Olefin Polymerization

coordination polym. lecture 23

reaction:

R = H, Me, alkyl, Ph...

PE (high density polyethylene

low density PE (ICI, radical process, > 300°C, ~ 1000 atm)

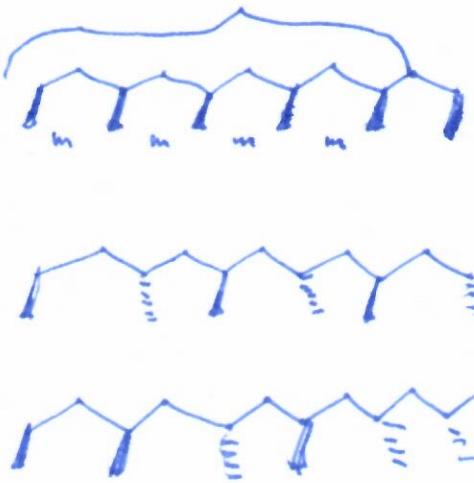
PP

HDPE ≥ 0.95 g/cm³

LLDPE (ethylene/α-olefin copolymer)

10^8 tons / year

PP = stereoregularity 'tacticity'



isotactic
crystalline, high m.p....

syndiotactic

atactic
amorphous
'random'

depends on catalyst
analysis of ^{13}C-NMR
dyad

('meso') ('racemic')

pentad
'mmmm'

---

catalysts.

Spring of '54

K. Ziegler

$CH_2=CH_2 \xrightarrow[25°C,\ 1atm]{TiCl_4/AlEt_3}$ PE · MW: 10^4-10^5

Nobel 1963!

G. Natta

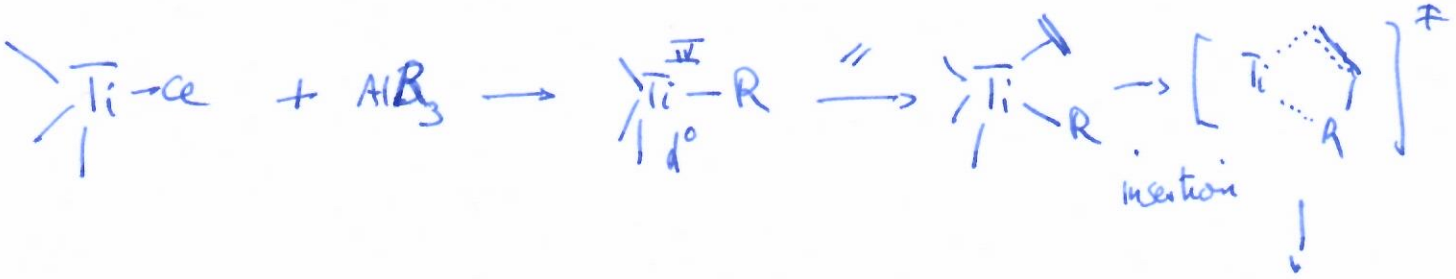
meanwhile Hogan / Banks Phillips Pet. 1951

CrO_3/SiO_2 catalyst for PE formation Cr^{III} vs Cr^{II}

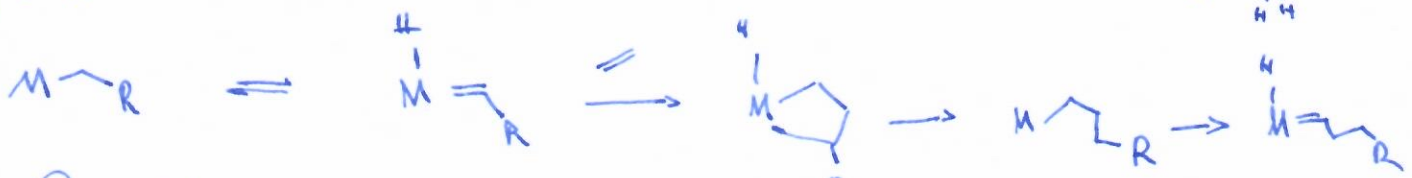
heterogeneous Cat, no cocatalyst, not very good for α-olefins

Phillips Catalyst review: A. Zecchina Chem. Rev. 2005, 105, 115

mechanism: Cossee J. Catal. 1964, 3, 80



rival proposal:



Green / Rooney JCS Chem. Commun. 1978, 604

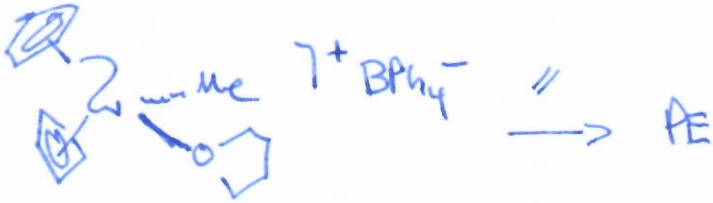
largely discounted today

---

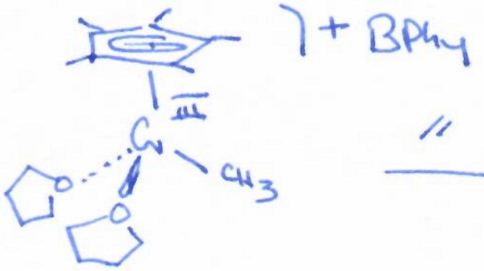
homogeneous model compounds:

Natta / Breslow $Cp_2TiCl_2 \xrightarrow{AlR_3} Cp_2Ti(Cl)R \xrightarrow{AlR_3} Cp_2Ti^{+}(R)\cdots Cl^{-}AlR_3$

R. Jordan cationic alkyls JACS 1986, 108, 1718



no cocatalyst needed!



// → PE

d[3], paramagnetic

Eur. J. Inorg. Chem. 1998, 15

'Union Carbide catalyst'

Cp_2Cr / SiO_2

---

homogeneous propene-polym.

1980 H. J. Sinn & W. Kaminsky

Angew. Chem. 1980, 19, 396

Cp_2ZrCl_2 + ($AlMe_3$ + H_2O) ⟶ PP low MW ~ 1000

↓ $-CH_4$

$[MeAlO]_n$

'methyl aluminoxane', MAO

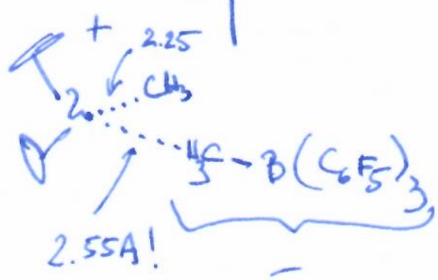
MAO used in large excess

200:1 or 2000:1

roles:

- alkylating agent
- scrubber of impurities (H_2O, O_2)
- supreme Lewis acid

Cp_2ZrMe_2 + $B(C_6F_5)_3$ ⟶



// → PE / PP

T. Marks, JACS 1991, 113, 3623