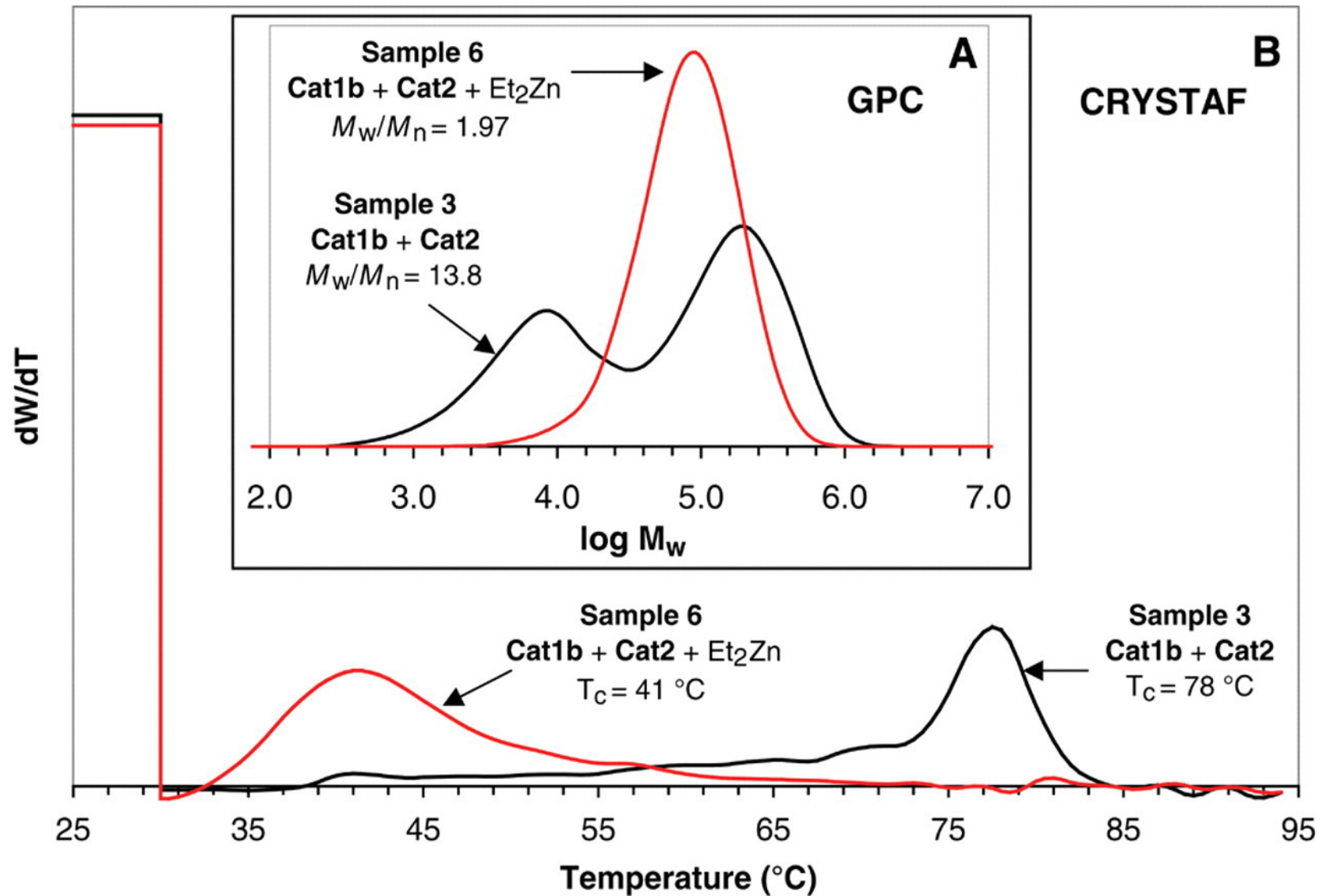


## **BLOCK COPOLYMERS VIA TRANSITION METAL CATALYZED CHAIN GROWTH ON ZINC**



- The process described can be efficiently conducted in a continuous mode of operation, wherein build up and decay rate is held constant by a continuous supply and withdrawal of catalyst
- The hard and soft segments consist of ethylene – octene-1 copolymers, the individual blocks containing different composition of the comonomer
- The catalyst system chosen permit the reaction to be conducted at 140° C to prevent the polymer from precipitation
- The process is catalytic with respect to hafnium and zirconium (approximately 250 chains per total catalyst) and stoichiometric with respect to zinc (two chains per zinc)
- Reversible chain transfer appears more efficient in a continuous mode since the reactor is populated with a steady state concentration of zinc polymeryl species. In a batch process, in the initial stages the concentration of zinc-polymeryl species is not large and hence only chain growth predominates, not exchange
- Narrow molecular weight distribution can be achieved by a rapid chain exchange reaction between two different catalysts. However, the same chemistry when extended to a continuous process results in a Schultz Flory distribution simply because there is a distribution of residence time in a continuous reactor. This is not really a disadvantage since we need for practical use a broader distribution of molecular weights

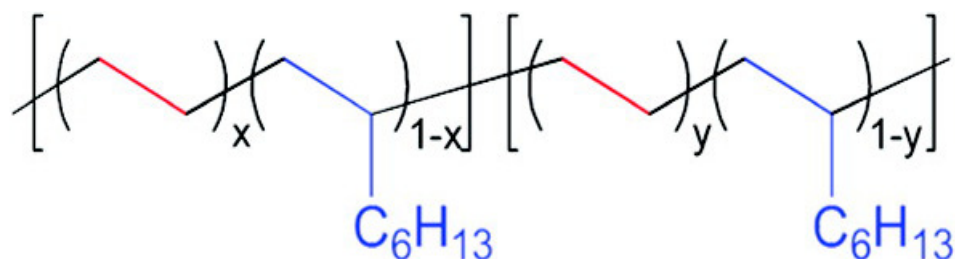
# BLOCK COPOLYMERS VIA TRANSITION METAL CATALYZED CHAIN GROWTH ON ZINC



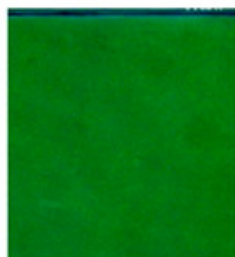
## PHOTONIC POLYETHYLENE FROM SELF-ASSEMBLED MESOPHASES OF POLYDISPERSE OLEFIN BLOCK COPOLYMERS

Phillip D. Hustad, Gary R. Marchand, Eddy I. Garcia-Meitin, Patricia L. Roberts, and  
Jeffrey D. Weinhold

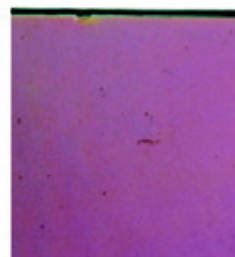
*Macromolecules*, **Article ASAP** • DOI: 10.1021/ma9002819 • Publication Date (Web):  
21 April 2009



$M_n < 70 \text{ kg/mol}$ , PDI  $\sim 2$



reflected colors



transmitted colors



Blue Morpho Butterfly



## ***SOME COMMERCIAL METALLOCENE CATALYST BASED PRODUCTS***

- EXXPOL based on X CAT HP ( Univation) for gas phase LLDPE and HDPE
- PRODIGY ( Univation) dual site catalyst for bimodal HDPE
- LUMICENE (Total) range of catalysts for PP, HDPE , MDPE nad LLDPE
- INSITE (Dow) for solution LLDPE
- ELITE (Dow) enhanced PE for oriented shrink films
- XLA (Dow) for fiber applications
- VERSIFY, AFFINITY (Dow) propylene-ethylene elastomers
- TAFMER (Mitsui) Propylene- butene copolymer
- VISTAMAXX ( Exxon Mobil) Ethylene-propylene copolymer
- INFUSE (Dow) Olefin Block Copolymers



## **EMERGING POLYOLEFIN SPECIALTY PRODUCTS**

- **High melt strength branched PP**
- **Rotomolding and thermoforming grades of PP**
- **Non crosslinked PE pipes for hot water transmission**
- **High speed BOPP resins with < 2 % soluble fraction for food packaging applications**
- **Low VOC reactor PP to replace CR-PP**
- **Oxygen barrier Polyolefins for packaging**
- **EVA (DuPont, Solutia) and polyolefin based films for solar wafer encapsulants**
- **Porous Polyolefins ( multilayer PE-PP) for separator films for Lithium ion battery( Ube, Asahi)**
- **Natural Fiber reinforced PP composites ( Jute, Sisal, Coir, pineapple fiber)**

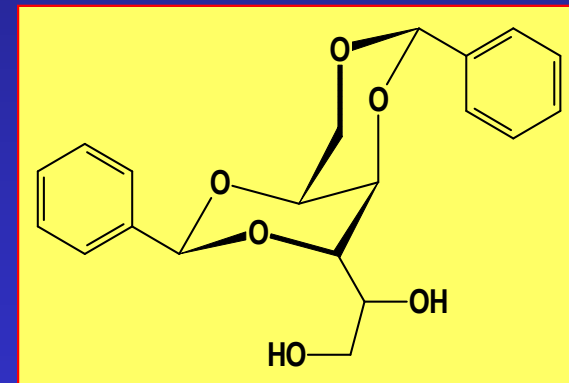
## **PROPYLENE-ETHYLENE VS PROPYLENE –BUTENE-1 COPOLYMER**



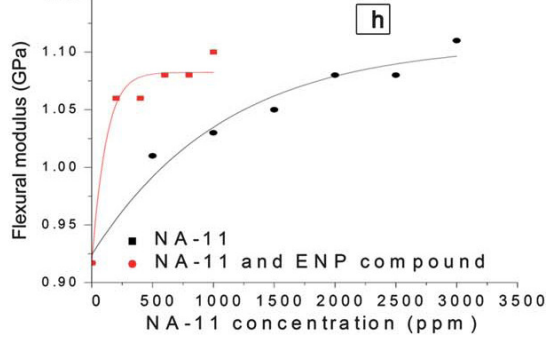
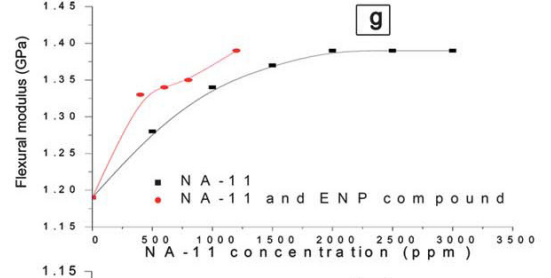
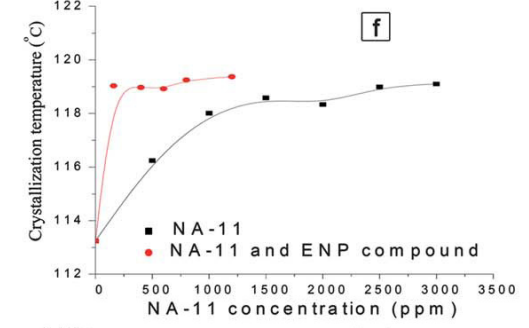
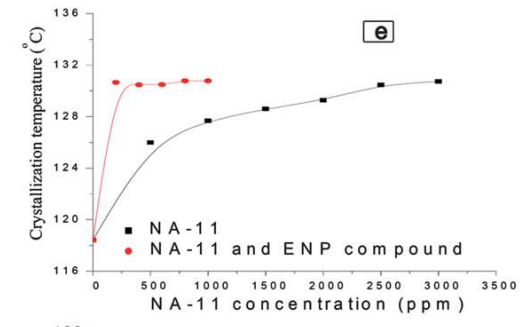
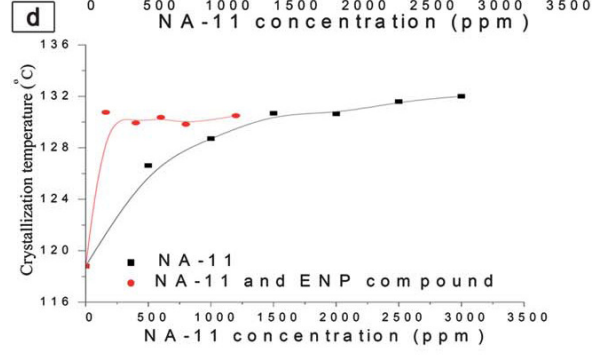
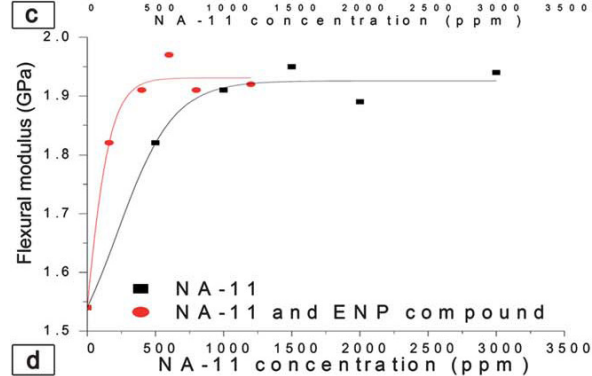
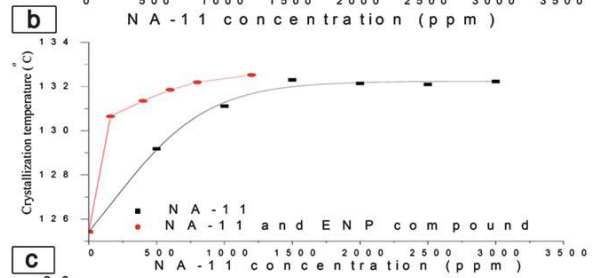
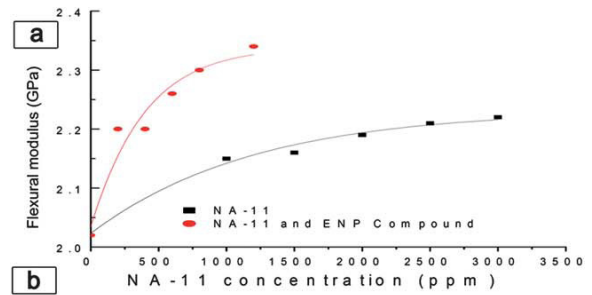
<b>Comonomer</b>	<b>Ethylene</b>	<b>Butene-1</b>
Melt flow index (g/10 min @190 °C)	2.8	3.0
DSC melting point (° C)	133	133
Secant flexural modulus (MPa)	524	690
Xylene solubles at 23° C (%)	10.5	7.0
n-Hexane extractables at 50° C(%)	2.8	1.3
Comonomer content : wt%	5.8	15
Comonomer content - mol %	8.0	12

## ***ADDITIVES : NUCLEATING AGENT (NA) FOR PP***

- Homogeneous and heterogeneous nucleating agents
- Improved dispersion of heterogeneous nucleating agents
- Use of NA as microemulsion in water
- Use of Xerogels of DBS
- In-situ nucleation



***Clarity of random PP extrusion blow molded products can now exceed PET With superior organoleptic properties with advanced clarifiers***



## **FURTHER READING**

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- Recent advances in polyolefin technology, J. Qiao et al, *Poly. Chem*; DOI:10 1039/Copy 00352b, 18 March 2011
- Metallocenes rise again, A. H. Tullo, *C&E News*, 88, 10-16 (2010)
- Recent progress in olefin polymerization catalyzed by transition metal complexes : new catalysts and new reactions, D. Takeuchi, *Dalton Trans.*, 39 311-328 (2010)
- Olefin polymer technologies: History and recent progress, P.S. Chum and K.W. Swogger, *Prog. Polym. Sci.*, 33 797-819 (2008)
- Nonbridged half metallocenes containing anionic ancillary ligands: New promising candidates as catalysts for precise olefin polymerization, K. Nomoura et.al, *J. Mol. Cat. A: Chemical* 267, 1-29 (2007)



***THANK YOU***

