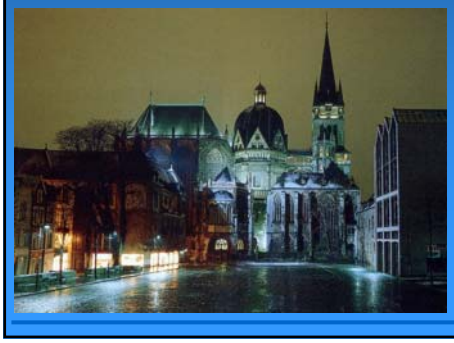
Homogeneous Polymerization Catalysts: New Materials Through Mechanistic Insights

1. Singapore Catalysis Forum
April 17, 2008



Jun Okuda
Chair of Organometallic Chemistry
RWTH Aachen University
Germany

Outline

Olefin Polymerization Catalysis

Single-Site Polymerization Catalysts

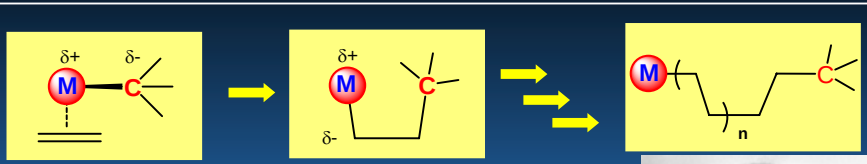
Stereoselective Polymerization of Styrene

Single-Site Catalysts for the
Isospecific Styrene Polymerization

Stereoselective Polymerization of Lactide

Initiators for the Heteroselective
Ring-Opening Polymerization of *rac*-Lactide

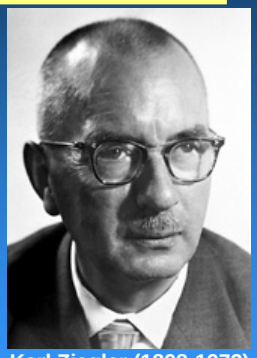
Coordinate Polymerization: Ziegler Catalysts



"Ionic" "Hard" "Soft" "Covalent"

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu									



Karl Ziegler (1898-1973)

Honor. Professor RWTH Aachen

Nobel Prize 1963

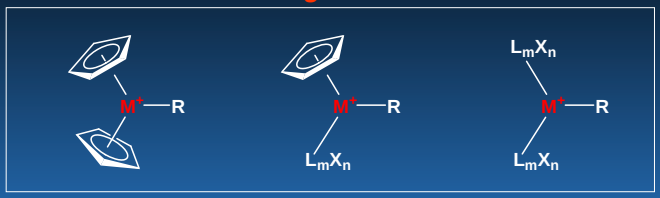
Polyethylene (PE)

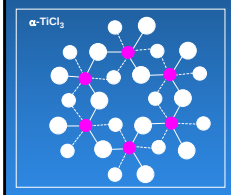
Polypropylene (PP)

>125,000,000 t/a 60% of the total polymer production

Single-Site Polymerization Catalysts

Single Site





Active Sites

Lewis Acidity/Electrophilicity: Preferably Cationic Metal

Facile Activation by Cocatalysts (AlR_3, MAO, $MgCl_2$, …)

Multiple Sites

Stereochemical Regulation

Enantiofacial Discrimination of Prochiral α-Olefins

Enantiomorphic Site Control

Chain End Control

Stereoselective Propylene Polymerization

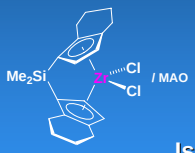
Walter Kaminsky

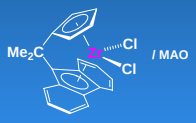
Hans-H. Brintzinger

(r m r m) r r

atactic

Low T_m





Isotactic

Syndiotactic

(m m m m) m m

T_m = 165 °C

(r r r r) r r

T_m > 150 °C

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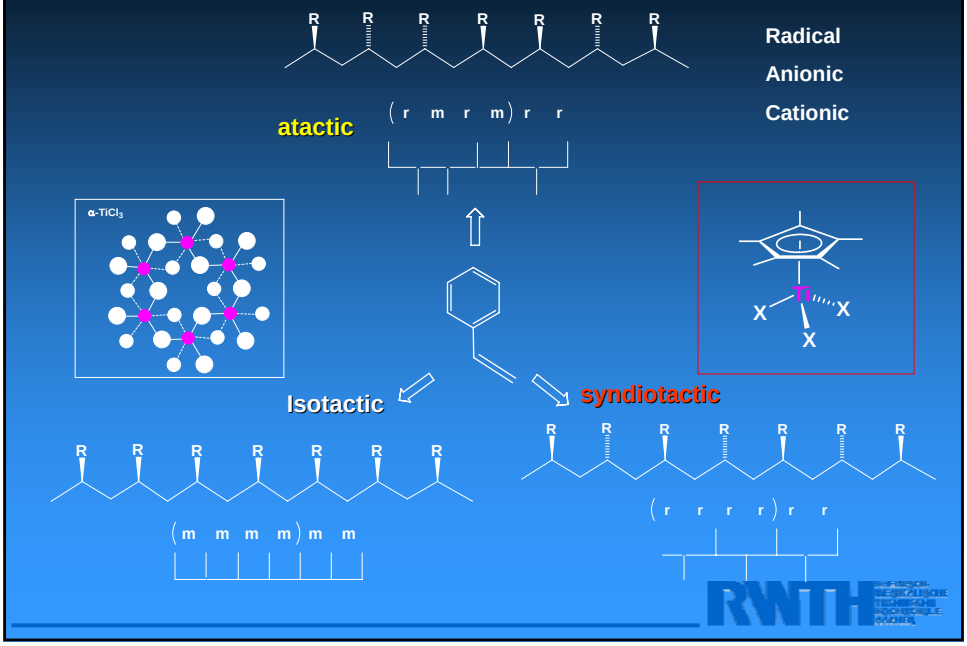
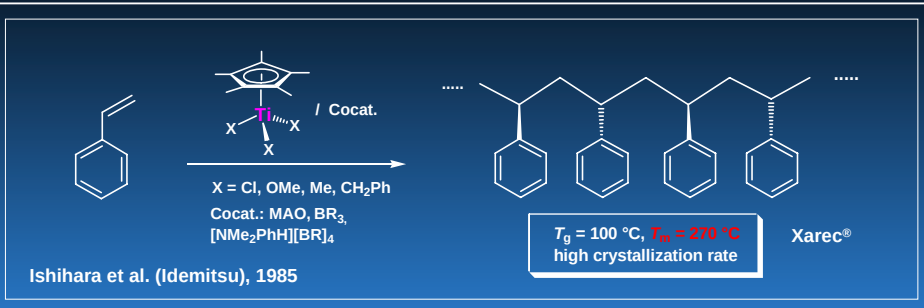
Stereoselective Styrene Polymerization

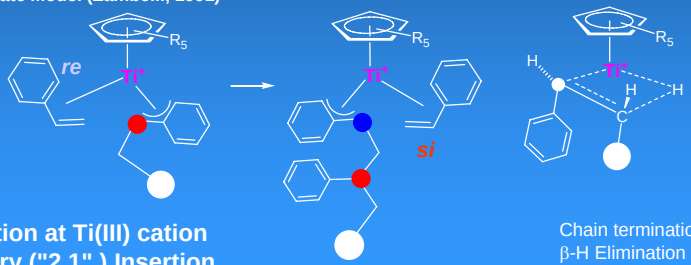


Syndiospecific Styrene Polymerization



Ishihara et al. (Idemitsu), 1985

Transition State Model (Zambelli, 1991)



cis-Addition at Ti(III) cation
Secondary ("2,1") Insertion
Markovnikov Regiochemistry

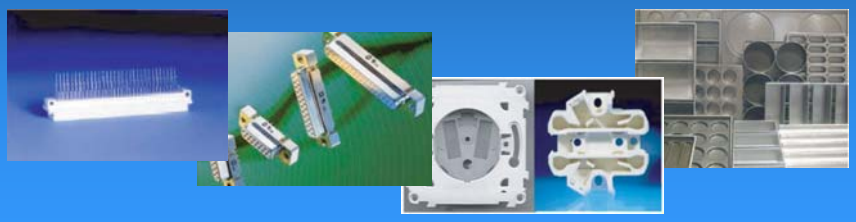
Chain termination by
β-H Elimination

Syndiotactic Polystyrene: Application

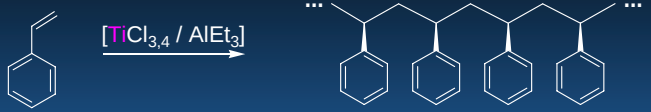
- **sPS Production**: Idemitsu and Dow Plastics
  World market: 5000 t/a (1996)
  20-80,000 t/a (2000-2002)
  15,000 t/a (2005) **?!**

- **High-tech engineering material** thermomechanical properties (high melting transition; brittleness) to be improved for easier processing

- **sPS Applications**: electronics, food contact and consumer uses



Stereoregular Styrene Polymerization



Isotactic (iPS)
T_g = 92 °C, T_m = 240 °C
low crystallization rate

Natta, Corradini, *Makromol. Chem.* 1955:
„Kristallstruktur des isotaktischen Polystyrols“

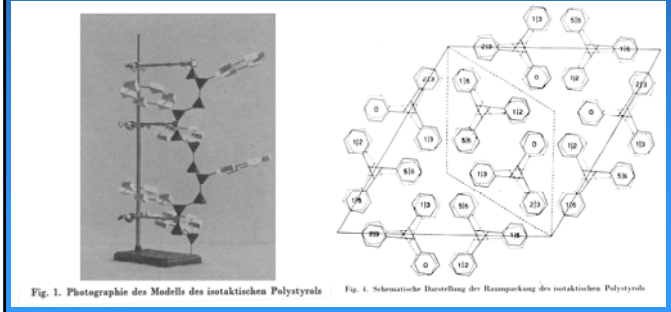
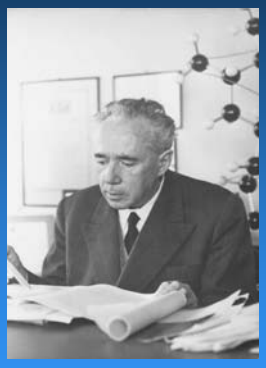


Fig. 1. Photographie des Modells des isotaktischen Polystyrols

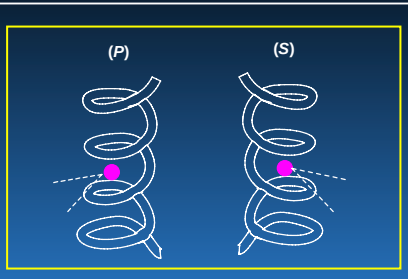
Fig. 4. Schematische Darstellung der Raumpackung des isotaktischen Polystyrols

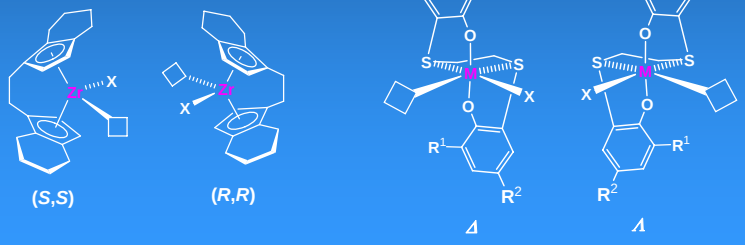


Giulio Natta (1903-1979)
Nobel Prize 1963

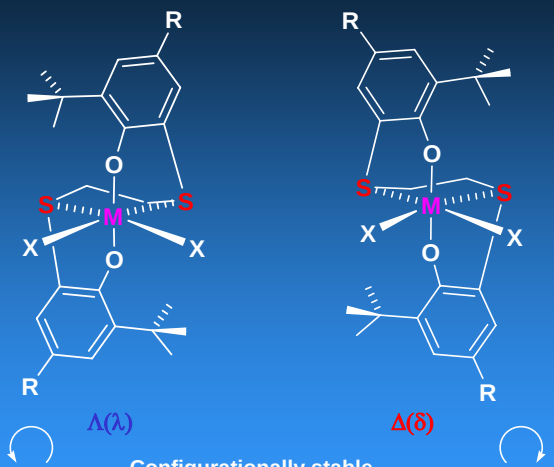
Chiral Metal Sites in an Helix

Chiral recognition of a (pro)chiral substrate in a groove of an **helix**



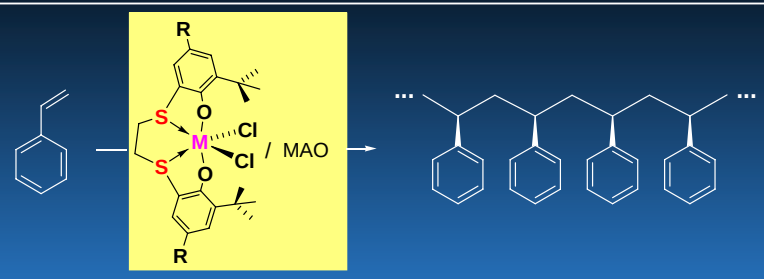


Configurational Stability of C_2-Symmetrical Complexes

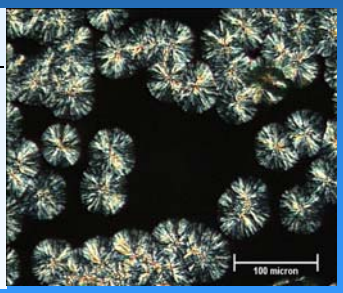


Configurationally stable
on the NMR time scale:
No racemization up to 100 °C

Isospecific Styrene Polymerization

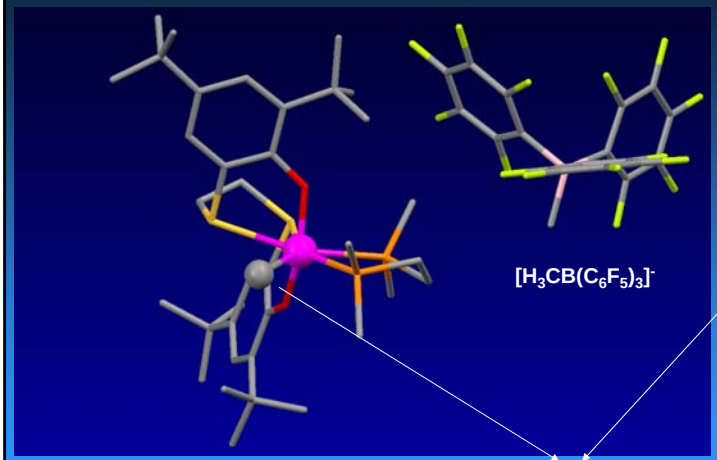


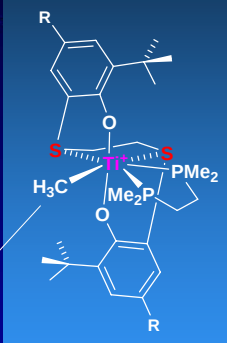
MX_2	Activity, g PS/mmol M h	M_n 10^{-4}	M_w/M_n	T_m, °C
$TiCl_2$	5400	265.4	2.0	223
$Ti(OiPr)_2$	1999	171.8	1.8	223
$Zr(CH_2Ph)_2$	77	16.3	1.9	218
$Hf(CH_2Ph)_2$	32	4.0	1.9	220



J. Am. Chem. Soc. **2003**, *125*, 4964

Characterization of a Stable Methyl Cation





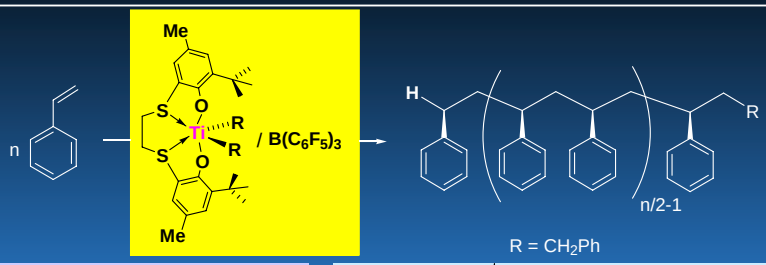
$\Delta(\delta)$

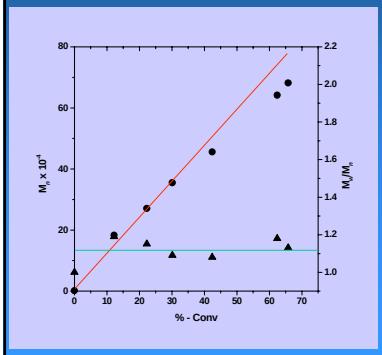
distorted pentagonal bipyramidal

^{1}H NMR: 1.32 ppm
^{13}C NMR: 88.6 ppm
^{31}P NMR: 19.8, 32.8 ppm

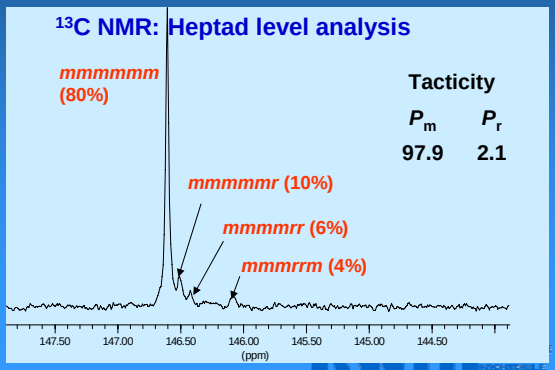
Angew. Chem. Int. Ed. **2007**, *46*, 8507.

Living Isospecific Styrene Polymerization





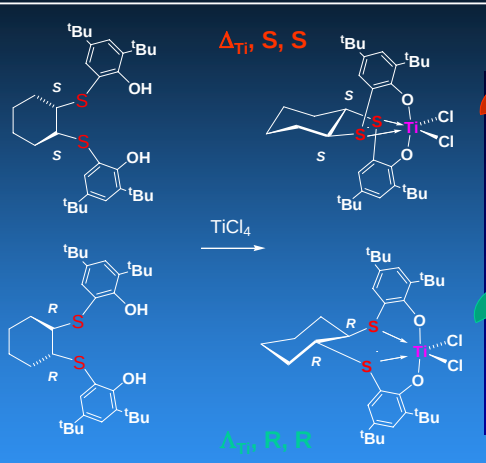
^{13}C NMR: Heptad level analysis

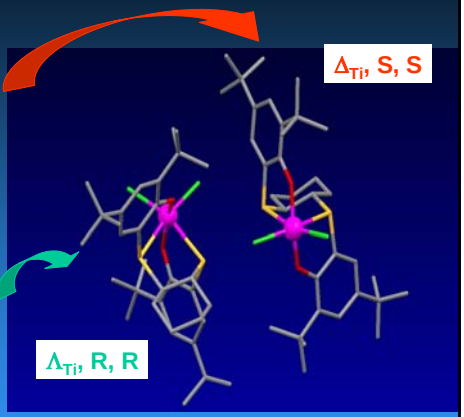


Tacticity	
P_m	P_r
97.9	2.1

Organometallics **2006**, *27*, 3019

C_2-Symmetrical Complexes: Diastereoselective Coordination



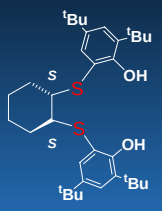


Racemic, *trans*

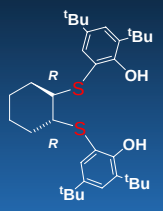
Possible Isomers	
Δ, S, S	Λ, R, R
Λ, S, S	Δ, R, R

Only one diastereomeric pair observed!

C_2-Symmetrical Complexes: Optical Activity



$[\alpha]_D^{25}$ = -74.3 ° ; mp = 115 °C



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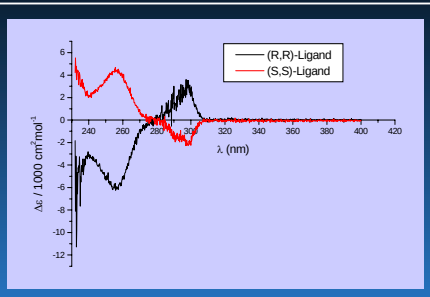
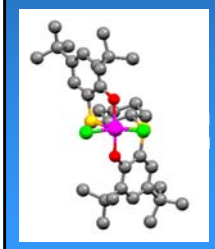
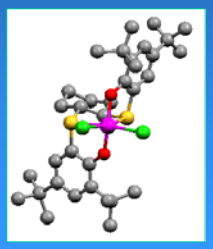




$[\alpha]_D^{25}$ = -140 ° (CH_2Cl_2)



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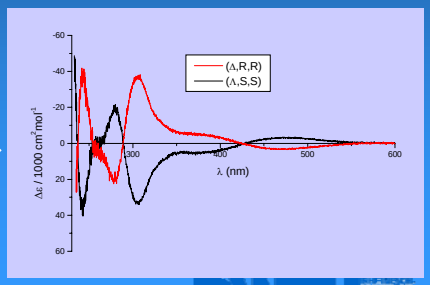
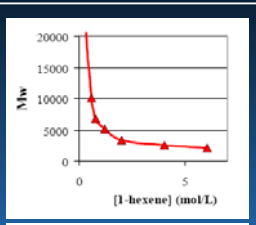
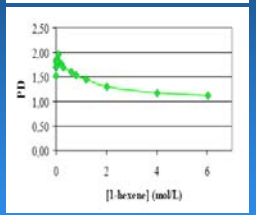


Isotactic Polystyrene: Chain Transfer by 1-Hexene

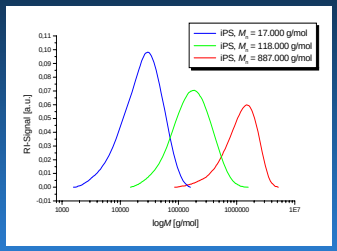
[1-hexene]:[styrene]	M_n
0	887,000
0.01	160,000
0.03	118,000
0.14	17,000

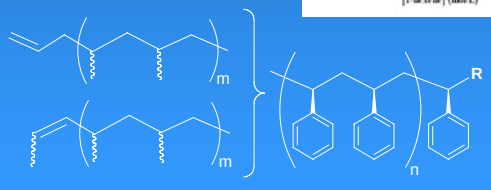
M_w/M_n = 1.5–1.8





HT GPC in 1,2,4-Trichlorobenzene;
RI Detection, PS Calibration



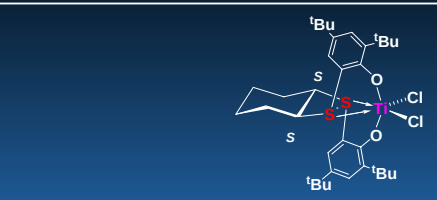


Growing iPS chain terminated by fast β-H elimination after α-olefin insertion

Isotactic Polystyrene with Oligopropylene Endgroups:

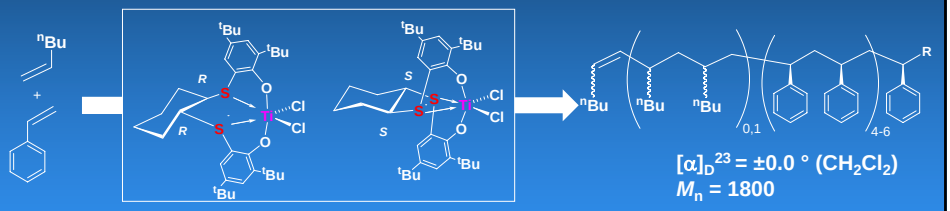
Macromolecules **2004**, *37*, 8918

Stereospecific Oligomerization



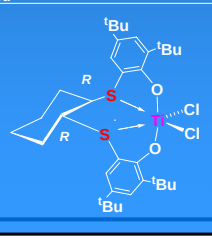
(+) Δ, S, S

$[\alpha]_D^{23}$ = +4.7(2)° (CH_2Cl_2)
$[\phi]_D^{23}$ = +90.7(1)° (CH_2Cl_2)



$[\alpha]_D^{23}$ = ±0.0 ° (CH_2Cl_2)
M_n = 1800

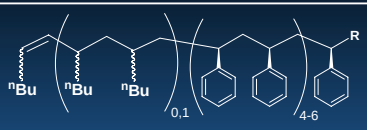
Racemate

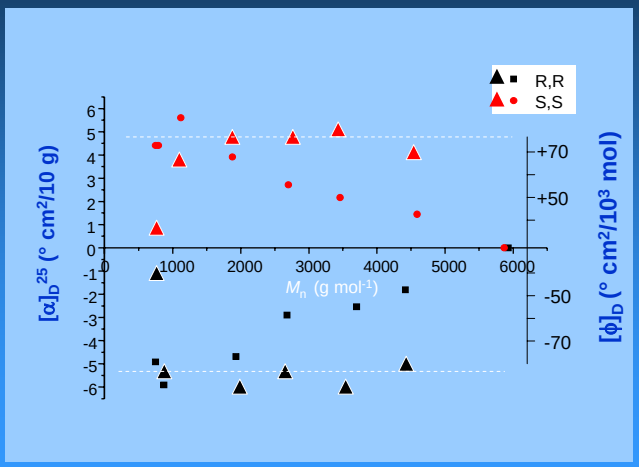


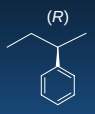
(-) Λ, R, R

$[\alpha]_D^{23}$ = -3.9(2)° (CH_2Cl_2)
$[\phi]_D^{23}$ = -73.3(2)° (CH_2Cl_2)

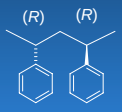
Stereospecific Oligomerization







$[\alpha]_D^{20}$ -6.2 ($CHCl_3$)
$[\phi]_D$ = -8.3



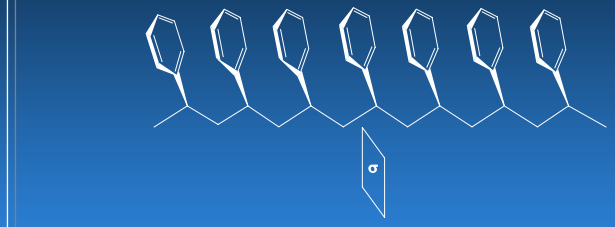
$[\alpha]_D^{30}$ -38.2 ($CHCl_3$)
$[\phi]_D$ = -85.7

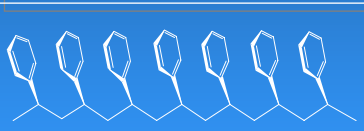
Angew. Chem. Int. Ed. **2007,** 119, 4790

Optically Active Isotactic Polystyrene ?

For **Homochiral** Isotactic Polystyrene No Optical Activity Observed

Cryptochirality

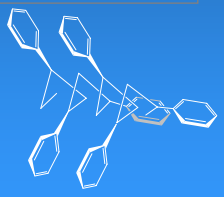




statistical coil
or
zigzag chain

?

nucleation



One-handed 3_1 Helix

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Single-Site Polymerization Catalysts

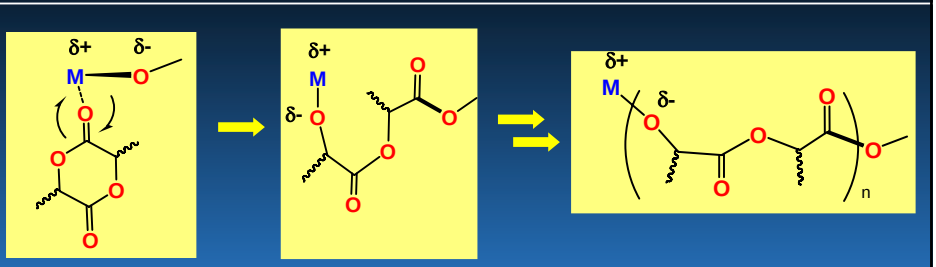
Stereoselctive Polymerization of Styrene

Single-Site Catalysts for the
Isospecific Styrene Polymerization

Stereoselective Polymerization of Lactide

Initiators for the Heteroselective
Ring-Opening Polymerization of *rac*-Lactide

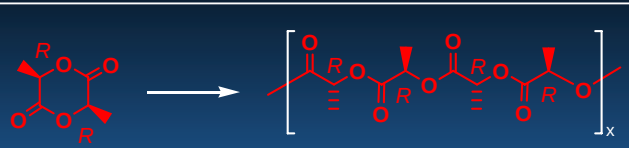
Ring-Opening Polymerization of Lactide



Characteristics:

- Controlled/living polymerization
- Large number of initiators (Al, Zn, Mg, Ca, Fe,..)
- Recent commercialization using Sn initiators
  Monomer from ***biorenewable*** sources (**Biorefinery**)

Polylactide



***(R)-L* Lactide**

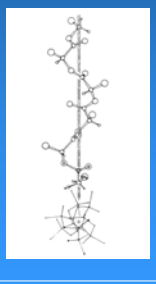
[RRRR]$_x$
isotactic ***PLLA***

PLLA can be processed like thermoplastics into **fiber** (using conventional melt spinning processes) and **film** (T_g = 50-65°C ; T_m = 170-190 °C)

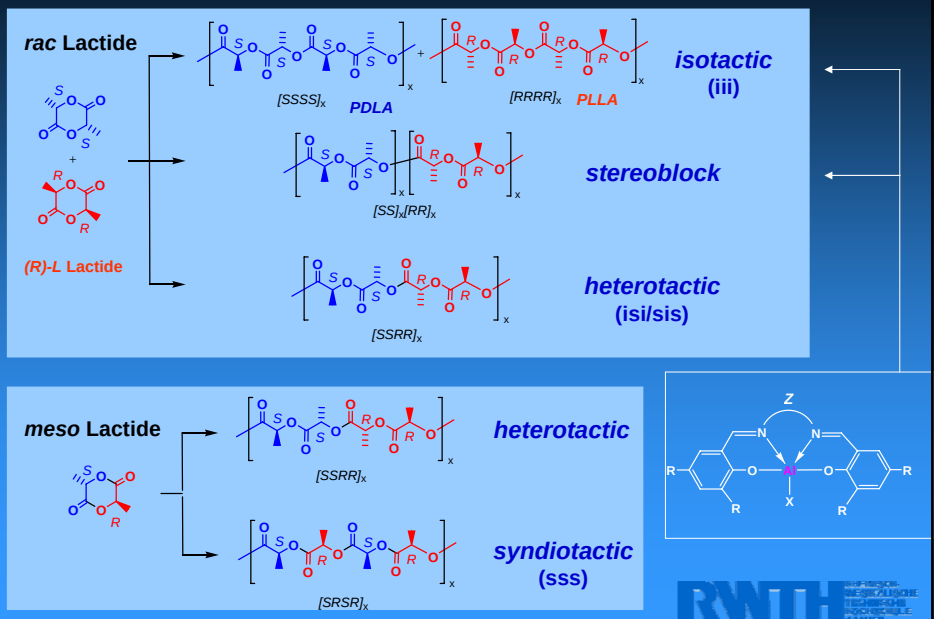
By physically blending the polymer with ***PDLA***

T_m can be increased to maximum of 230°C
T_g can be increased to up to 190 ° C

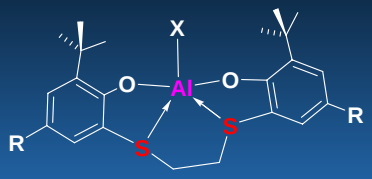
• **3_1 or 10_3 Helix**



Ring-Opening Polymerization of Lactide

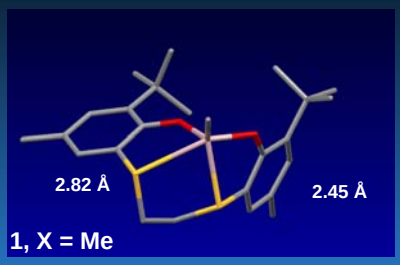


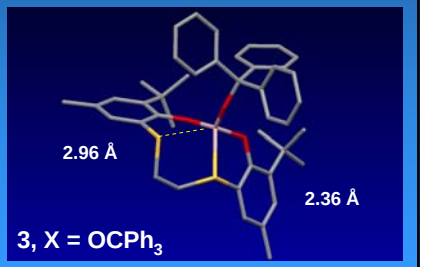
Ring-Opening Polymerization of Lactide



X = 1, Me; 2, Et; 3, $OCPh_3$

Distorted tetrahedral; highly fluxional



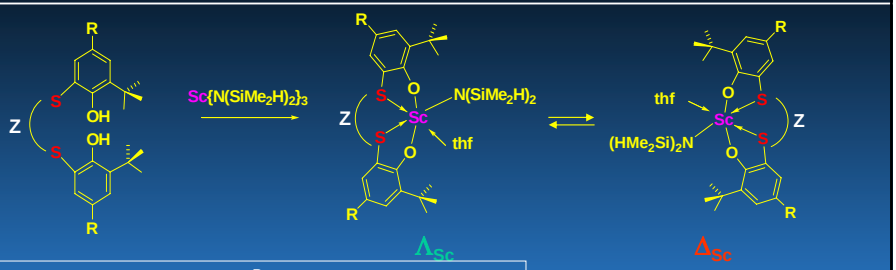


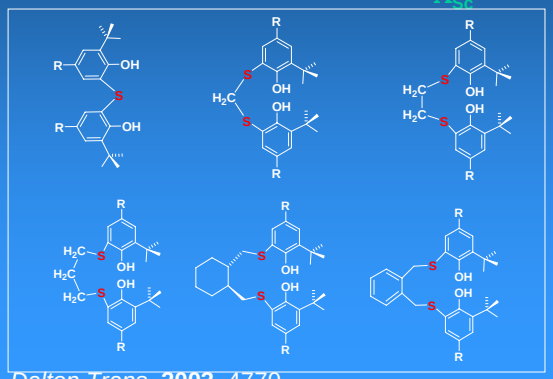
	time (h)	conv (%)	M_n(SEC)	M_w/M_n	P_r
1	1	31	7830	1.06	0.49
1	10	92	20430	1.04	0.50
2	10	93	20340	1.04	0.49
3	22	33	10580	1.08	0.64
3	118	92	20500	1.07	0.65

atactic

Dalton Trans. **2005**, 721

Scandium Complexes



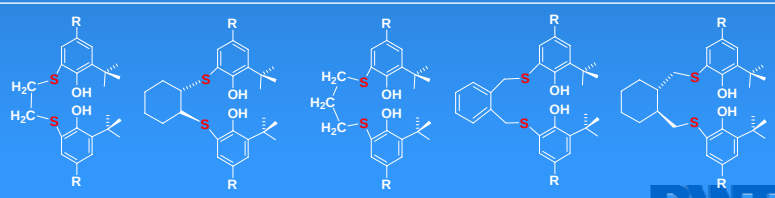


Labile THF coordination; highly fluxional on the NMR time scale

Dalton Trans. **2003**, 4770

Ring-Opening Polymerization of Lactide

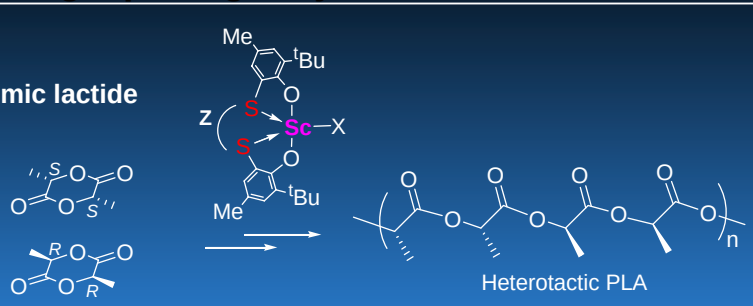
Z	[^{i}PrOH]$_0$ /[Sc]$_0$	time (h)	conv. (%)	M_n (10^4)	M_w/M_n	P_r
$(CH_2)_2$	-	9	82	17.8	1.89	0.78
cycl	-	9	79	23.8	1.88	0.82
$(CH_2)_3$	-	8	81	12.6	1.85	0.95
xyl	-	21	89	14.3	1.88	0.94
cycm	-	5	75	28.5	1.60	0.94
$(CH_2)_3$	1	8	63	5.38	1.55	0.96
$(CH_2)_3$	2	8	59	1.88	1.15	0.94
$(CH_2)_3$	3	8	40	1.09	1.12	0.90



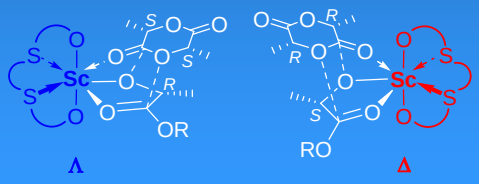
cycl xyl cycm

Ring-Opening Polymerization of Lactide

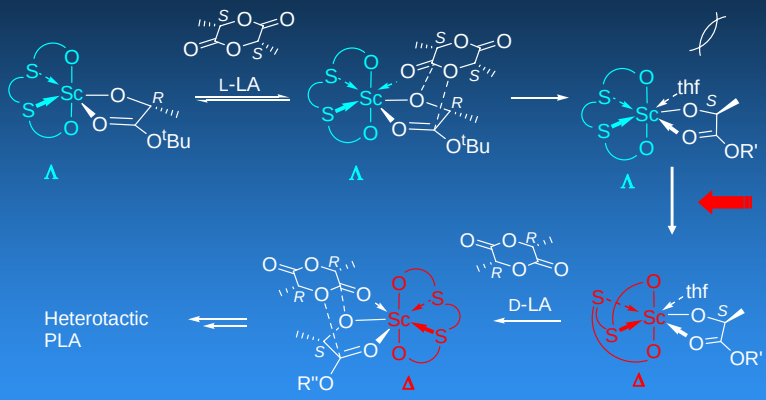
Racemic lactide



Enantiomer Recognition

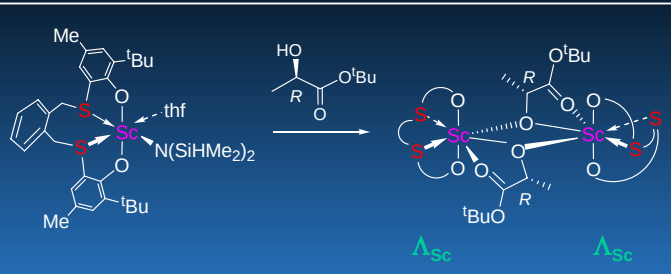


Ring-Opening Polymerization of Lactide



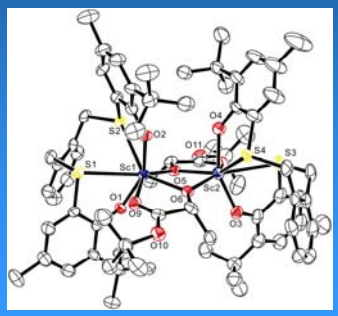
(S)-Lactate induces Δ configuration

Scandium Lactate Complexes



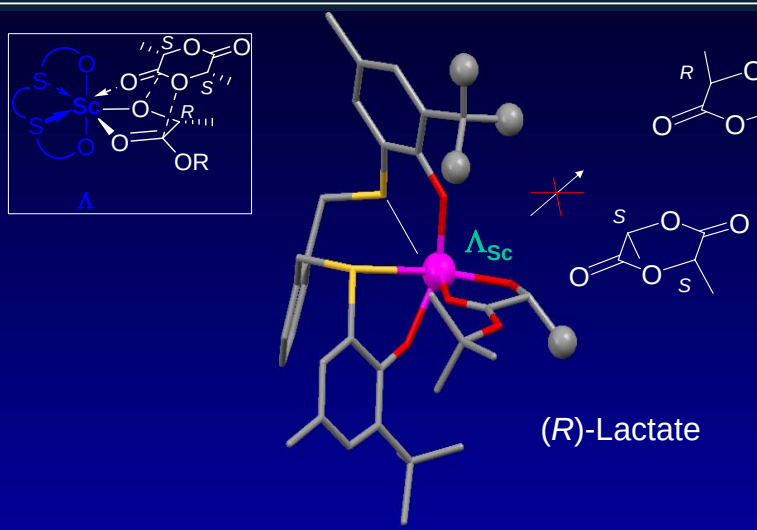
(R)-Lactate selectively induces Λ configuration

Homochiral dimer: Self-recognition of distorted pentagonal bipyramidal metal centers



Angew. Chem. Int. Ed. **2006**, 45, 7818

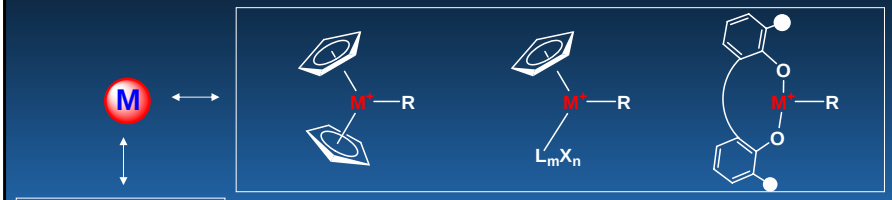
Scandium Lactate Complexes

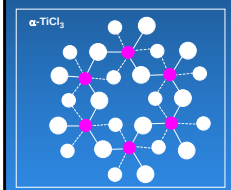


Poly(lactic acids)

- **Current production:**
  ca 140,000 t/a (isotactic)
- **Biodegradable** and biocompatible material with mechanical properties similar to PS and PET
- **Packaging and fibers:**
  - Films
  - Containers
  - Clothing
- **Biomedical applications:**
  - Cartilage repair units
  - Intravascular stents
  - Controlled drug delivery

Single-Site Polymerization Catalysts





Expansion of Metal-Ligand Combinations
Non-cyclopentadienyl ligands, late transition metals, ...

Expansion of Monomer Basis
α-Olefins, internal olefins, styrene, polar monomers, ...

New Catalyzed Polymerizations
Copolymerization, living polymerization, tandem polymerization,...

Novel Macromolecular Architectures and Functions
Block copolymers, chiral macromolecules, ...

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