EARLY AND LATE TRANSITION METAL COMPLEXES FOR THE POLYMERIZATION OF OLEFINS : NOVEL BRANCHED AND FUNCTIONAL POLYOLEFINS

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IISER -PUNE

November 8, 2011

2011
C
CHEMISTRY

International Year of
CHEMISTRY
2011

1950-2010
NCL
Celebrating Sixty Years of Science

- 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

- ➢ 100th anniversary of the discovery of superconductivity
- ➢ Birth centenary of Melvin Calvin
- ➢ Bicentenary of the publication of the hypothesis by Avogadro stating that ”equal volumes of gases at the same temperature and pressures contain equal numbers of molecules”

Madame Curie, Nobel Prize in Chemistry , 1911

Earnest Rutherford, The Structure of the Atom. 1911

MARIE SKLODOWSKA CURIE
(1867 – 1934)

- The first woman to get a Ph D in Europe
- The first woman to be appointed a full Professor in Sorbonne in 1906 , but only after the death of her husband and after having won a Nobel Prize
- The first woman to win a Nobel Prize , in 1903 for Physics based on her Ph D thesis
- The only woman to have won two Nobel Prizes
- The only person to have won two Nobel Prizes for two different branches of science, Physics and Chemistry (1911)
- The only mother and daughter pair to win Nobel Prizes in Chemistry

" You cannot hope to build a better world without improving the individuals; To that end , each one of us must work for our own improvement, and at the same time share a responsibility for all humanity. Our particular duty being to aid those to whom we think we can be most useful" : Marie Curie

I am inclined to think that the development of polymerization is, perhaps, the biggest thing that chemistry has done, where it has the biggest effect on everyday life

Lord Alexander Todd (1907-1997)

Nobel Laureate, 1957

METAL CATALYZED OLEFIN POLYMERIZATION

1950 - 2010
NCL
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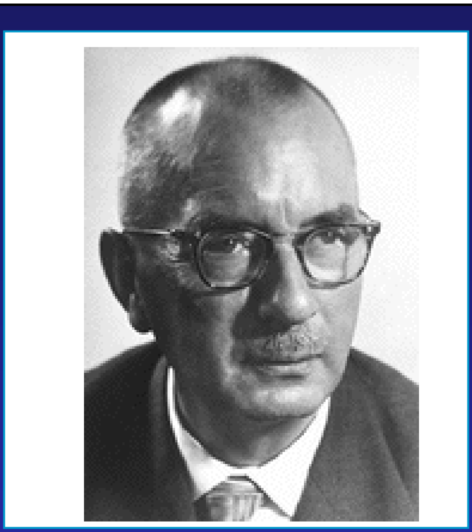
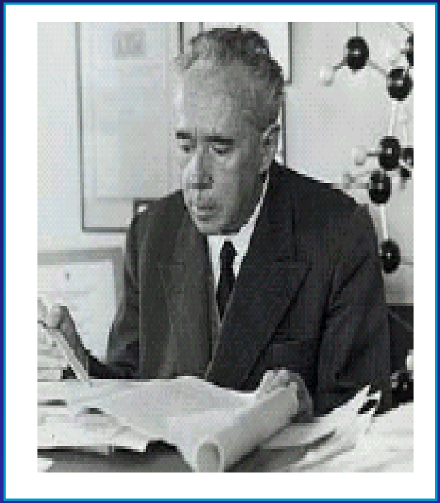
Years of Science





BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM
14. APRIL 1960

DEUTSCHES PATENTAMT

PATENTSCHRIFT
№ 973 626
KLASSE 39c GRUPPE 25 01
INTERNAT. KLASSE C 08f
Z 3799 IVb / 39c

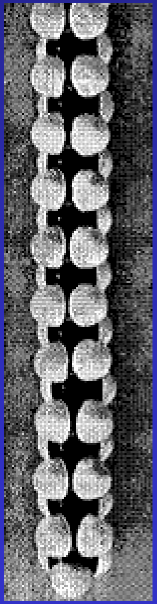
Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr,
Dr. Heinz Breil, Oberhausen (Rhld.), Dr. Erhard Holzkamp, Düsseldorf,
und Dr. Heinz Martin, Mülheim/Ruhr
sind als Erfinder genannt worden

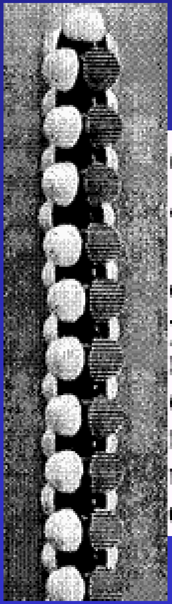
Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr

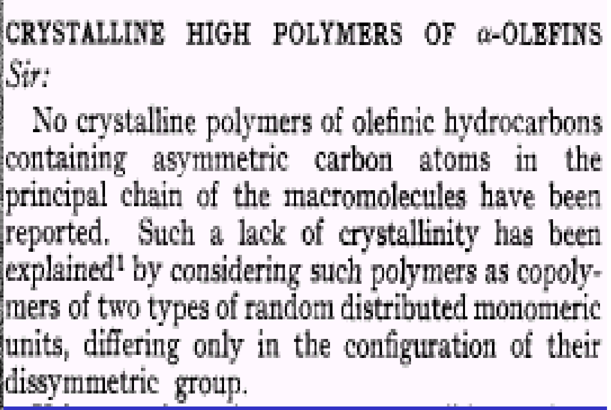
Verfahren zur Herstellung von hochmolekularen Polyäthylenen

Patentiert im Gebiet der Bundesrepublik Deutschland vom 18. November 1953 an
Patentanmeldung bekanntgemacht am 4. Oktober 1956
Patenterteilung bekanntgemacht am 24. März 1960

DE 973626
Nov 18, 1953







CRYSTALLINE HIGH POLYMERS OF α-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[1] 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)

ZIEGLER-NATTA CATALYSTS AND POLYMERIZATION THE BIRTH OF A SCIENCE

Process for preparing high molecular weight polyethylene,

Ger Pat 973, 626, 1960 dated November 18, 1953

to K. Ziegler, H. Breil, E. Holzkamp and H. Martin

- ***Exemplary claim***

  A method for preparing high molecular weight polyethylene

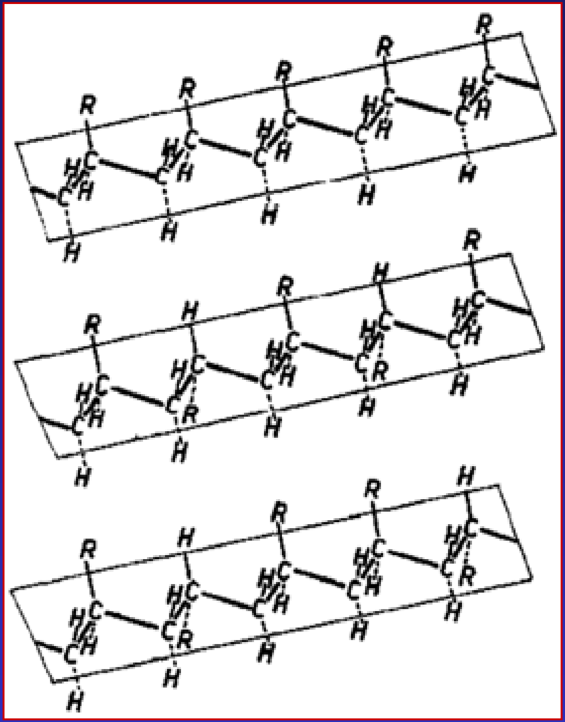
  using aluminum alkyls as catalysts, characterized by bringing together ethylene at pressures >10 atm and temperatures above 50°C with mixtures of aluminum trialkyls and compound of the metals of Group IVa to VIa of the periodic table with the atomic numbers 22 to 74
- **Land mark experiment carried out on October 26, 1953, in the Max Planck Institute fur Kohlenforschung in Mulheim an der Ruhr**
- **A patent was issued to Natta et al (US Pat 3, 112, 200 on June 8, 1954) for the preparation of isotactic polypropylene**

DISCOVERY OF ISOTACTIC POLY(PROPYLENE)S

- **An Italian company Montecatini Edison signs a license from Karl Ziegler to make polyethylene**
- **The Italian company sponsored three of its staff to Mulheim to gain experience in this new chemistry in early 1953**
- **Professor Natta, at Milan Polytechnic, an X-ray crystallographer, was a consultant to Montecatini. He had, therefore, access to all the information from K. Ziegler's laboratory – much of it then unpublished**
- **On March 11, 1954, Natta and coworkers succeeded in polymerizing propylene using Ziegler's catalyst system to a tacky solid (G. Natta, P. Pino and G. Mazzanti, US Pat 3,112,200, June 8, 1954)**

DISCOVERY OF ISOTACTIC POLY(PROPYLENE)S

- Natta recognized that the material is composed of different diastereoisomers. Fractionation from diethylethers and heptane, resulted in an “amorphous” soluble fraction and insoluble “crystalline” fraction (with a Tm ~ 160°C)
- Natta applied X-ray crystallography to deduce the structure of crystalline polymer and termed them as isotactic, syndiotactic and atactic
- The concept of polymer strereoregularity in conjunction with transition metal catalyzed stereospecific polymerization by means of enantiomorphic catalytically active site had far reaching impact on the progress of polymer science and technology



Montecatini starts manufacture of polypropylene in 1957 at Ferrara, Italy

ZIEGLER AND NATTA AWARDED NOBEL PRIZE IN 1963

Karl Ziegler

Citation

For their discovery in the field of chemistry and technology of high polymers

> *"Nature synthesises many stereoregular polymers (cellulose, rubber, biomacromolecules). This ability has so far been thought to be a monopoly of nature operating with biocatalysts known as enzymes. But Professor Natta has broken this monopoly"*
>
> *A. Fredga, Nobel Presentations, 1963*

Giulio Natta

Quintessential Chemistry : Formation of Carbon –Carbon Bonds

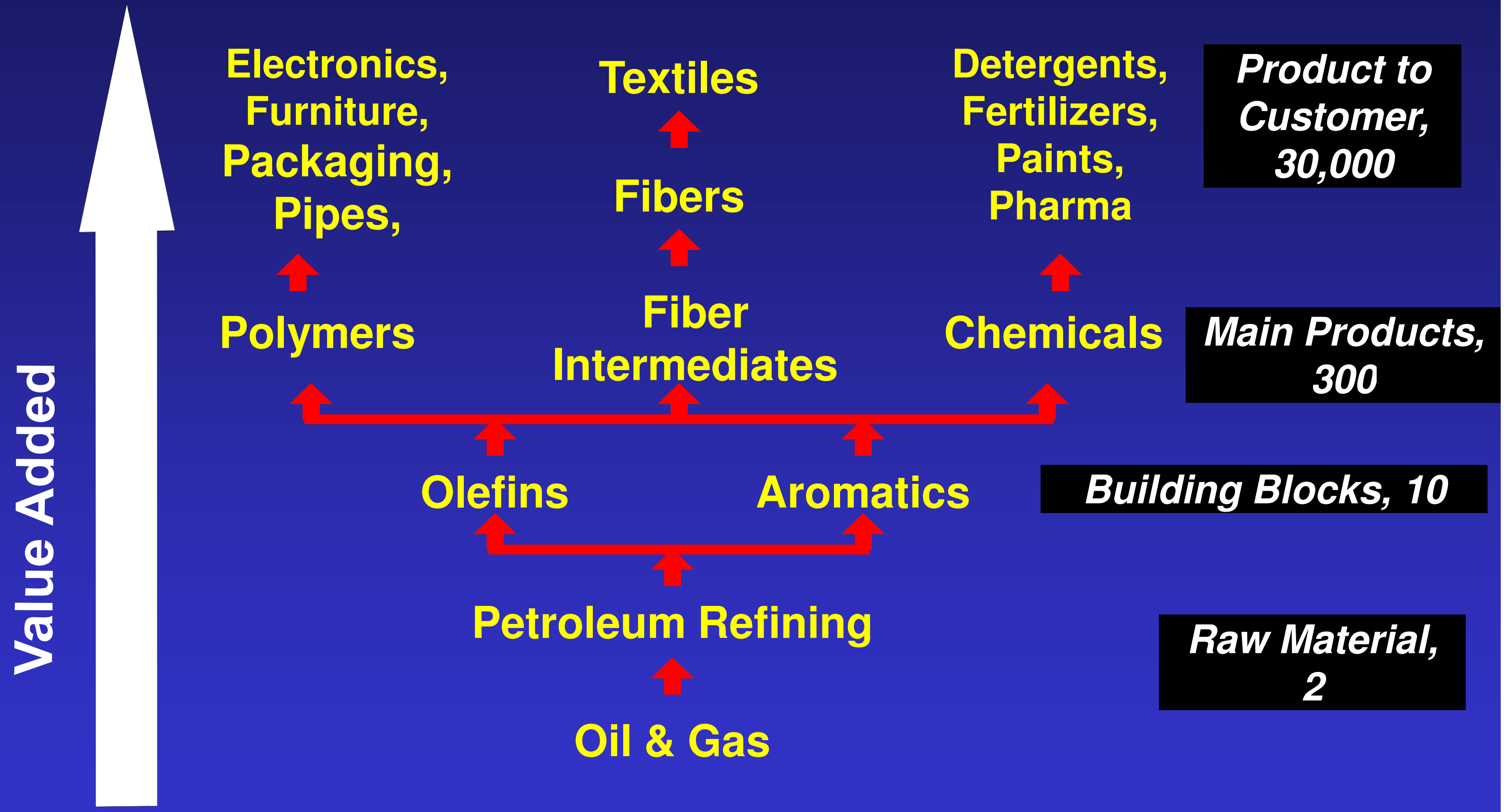
Since Victor Grignard in 1912 more than ten Noble Prizes in Chemistry have been awarded to chemists who discovered new ways to make carbon-carbon bonds, the latest being Suzuki, Negishi and Heck in 2010

"I set out to follow a broad course of study in which my only guide was , initially, just the desire to do something which gave me pleasure. The course threw up many interesting conclusions , many of them of highly practical value, and one of them led ultimately to a method of making polyethylene "

Karl Ziegler

Nobel Address

STRUCTURE OF THE PETROCHEMICAL INDUSTRY



Electronics, Furniture, Packaging, Pipes,

Textiles

Detergents, Fertilizers, Paints, Pharma

Product to Customer, 30,000

Fibers

Polymers

Fiber Intermediates

Chemicals

Main Products, 300

Olefins

Aromatics

Building Blocks, 10

Petroleum Refining

Raw Material, 2

Oil & Gas

Value Added

Ninety five per cent of the organic chemical industry is derived from ten building blocks, namely, methane, ethylene, propylene, C-4 paraffins, C-4 olefins, C-5 olefins, butadiene, benzene, toluene and xylene

RESEARCH THEME

A Recurrent Theme

- **Introduction of functional groups in polymers**
  - ***in the chain***
  - ***at the terminal end of the chain***
- **Control of polymer structures**
  - ***blocks, comb and branched***

Expanding the synthetic chemistry tool box by learning to manipulate a diversity of chain ends, radical, anionic and metal – carbon bonds

POLYOLEFINS via CATALYSIS INVOLVING NOVEL METALS AND LIGANDS

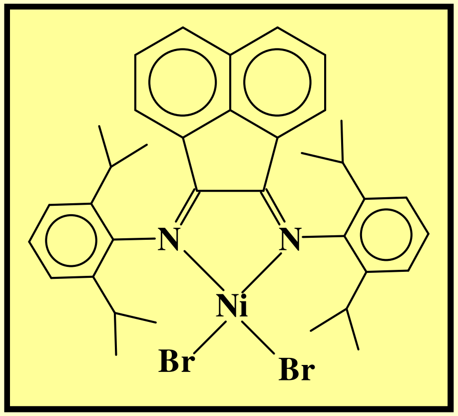
CATALYSTS

- **Group 4 (Ti-Mg)**
- **Group 4 metallocenes**
  - **Ligands, bis Cp, mono Cp, bridged Cp, non Cp**
- **Group 4 metal complexes**
  - **Bis(salicylaldiimine)**
- **Group 8 Metal complexes**
  - **Fe(II), bis(imino)pyridine**
- **Group 10 metal complexes**
  - **Ni(ii) / Pd(ii) α-diimine**
  - **Neutral nickel**
- **Group 11 metal complexes**
  - **Cu(II) complexes**

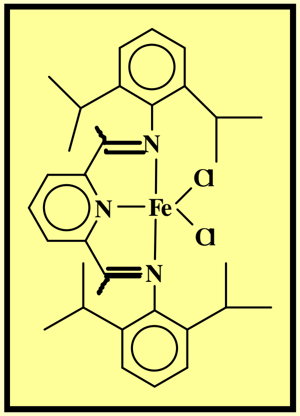
POLYOLEFIN HOMO AND COPOLYMERS

- **iPP/Syndio PP**
- **Elastic PP**
- **Plastomers**
- **EPDM’s**
- **Syndio polystyrene**
- **Ethylene-styrene interpolymers**
- **Cyclic olefin copolymers**
- **In-situ branched PE’s without comonomers (Versipol, CGC)**
- **Polar copolymers at ends of branches**
- **In chain polar olefin copolymers**

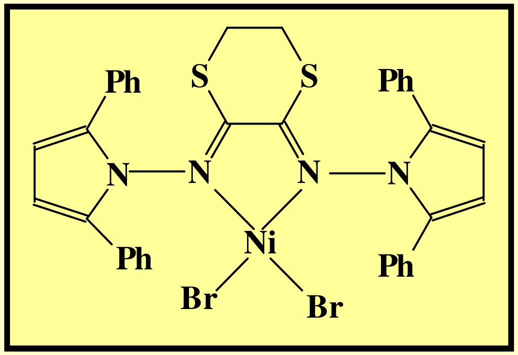
NEWER METALS AND LIGANDS FOR OLEFIN POLYMERIZATION



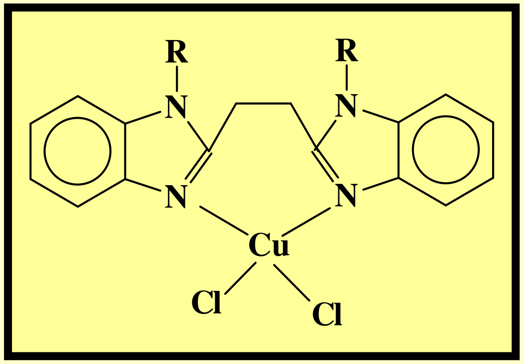
Brookhart(1995)



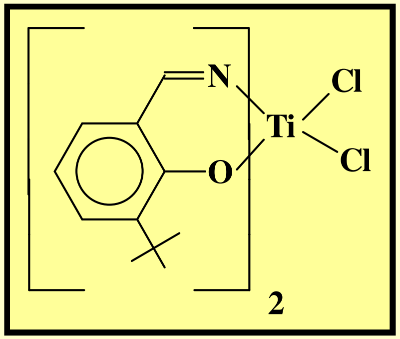
Gibson(1999)



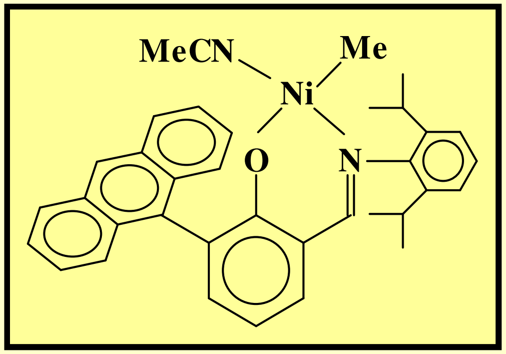
Eastman Chemicals (2000)



Exxon Mobil (2000)



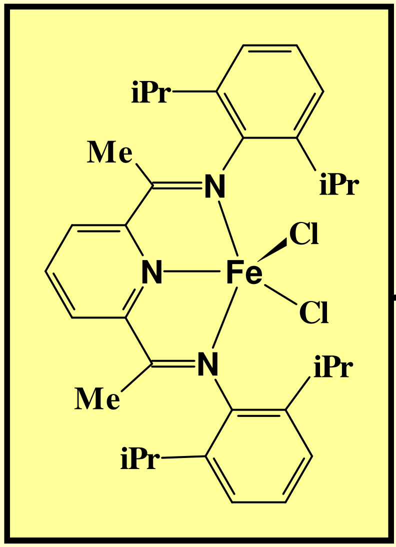
Fujita(2002)



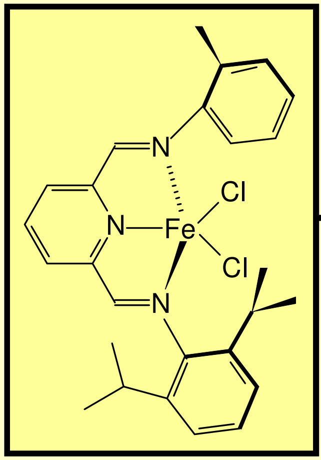
Grubbs(2003)

V.C.Gibson and S.K.Spitzmesser; *Chem.Rev.*, 103, 283-315 (2003)

LATE TRANSITION METAL COMPLEXES FOR OLEFIN POLYMERIZATION

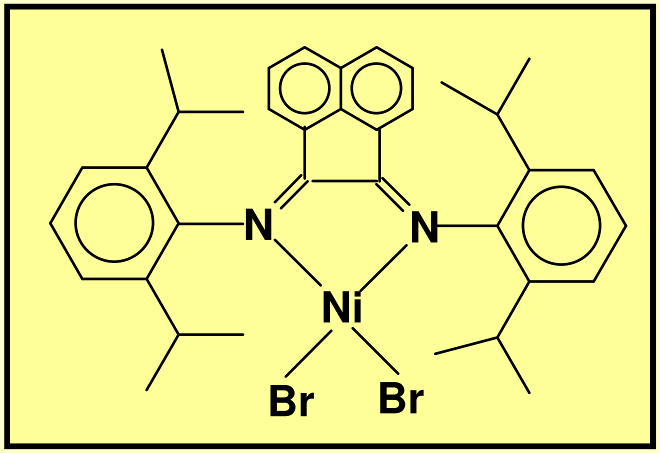


- Sterically bulky ortho-substituents reduce the rate of β-H tranfer and result in high Mw polyethylene
- Chain transfer aluminium alkyl: Broad/Bimodal MWD

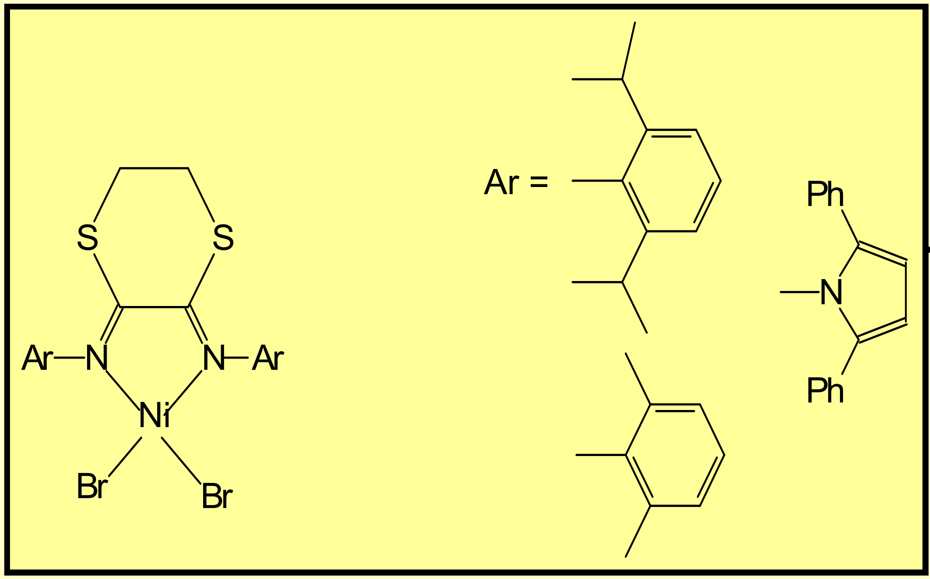


- C1-symmetric complex
- Simultaneous polymerization and oligomerization
- Highly crystalline PE
- Oligomerization highly selective with 95 % α-olefins

LATE TRANSITION METAL COMPLEXES FOR OLEFIN POLYMERIZATION

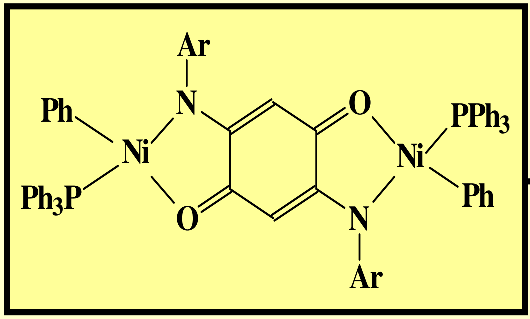


- Polymerize ethylene and α-olefins to high molecular weight polymers
- Linear to branched polymers
- Narrow MWD
- Copolymerization of ethylene with polar monomers

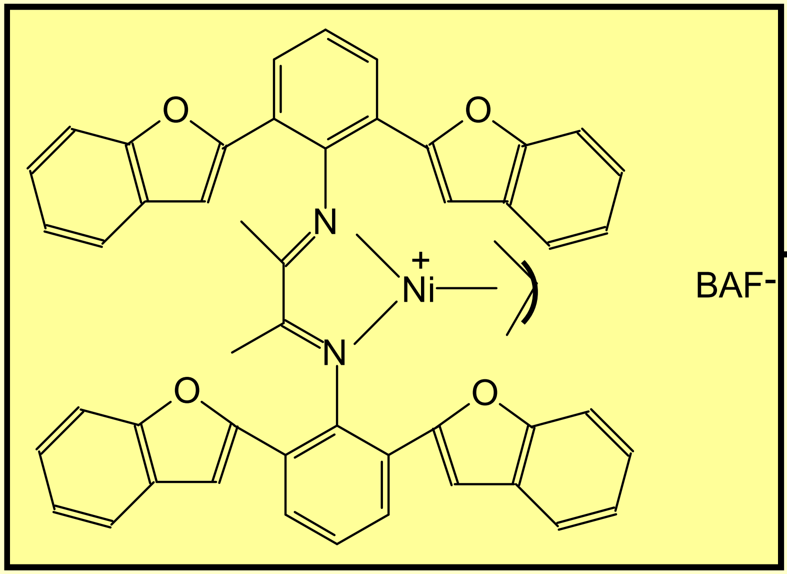


- GAVILAN technology
- Excellent catalyst activity and thermal stability
- Copolymerization of ethylene with cyclic olefins, polar monomers
- Narrow MWD and composition distribution

LATE TRANSITION METAL COMPLEXES FOR OLEFIN POLYMERIZATION

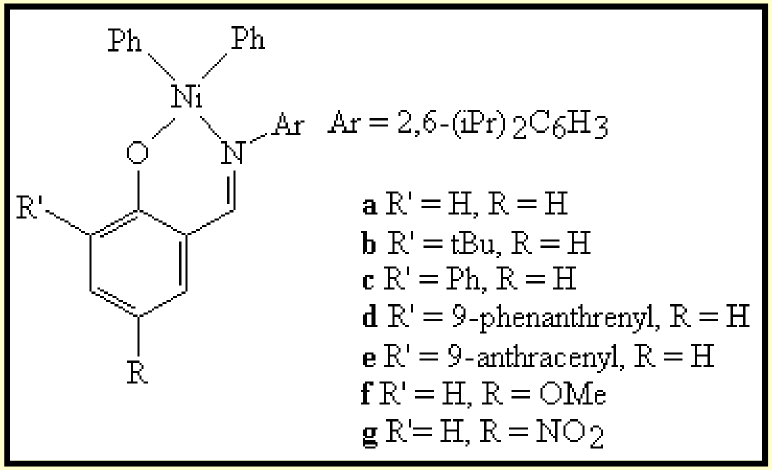


- Neutral, single-component binuclear catalyst
- Moderately branched PE with broad MWD
- Presence of more than one active species due to interaction between the metal centers



- High thermal stability ; Catalyst activity retained even at 150°C
- Ultrahigh molecular weight PE (Mw > 2.5 million at 70 °C)

LATE TRANSITION METAL COMPLEXES



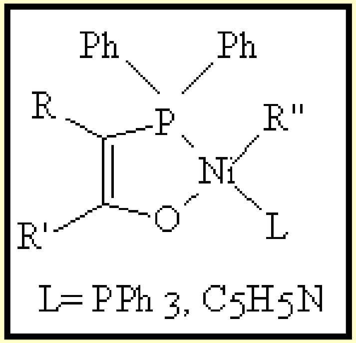
Ar = 2,6-(iPr) $_2C_6H_3$

a R' = H, R = H
b R' = tBu, R = H
c R' = Ph, R = H
d R' = 9-phenanthrenyl, R = H
e R' = 9-anthracenyl, R = H
f R' = H, R = OMe
g R'= H, R = NO_2

N,O donors

Neutral Ni(II) salicyldiminato complexes produce poly(ethylene)s with 30-55 branches/1000 C

Grubbs, R. H. *Organometallics,* 1998, 17, 3149

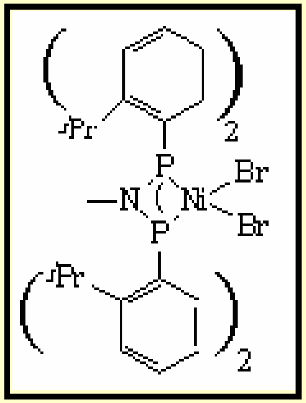


L= PPh $_3$, C_5H_5N

P,O donors

Activity of 5300 gmmol^{-1} Ni^{-1} h^{-1} bar^{-1} when R = COOR, R´ = CF_3, C_3F_7 or C_6F_5 for oligomerization of ethylene

Claverie, J. *Macromolecules,* 2001, 34, 2438.



P,P donors

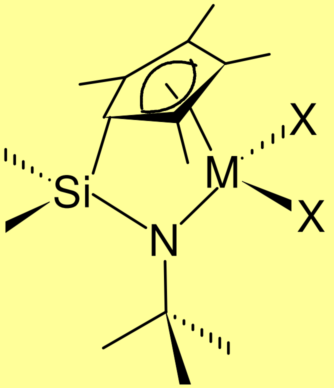
Activity of 2200 gmmol^{-1} Ni^{-1} h^{-1} bar^{-1} resulting in a linear high molecular weight PE

Wass, D.F *Organometallics,* 2001, 20, 4769.

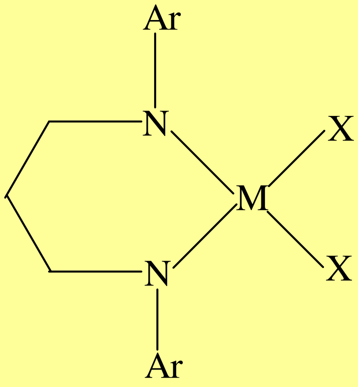
POLYMERIZATION OF ETHYLENE USING ansa - η5 - MONOFLUORENYL COMPLEXES OF GROUP 4 METALS

A. Rajesh and S. Sivaram, Polymer Bulletin, 67(3), 383 (2011)

NON-METALLOCENE EARLY TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATION



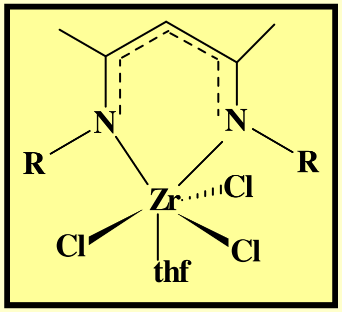
- **Mono-Cp complexes with covalently linked amide donor and a short bridging group**
- **Cp-M-N angle < 115°**
- **Long chain branched PE**
- **Copolymerization of ethylene with α-olefins, styrene, cyclic olefins etc**



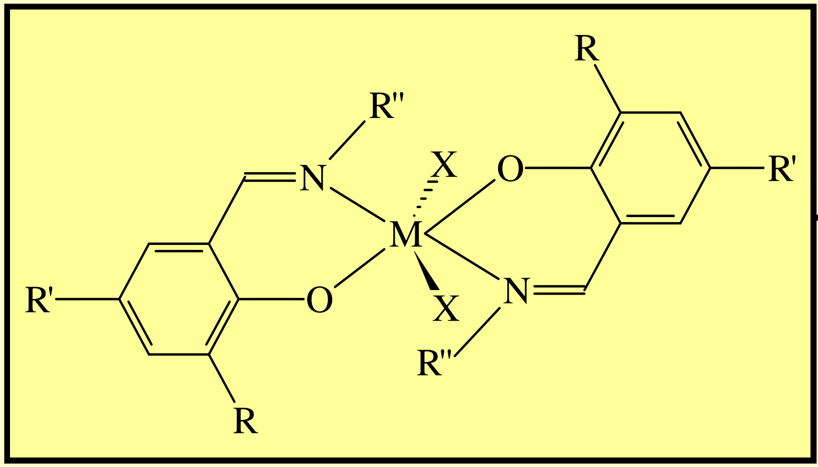
M = Ti, Zr
X = Cl, Me, CH_2Ph

- **Polymerization of higher α-olefins with high activities (>105 g poly(hexene) mmol-1 Ti h-1)**
- **Chain transfer to aluminum in presence of MAO**
- **Living polymerization in presence of B(C6F5)3**

NON-METALLOCENE EARLY TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATION

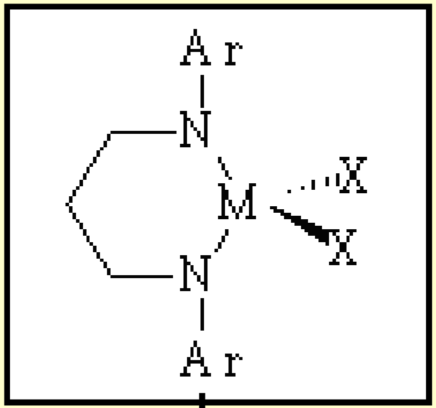


- **Very low activities for mono(β-diketiminates)**
- **Bis(β-diketiminates) exhibit higher activities**
- **Higher activities when R = p-CF3C6H3**



- **Very high catalyst activities and polymer molecular weights**
- **Bulky R” leads to higher Mw**
- **Bulky R group increases catalyst activity**
- **Living polymerization: Block copolymers**

EARLY TRANSITION METAL CATALYSTS

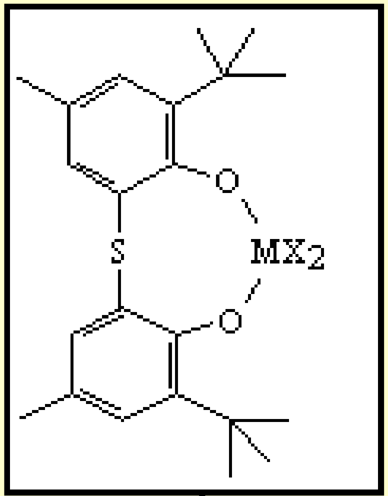


Chelating diamide ligands

Active catalyts for hexene-1 polymerization in combination with MAO

A = 350 x10^3 $gmmol^{-1}$ Zr^{-1} h^{-1} bar^{-1} , X = Me, Ar = 2,6-$^{i}Pr_2$-C_6H_3

McConville, D. H. Macromolecules, 1996, 29, 5241.

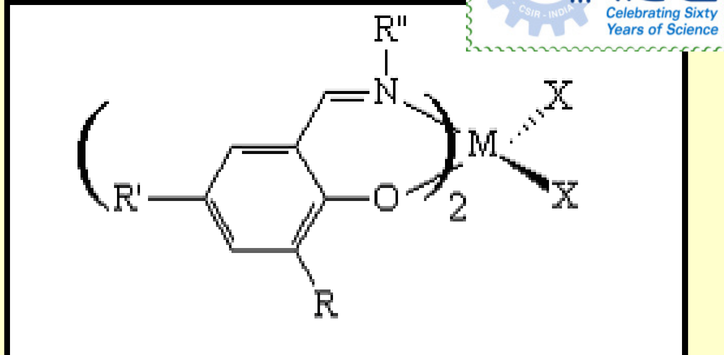


Chelating phenoxide ligands

Active catalysts for ethylene polymerization with 500 eqv MAO

A = 1580 $gmmol^{-1}$ Ti^{-1} h^{-1} bar^{-1}

van der Linden, A.; Schaverien, C. J. J. Am. Chem. Soc. 1995, 117, 3008.



a R = tBu, R' = H, R" = Ph
b M = Zr, R = tBu, R" = H
c M = Zr, R = cumyl, R' = Me, R" = Cy

Salicylaldiminato ligands

Active catalysts for ethylene polymerization

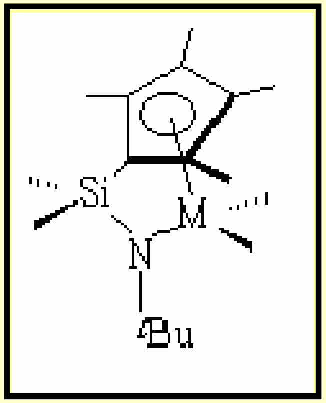
3a. A = 519 x 10^3 $gmmol^{-1}$ Zr^{-1} h^{-1} bar^{-1}

3b. A = 550 x 10^3 g $mmol^{-1}$ Zr^{-1} h^{-1} bar^{-1} R"=Ph

3c. A = 43x 10^5 $gmmol^{-1}$ Zr^{-1} h^{-1} bar^{-1}

Fujita, T. J. Am. Chem. Soc. 2001, 123, 6847

MIXED LIGANDS



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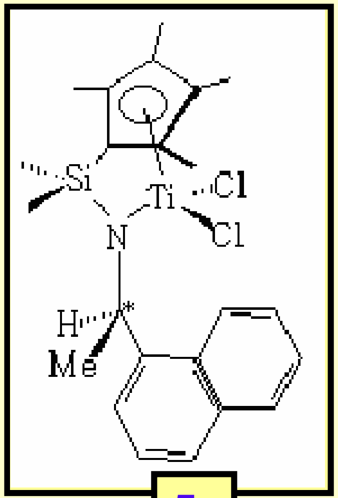

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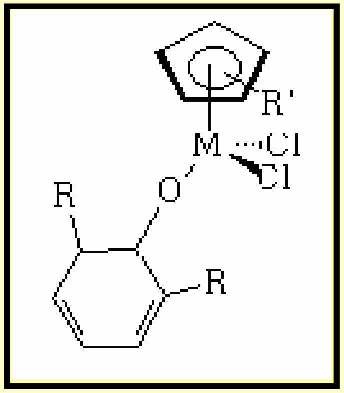

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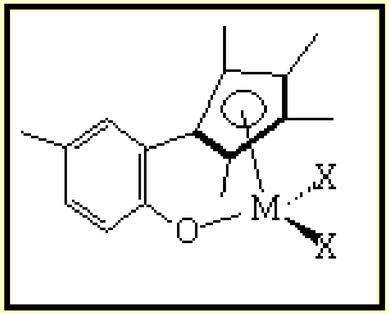


7

Complex 4 is the well kmown constraint geometry catalyst

Complex 5 is an active catalyst for the polymerization of propylene resulting in a PP with 56% isotacticity

McKnight, A. L.; Waymouth, R. M. Chem. Rev. 1998, 98, 2587.

Fink, G. J. Mol. Catal. A: Chem, 2000, 157, 83.

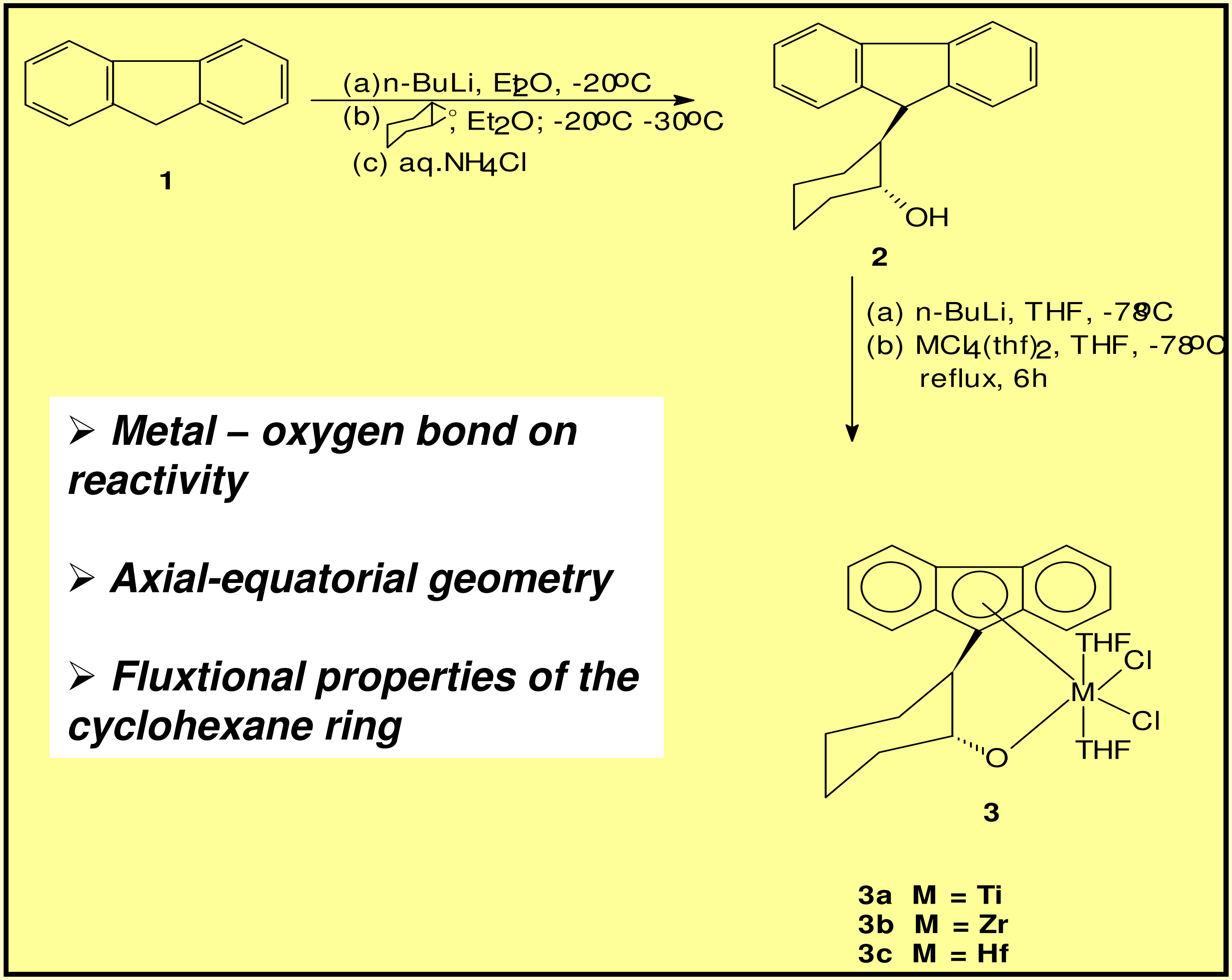
Zr complex 6 (R= tBu, R' = Me$_5$) exhibits an activity of 4260 gmmol^{-1} Zr^{-1} h^{-1} bar^{-1} for the polymerization of ethylene

7/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ is an active catalyst for ethylene polymerization; A = 2100 gmmol^{-1} Ti^{-1} h^{-1} bar^{-1}

Nomura, K. Organometallics, 1998, 17, 2152.

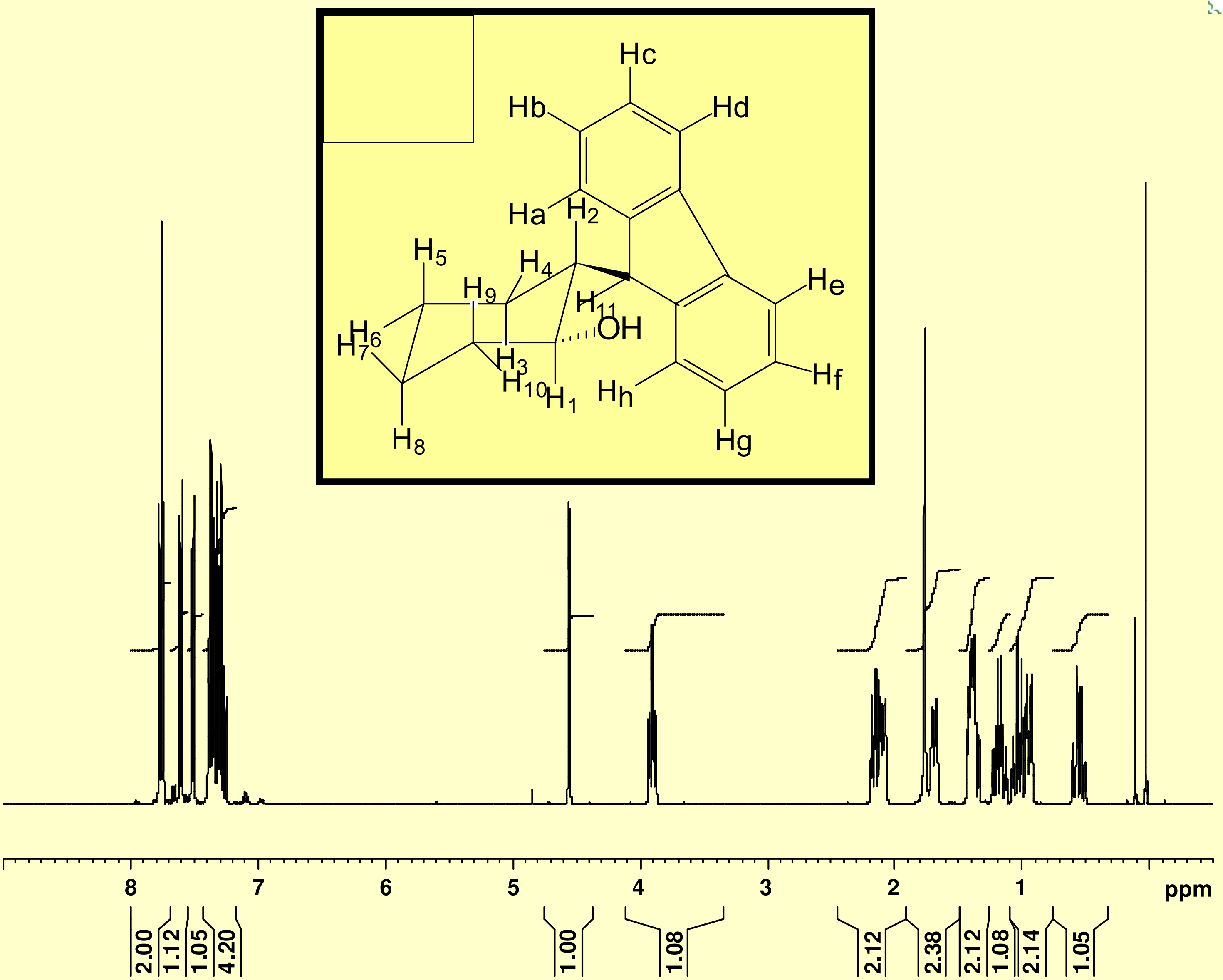
Marks, T. J. Organometallics, 1997, 16, 5958.

SYNTHESIS GROUP 4 METAL COMPLEXES OF TRANS-2-[9-(H) FLUORENYL] CYCLOHEXANOL



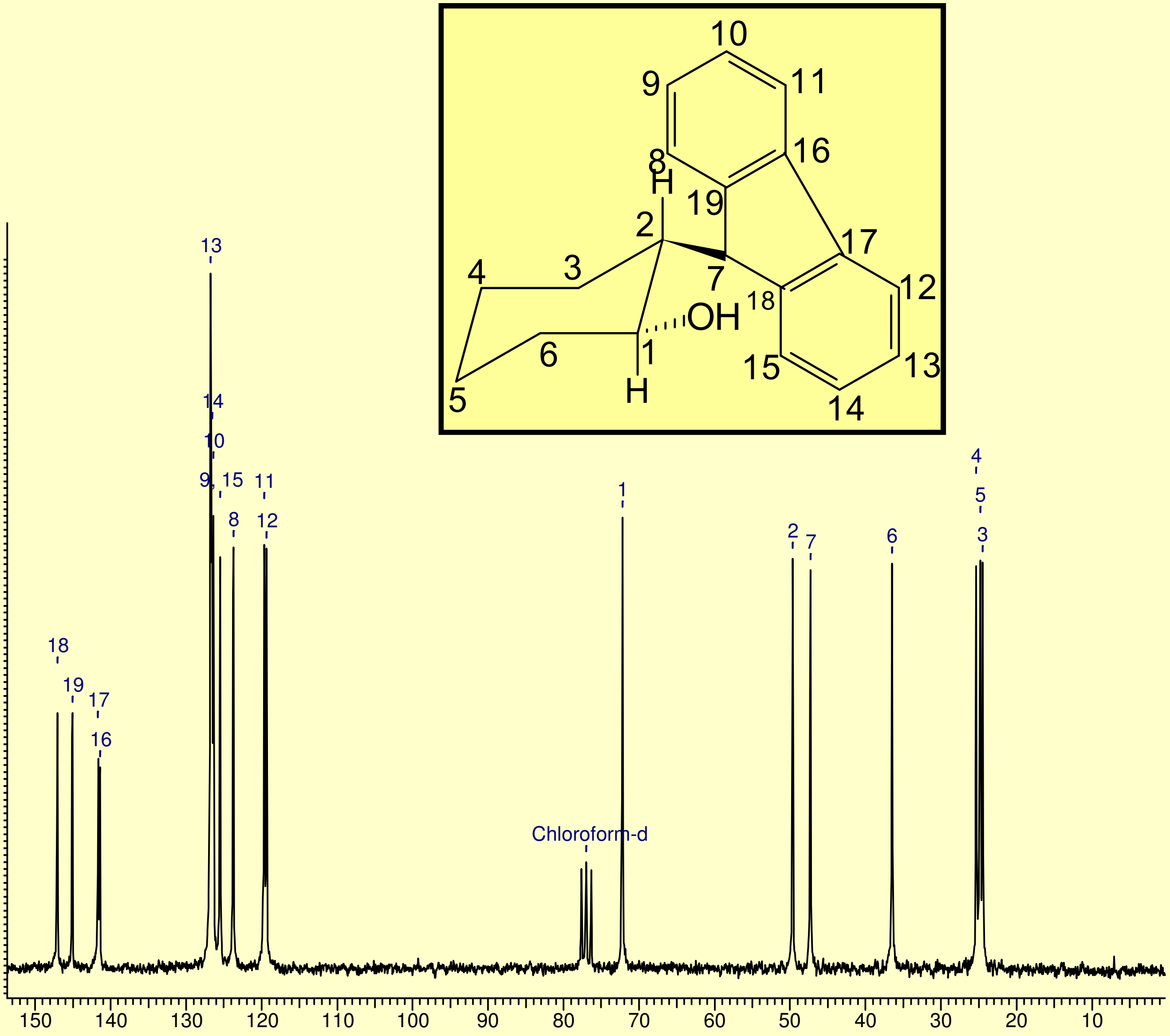
- ***Metal – oxygen bond on reactivity***
- ***Axial-equatorial geometry***
- ***Fluxtional properties of the cyclohexane ring***

^{1} H NMR SPECTRUM OF THE LIGAND

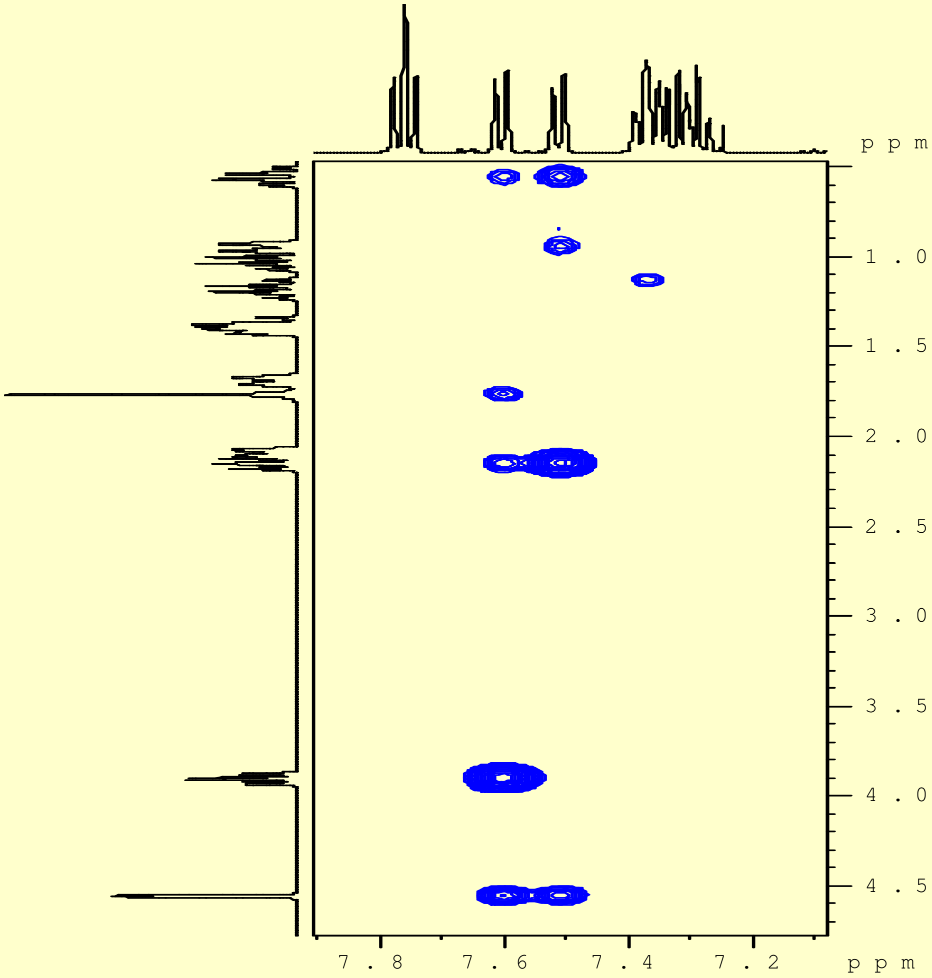


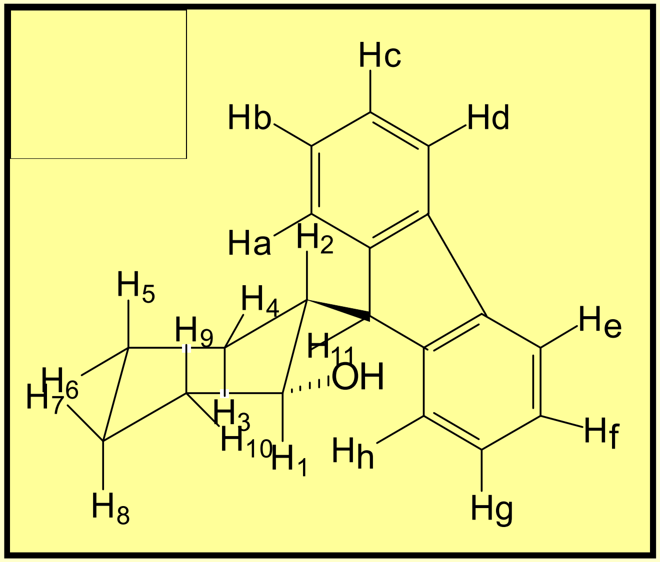
^{13}C NMR SPECTRUM OF THE LIGAND

1950 - 2010
Celebrating Sixty Years of Science



NOESY SPECTRUM PROVIDES EVIDENCE FOR THE AXIA EQUATORIAL GEOMETRY OF THE LIGAND





- ➢Strong NOE observed between H_2(2.14 ppm) and H_a(7.51 ppm) and between H_1 (3.98 ppm)and H_h (7.60 ppm)

POLYMERIZATION OF ETHYLENE AT 5 BAR: NATURE OF METAL

Toluene(30 mL); MAO; Al/M: 2000; PC2H4: 5 bar; time: 1 h

Complex	Complex (μmol)	Tp (°C)	Yield (g)	Activity g PE mmol^{l-1}M.h^{-1}	$[\eta]^b$ dL/g	Mw (x10^4)	M_w/ M_n	Tm (°C
3a (Ti)	19.0	25	0.20	10	5.2	n.d	n.d	142
3b(Zr)	17.6	25	1.0	57	5.1	n.d	n.d	134
3c(Hf)	15.5	25	0.04	2.6	2.8	n.d	n.d	133
3a(Ti)	19.0	80	0.30	16	2.5	n.d	n.d	140
3b(Zr)	17.6	80	3.7	210	0.9	12.2	BM	122
3c(Hf)	15.5	80	0.07	4.5	2.0	n.d	n.d	134

[b] measured in decahydronaphthalene at 135°C

➢Lower catalyst activity of hafnium complex 3c when compared to 3a and 3b can be attributed to stronger Hf-C bond which slows down monomer insertion and chain propagation

➢Titanium and zirconium complexes produce poly(ethylene)s in the ultra high molecular weight range

➢Titanium complex 3a resulted in poly(ethylene)s with exceptionally high crystalline melting point

POLYMERIZATION OF ETHYLENE USING 3 b / MAO: EFFECT OF MAO CONCENTRATION

Toluene(30 mL); Zr: 17.6 μmol; MAO; PC2H4: 5 bar; time: 1 h

Al/Zr	Tp (°C)	Yield(g)	Activity g PE $mmol^{-1}Zr.h^{-1}$	$[\eta]^b$ dL/g	Tm(°C)
500	25	0.9	51	6.55	132
1000	25	0.96	55	6.30	132
2000	25	1.0	57	5.13	134
500	80	2.5	142	1.25	127
1000	80	2.8	159	1.35	122
2000	80	3.7	210	0.93	122

[b] measured in decahydronaphthalene at 135°C

Very high molecular weight poly(ethylene)s at 25° C; MW exceeding Fujita's catalysts

EFFECT OF TEMPERATURE

Toluene (30 mL); Zr: 17.6 μmol; MAO; Al/Zr: 2000; P_{C2H4} : 5 bar; time : 1 h

Tp (°C)	Total yield (g)	Acetone insoluble fraction (Fraction A) (g)	Acetone soluble fraction (Fraction B) (g)	Toluene soluble fraction (Fraction C) (g)	Activity g PEmmol^{-1}Zr.h^{-1}
25	1.0	1.0	nil	nil	57
40	0.96	0.96	nil	nil	55
60	3.9	1.9	1.1	0.9	222
80	3.7	1.8	1.1	0.8	210
100	2.8	1.7	0.5	0.6	159

- Oligomerization favored above 60°C due to increased rate of chain transfer reactions

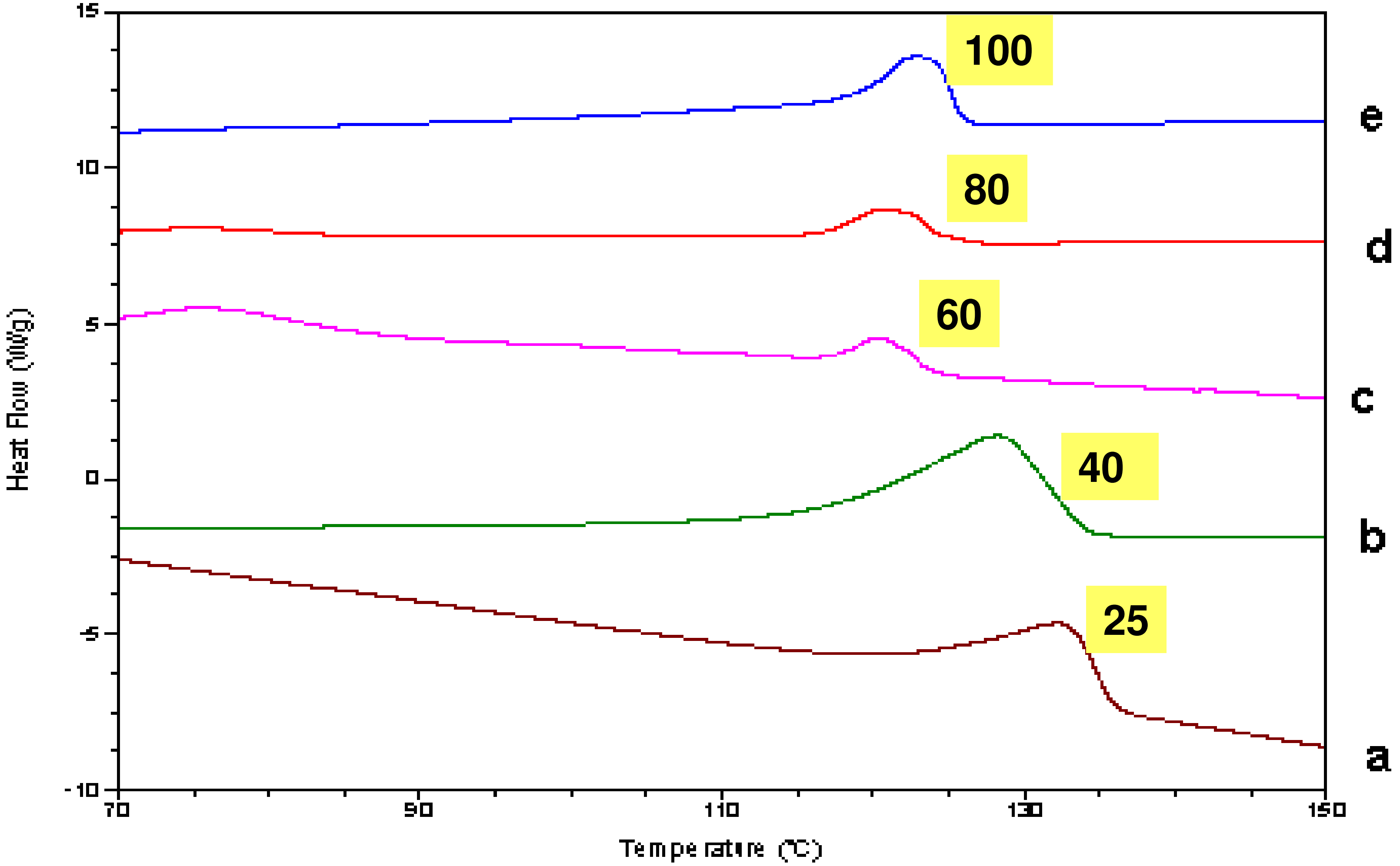
- Decrease in catalyst activity at 100°C may be due to deactivation of the active species

ANALYSIS OF FRACTION A

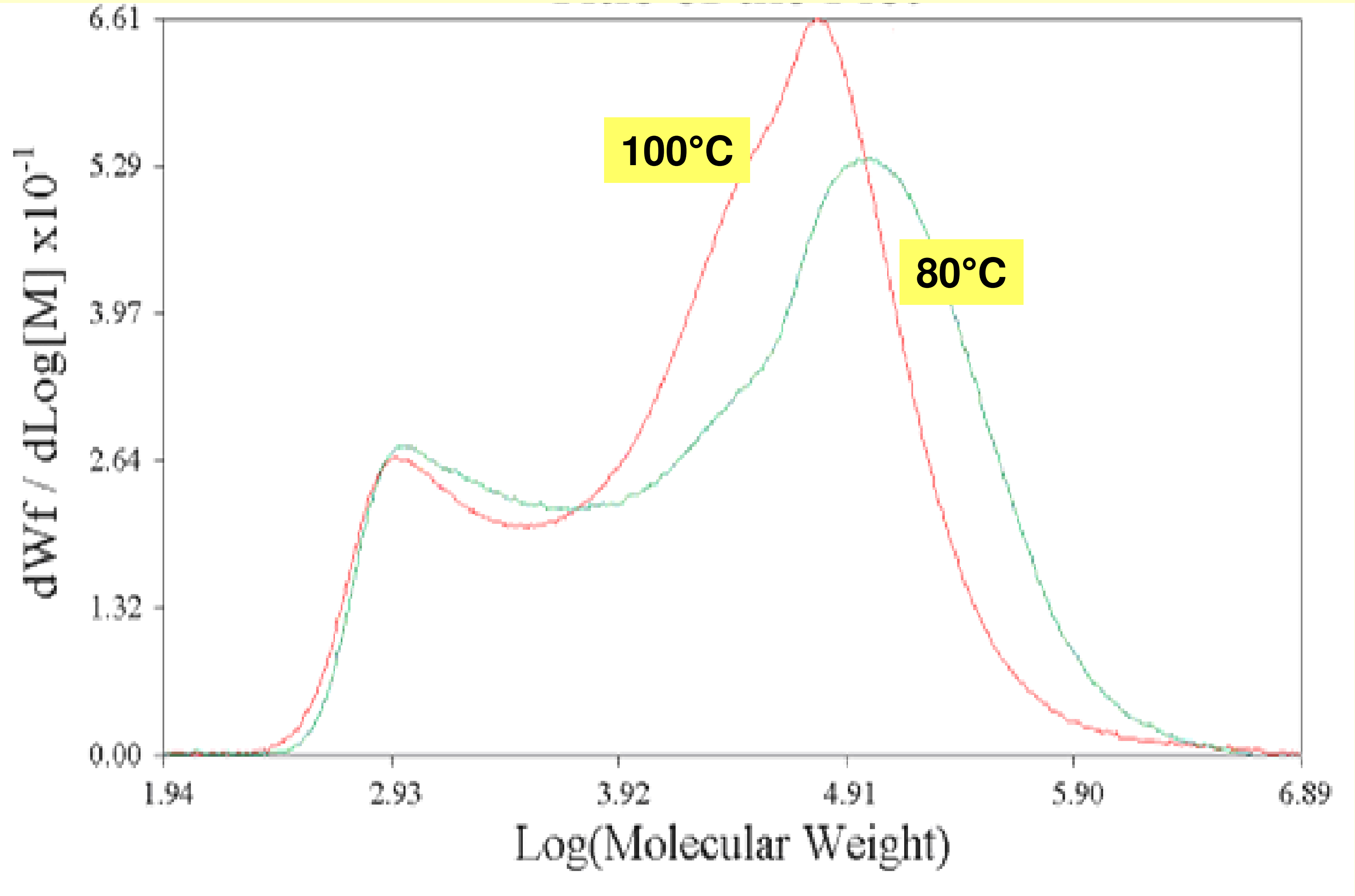
Tp (°C)	[η] dL/g	Mw ($x10^4$)	Mw/Mn	Tm (°C)
25	5.1	n.d	n.d	132
40	4.7	n.d	n.d	130
60	1.04	n.d	n.d	125
80	0.93	12.2	Bimodal	121
100	0.59	7.7	Bimodal	123

- ➢ Progressive decrease in crystalline melting point (Tm) with increasing temperature indicates increase in degree of branching
- ➢Bimodal molecular weight distribution implies the presence of more than one active center

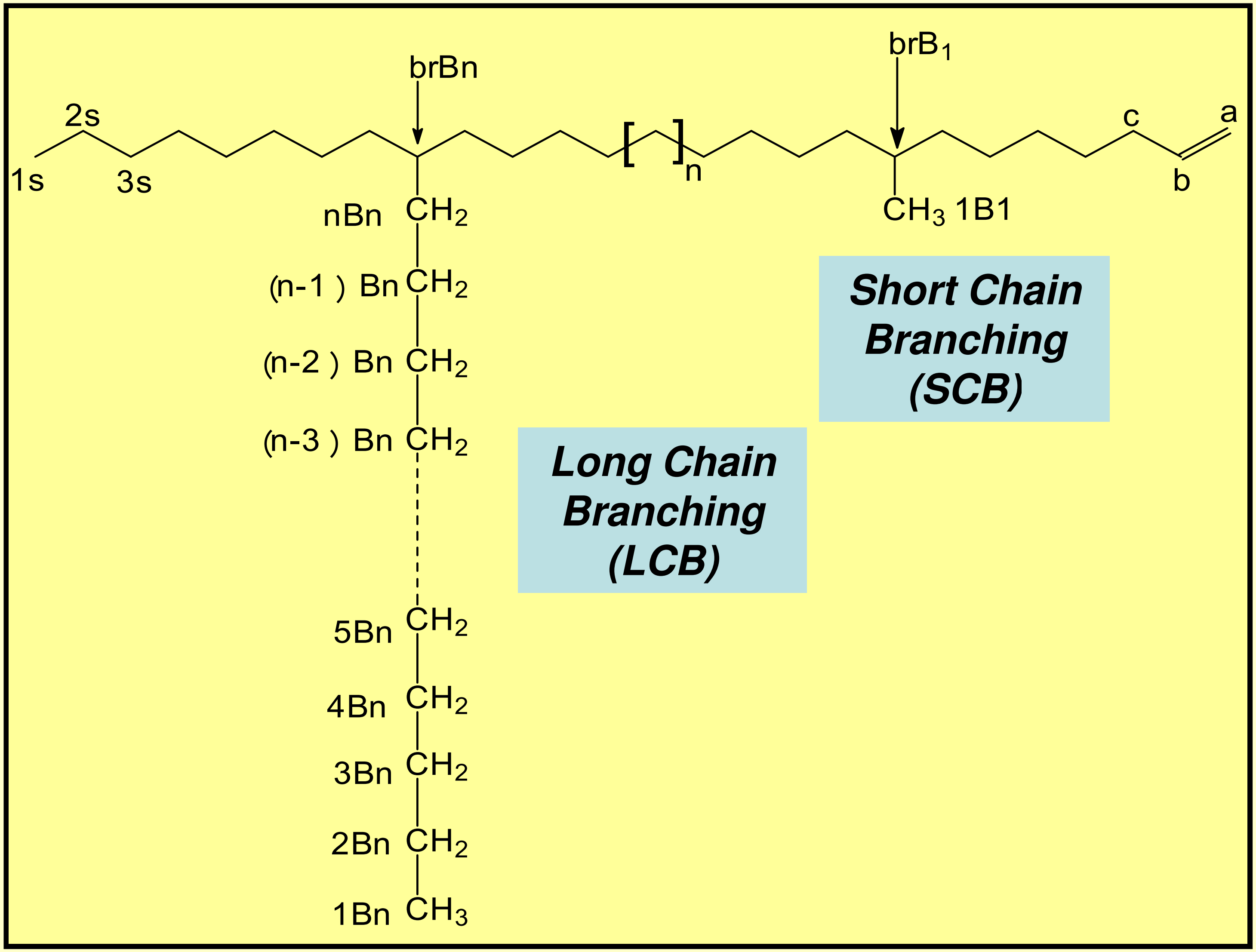
DSC THERMOGRAMS OF FRACTION A



GPC OF FRACTION A OBTAINED USING 3b / MAO



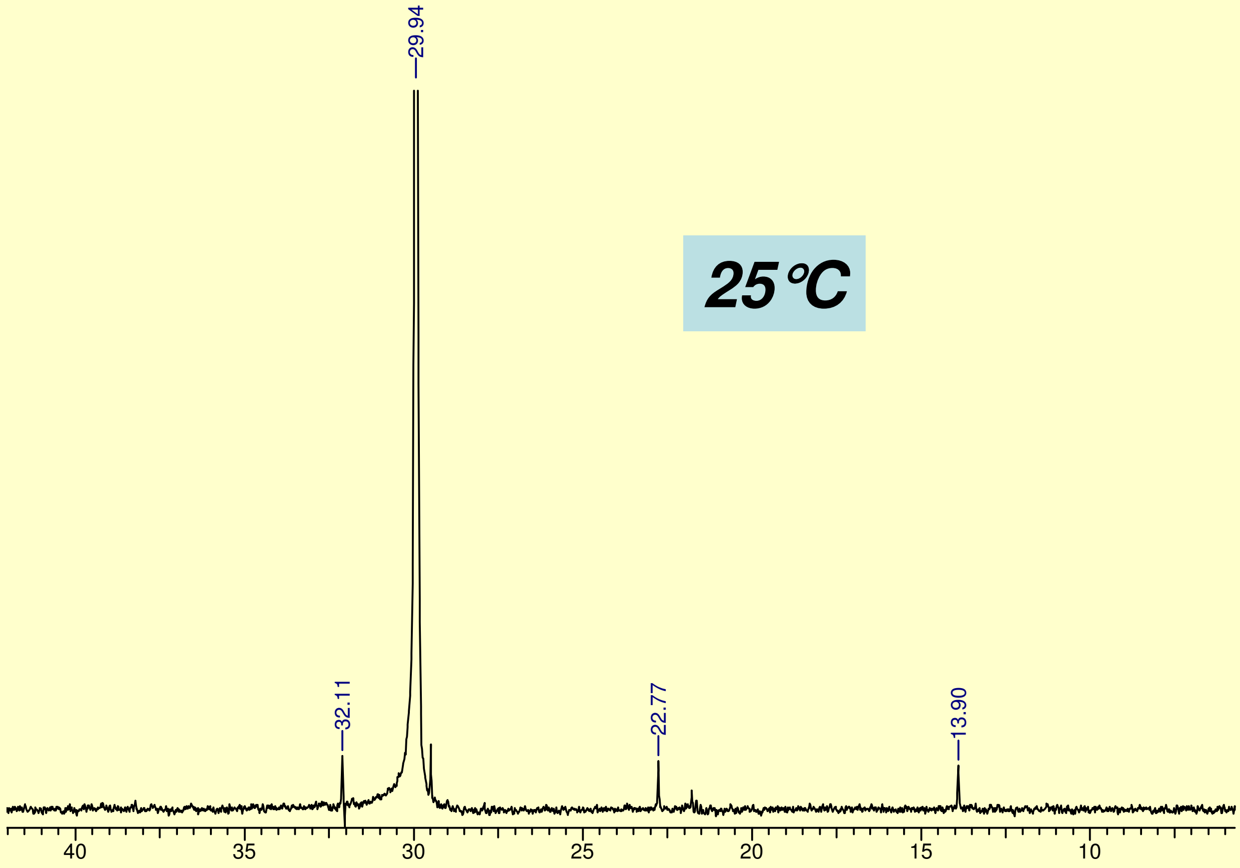
NOMENCLATURE FOR BRANCHED POLYETHYLENE



Short Chain Branching (SCB)

Long Chain Branching (LCB)

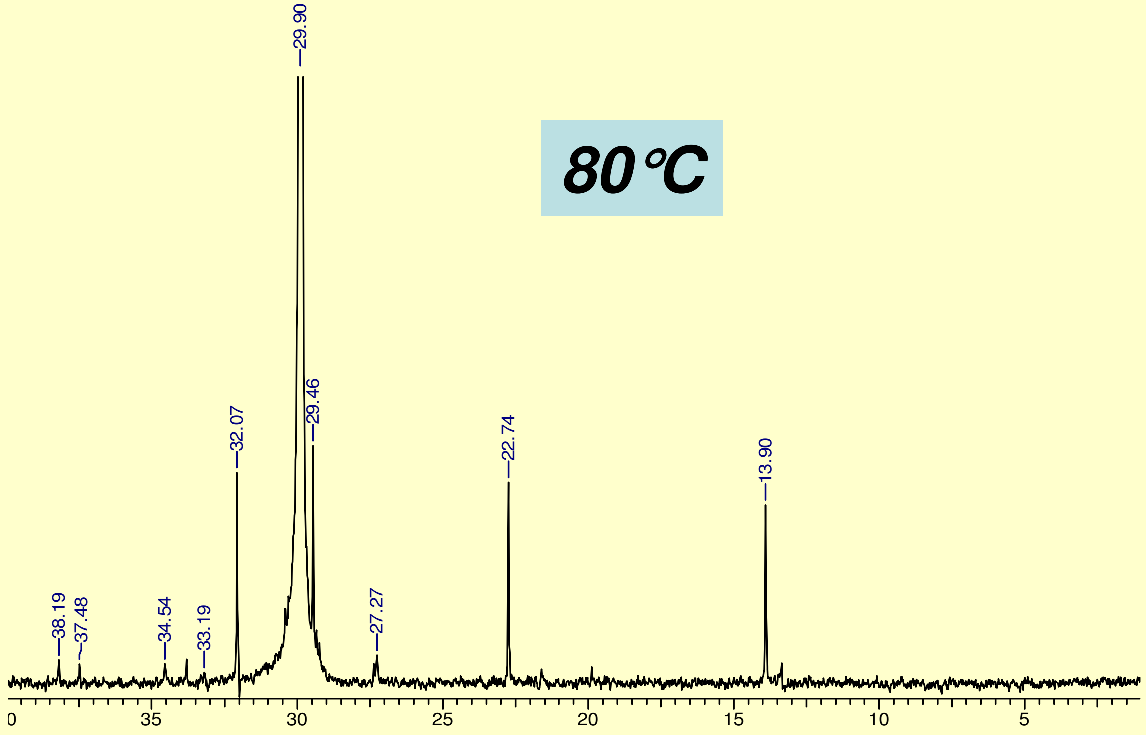
QUANTITATIVE 13C NMR SPECTRUM (IN ODCB/C_6D_6) OF FRACTION A OBTAINED FROM 3 b / MAO



25°C

- **Absence of peak at 38.19 ppm implies that the polymer is linear**
- **Chain ends completely saturated (chain ends : methyl group)**

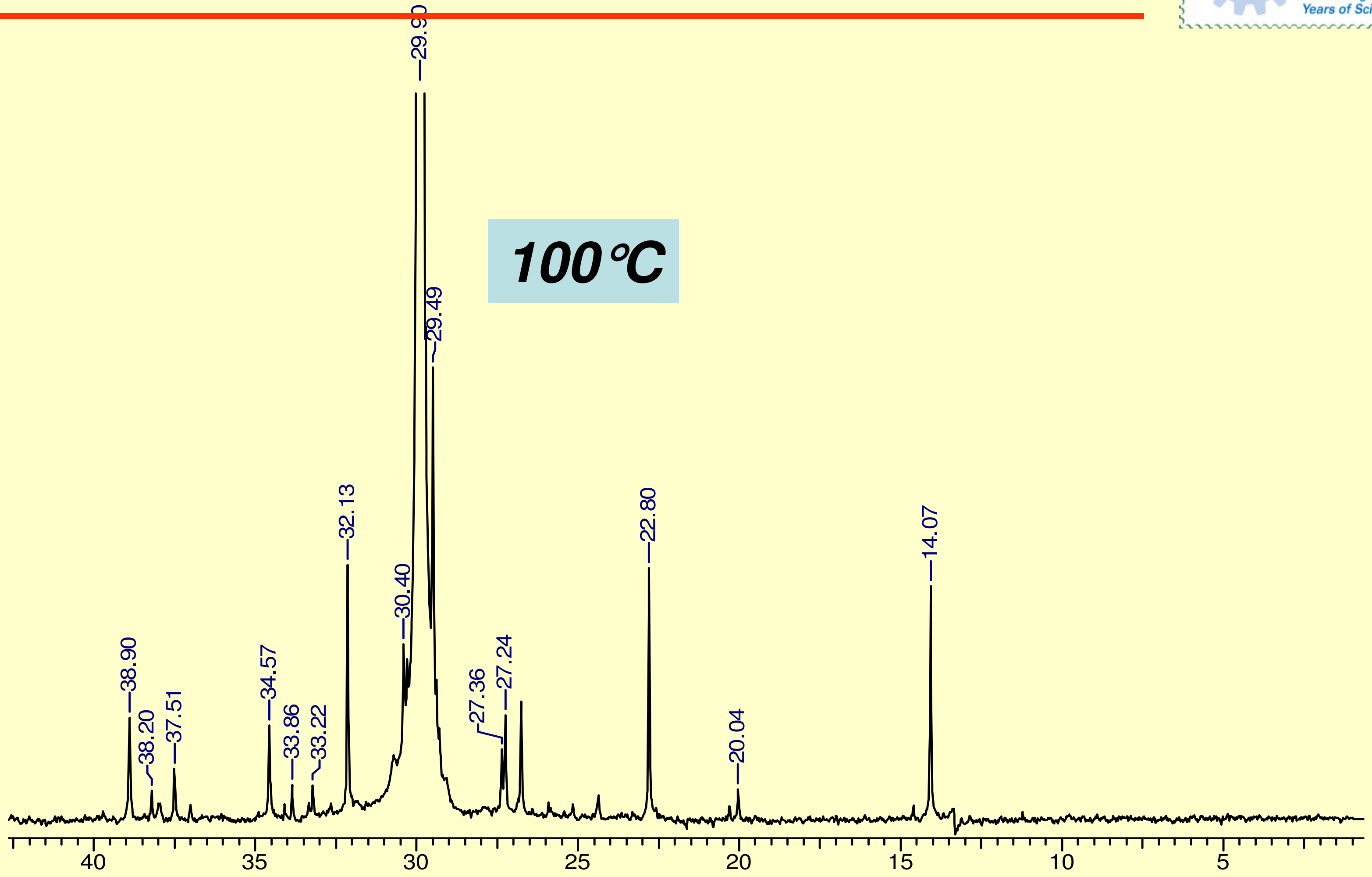
QUANTITATIVE 13C NMR SPECTRUM OF FRACTION A OBTAINED FROM 3 b / MAO



80°C

- Branching confirmed by the presence of peak at 38.19 ppm
- Only long chain branches(more than 6 carbon atoms in the branch)

QUANTITATIVE 13C NMR SPECTRUM OF FRACTION A OBTAINED FROM 3 b / MAO



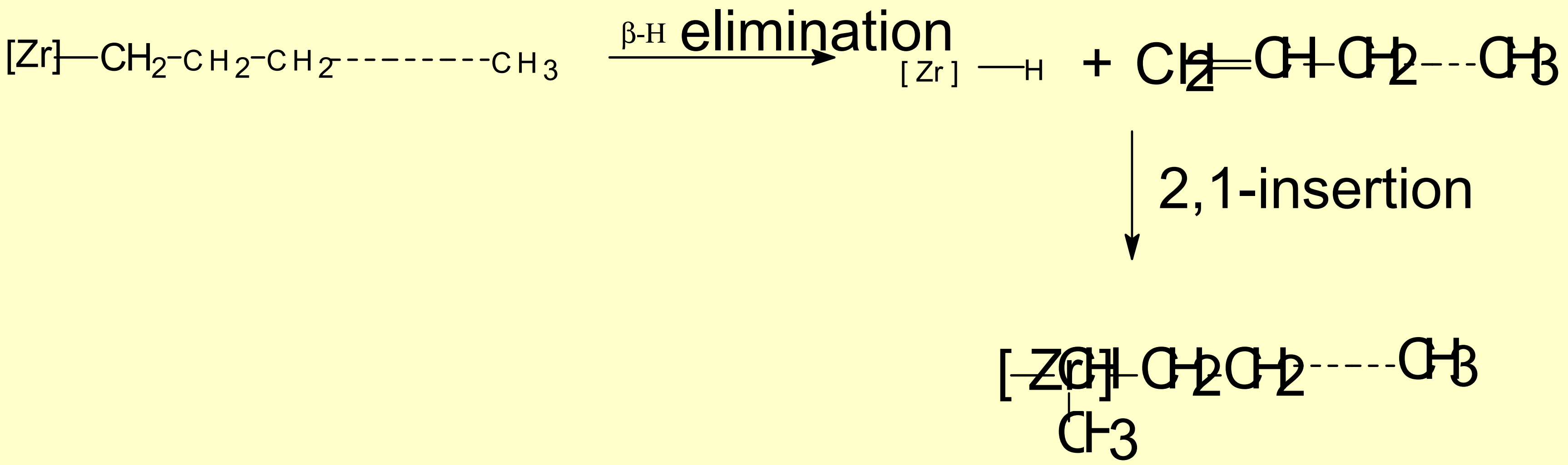
- **Signals at 20.04 and 37.47 ppm indicates presence of methyl branches in addition to long chain branches**

NATURE OF BRANCHING AND BRANCHING DISTRIBUTION OF FRACTION A OBTAINED USING 3b / MAO

Temp.	Total branching/1000 C	Branching with respect to total	
		Methyl (%)	Long chain (%)
25	0	0	0
40	0	0	0
60	0.7	0	100
80	1.4	0	100
100	2.6	60	40

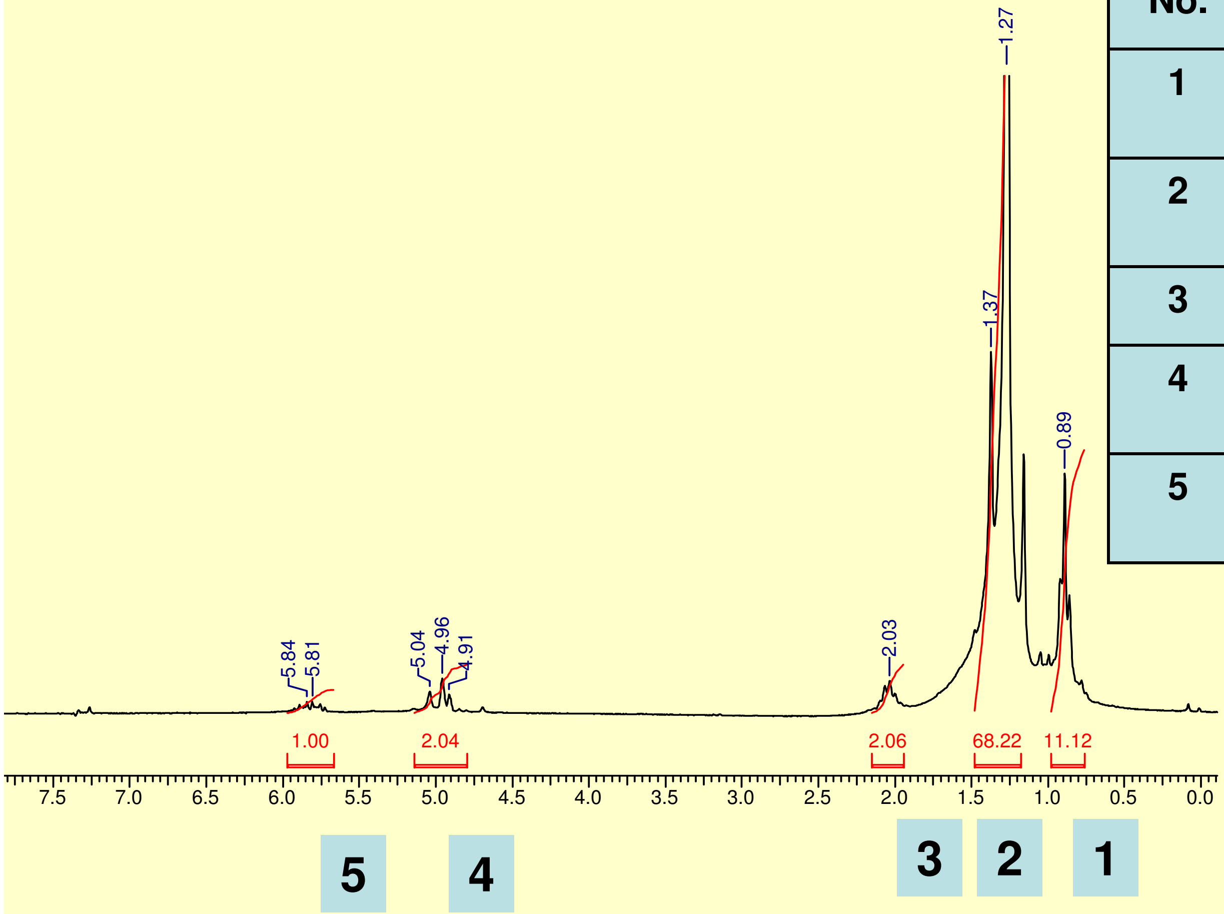
- **Formation of methyl branches in addition to long chain branches at 100°C**

MECHANISM FOR THE FORMATION OF METHYL BRANCHES



- ➢ **Methyl branches result from β-H elimination followed by 2,1-insertion of the α-olefin into the [Zr – H] species (Regio-errors)**
- ➢ **2,1-insertion favored at higher temperatures**

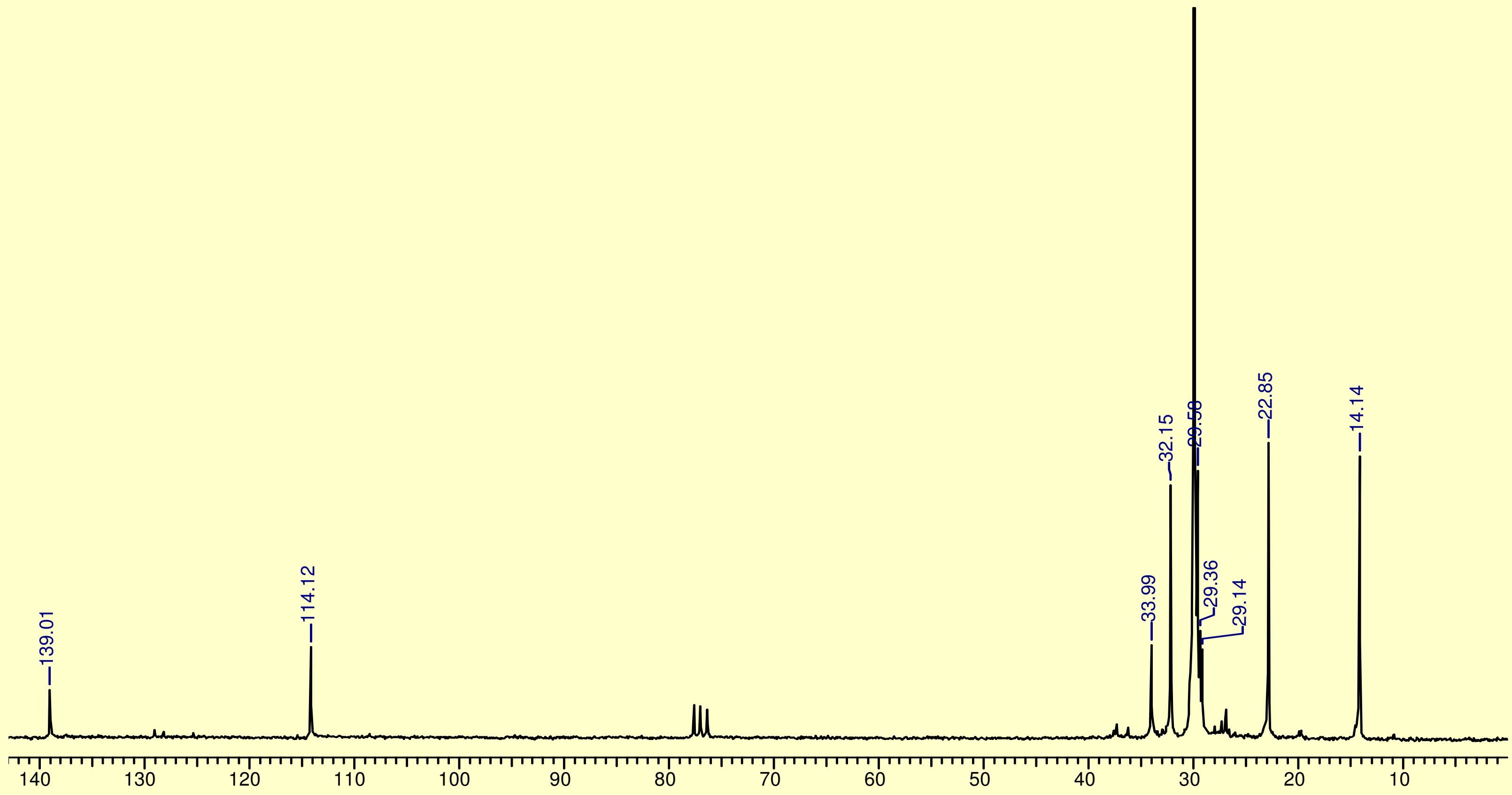
1H NMR SPECTRUM OF FRACTION B



Peak No.	Chemical shift (ppm)	Assignments
1	0.89	$-CH_3$
2	1.27-1.37	$-(CH_2-)_n$
3	2.04	$-CH_2-CH=CH_2$
4	4.91-5.06	$-CH_2=CH$
5	5.70-5.78	$-CH_2=CH-$

Presence of terminal unsaturation and methyl groups

13C NMR SPECTRUM FRACTION B



- **Absence of signal at 38.19 ppm indicates linear nature of the oligomer**
- **Signals at 14.14, 22.85 and 32.15 ppm due to saturated chain ends**
- **Signals arising from unsaturated chain ends appear at 114.12 and 139.01 ppm**
- **Mixture of linear α-olefins and long chain alkanes**

CHARACTERIZATION OF FRACTIONS B AND C

Tp (° C)	% alkanes		Mn	
	Fraction B	Fraction C	Fraction B	Fraction C
60	76	78	320	300
80	69	61	310	250
100	50	57	280	200

- Low molecular weight oligomers (DP ~ 10) comprise of mixtures of n-alkanes and α-olefins
- Oligomers are rich in n-alkanes implying that chain transfer to aluminium is a dominant chain breaking event
- Content of α-olefins increases with temperature ; Rate of β-H transfer becomes competitive with chain transfer to aluminium at higher temperatures

CONCLUSIONS

- *Ansa* - η5 - monofluorenyl Group 4 metal complexes (3a-3c) exhibit moderate activity for the polymerization of ethylene at 5 bar pressure
- Catalyst activity decreases in the order Zr > Ti > Hf
- Titanium complex 3a at 25°C produce ultra high molecular weight poly(ethylene)s with unusually high crystalline melting point. This indicates that the PE is defect free and linear with methyl terminal chain ends
- Zirconium complex 3b at 25°C also produce ultra high molecular weight poly(ethylene)s; however, the crystalline melting points are lower, similar to conventional HDPE

CONCLUSIONS

- **Zr complex 3b exhibits activity even at 100°C. The thermal stability of the catalyst system can be attributed to the metal-oxygen bond in the complex**

- **At 60, 80 and 100°C, a mixture of insoluble solid polymer and soluble liquid oligomers was obtained**

- **The solid poly(ethylene)s consists of exclusively long chain branches (> 6 carbons) at 60 and 80°C, whereas, at 100°C, methyl branches are also observed in addition to long chain branches**

- **Long chain branches are formed as a result of β-H transfer reaction followed by reincorporation of the resulting long chain α-olefin (macromonomers of ethylene)into the growing polymer chains**

CONCLUSIONS

- **Methyl branches result from β-H elimination followed by 2,1-insertion of the α-olefin into the [Zr]-H centers , (Regio- errors). This reaction is favored at 100° C**

- **The soluble oligomer was found to be a mixture of linear α-olefins and long chain alkanes, providing further evidence that the dominant chain breaking events at higher temperatures are β-H elimination and chain transfer to alkylaluminum**

- **Bimodal MWD observed at higher temperatures indicate the presence of at least two active centers, one capable of selective oligomerization and the other capable of either homo-polymerization or copolymerization of ethylene with higher α-olefins**

CONCLUSIONS

- First example of a single zirconium complex that exhibits such diverse polymerization behavior producing a range of poly(ethylene) s from linear high molecular weight to lower molecular weight polymers with short and long chain branching as well as single site as well dual site behavior

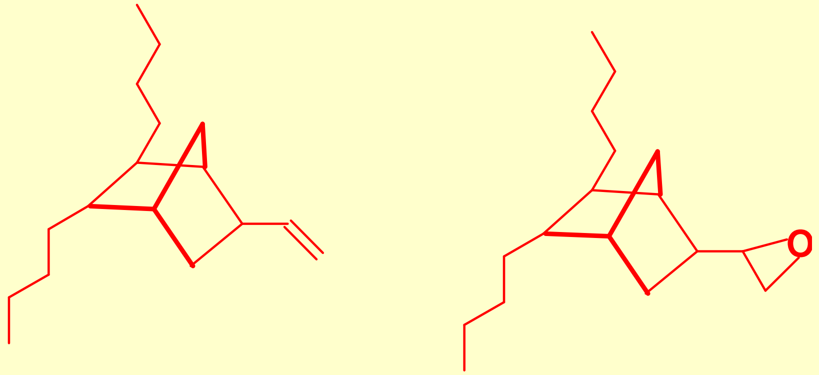
- This behavior can be tuned only with one variable, namely, temperature of polymerization

- The Cp - Zr – O bite angle increases with temperature due to the increased conformational mobility of the cyclohexane at higher temperatures, resulting in β-H elimination, reinsertion and 2,1- insertion.

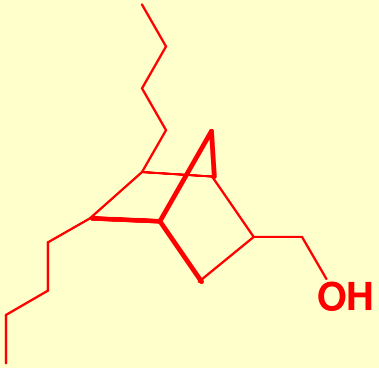
SYNTHESIS OF FUNCTIONAL POLY(OLEFIN)S

- *IN CHAIN FUNCTIONAL POLY(OLEFIN)S*
  - ***Copolymerization with functional monomers***
  - ***Use of comonomers with protected functional groups***
  - ***Introduction of functional groups on preformed polymers***
- *CHAIN END FUNCTIONAL POLY(OLEFIN)S*
  - ***Introduction of terminal functional groups by reaction on pre formed polymers***
  - ***Use of chain transfer agents to introduce chain end functionality***

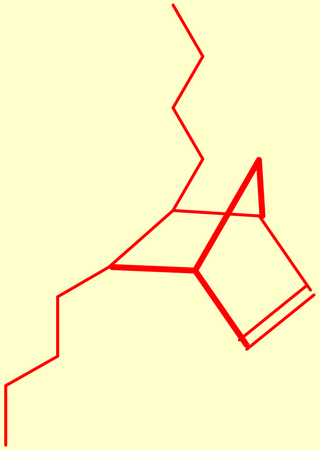
IN CHAIN FUNCTIONALIZATION OF POLY(OLEFIN)S



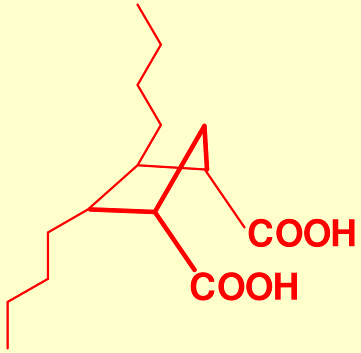
S. Marathe(1994)



K. Radhakrishnan (1998)



K. Radhakrishnan (1998)

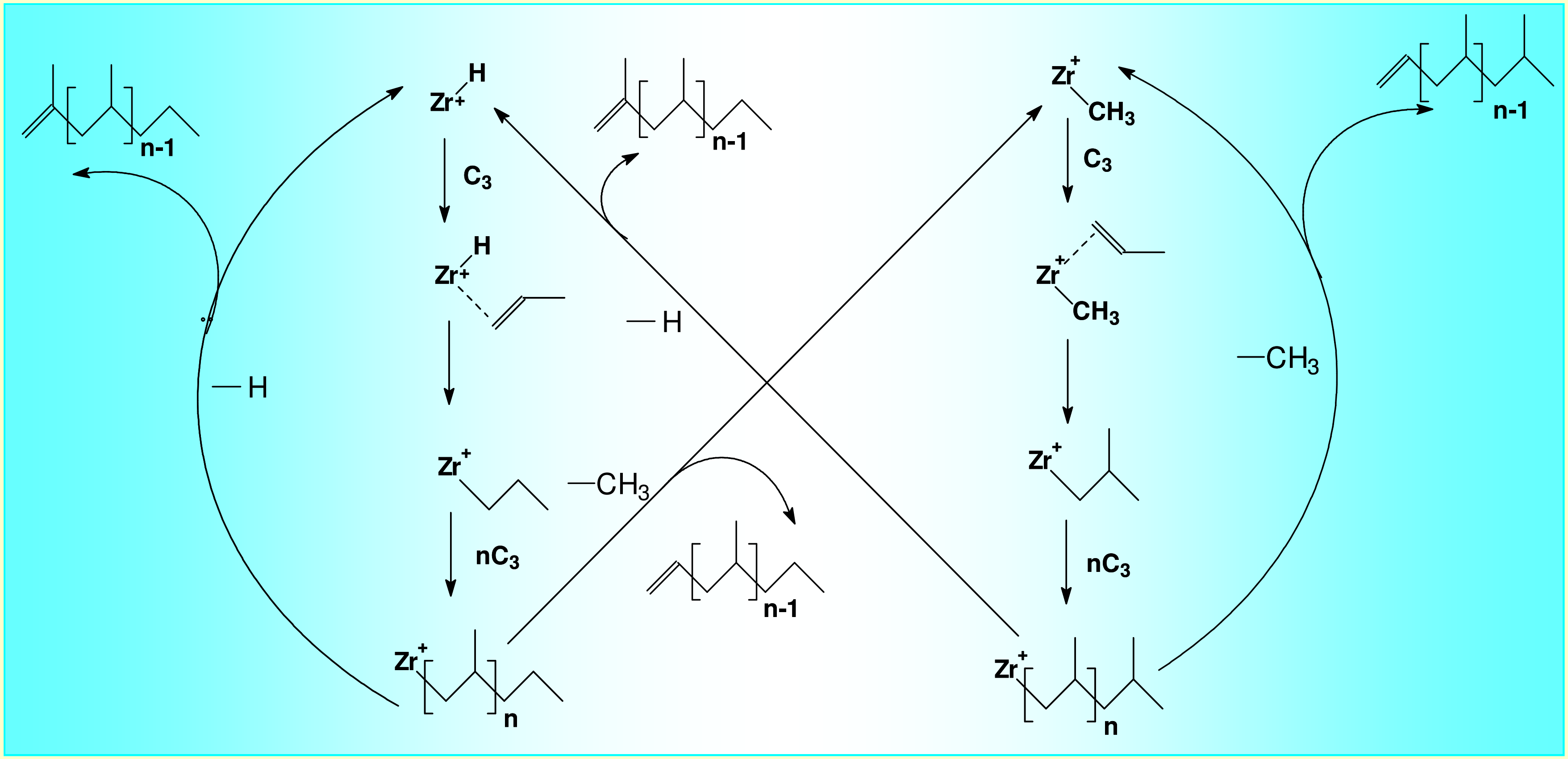


K. Radhakrishnan, M.J. Yanjarappa (2000)

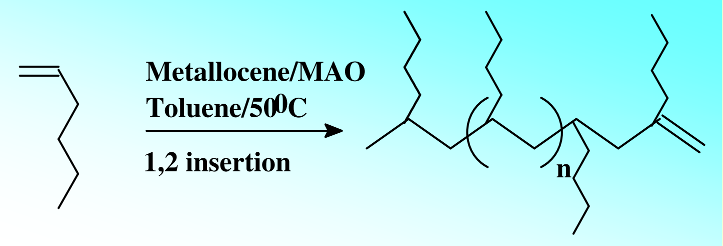
SYNTHESIS OF TERMINAL VINYLIDENE UNSATURATED POLY(HEXENE-1)S

OBJECTIVES

To exploit the chain transfer reactions in metallocene catalyzed polymerization of olefins for the synthesis of terminally functionalized poly(olefin)s



SYNTHESIS OF VINYLIDENE TERMINATED OLIGO(1-HEXENE)



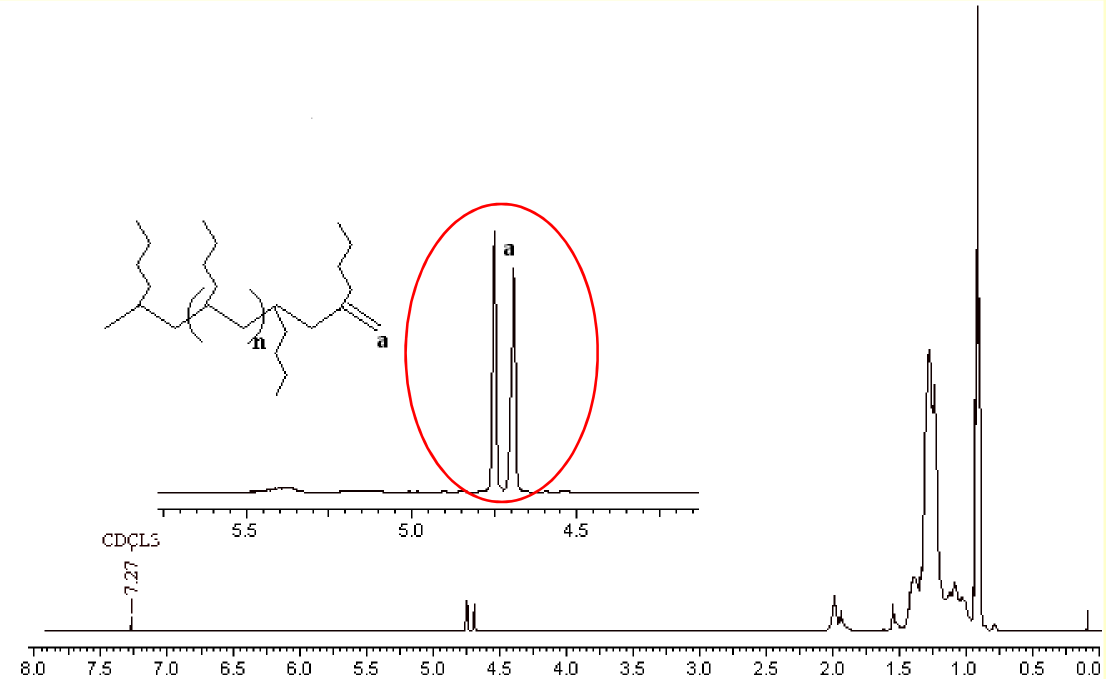
Mn = 300 - 2000

Fn > 95%, Mw/Mn = 2

n = 3-10

Metallocene	Temp (^{0}C)	Mn by VPO	Mn by ^{1}H NMR	mol% Vinylidene unsaturation
Cp_2ZrCl_2	50	370	380	98
	40	580	600	96
	30	860	900	95
$n\text{-}BuCp_2ZrCl_2$	50	440	460	98
	40	700	730	96
	30	1020	1100	93

^{1}H NMR OF POLY(HEXENE-1) (Mn : 400) PRODUCED BY CP$_2$ZrCl$_2$/MAO CATALYST



REACTION CONDITIONS: Temperature = 50^{0}C, Zr = 9.6x10^{-5} mol/L, Al/Zr = 8000.

Vinylidene double bond which arises due to β-H transfer after 1,2 insertion was observed as major end group at 50^{0}C

SYNTHESIS OF ACRYLAMIDO END FUNCTIONALIZED POLY(OLEFIN)S USING METALLOCENE CATALYSTS

M.J. Yanjarappa and S. Sivaram, Macromolecules, 37, 8499 (2004)

RITTER REACTION USING VINYLIDENE TERMINATED OLIGO(HEXENE-1)

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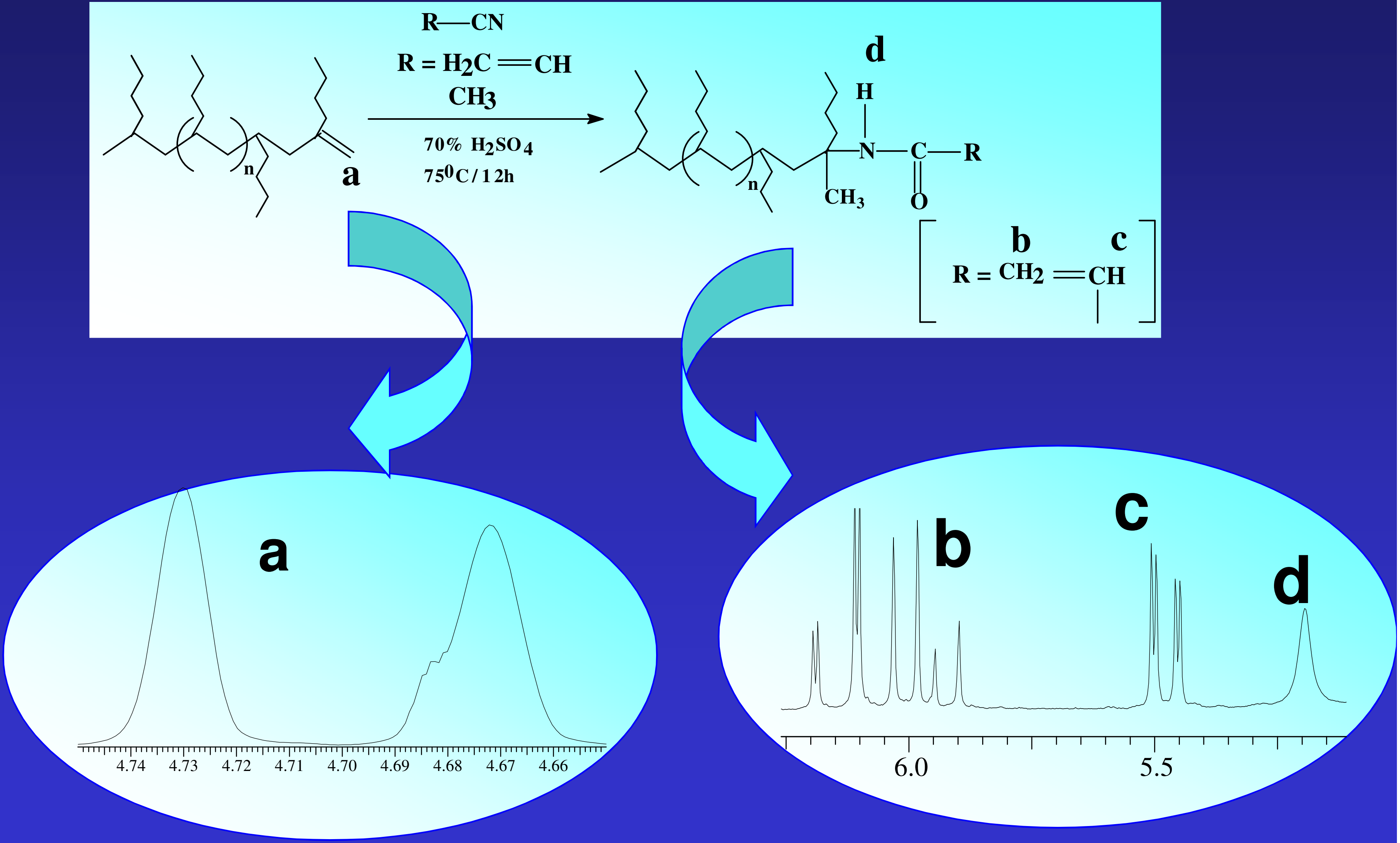
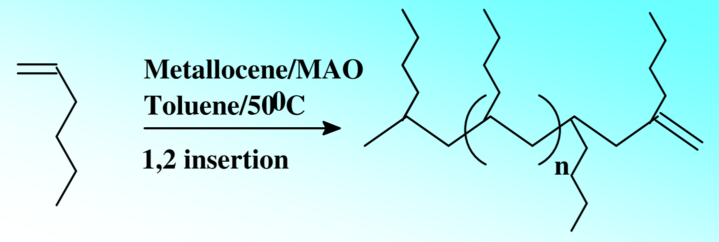


SYNTHESIS OF VINYLIDENE TERMINATED OLIGO(1-HEXENE)



Mn = 300 - 2000

Fn > 95%, Mw/Mn = 2

n = 3-10

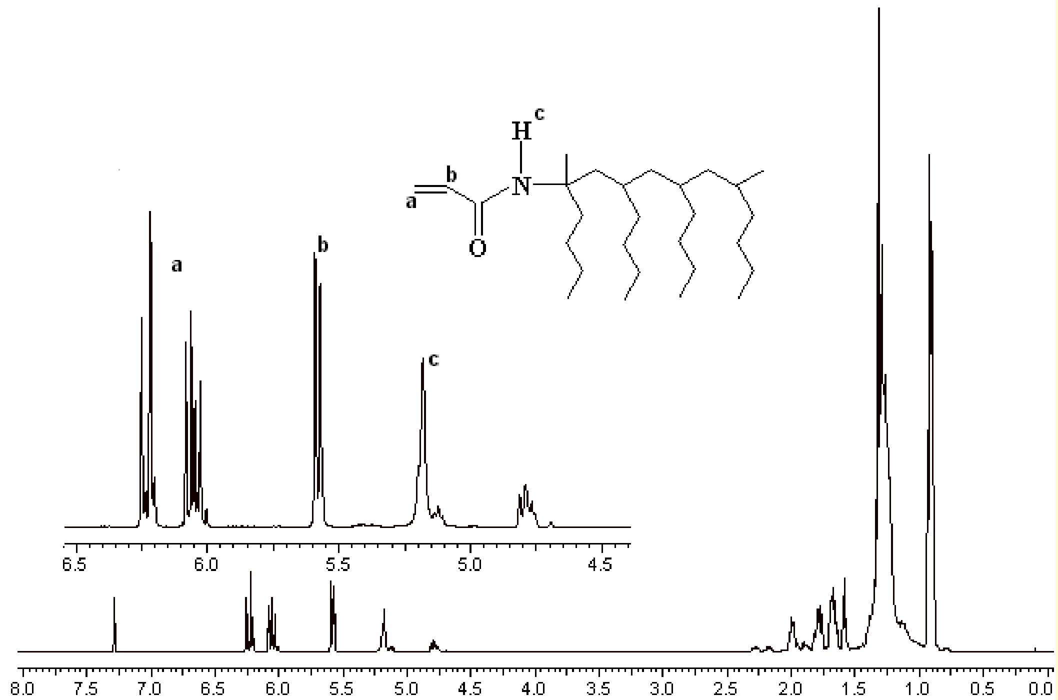
Metallocene	Temp (^{0}C)	Mn by VPO	Mn by ^{1}H NMR	Mol% Vinylidene unsaturation
Cp_2ZrCl_2	50	370	380	98
	40	580	600	96
	30	860	900	95
n-$BuCp_2ZrCl_2$	50	440	460	98
	40	700	730	96
	30	1020	1100	93

RITTER REACTION OF VINYLIDENE TERMINATED POLY(HEXENE-1) WITH ACRYLONITRILE

Run no.	Poly(hexene-1)				Mn after functionalization		Fn (mol%) a / b
	Mn	mol	End groups (mol%)		VPO a	^{1}H NMR b	
			vinylidene	internal			
1	380	0.01	98	2	440	490	89
2	1080	0.005	94	6	1140	1440	80
3	2760	0.0025	90	10	2820	5660	50
4	10 020	0.001	83	17	10 080	34 760	29

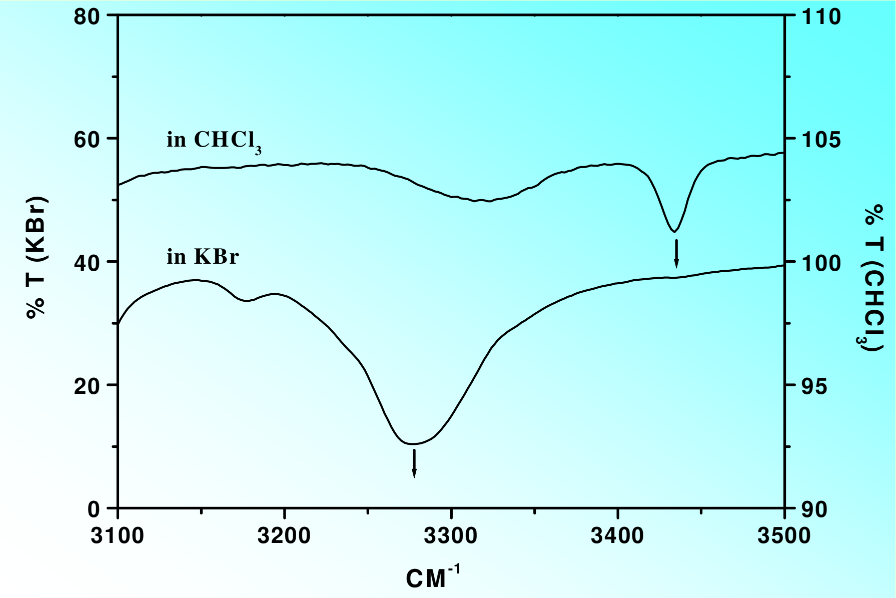
Reaction conditions: 2 mL of 70% H_2SO_4 catalyst, Temperature = 70^{0}C, Nitrile/Olefin = 5 mol/mol,

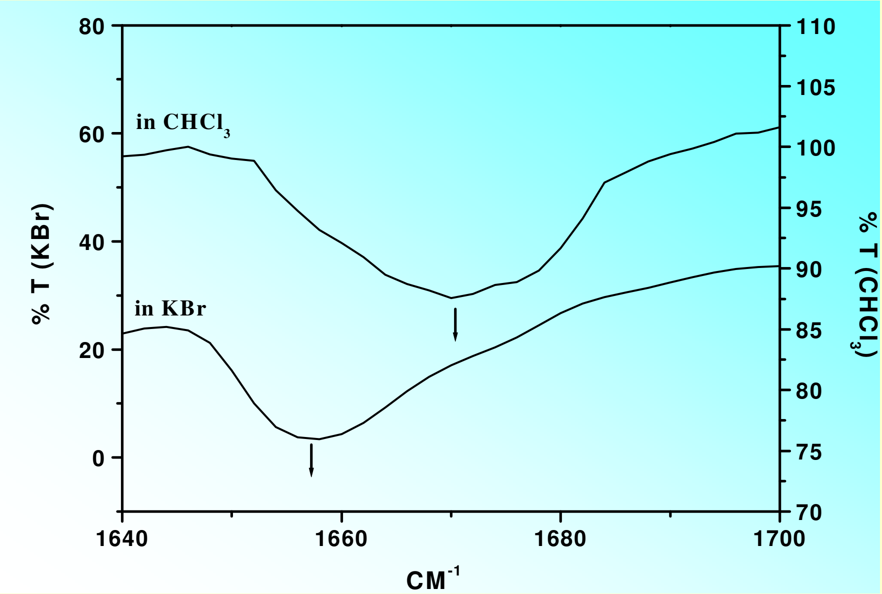
The number average degree of functionality (Fn) decreases with increase in number average molecular weight of poly(hexene-1)s.



^{1}H NMR OF N-POLY(ALKENYL)ACRYLAMIDE

EVIDENCE OF INTERMOLECULAR HYDROGEN BONDING (FT-IR)





N-H strech

KBr = 3278 cm^{-1}

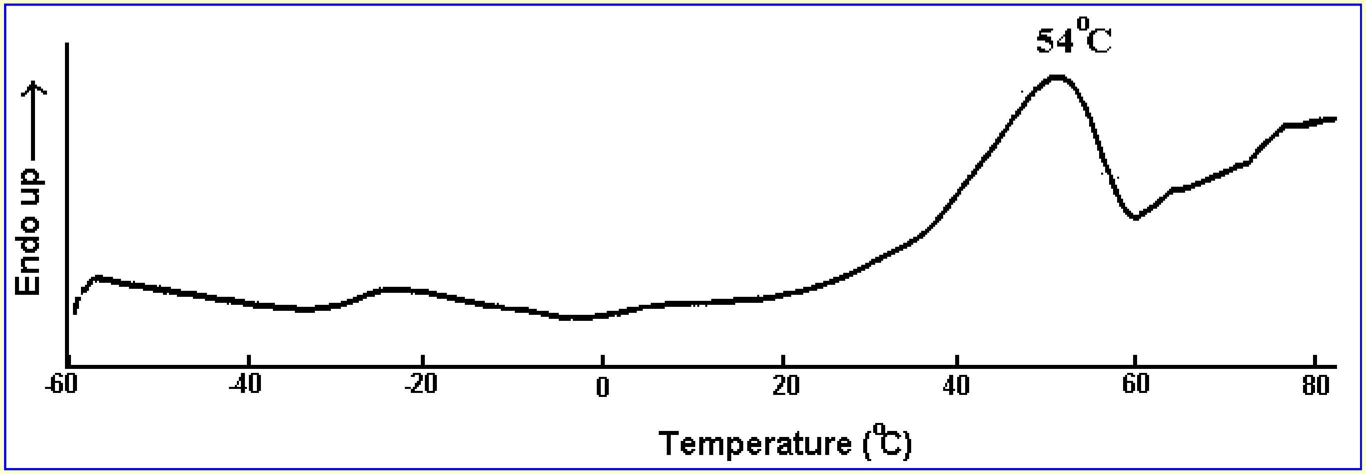
CHCl$_3$ = 3434 cm^{-1}

C=O strech

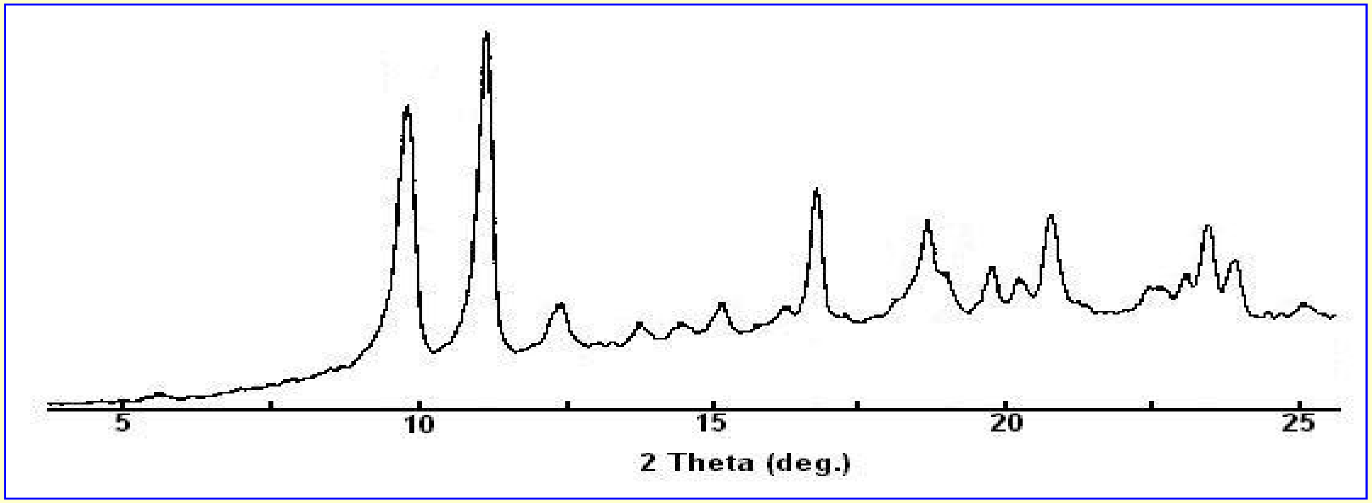
KBr = 1658 cm^{-1}

CHCl$_3$ = 1670 cm^{-1}

INDUCED CRYSTALLINITY DUE TO AMIDE FUNCTIONALITY



DSC of N-poly(alkenyl) acrylamide.



WAXS of N-poly(alkenyl) acrylamide

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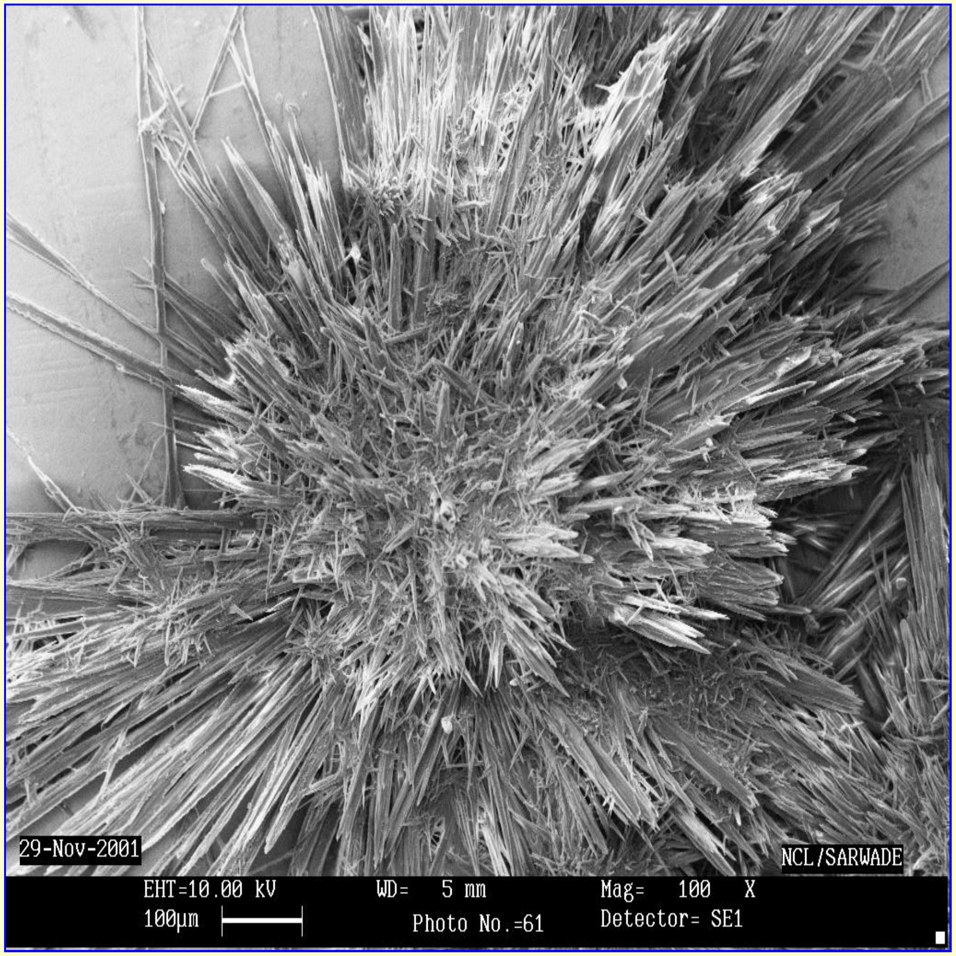
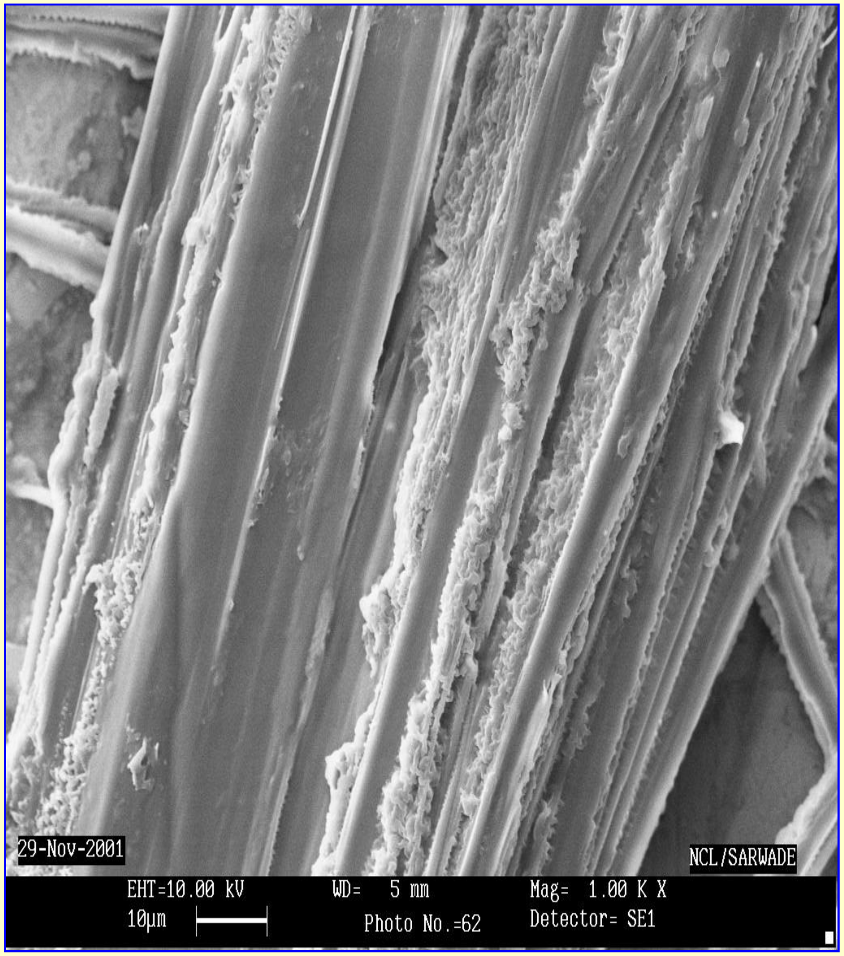
SCANNING ELECTRON MICROSCOPY



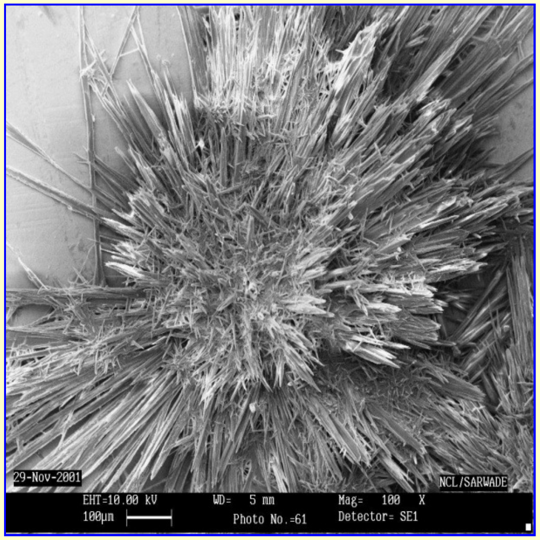


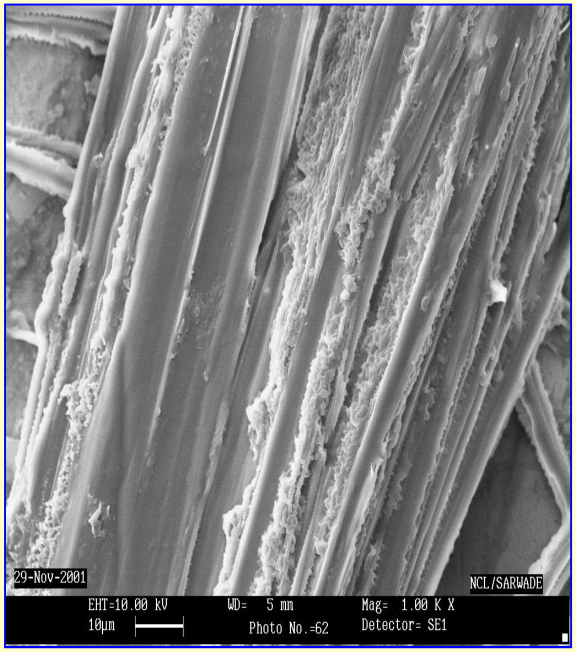
CONCLUSIONS

Amphiphilic in nature.

Amide groups were found to be intermolecularly hydrogen bonded.

- **DSC exhibits a melting endotherm arising due to the dissociation of hydrogen bonds**
- **The oligomer crystallizes to form rod like dendritic structure from n-pentane solution**





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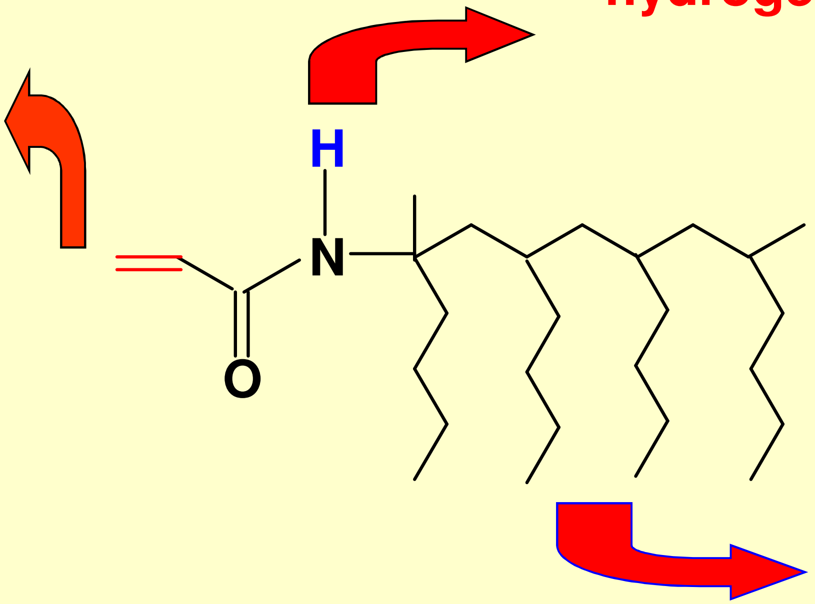
N-POLY(ALKENYL) ACRYLAMIDES : NOVEL AMPHIPHILIC MACROMONOMERS



Hydrophilic Amide
capable of
hydrogen bonding

Reactive
Unsaturation

Hydrophobic
alkyl group

SUMMARY

N-poly(alkenyl) acrylamides were found to be

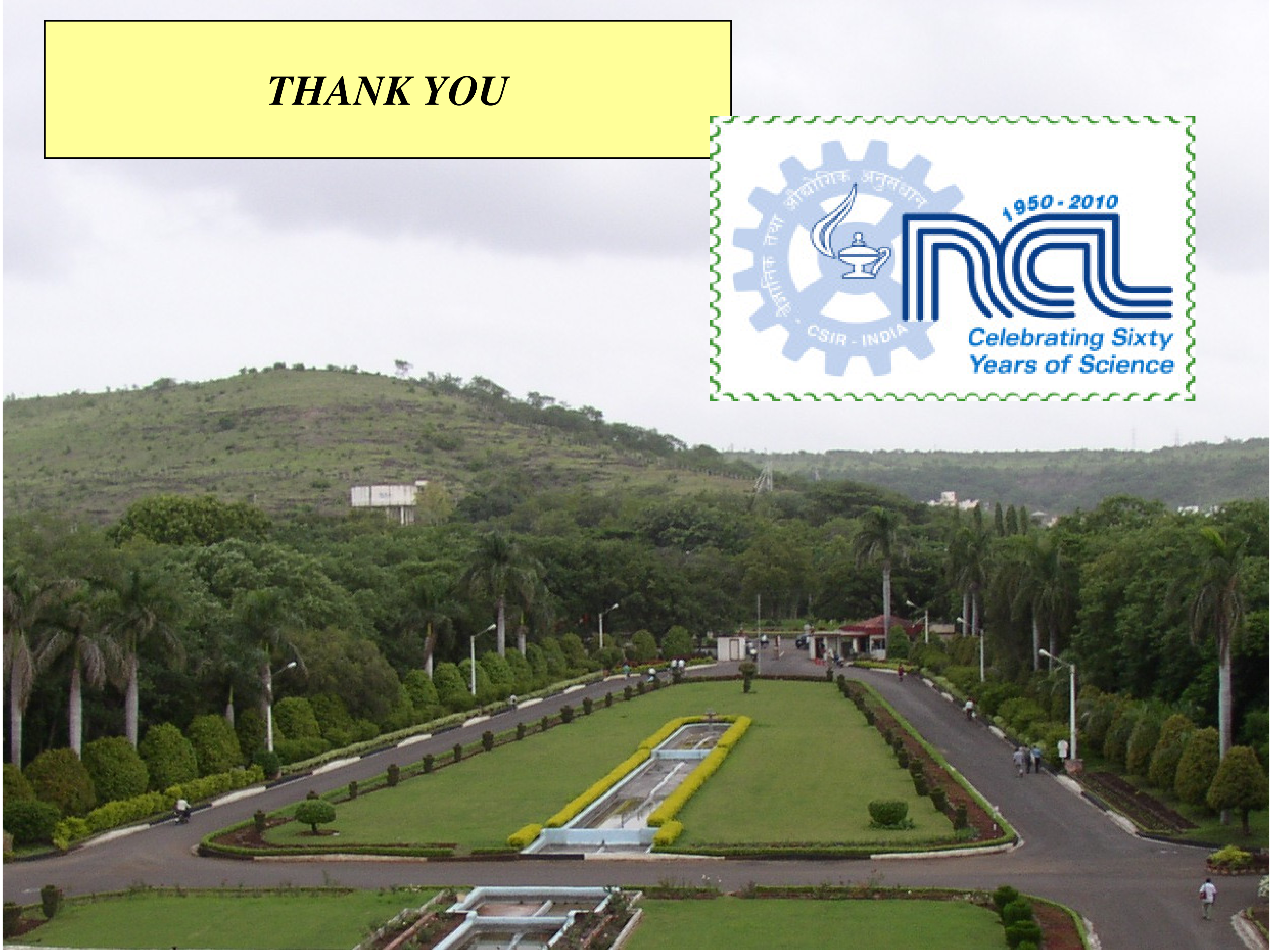
- **Amphiphilic in nature.**
- **Amide groups were found to be intermolecularly hydrogen bonded.**
- **DSC exhibits a melting endotherm arising due to the dissociation of hydrogen bonds**
- **The oligomer crystallizes to form rod like dendritic structure from n-pentane solution**

CHEMISTRY OF OLEFIN POLYMERIZATION

A seven hour video lecture
on
the chemistry, kinetics, stereochemistry and mechanism as well as industrial practice of the manufacturing processes

Olefin Polymerization_Video.mp4

THANK YOU



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