Advances in Ziegler-Natta Catalyst Technologies for Ethylene Polymerization in the Solution Process

Isam Jaber

NOVA Chemicals Corporation

Calgary, Alberta

91st CSC Edmonton, Alberta

May 24-28, 2008

Outline

- NOVA Chemicals Corporation Overview
- Ziegler-Natta Catalyst Technologies for Ethylene polymerization
- Solution Phase Polyethylene Process
- Experimental Results
- Conclusions
- Acknowledgment

NOVA Chemicals

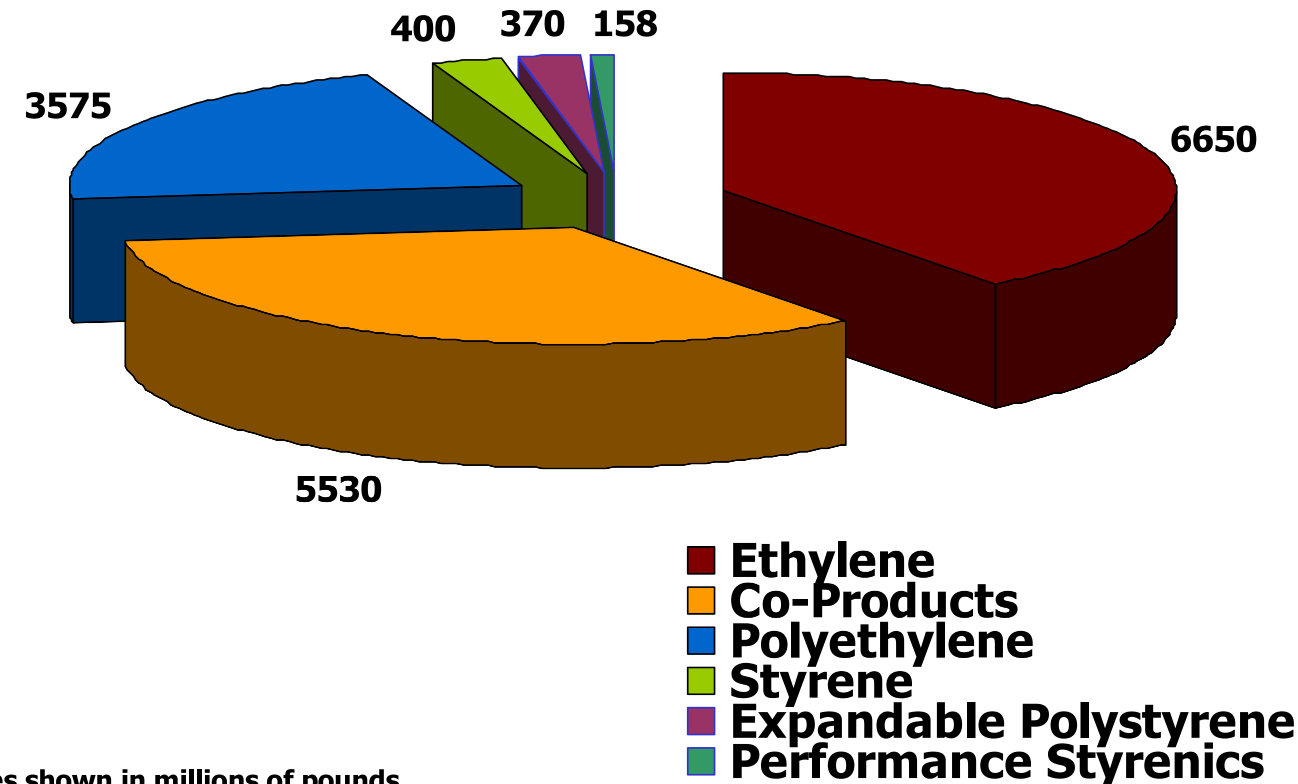
NOVA Chemicals .. Overview

NOVA Chemicals produces plastics and chemicals that are essential to everyday life.

Our employees develop and manufacture materials for customers worldwide that produce consumer, industrial and packaging products.

- **Revenue:** Approximately $6.5 billion
- **Employees:** Approximately 2800
- **Sites:** Seven manufacturing sites in North America

2007 Production Capacities



All capacities shown in millions of pounds

- Source: NOVA Chemicals Annual Report
- Does not include INEOS NOVA capacity

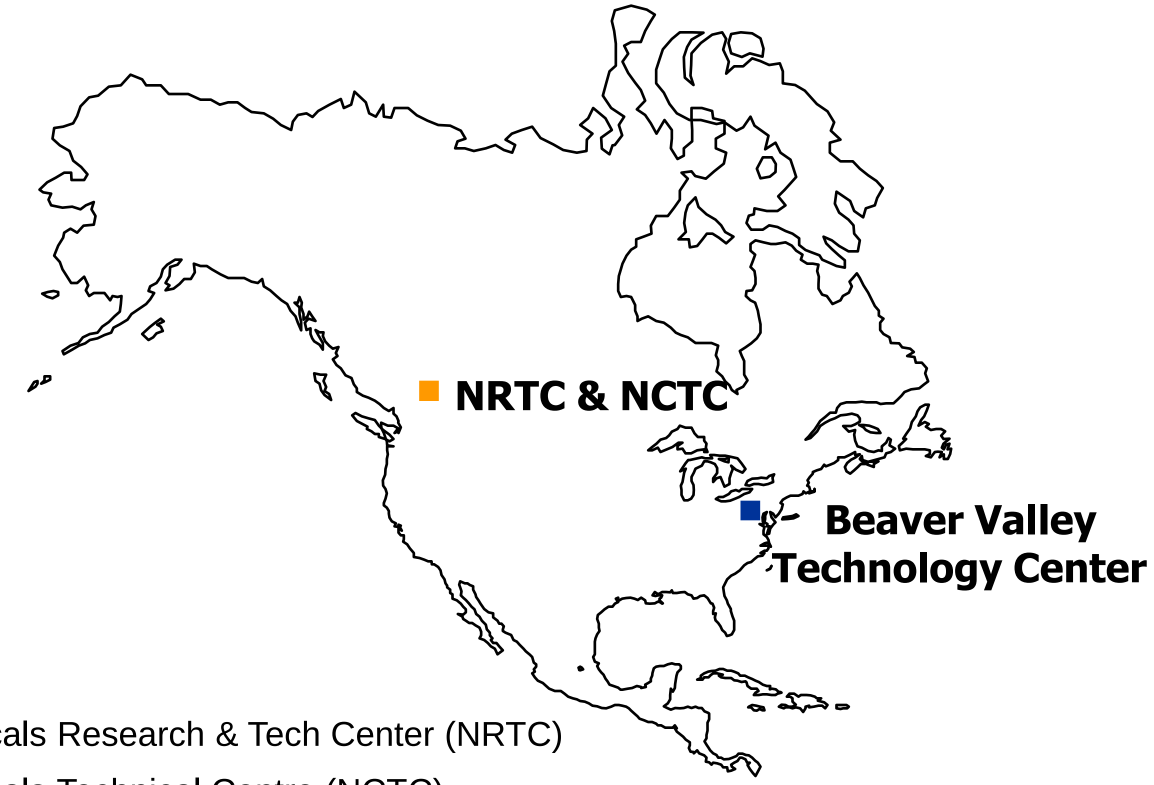
Manufacturing Sites

LEGEND

- ▲ **NOVA Chemicals Ethylene/Polyethylene Site**
- ● **NOVA Chemicals Performance Styrenics Site**

* Long-term tolling arrangement

Research & Technology Centers



- NOVA Chemicals Research & Tech Center (NRTC)
- NOVA Chemicals Technical Centre (NCTC)
  — Calgary, Alberta, Canada
- Beaver Valley Technology Center & Pilot Plant
  — Monaca, Pennsylvania, USA

Ziegler-Natta Catalyst Technologies

- Typical Components
- Metal Alkyls
- Experimental Design
- Catalyst Formation

Typical components

Mg alkyls

($MgR_2/AlEt_3$)

Me_2-Mg (nHex)$_2$-Mg,

di-t-BuMg Mg-dibenzyl

(nBu)$_2$-Mg (nOctyl)$_2$-Mg

Aluminum alkyls

$AlEt_3$ $AlMe_3$

Al(iBu)$_3$ Al(nHex)$_3$

Al(nOctyl)$_3$ Et_2AlCl

Et_2AlOEt $EtAlCl_2$

Transition Metals

Most common Ti, V, Zr

Metal Alkyls

BuEtMg / $AlEt_3$

$(n\text{-}Hex)_2Mg$

$(n\text{-}Bu)_2Mg$

$AlMe_3$

$Me_2\text{-}Al\text{-}OSi\text{-}tBuMe_2$

$Me_2\text{-}Al\text{-}OEt$

Al-alkyls that were not available commercially were made inline

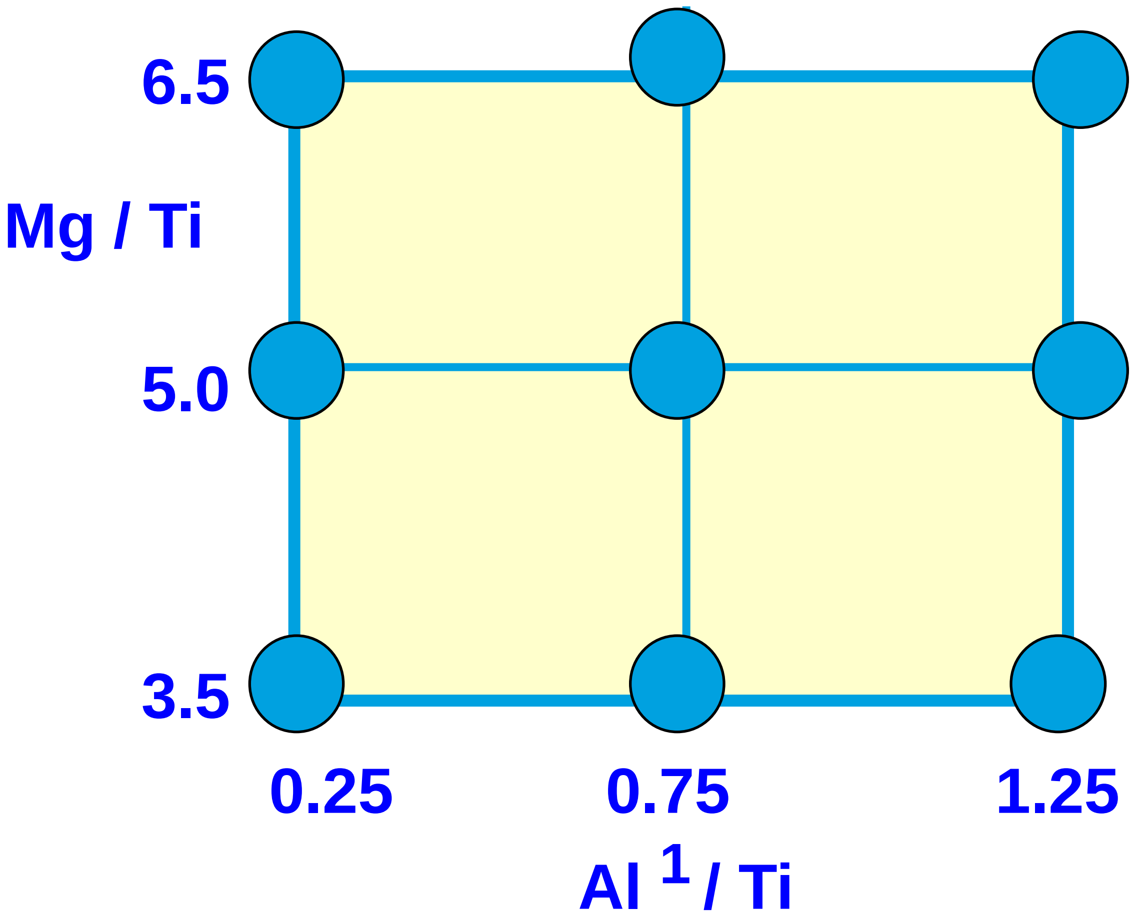
$AlMe_3 + HO\text{-}Si\text{-}tBuMe_2 \rightarrow Me_2\text{-}Al\text{-}OSi\text{-}tBuMe_2$

Similarly

$AlMe_3 + EtOH \rightarrow Me_2\text{-}Al\text{-}OEt$

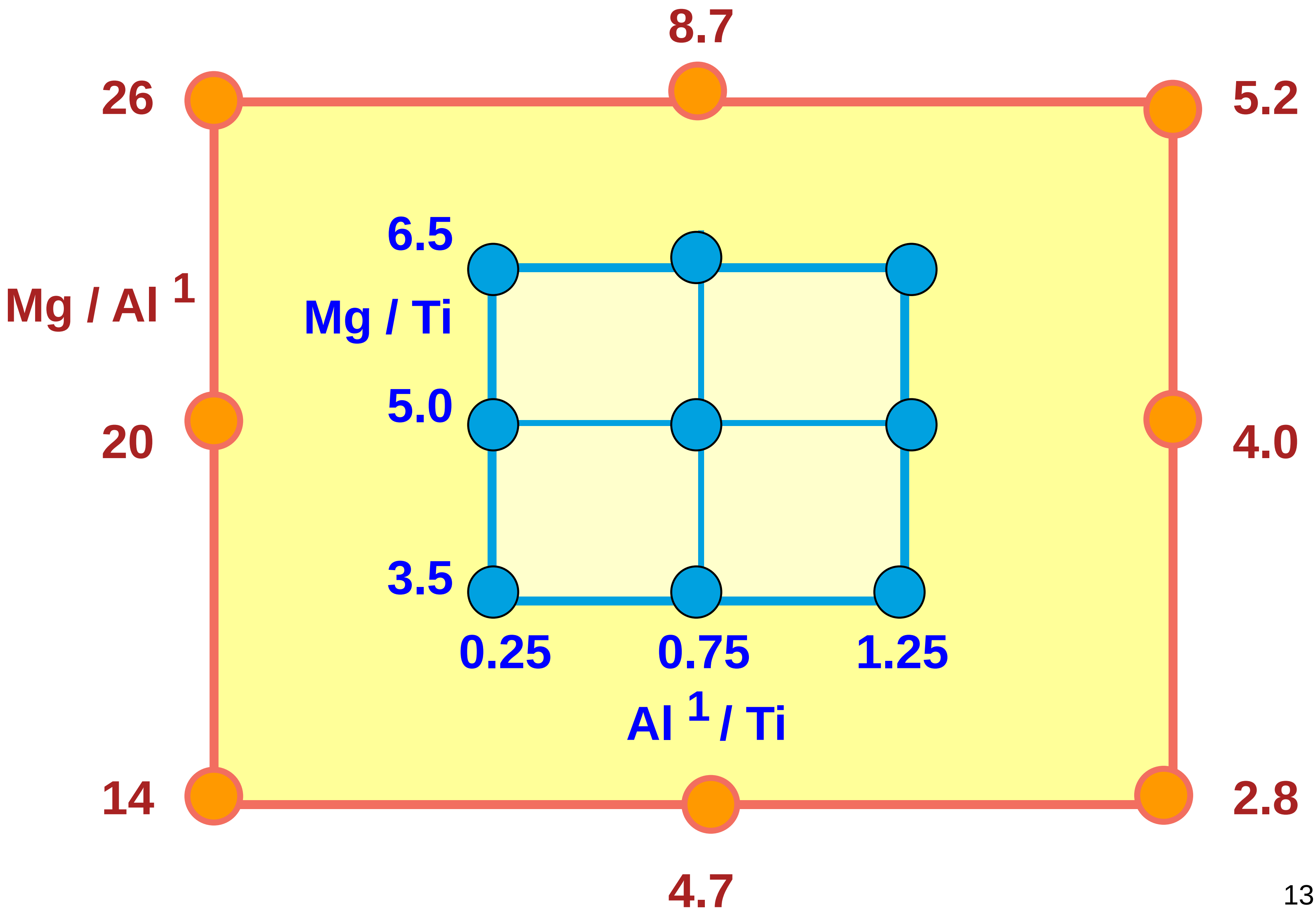
Experimental Design (mol ratios)

NOVA Chemicals



Experimental Design (mol ratios)

NOVA Chemicals



Catalyst Formation

$MgCl_2$ formation

$[R_2Mg / AlR_3] + 2(t\text{-}BuCl) \rightarrow RMgCl/AlEt_3$ or $MgCl_2/AlEt_3$

Deposit $TiCl_4$ on the $MgCl_2/AlEt_3$

$MgCl_2/AlEt_3 + TiCl_4 \rightarrow MgCl_2/TiCl_3 + AlEt_2Cl$

Catalyst Formation

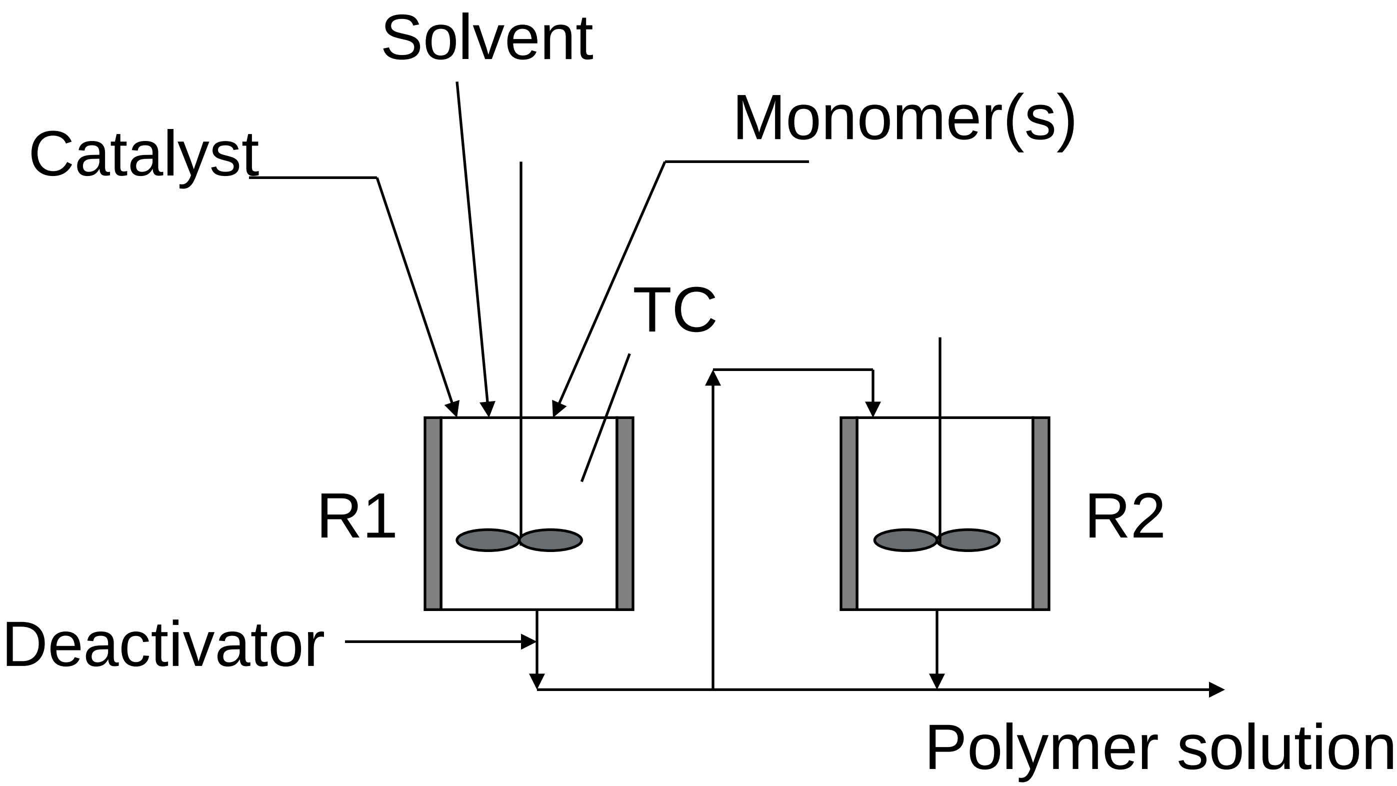
Reaction with 2nd Al-alkyl

Al-alkyls play three main roles in olefin polymerization

- Scavenging
- Alkylation
- Reduction of Ti

Solution Phase Polyethylene Process

- **Schematics**
- **Features**
- **Typical Conditions**


Solvent
Catalyst
Monomer(s)
TC
R1
R2
Deactivator
Polymer solution

Features

- Catalyst made in-line
- Fed continuously
- Product pumped out continuously
- Polymer solution flashed out to atm pressure
- Online GC measurement of C2 consumption
- Lab Polymerization unit runs 24 / 5
- Fast turn around
- Various Catalysts & Activators
- Supported and un-supported catalysts
- Multiple reactors

Typical Conditions

(Lab polymerization unit)

- T = 200 ^{o}C
- Total solution feed rate = 27 mL/min.
- Residence time = 2.6 min.
- Ethylene (wt.%) = 10
- $\propto$-Olefin co-monomer / ethylene = ~ 1.0 g/g

Experimental Results

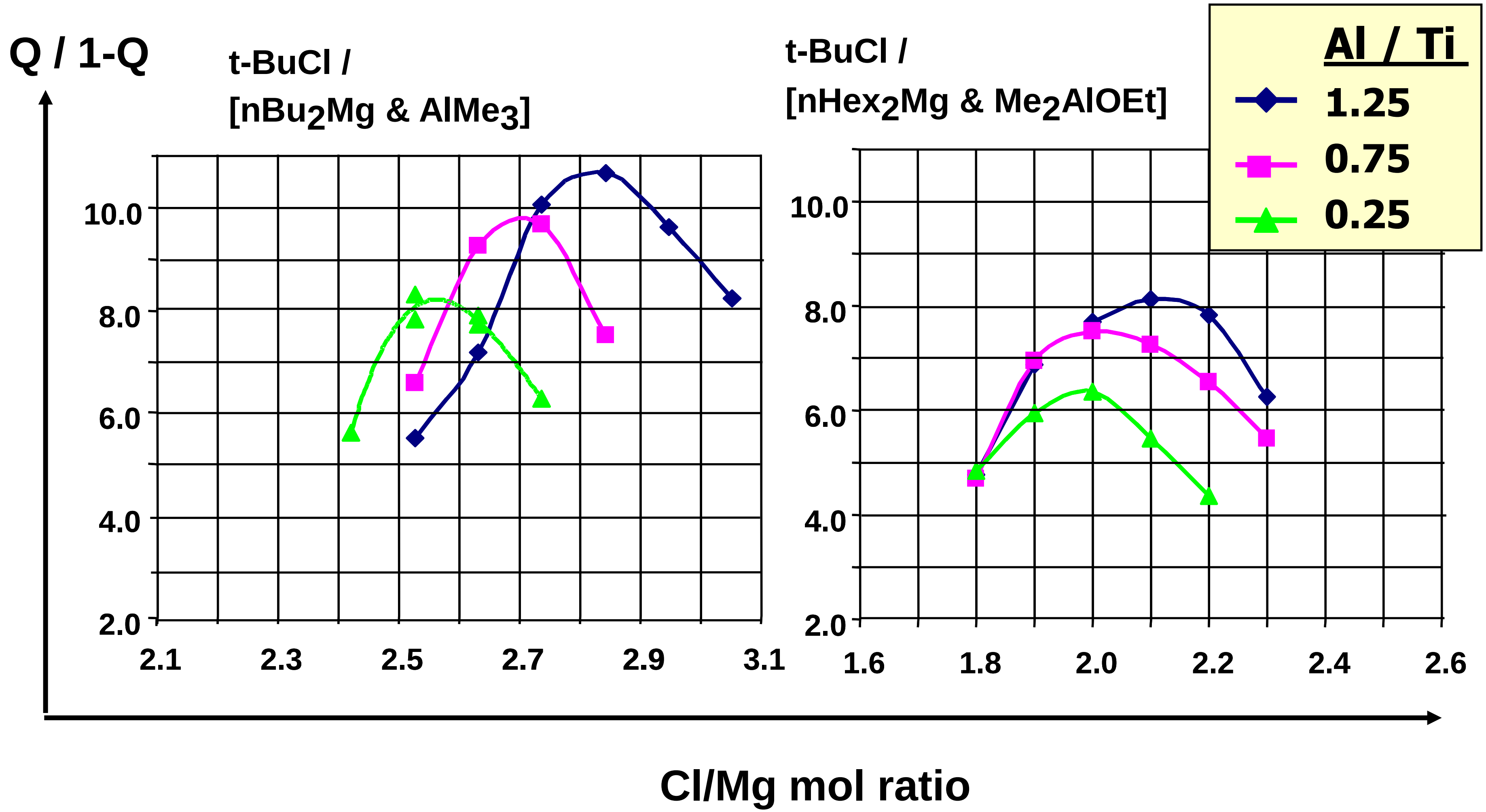
- Cl / Mg optimal ratio
- Catalyst Activity (Kp)
- Polymer Molecular Weight (MW)
- Polymer Density

Cl / Mg Optimal ratio

The optimal Cl/Mg mole ratio can shift from about 1.8 to about 2.8 due to

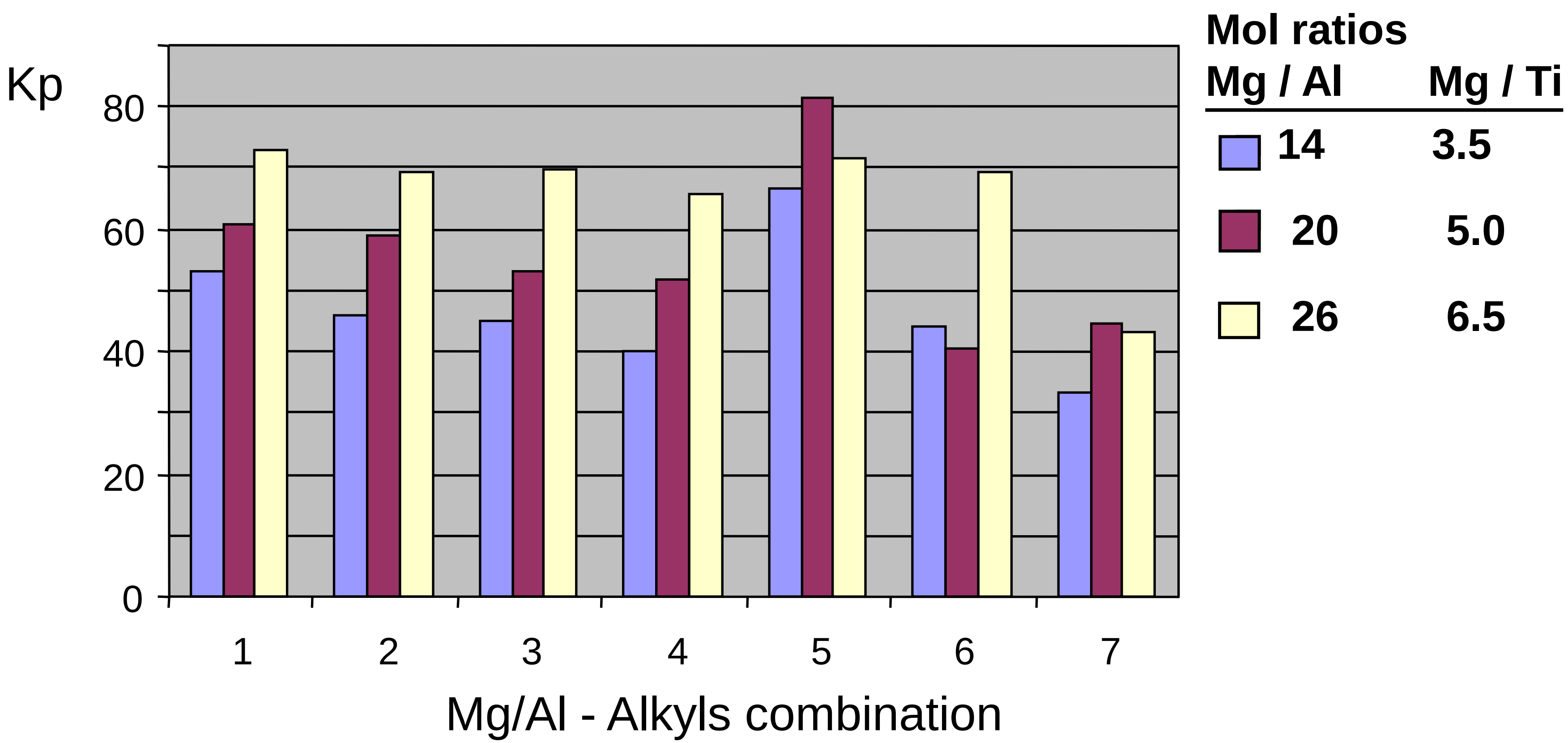
- Reaction rate of t-BuCl with the MgR_2
- Reactions of the 1st Al-alkyl present with the MgR_2

Cl/Mg mole ratio optimization



Catalyst Activity

(Kp = L / mmolTi . min)



1- BuEtMg/AlEt3

2- (nHex)2Mg/AlMe3

3- (nHex)2Mg /Me2AlOSi-tBuMe2

4- (nHex)2Mg /Me2AlOEt

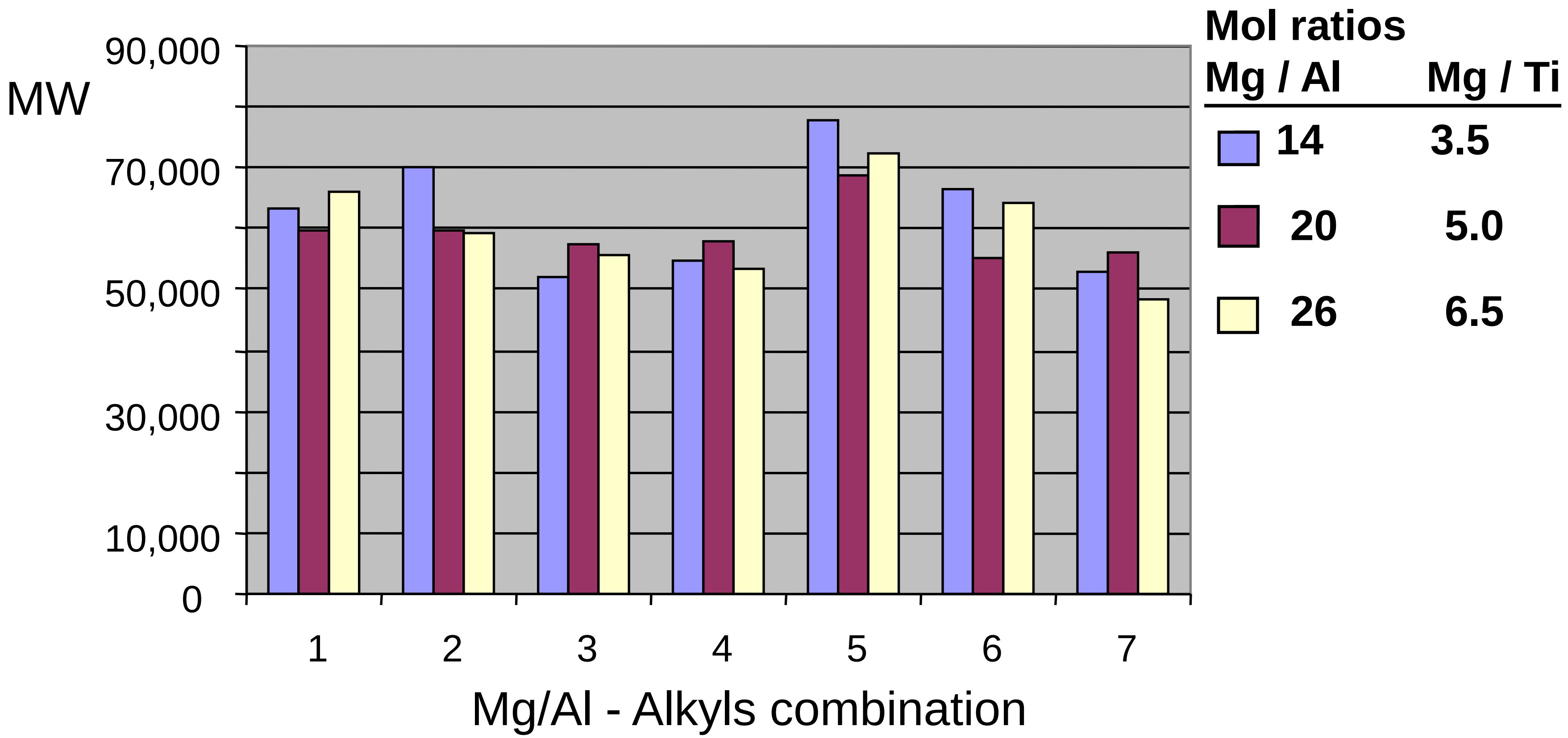
5- (nBu)2Mg/ AlMe3

6 - (nBu)2Mg/ Me2AlOSi-tBuMe2

7- (nBu)2Mg/ Me2AlOEt

Polymer Molecular Weight

g/mol measured by gel permeation chromatography (GPC)



1- BuEtMg/AlEt3

2- (nHex)2Mg/AlMe3

3- (nHex)2Mg /Me2AlOSi-tBuMe2

4- (nHex)2Mg /Me2AlOEt

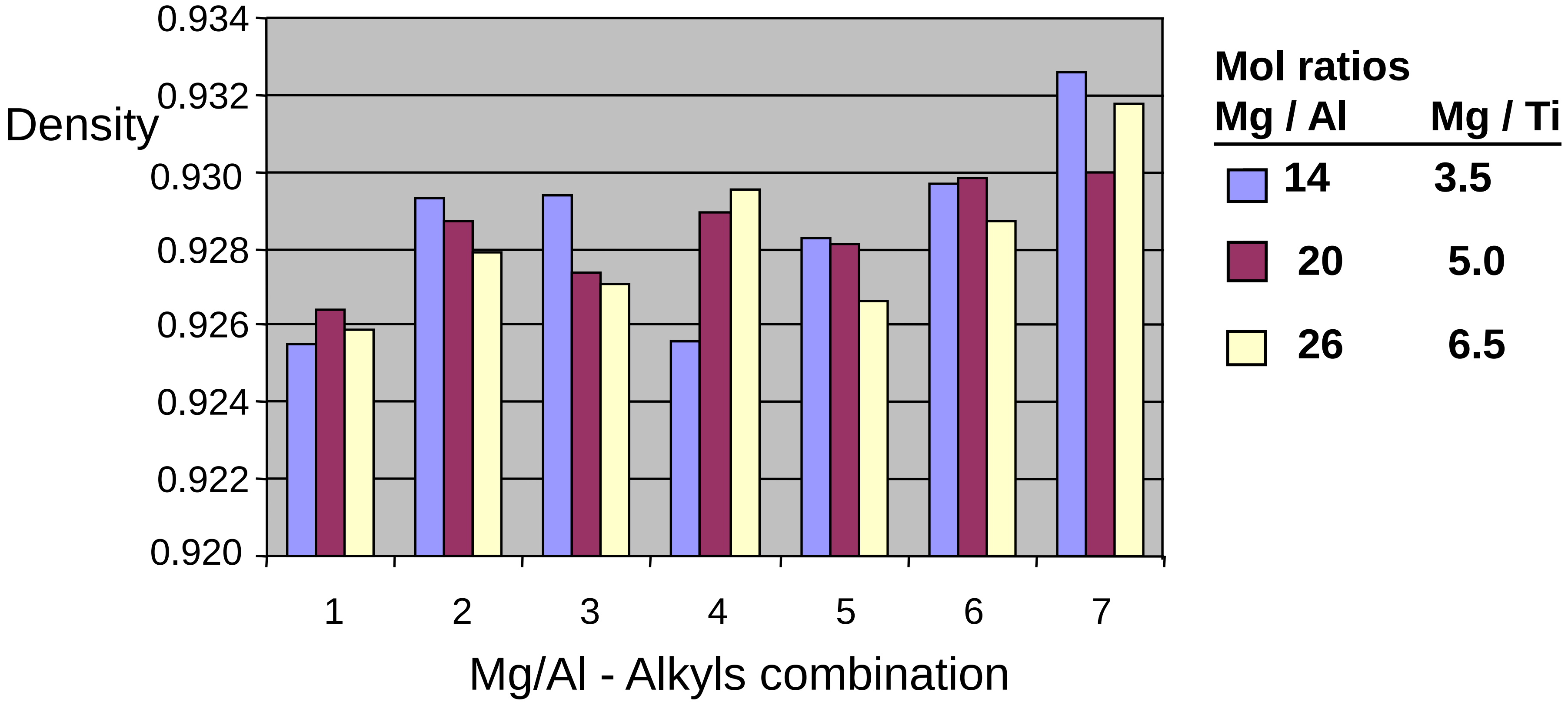
5- (nBu)2Mg/ AlMe3

6 - (nBu)2Mg/ Me2AlOSi-tBuMe2

7- (nBu)2Mg/ Me2AlOEt

Polymer Density

(g/cc)



1- BuEtMg/AlEt3

2- (nHex)2Mg/AlMe3

3- (nHex)2Mg /Me2AlOSi-tBuMe2

4- (nHex)2Mg /Me2AlOEt

5- (nBu)2Mg/ AlMe3

6 - (nBu)2Mg/ Me2AlOSi-tBuMe2

7- (nBu)2Mg/ Me2AlOEt

Conclusions

- Catalyst activity is dependent on the Mg/Ti mole ratio
    - Higher Mg/Ti mole ratio leads to higher activity
- Optimal Cl/Mg mole ratio is dependent on metal alkyl combination
- Polymer properties show little dependency on the variation of metal alkyls to Ti

Acknowledgment

- NOVA Chemicals Corporation
  - Leadership
  - New Catalyst & Polymers
  - Lab Operations
  - Testing Services