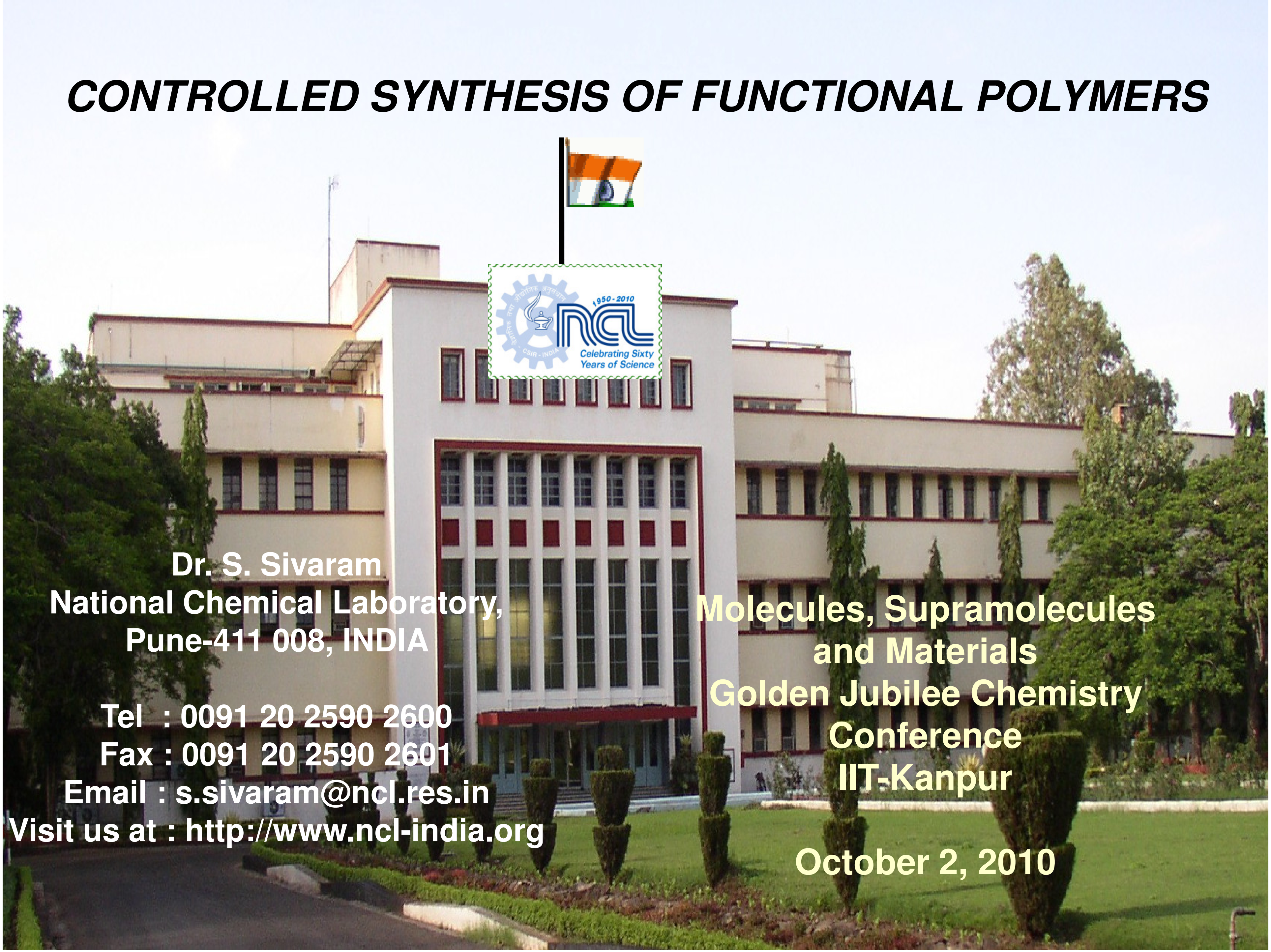
CONTROLLED SYNTHESIS OF FUNCTIONAL POLYMERS



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Molecules, Supramolecules
and Materials
Golden Jubilee Chemistry
Conference
IIT-Kanpur

October 2, 2010

DEPARTMENT OF CHEMISTRY, IIT KANPUR (1965-67)

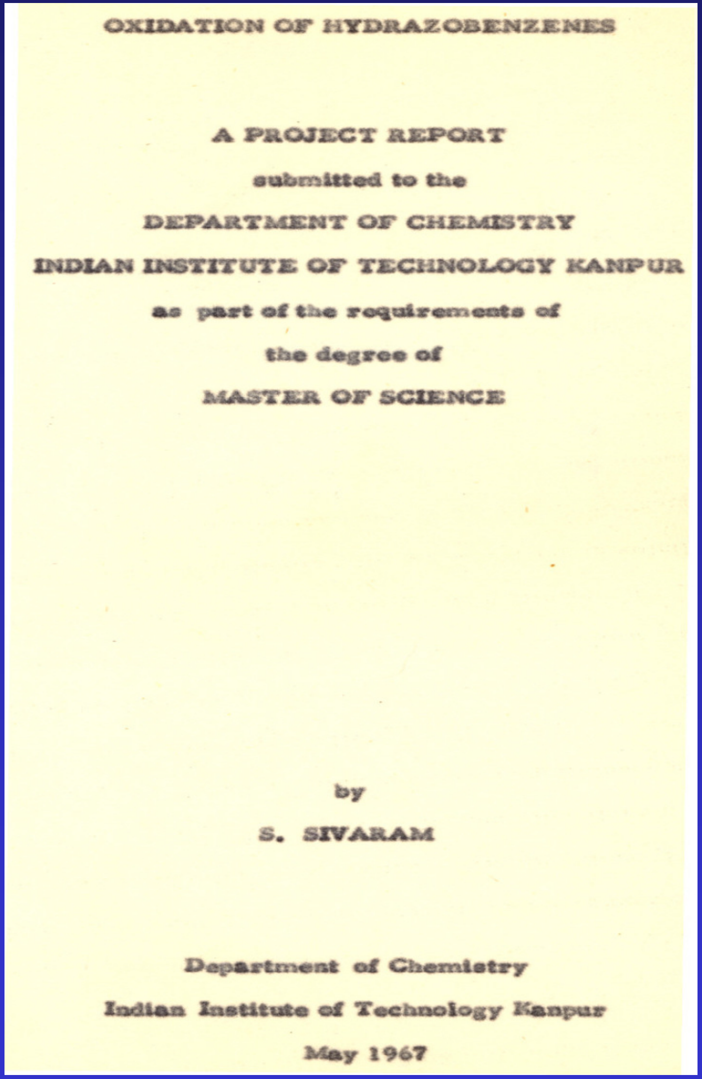
- A class of seven – first batch of MSc in IIT Kanpur
- Extraordinary faculty with exceptional pedigree (Prof Rao – Kenneth Pitzer, Professor Narasimhan – Karplus, Professor George – Gilman, Barton and Huisgen, Professor Ranganathan-Newman,Woodward, Professor Chakravorti – Cotton etc.
- The universities they came from were astounding, Harvard, Berkeley, Purdue, Columbia, Munich, MIT, Imperial College , London !

DEPARTMENT OF CHEMISTRY, IIT KANPUR (1965-67)

- **Research in the air; frequent seminars and lectures; lights burning in the lab late in the night !**
- **A large number of Ph D students – feel elevated in their company**
- **Continuous evaluation; surprise quizzes; no final examinations**
- **Over thirty books given free by US AID; The beginning of the personal library**
- **Faculty exceedingly informal and accessible**
- **Summer and M. Sc research in Professor George's laboratory in 1965**

Teach less; encourage self learning; make learning a pleasure

THE FIRST TASTE OF RESEARCH



OXIDATION OF HYDRAZOBENZENES

A PROJECT REPORT
submitted to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
as part of the requirements of
the degree of
MASTER OF SCIENCE

by
S. SIVARAM

Department of Chemistry
Indian Institute of Technology Kanpur
May 1967

- **Oxidation of hydrazobenzenes to azobenzenes using radical anions**
- **Na and K Naphthalene as radical anion source**
- **Effect of para substituent on the rate of oxidation**
- **Rate measured using a Beckman DU UV-Visible Spectrophotometer**

Pay attention to details; small things are important in science

A MENTOR SETS THE COURSE

Professor C. N. R. Rao

- In June 1967, Professor Rao asks me what I propose to do after M.Sc
- He suggests I go abroad for doing my Ph. D
- When I say that I am interested in Organic Chemistry he suggests that I work with Professor H.C Brown at Purdue University
- He writes a letter on my behalf to Professor Brown ; I receive a letter of appointment as a fully paid research assistant from Professor Brown in August 1967

- ***A true mentor is one who is more concerned about his student, not himself***
- ***A true mentor is one who shows you the way when you do not know where you want to go***

A LETTER FROM PROFESSOR RAO

“He was an outstanding postgraduate student of the department and had a cumulative performance index of 10 out of 10. This is certainly a remarkable record by all standards……………..We would have been happy to keep Sivaram for the Ph D programme in this department, but encouraged him to go out to enable him to get the best out of his post graduate training period “

Professor C. N.R. Rao, F.R.S
July 30, 1967

LIFE`S LESSONS

- The power of the mentors -encounters with great minds who see farther than you do
- Being at the right place at the right time; an opportunity to be associated with great institutions
- Building a robust foundation
- Liberal education that teaches you to keep your mind open and observe your environment critically
- Repeated learning and relearning experiences
- An opportunity to build both character and competence

In a life's journey, every encounter is a matter of chance
What great minds and institutions teach you is to stand tall, look at the skies, dream passionately and relentlessly work to convert dream into reality

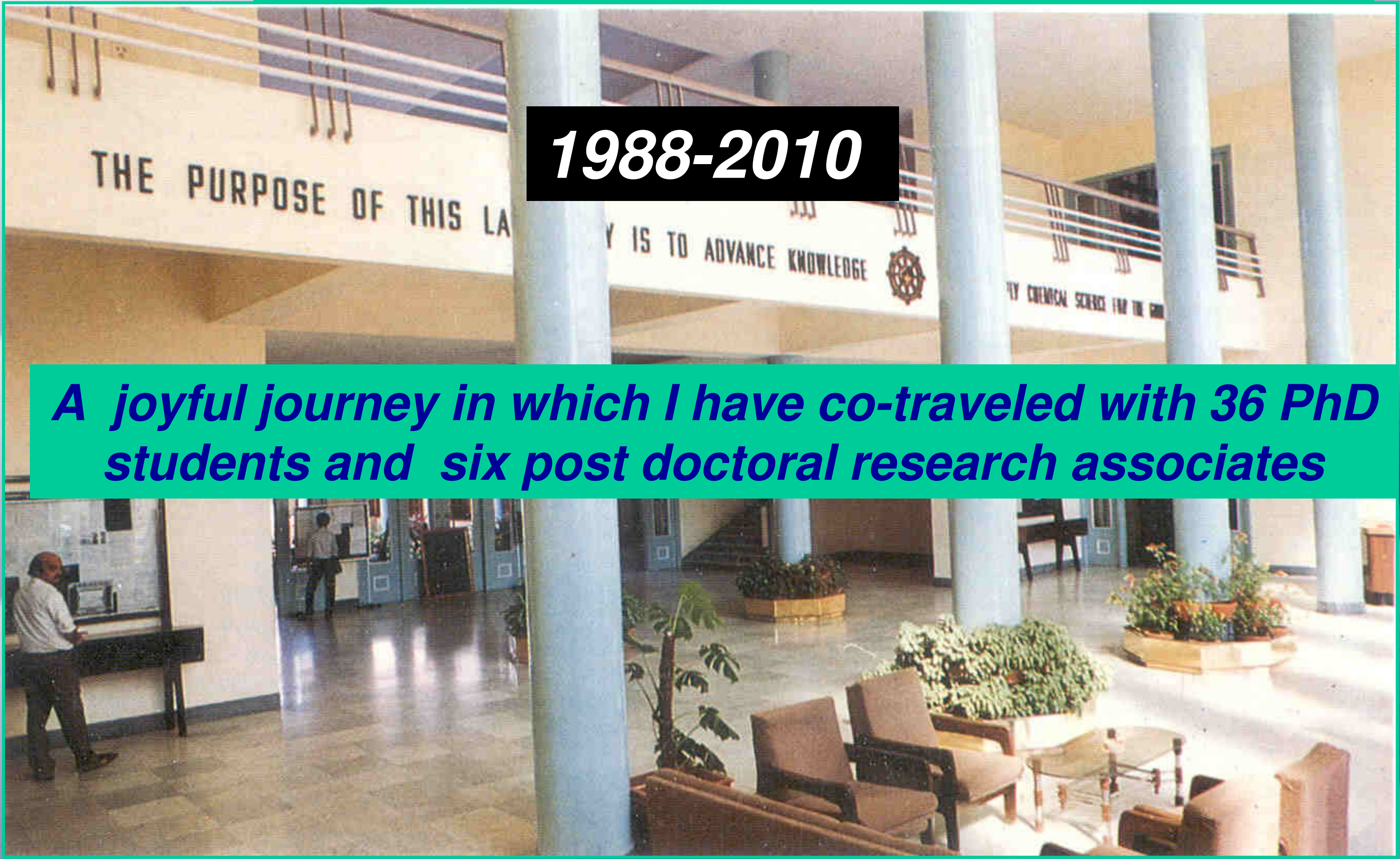
The moving finger writes; and having writ,
Move on : nor all your piety nor writ
Shall lure it back to cancel half a line
Nor all your tears wash out a word of it

Fitzgerald's Translation
Rubaiyat of Omar Khayyam

1950-2010
Celebrating Sixty Years of Science

THE PURPOSE OF THIS LABORATORY IS TO ADVANCE KNOWLEDGE AND TO APPLY CHEMICAL SCIENCE FOR THE GOOD OF THE PEOPLE

J W McBain



1988-2010

A joyful journey in which I have co-traveled with 36 PhD students and six post doctoral research associates

TWENTY YEARS OF RESEARCH AT NCL (1989-2009)

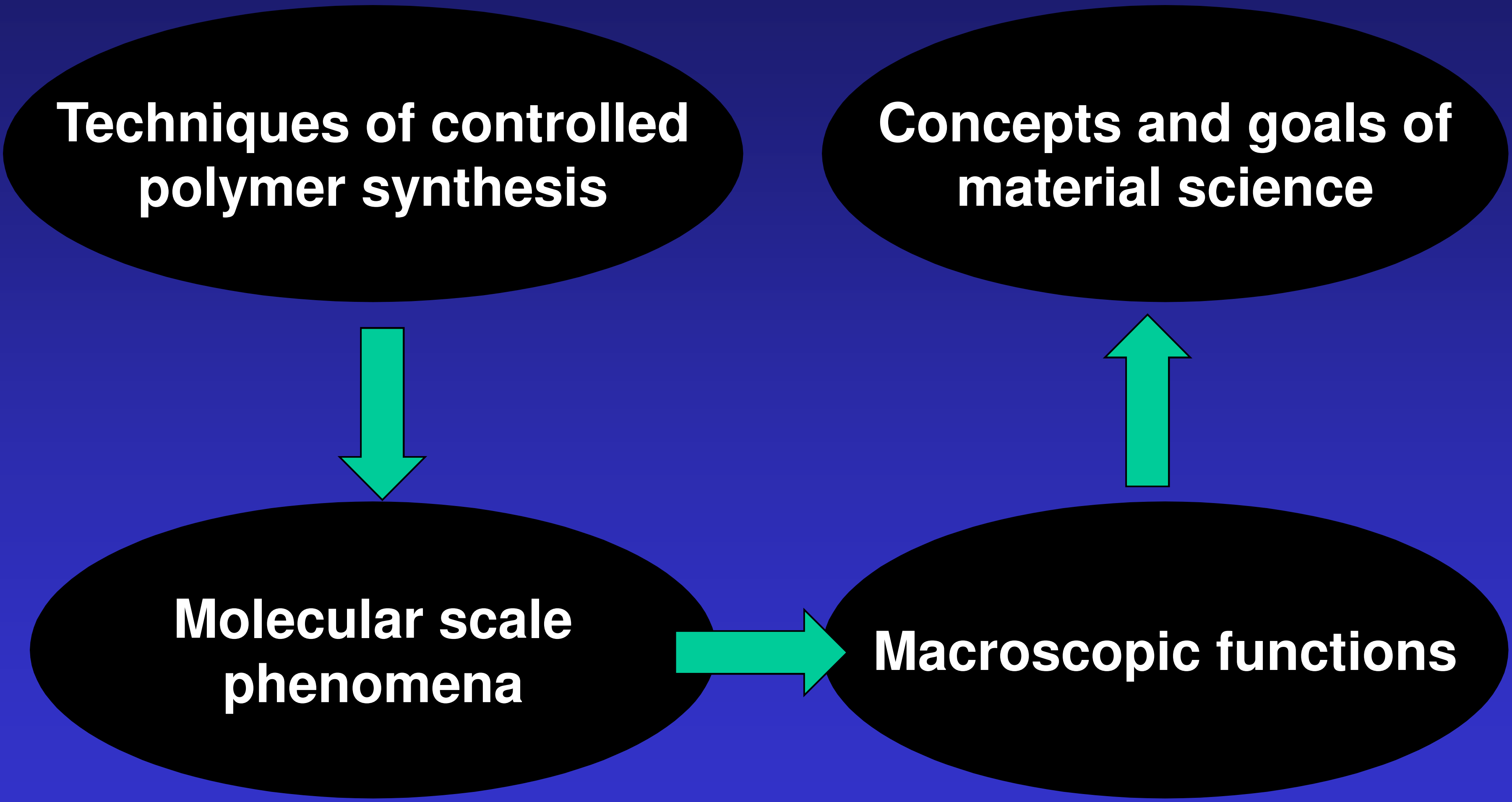
A Recurrent Theme

- **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

OUR OBJECTIVES…….

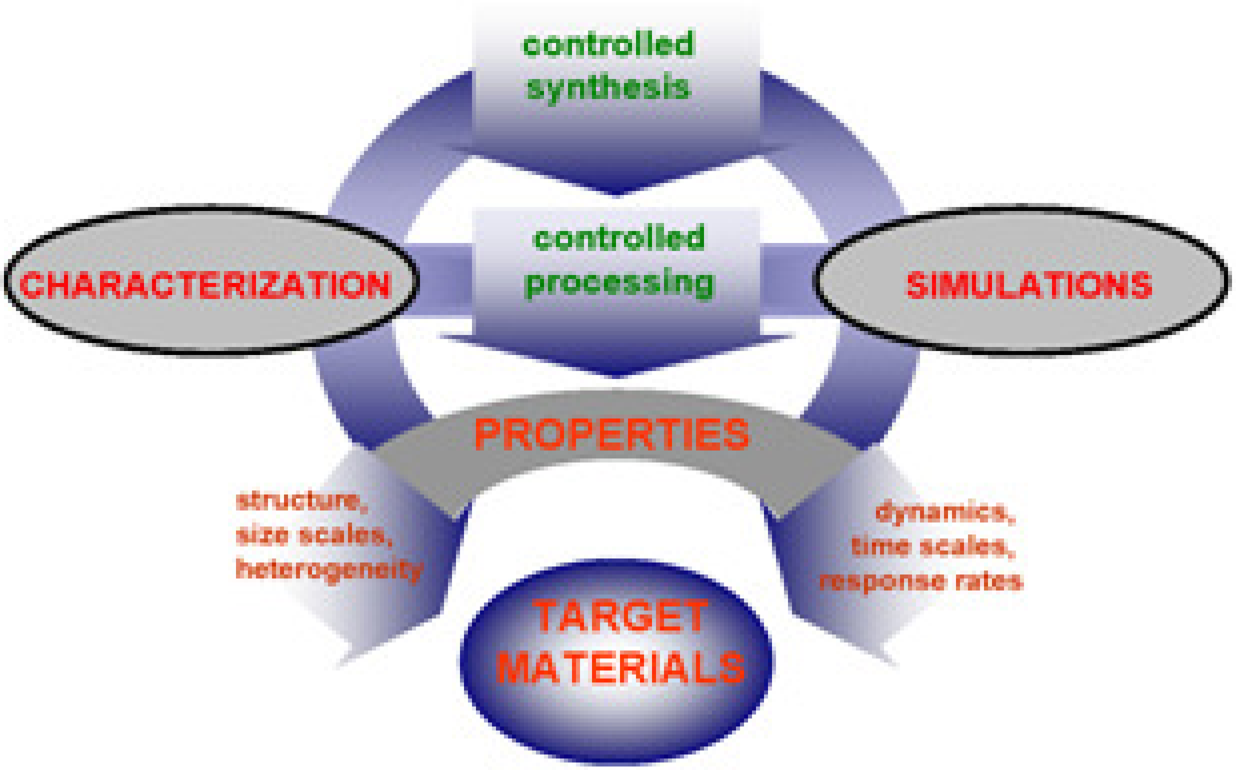


Techniques of controlled polymer synthesis

Molecular scale phenomena

Macroscopic functions

Concepts and goals of material science



controlled synthesis

controlled processing

CHARACTERIZATION

SIMULATIONS

PROPERTIES

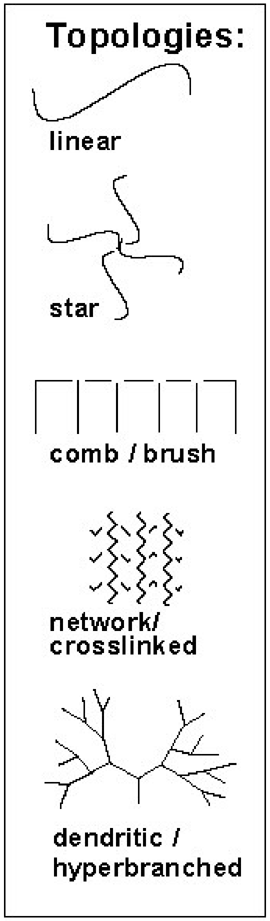
structure, size scales, heterogeneity

dynamics, time scales, response rates

TARGET MATERIALS

What Can Controlled/ Living Polymerizations Do ?

$DP_n = \Delta[M]/[I]_o$; $200<M_n<10^6$ (or more?); $1.01<M_w/M_n < 1.5$ & designed MWD; tacticity



Topologies:

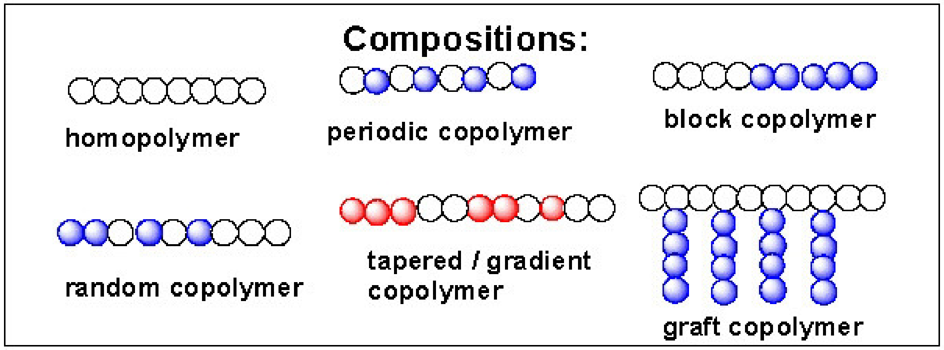
linear

star

comb / brush

network/
crosslinked

dendritic /
hyperbranched



Compositions:

homopolymer

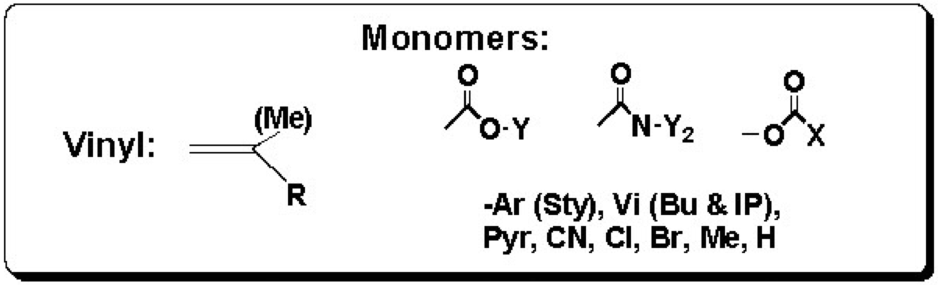
periodic copolymer

block copolymer

random copolymer

tapered / gradient
copolymer

graft copolymer



Monomers:

-Ar (Sty), Vi (Bu & IP),
Pyr, CN, Cl, Br, Me, H

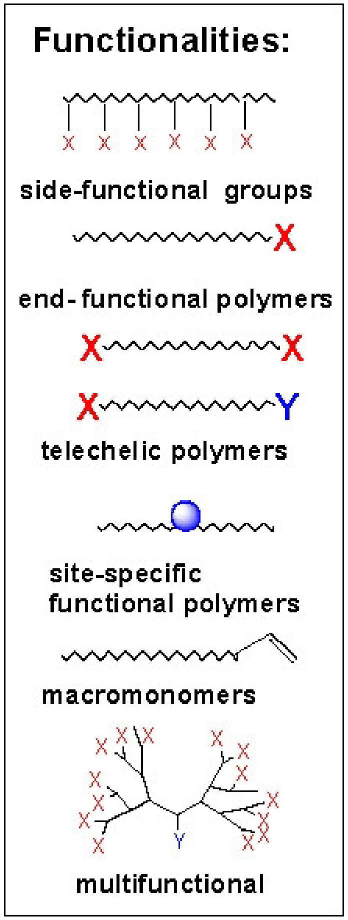
Systems: bulk, solution (org., H_2O, CO_2), suspension, emulsion, ...

Transformations:

⊕ → ⊙
⊖ → ⊙
⊙ → ⊕

Z-N → ⊙
ROMP → ⊙
PCond. → ⊙

Hybrids:
synthetic/natural
organic/inorganic
surfaces; IPN; etc.



Functionalities:

side-functional groups

end-functional polymers

telechelic polymers

site-specific
functional polymers

macromonomers

multifunctional

WHY FUNCTIONAL POLYMERS?

- Polymers are generally recognized as structural materials devoid of function

- However, functional polymers are increasingly becoming important in many specialty applications
  - -Molecular electronics
  - -Macromolecular surfactants
  - -Reactive adhesives
  - -Reactive surfaces
  - -Functional dendrimers
  - - Polymers in therapeutics

ISSUES IN POLYMER FUNCTIONALIZATION

- Introduction of reactive functionality difficult since many functional groups interfere with initiators and catalysts used for polymerization
- Polymer chain growth reactions are accompanied by several chain transfer/breaking processes.This leads to less than quantitative chain end functionality
- Routine extrapolation of functional group transformations used in organic chemistry to polymers is often difficult due to incompatibility of reagents and solvents with polymerization conditions
- Analysis of functionality in polymer poses unique problems due to its low concentration on a mole basis

NCTIONAL POLYMERS THROUGH CONTROLLED CHAIN GROWTH POLYMERIZATION

- Functional initiators
  - *Anionic,* cationic, *free radical*, GTP, ROP
- Functional monomers
  - Free radical, GTP
- Protected functional monomers
  - Anionic, GTP, metal catalyzed polymerization
- Functional termination of living chain ends
  - Anionic, GTP, cationic, free radical
- Controlled catalytic chain transfer
  - Free radical, *metal catalyzed polymerization*

CONTROLLED SYNTHESIS OF FUNCTIONAL POLYMERS

- **Synthesis of end functionalized poly(methyl methacrylate)s *via* living anionic polymerization, group transfer polymerization and atom transfer radical polymerization**

- **Synthesis of functionalized poly(olefin)s using metal catalyzed coordination polymerization**

SYNTHESIS OF FUNCTIONAL POLY (METHYLMETHACRYLATE)S

- **Chain end functional polymers through the use of protected and unprotected functional initiators**

- **Functionalization of a growing polymer chain end using a C-C bond forming reaction**

Both these approaches require that the conditions chosen for polymerization are free of chain breaking reactions, namely, transfer and termination; otherwise, every chain will not have the functional group and the efficiency of functionalization (Fn) will be less than 1.0

Synthesis of Functional Polymers *via* Anionic Polymerization

Living Anionic Polymerization is the most versatile and controlled method for preparing end-functional polymers

Absence of termination and transfer

↓

Excellent control over molecular weight, MWD, microstructure, functionality

Living anionic polymerization enables synthesis of functional polymers with well-defined structures

Functional Polymers : Synthesis

Strategies for polymer functionalization

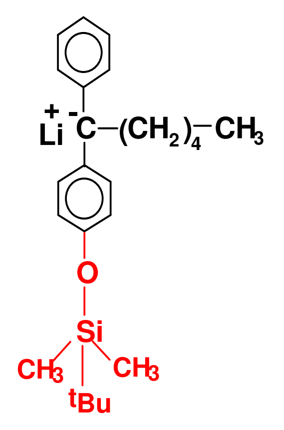
Electrophilic termination

- Method more general
- Functionalization usually not quantitative ⇒ Unfunctionalized chains
- Undesirable side-reaction ⇒ Polymeric side-products

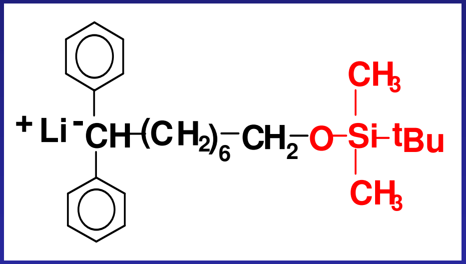
Functional initiation

- Simpler and quantitative method
- Functional groups need to be protected
- Can be used for making telechelic polymers, functional-block and star copolymers

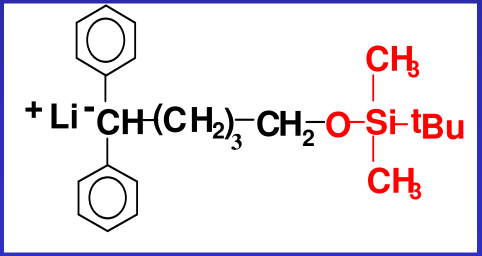
Synthesis of Hydroxyl End-functionalized PMMA Using Protected Hydroxyl-functionalized Initiators



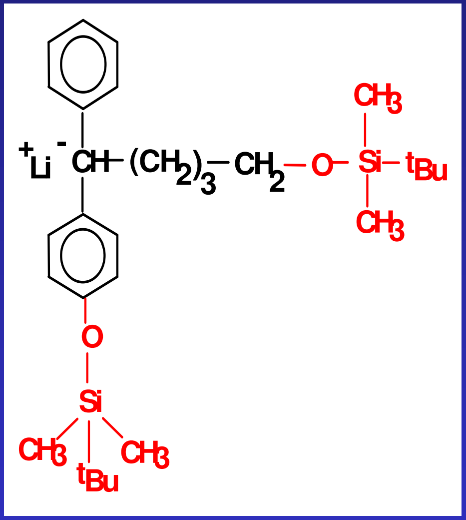
F1



F2



F3

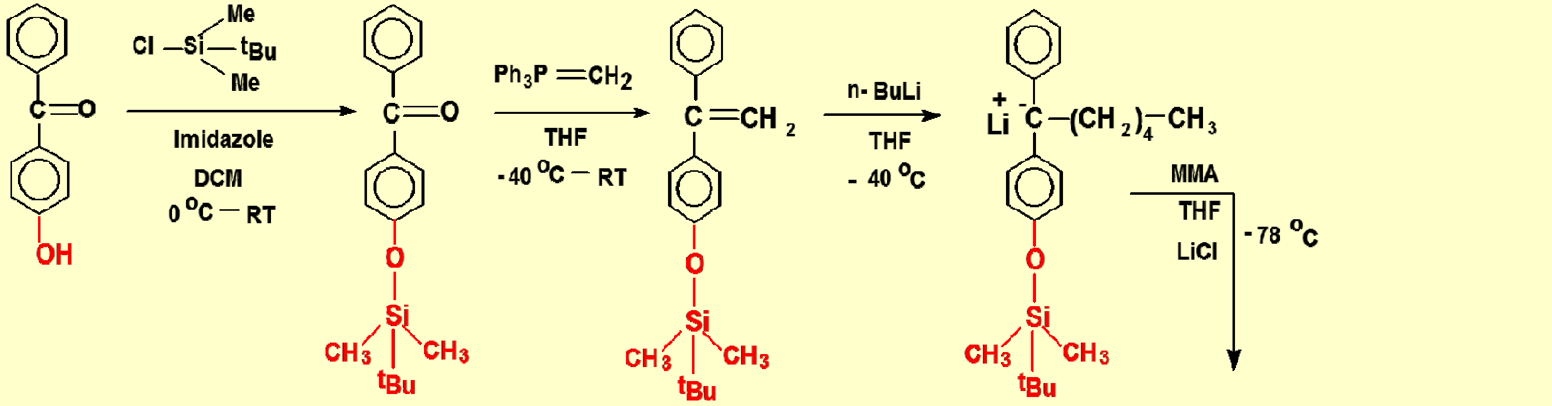


F4

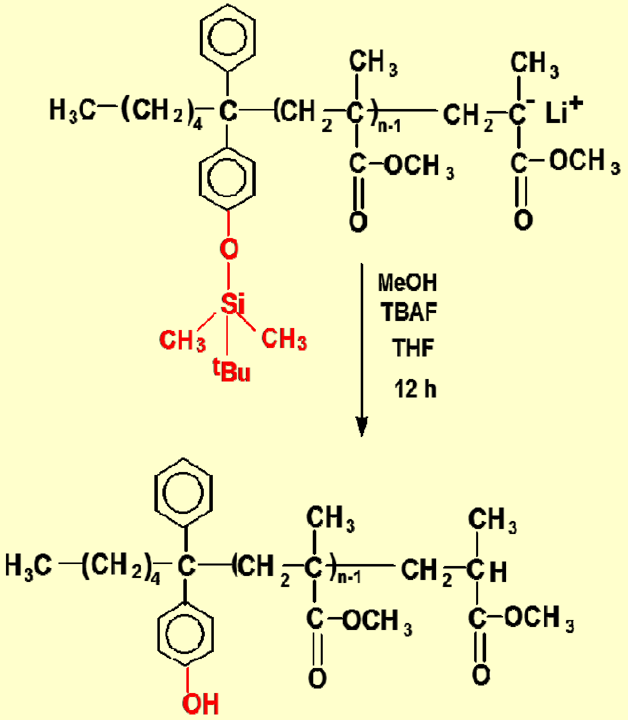
Hydroxyl end-functional PMMA can be prepared by living anionic polymerization of MMA using protected hydroxyl-functionalized initiators

Synthesis of Hydroxyl End-functionalized PMMA Using F1

F1 ☞ *Adduct of 1-(p-hydroxyphenyl)-1'-phenyl ethylene and n-BuLi*



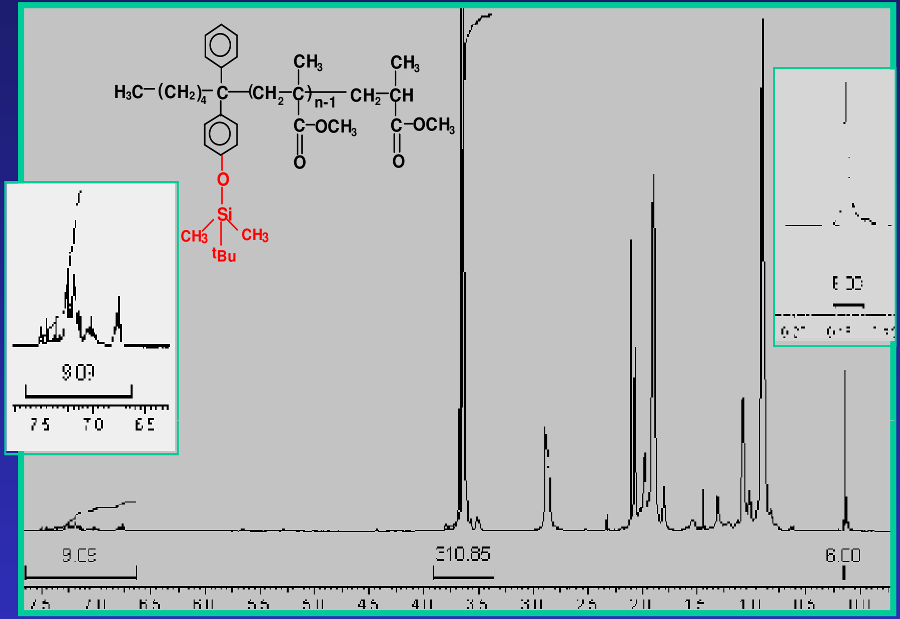
Run no.	$[I]_0$ x10^{-3} m/L	$[M]_0$ m/L	Conv. %	$\overline{M}_{n,sec}$ x10^{-3}	$\overline{M}_{n,calc}$ x10^{-3}	MWD	$f = \overline{M}_{n,calc} / \overline{M}_{n,sec}$
1	3.67	0.12	~100	3.2	3.3	1.07	1.03
2	2.70	0.18	90	10.8	9.8	1.06	0.91
3	2.88	0.41	90	14.1	14.4	1.09	1.02



- **Well-controlled polymerization**
- **Functionality confirmed by ^{1}H NMR,MALDI-TOF MS**

Hydroxyl End-functionalized PMMA Using F1: Characterization by NMR & MALDI-TOF MS

^{1}H NMR (500 MHz, acetone-d6) spectra of silyl-protected hydroxy-PMMA (Mn,sec=10800)

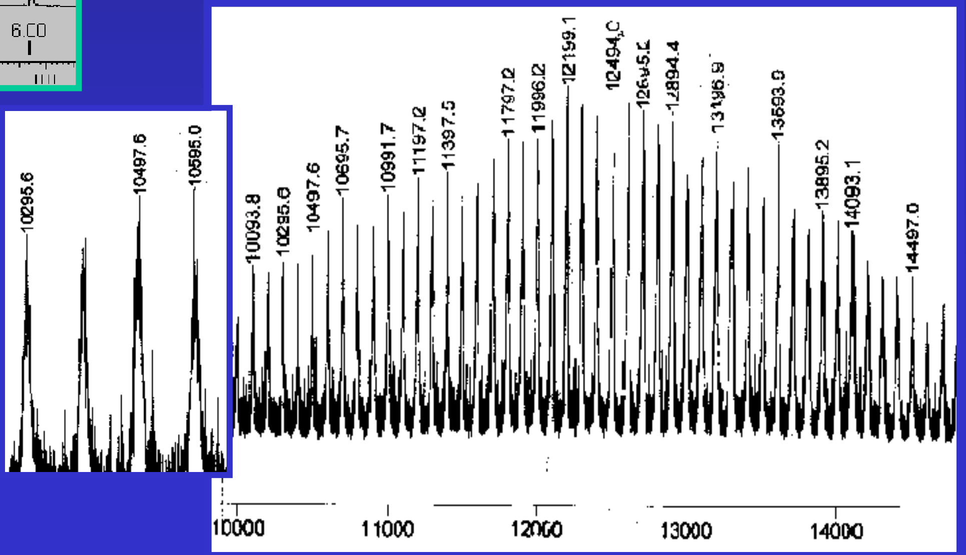


δ 0.0	6 H of -Si$(CH_3)_2$
δ 6.7-7.6	9 H for 2 phenyl groups
δ 3.58	310 H for $-OCH_3$ protons of PMMA

⇩

quantitative functionalization of PMMA chains

MALDI-TOF mass spectra of hydroxy-PMMA (Mn, sec=10800)



End-grp. mass from any m/z, say 10595.0 and 14093.1 are 395 and 393.2 respectively

Theoretical end-group mass = 253+101+39 = 393

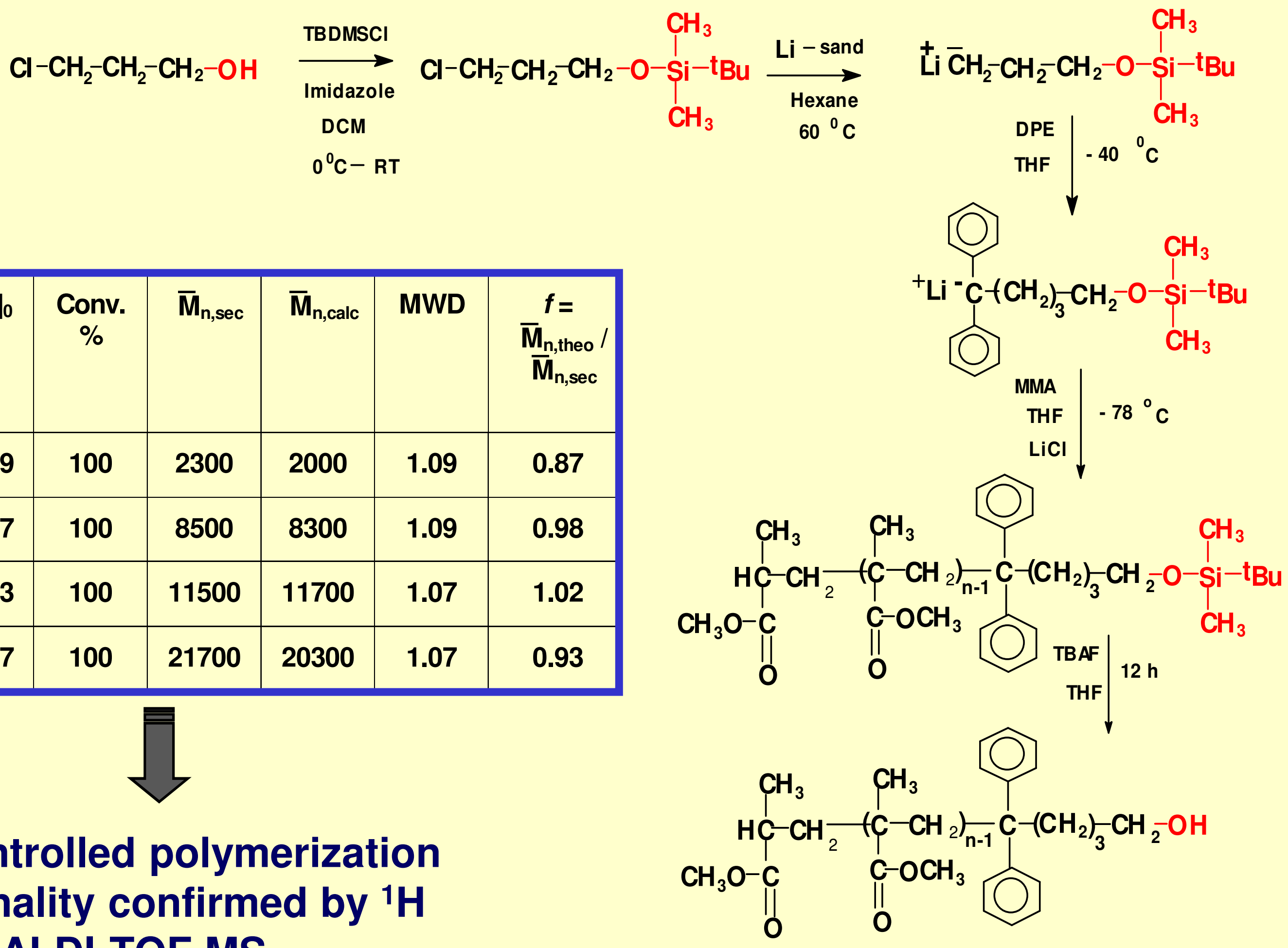
Also, single generation of polymers

⇩

Presence of protected –OH at all chain-ends

Synthesis of Hydroxy End-functional PMMA Using F3

F3 : *Adduct of 1,1'-diphenyl ethylene and protected hydroxy propyllithium*

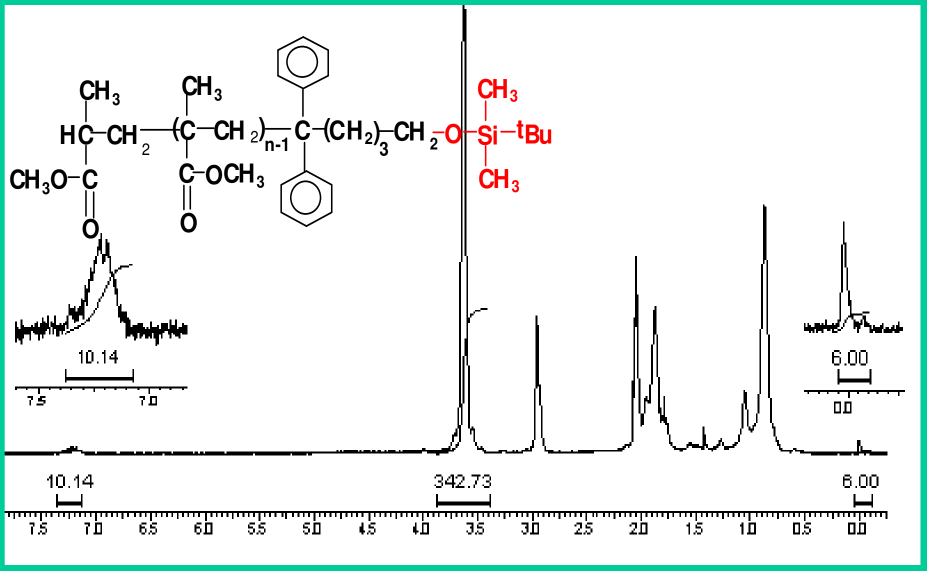


Run no.	$[I]_0$ x10^{-3} m/L	$[M]_0$	Conv. %	$\overline{M}_{n,sec}$	$\overline{M}_{n,calc}$	MWD	*f* = $\overline{M}_{n,theo}$ / $\overline{M}_{n,sec}$
1	4.45	0.09	100	2300	2000	1.09	0.87
2	3.22	0.27	100	8500	8300	1.09	0.98
3	2.79	0.33	100	11500	11700	1.07	1.02
4	1.84	0.37	100	21700	20300	1.07	0.93

- **Well-controlled polymerization**
- **Functionality confirmed by ^{1}H NMR,MALDI-TOF MS**

Hydroxyl End-functionalized PMMA Using F3: Characterization by NMR & MALDI-TOF MS

^{1}H NMR (500 MHz, acetone-d6) spectra of silyl-protected hydroxy-PMMA (Mn,sec=11500)

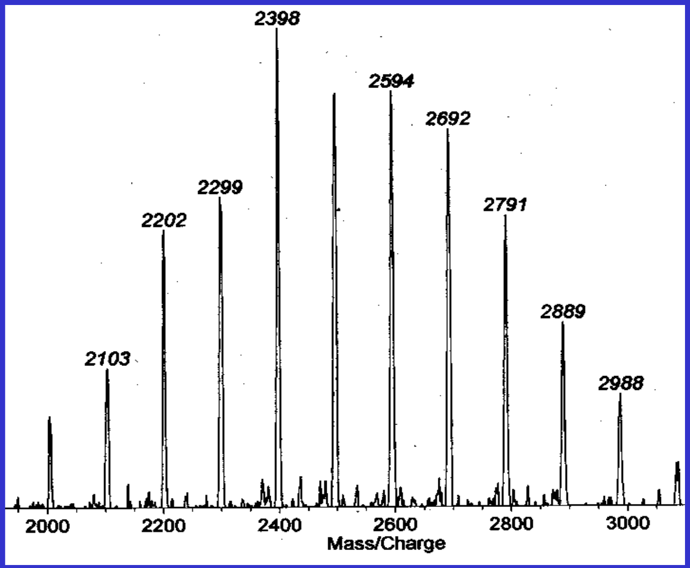


δ 0.0	6 H of $-Si(CH_3)_2$
δ 6.7-7.6	10 H for 2 phenyl groups
δ 3.58	342 H for $-OCH_3$ protons of PMMA

⇩

quantitative functionalization of PMMA chains

MALDI-TOF mass spectra of hydroxy-PMMA (Mn, sec=2300)



End-group. mass from any say, m/z = 2597 and 2791 are 494 and 491 respectively

Theoretical end-group mass = 354+101+39= 493

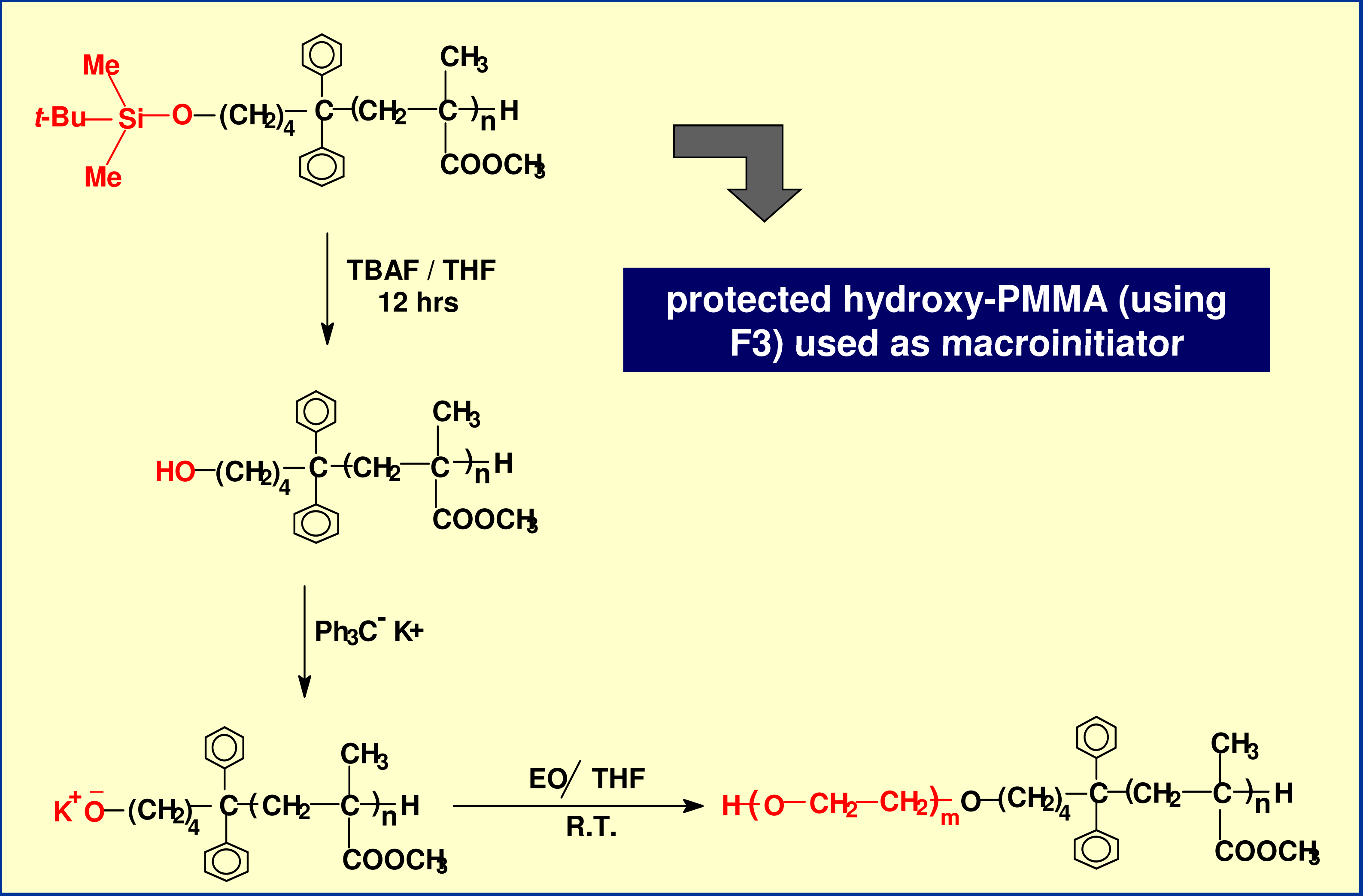
Also, single generation of polymers

⇩

Presence of free –OH at all chain-ends

Synthesis of PMMA-*block*-PEO Copolymer

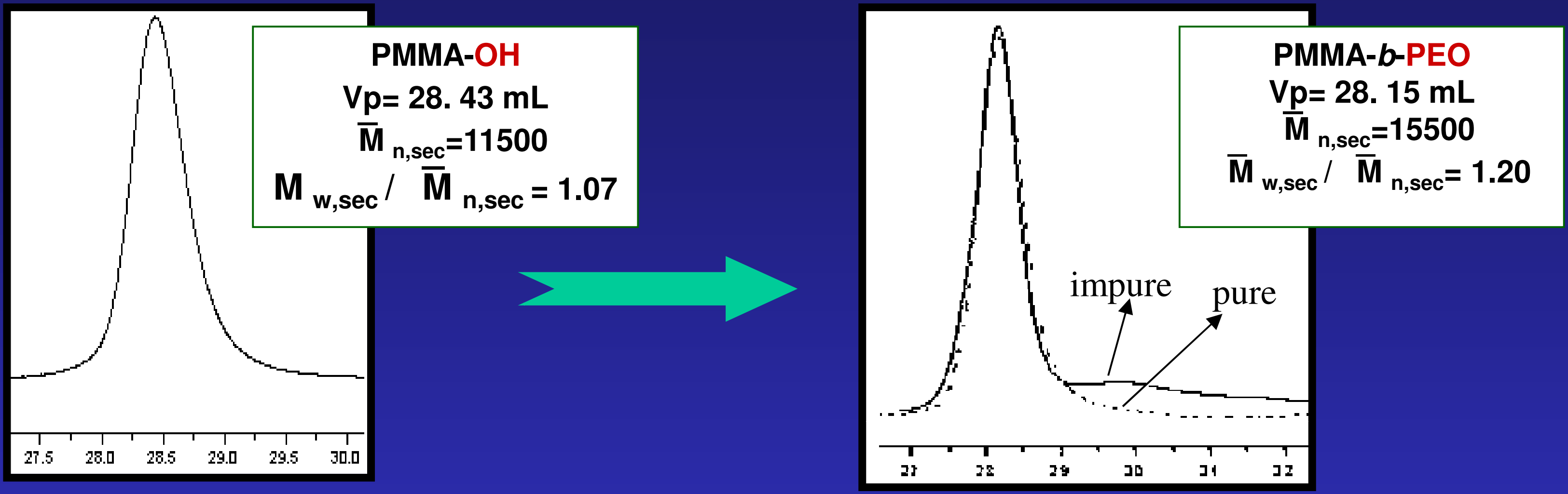
Hydroxy-PMMA prepared using F1, F2 and F3 were used as macro-initiators for the synthesis of PMMA-*block*-PEO



protected hydroxy-PMMA (using F3) used as macroinitiator

CHARACTERIZATION OF PMMA-BLOCK-PEO COPOLYMER

GPC Analysis



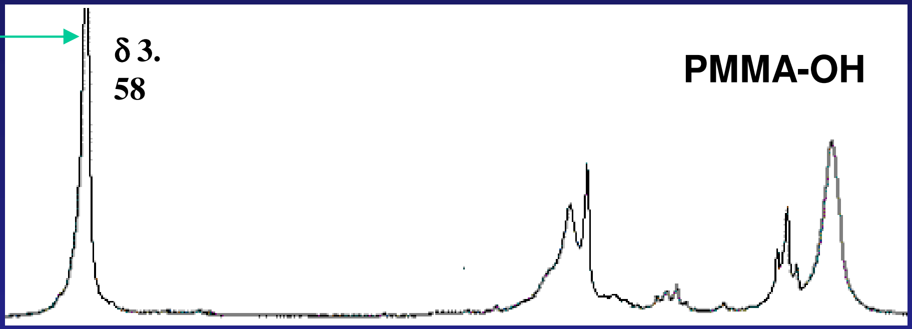
PMMA-OH
Vp= 28. 43 mL
$\overline{M}_{n,sec}$=11500
$M_{w,sec}$ / $\overline{M}_{n,sec}$ = 1.07

PMMA-*b*-PEO
Vp= 28. 15 mL
$\overline{M}_{n,sec}$=15500
$\overline{M}_{w,sec}$ / $\overline{M}_{n,sec}$= 1.20

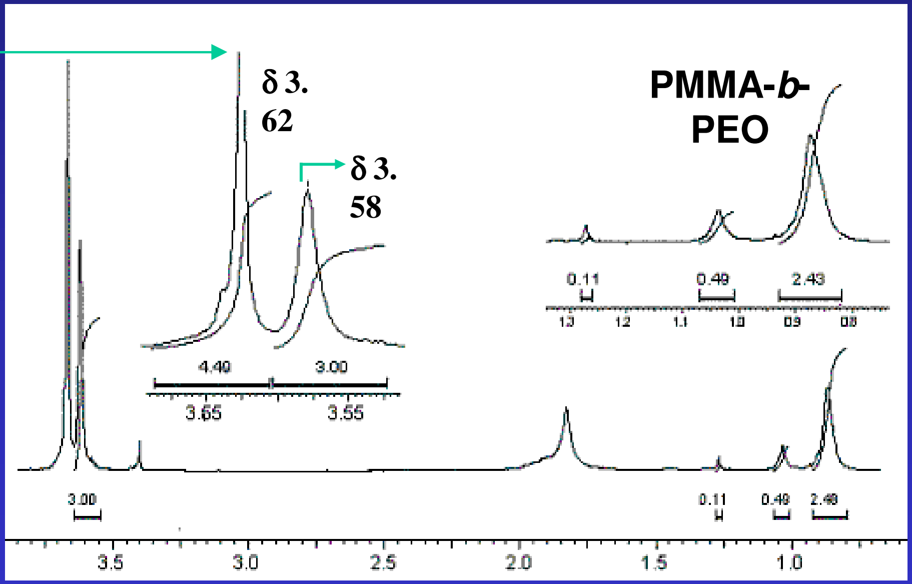
- **Increase in molecular weight**
- **Elugram of block copolymer show tailing in low molecular weight region**
- **Tailing disappears on washing the copolymers with water**
- **Water-soluble portion (~3.0 % by wt.) was found to be PEO homopolymer**

Characterization of PMMA-*block*-PEO Copolymer

^{1}H NMR (500 MHz) spectroscopic analysis



-OCH_3 group of precursor PMMA



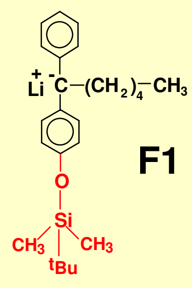
-OCH_2 group of PEO block of PMMA-*b*-PEO

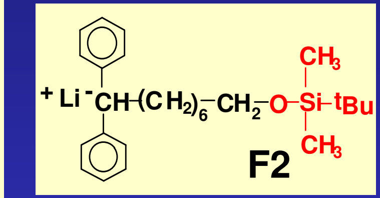
- Additional peak at δ 3.62 due to –OCH_2 protons in PMMA-*b*-PEO
- Ratio of peak intensities due to –CH_3 and –OCH_3 protons is 1:1

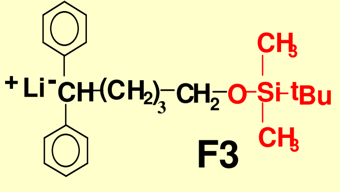
Appearance of new peak due to –OCH_2 protons confirm formation of the diblock
Presence of equal number of methyl and methoxy groups suggest insignificant amount of transesterification reaction

Characterization of PMMA-*block*-PEO Copolymers : GPC & NMR

Run no.	PMMA-OH			[MMA]:[EO] in feed	PMMA-*b*-PEO			
	Sample no.	$\overline{M}_n$ (SEC)	$\overline{M}_w/\overline{M}_n$ (SEC)		Conv.	$\overline{M}_n$ (SEC)	$\overline{M}_w/\overline{M}_n$ (SEC)	[MMA]: [EO] (by NMR)
1	F3	11500	1.07	3.3:6.7	0.51	15400	1.20	3.9:6.1
2	F3	11500	1.07	2.7:7.3	0.53	15900	1.20	3.1:6.9
3	F3	14000	1.08	4.1:5.9	0.49	16400	1.21	4.9:5.1
4	F3	14000	1.08	3.8:6.2	0.56	17300	1.15	4.1:5.9
5	F3	8500	1.09	4.9:5.1	0.60	14400	1.13	-
6	F3	21700	1.07	4.6:5.4	0.62	27100	1.25	5.2:4.8
7	F2	5000	1.08	2.4:7.6	0.50	8000	1.27	3.0:7.0
8	F2	8900	1.11	2.5:7.5	0.58	13700	1.18	2.7:7.3
9	F2	8900	1.11	1.1:8.9	0.61	15500	1.13	-
10	F1	16200	1.10	2.0:8.0	0.55	40700	1.27	1.2:8.8

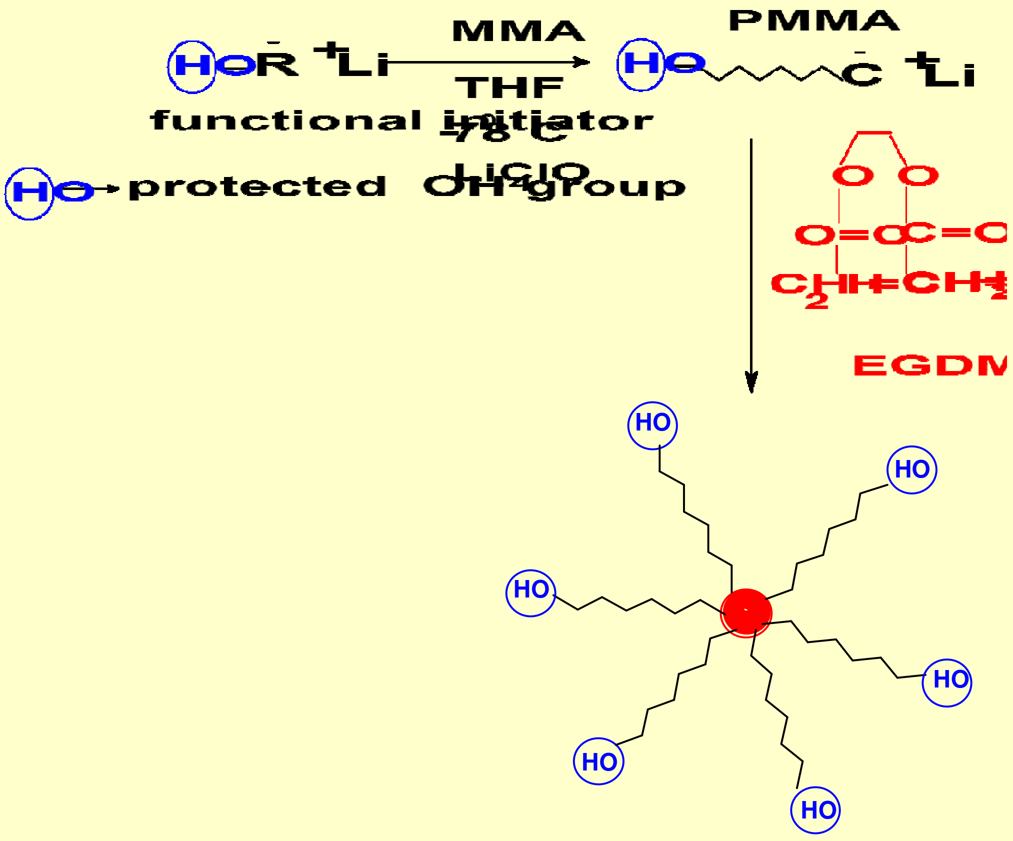






- NMR and GPC results prove the formation of PMMA-*b*-PEO from the precursor PMMA-OH
- Simple process of purification yields well-defined block copolymers with unimodal and fairly narrow MWD
- Run nos. 5 and 9 resulted in water-soluble PMMA-*b*-PEO copolymers

Synthesis of Hydroxyl-functionalized PMMA Star polymer



Protected hydroxy-functional star-PMMA

Synthetic procedure

Step 1: Anionic polymerization of MMA using functional initiators

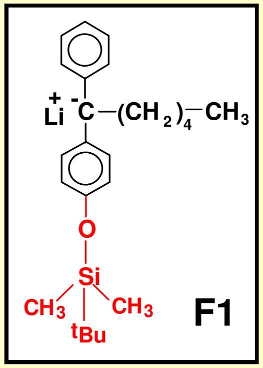
Step 2: Living chains coupled with bis-unsaturated monomer

Well-defined PMMA-star polymers with hydroxy functions at the chain ends could be successfully synthesized

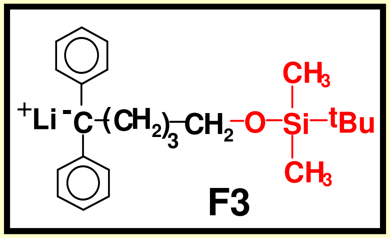
Controlled synthesis of hydroxyl-functional PMMA-star

Effect of arm length & [EGDA]:[I] on no. of branches

Sample	EGDMA/ initiator	Arm			Star				No. of arms (by -OH titrn.)
		$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$ (SEC) x 10^{-3}	$\bar{M}_w/\bar{M}_n$ (SEC)	$\bar{M}_w$ (LS) x10^{-3}	$\bar{f}_w$	
F3-S1	3:1	7000	7600	1.09	55.0	1.11	74.6	9.8	9.3
F3-S2	3:1	8500	9100	1.07	54.5	1.12	70.0	7.7	7.4
F3-S3	3:1	11000	11700	1.07	60.0	1.09	75.4	6.4	6.0
F3-S4	3:1	19700	21000	1.07	97.8	1.15	120.0	5.7	-
F3-S5	6:1	8600	9400	1.08	75.0	1.10	90.0	9.5	9.0
F1-S1	3:1	5100	5500	1.08	35.0	1.10	39.0	7.1	-
F1-S2	6:1	5000	5500	1.09	48.0	1.12	-	-	9.4



F1



F3

$\bar{f}_w = \bar{M}_{w,LS}\,(\text{star}) / \bar{M}_{w,sec}\,(\text{arm})$

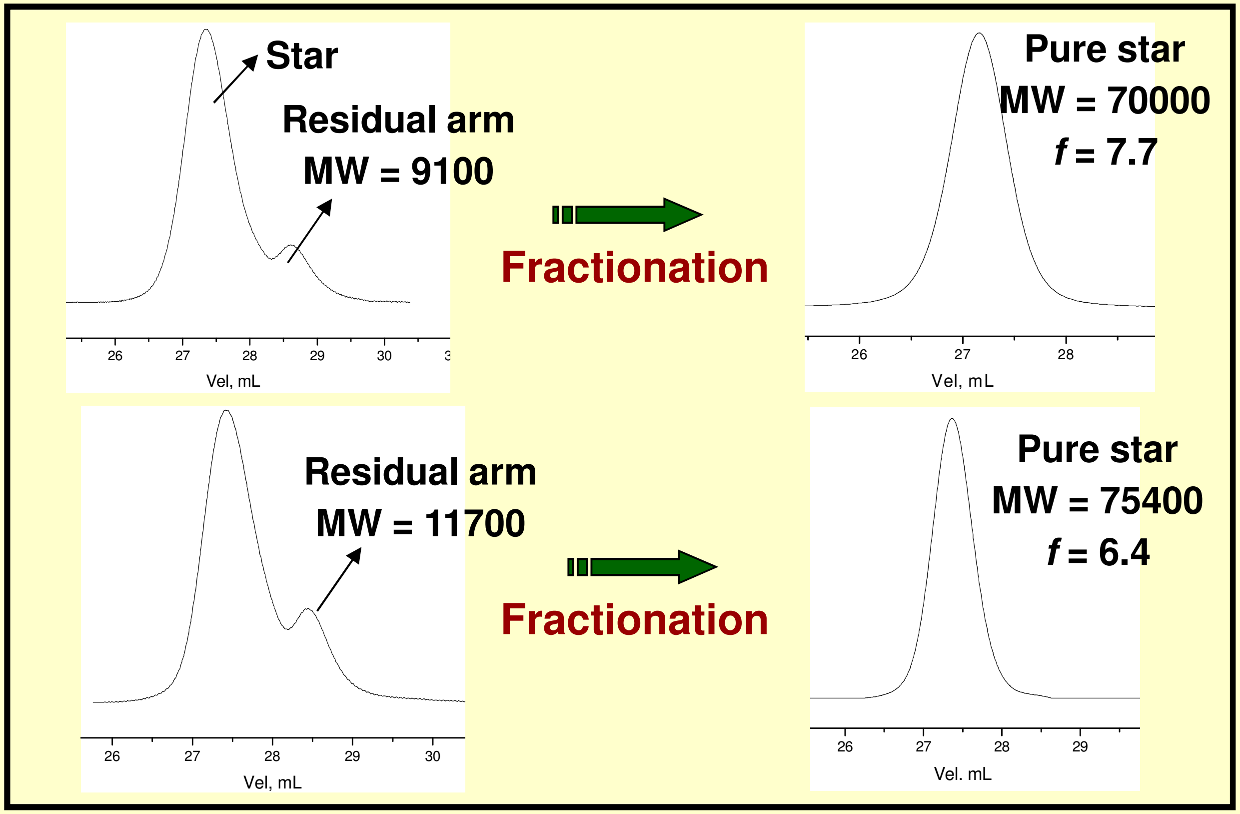
☞ Degree of branching increases with

- increase in EGDMA : initiator ratio
- decrease in arm molecular weight

•Smaller arm offers less steric hindrance to further arm incorporation

•Larger core size provides greater space to accommodate more number of arms

Purification of PMMA-star : Removal of unreacted arm



Higher arm MW

Lower incorporation into star

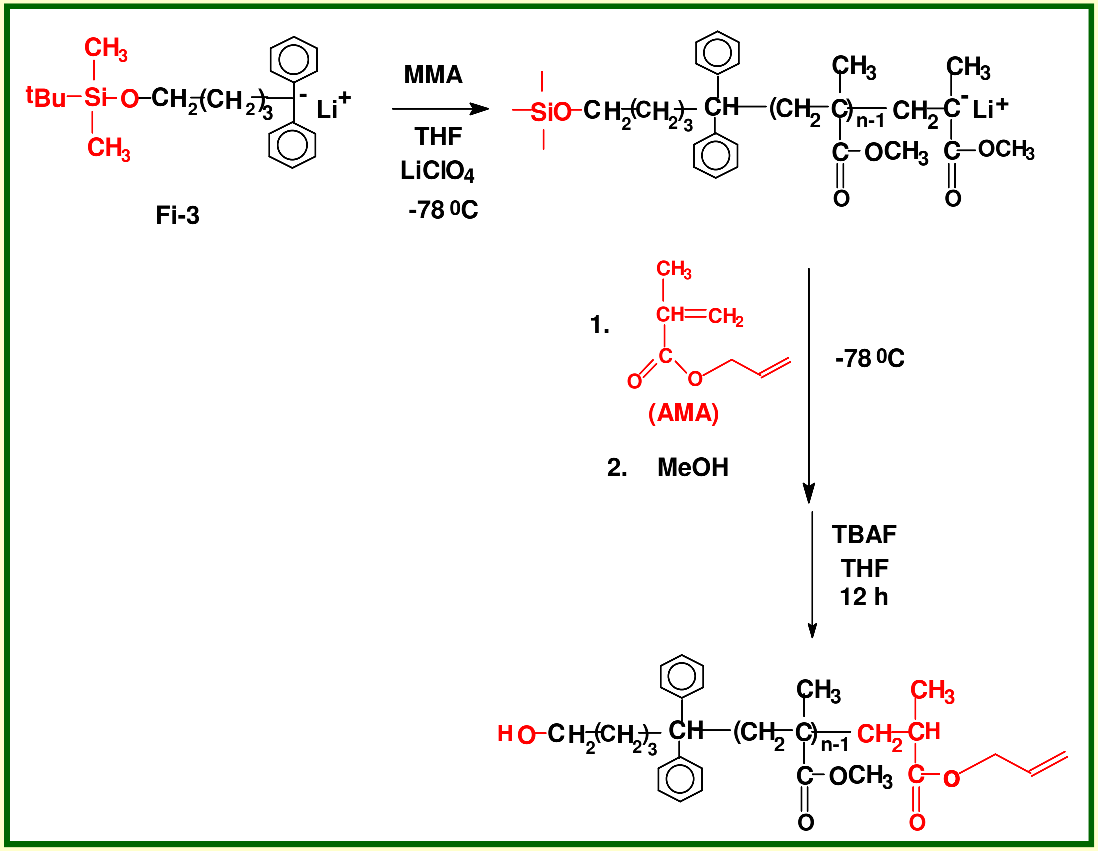
Higher residual arm content

- Addition of dilute toluene solution of deprotected hydroxy-PMMA star to excess cold methanol causes the star to preferentially precipitate

PMMA stars with free –OH groups can be easily purified form free residual arms contamination

Controlled Synthesis of Functional PMMA-macromonomers

Synthesis of α-hydroxy-ω-allyl PMMA in THF at –78 ° C using F3 as initiator and allyl methacrylate as end-capper



Step 1. Anionic polymerization of MMA using functional initiator F3

Step 2. Electrophilic termination of living chains by allyl methacrylate

Sample	$[I]_0$ x10^{-3} m/L	$[M]_0$ x10 m/L	Temp. °C	Time of rxn. (mins)	Yield %	$M_{n,theo}$	$M_{n,sec}$	MWD	*f*
F3-PMAM-1	3.0	1.75	-78 °C	30	100	5800	6000	1.09	0.96

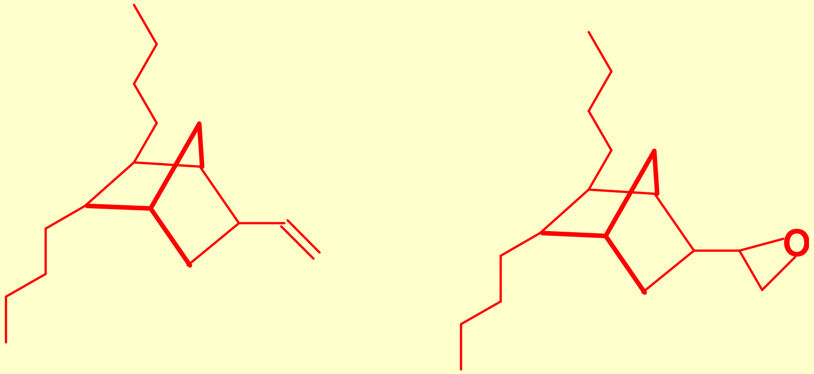
CONCLUSIONS

- Unambiguous synthesis of hydroxyl end functionalized PMMAs
- First unequivocal synthesis of amphiphilic PMMA-b-PEO using hydroxyl end functionalized PMMA as the macro initiator
- Living arms of protected hydroxy-PMMA have been coupled using a cross-linker to yield well-defined PMMA stars with peripheral hydroxyl functionalities

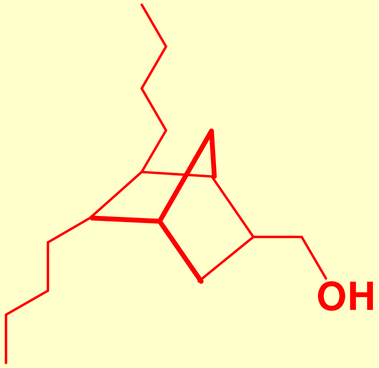
CONTROLLED OR “LIVING” POLYMERIZATION OF OLEFINS

- Controlled catalytic polymerization of olefins is still an elusive goal
- Evidence of “living” nature of chain ends not complete. True A-B and A-B-A block polymers of olefins are rare in the literature
- Several catalyst show features such as narrow molecular weight distribution for polyolefins. However, this alone is not very interesting
- The conversion of an active carbon metal bond to a well defined end functionality does not appear to be a general one except for C-V bonds
- Thus, indirect methods must be resorted to for the synthesis of functional polyolefins

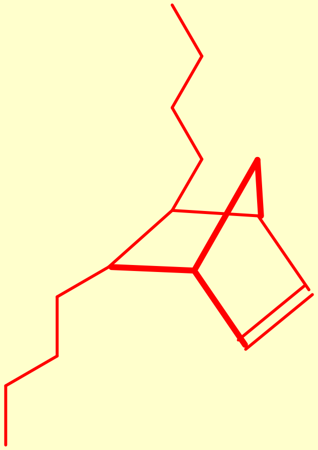
IN CHAIN FUNCTIONALIZATION OF POLY(OLEFIN)S



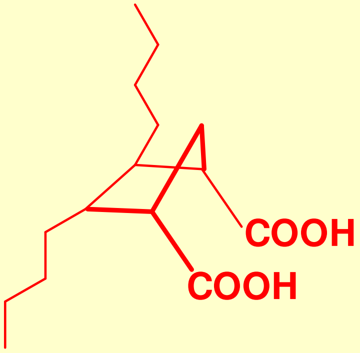
S. Marathe(1994)



K. Radhakrishnan (1998)



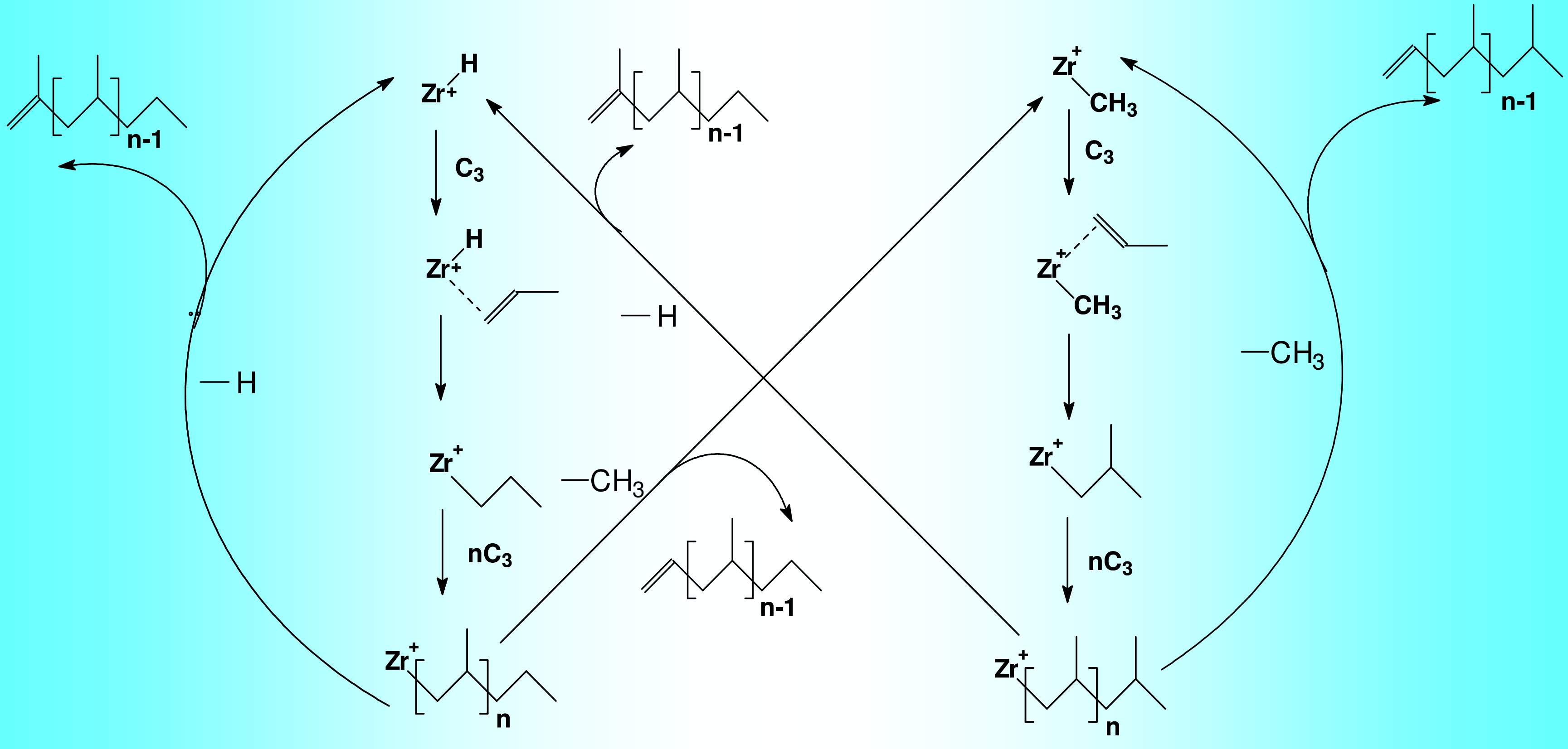
K. Radhakrishnan (1998)



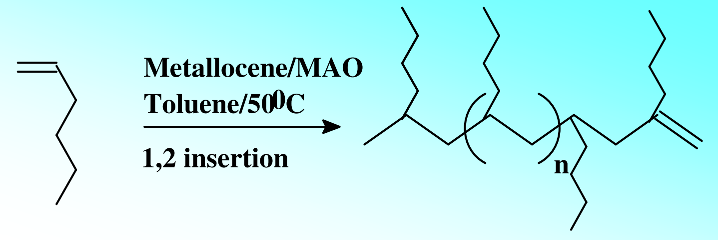
K. Radhakrishnan, M.J. Yanjarappa (2000)

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-$BuCp_2ZrCl_2$	50	440	460	98
	40	700	730	96
	30	1020	1100	93

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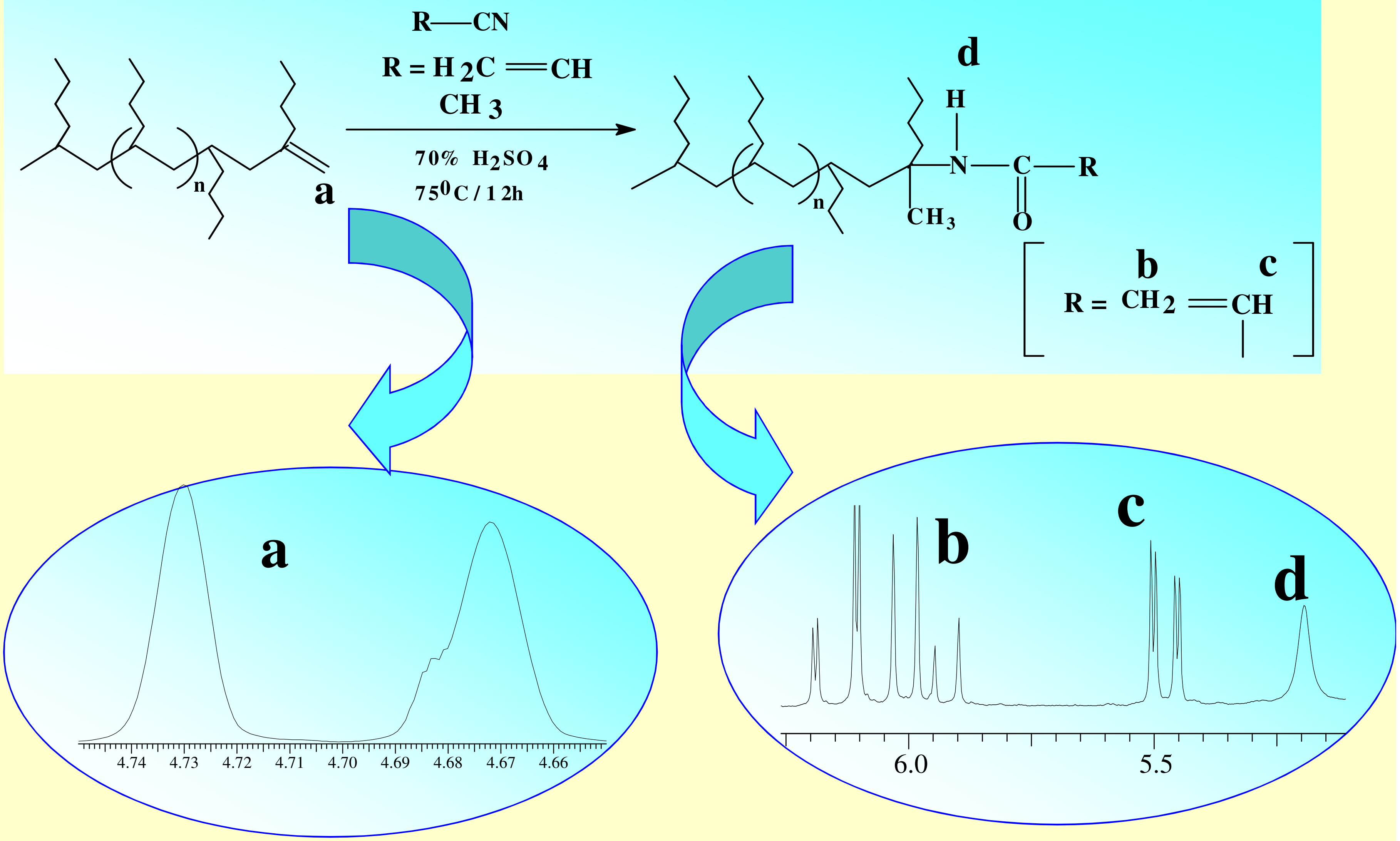
RITTER REACTION USING VINYLIDENE TERMINATED OLIGO(HEXENE-1)



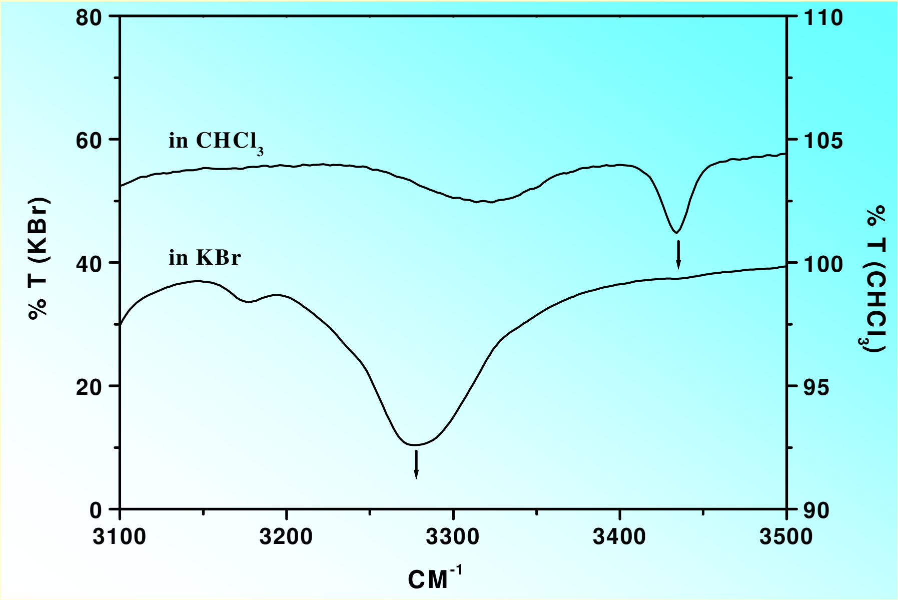
RITTER REACTION OF VINYLIDENE TERMINATED POLY(HEXENE-1) WITH ACRYLONITRILE

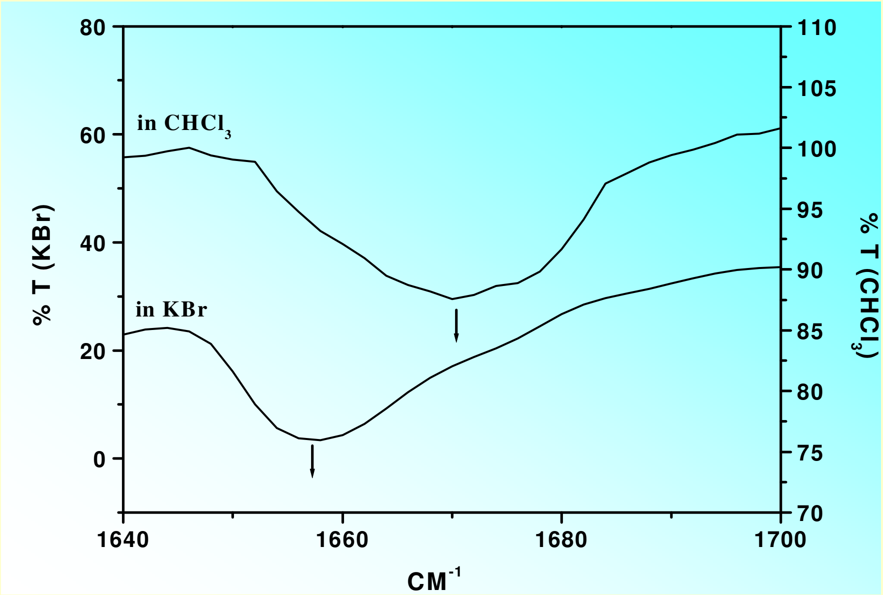
Run no.	Poly(hexene-1)				Mn after functionalization		Fn (mol%) a / b
	Mn	mol	End groups (mol%)		VPO a	^{1}H NMR b	
			vinylidene	internal			
1	380	0.01	98	2	440	490	89
2	1080	0.005	94	6	1140	1440	80
3	2760	0.0025	90	10	2820	5660	50
4	10 020	0.001	83	17	10 080	34 760	29

Reaction conditions: 2 mL of 70% H_2SO_4 catalyst, Temperature = 70^0C, 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.

EVIDENCE OF INTERMOLECULAR HYDROGEN BONDING (FT-IR)





N-H strech

KBr = 3278 cm^{-1}

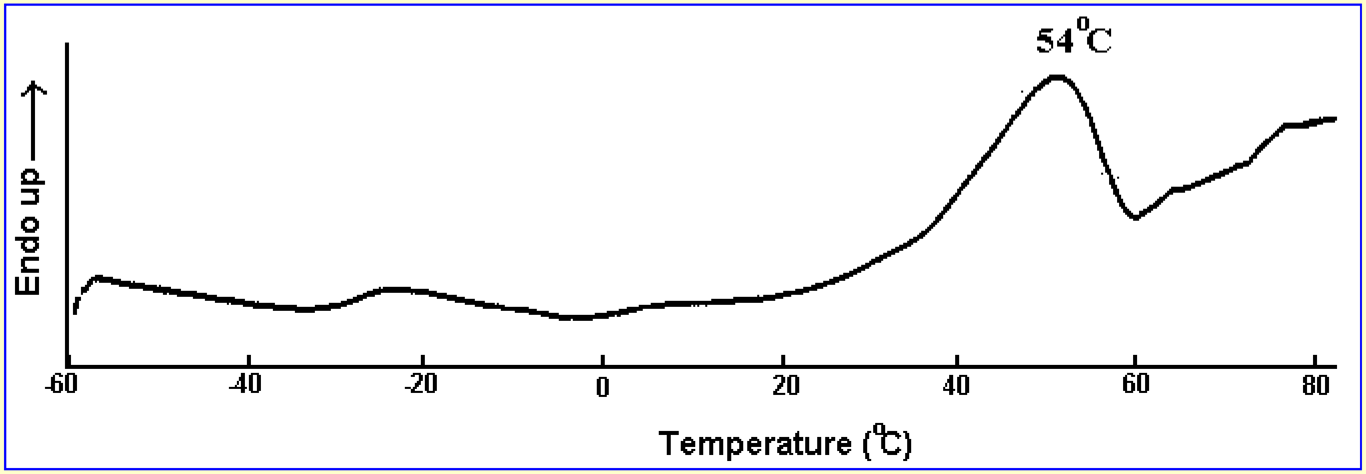
CHCl$_3$ = 3434 cm^{-1}

C=O strech

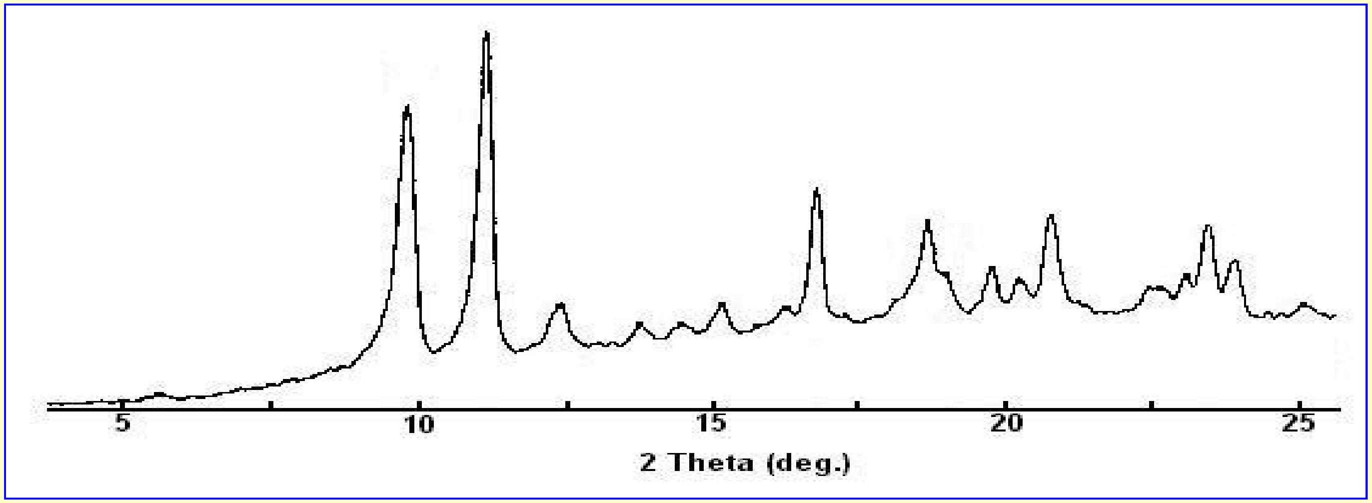
KBr = 1658 cm^{-1}

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

CRYSTALLINITY DUE TO AMIDE FUNCTIONALITY



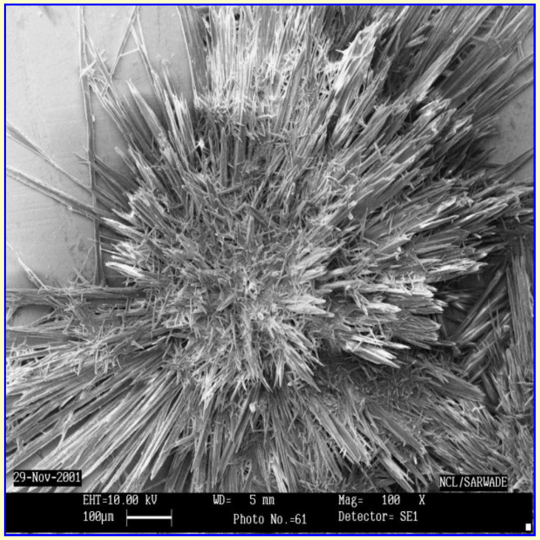
DSC of N-poly(alkenyl) acrylamide.

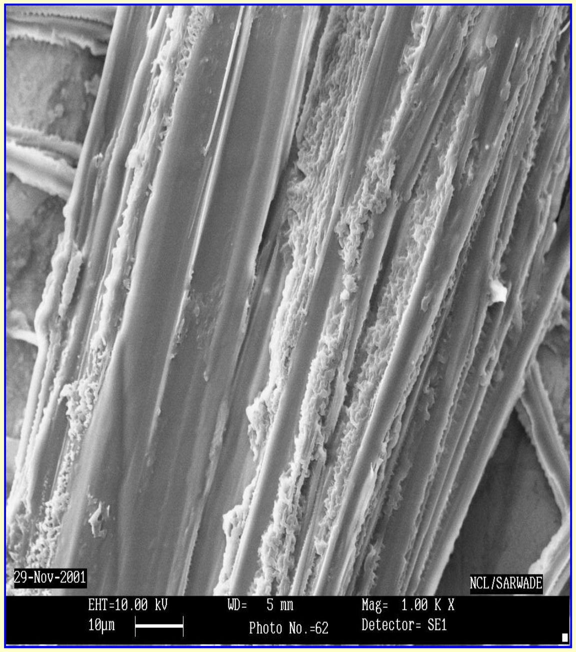


WAXD of N-poly(alkenyl) acrylamide

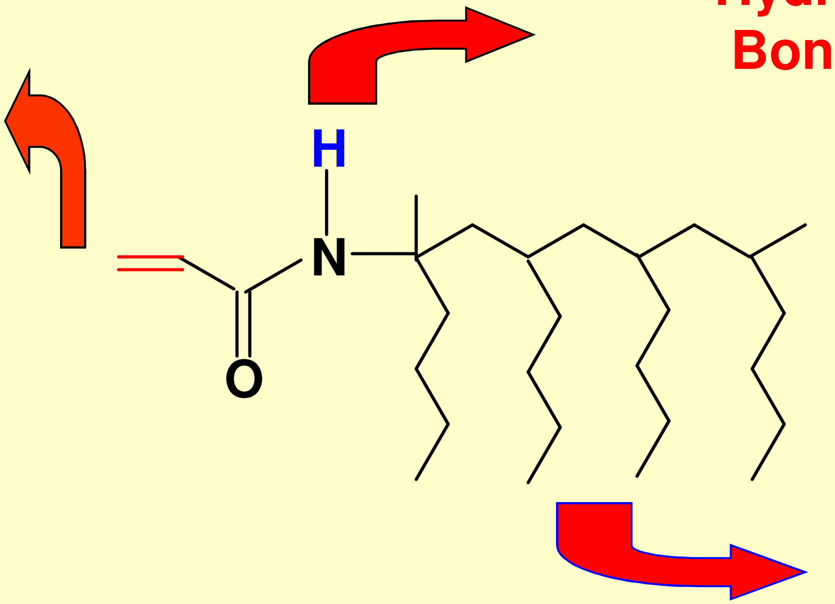
CONCLUSIONS

- Ampiphilic 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





N-POLY(ALKENYL) ACRYLAMIDES : NOVEL AMPIPHILIC MACROMONOMERS



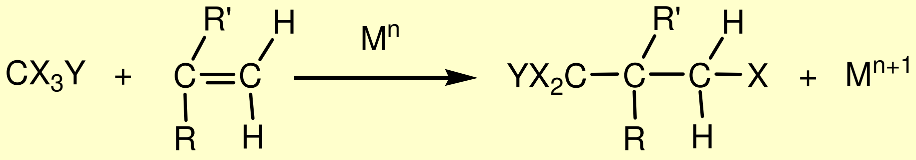
Reactive Unsaturation

Hydrophilic Amide Capable of Hydrogen Bonding

Hydrophobic alkyl group

Development of Atom-transfer Radical Polymerization (ATRP)

- **Atom transfer radical addition**



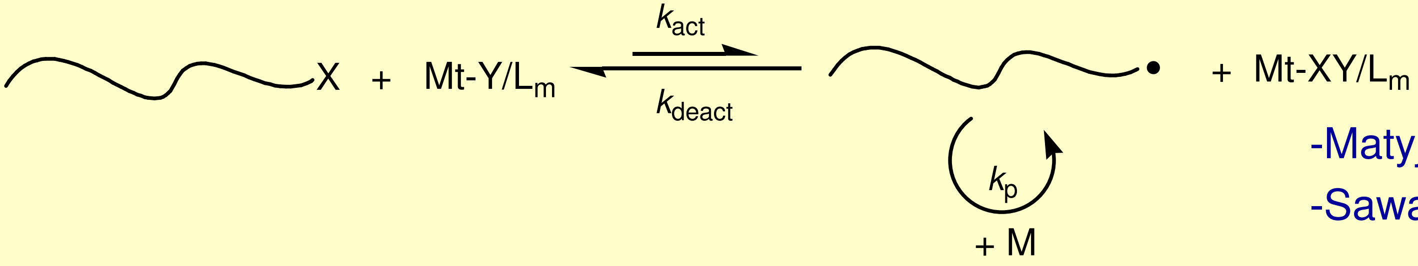
$$CX_3Y + \underset{R}{\overset{R'}{C}}{=}\underset{H}{\overset{H}{C}} \xrightarrow{M^n} YX_2C-\underset{R}{\overset{R'}{C}}-\underset{H}{\overset{H}{C}}-X + M^{n+1}$$

X = halogen; Y = H (or) electronegative group; M = Cu or Ni

Morris Kharash

(1938)

- **Atom transfer radical polymerization**

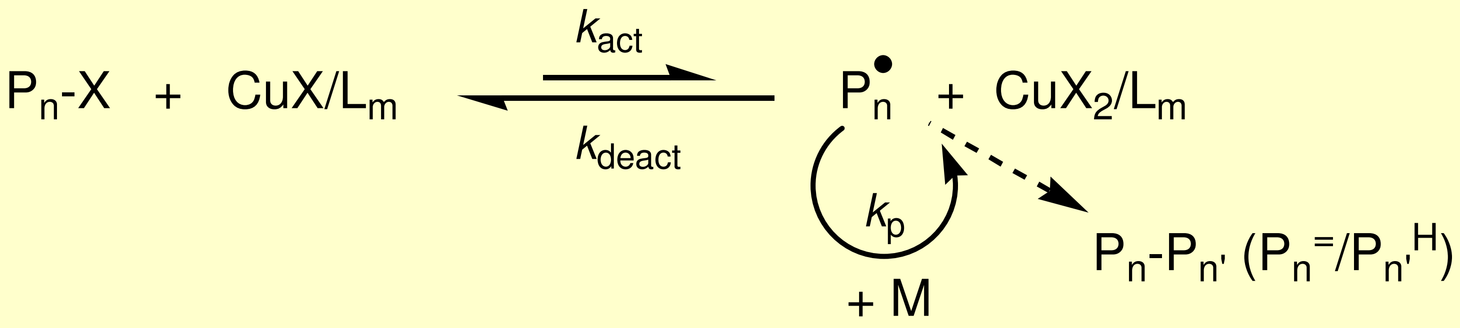


-Matyjaszewski (1995)

-Sawamoto (1995)

X and Y- halogen; Mt -Cu^{I}, Ru^{II}, Fe^{II}, Ni^{II}, etc; M- vinyl monomer, L-Ligand

Advantages of Copper-mediated ATRP



$$P_n\text{-}X \;+\; CuX/L_m \;\underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}}\; P_n^{\bullet} \;+\; CuX_2/L_m$$

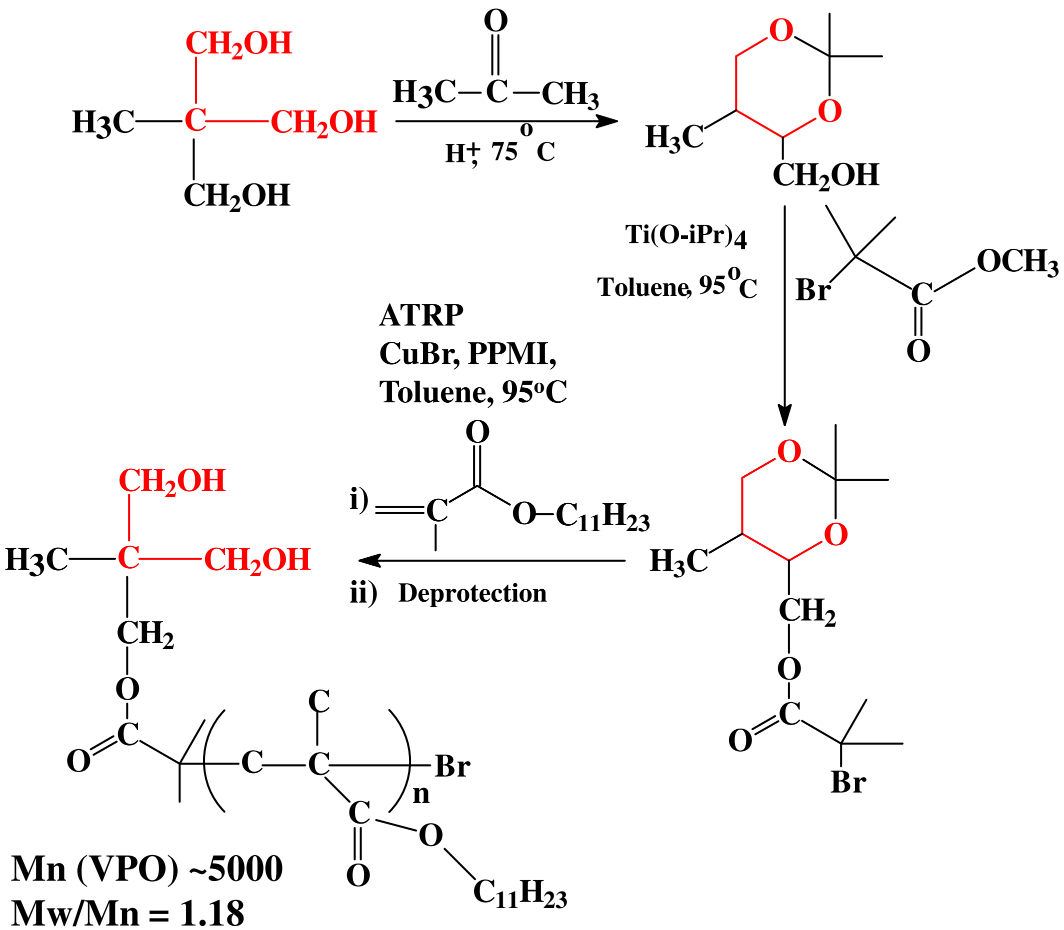
k_p

$+ M$

$P_n\text{-}P_{n'}\ (P_n^{=}/P_{n'}^{H})$

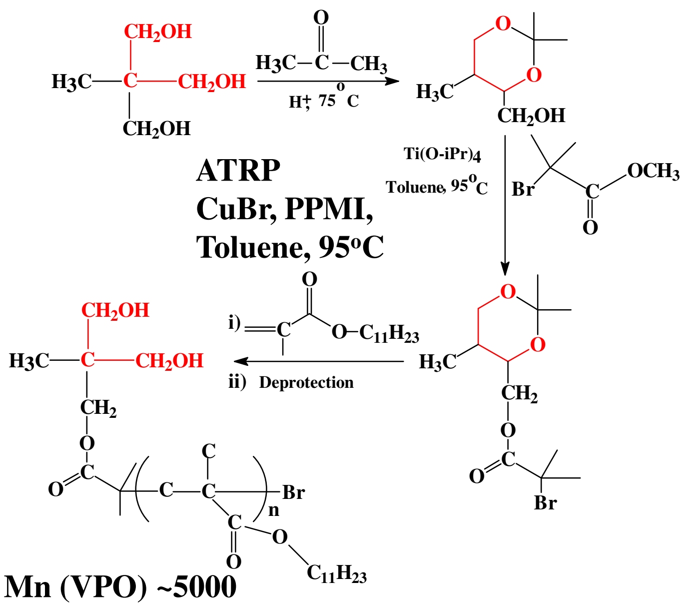
- Significantly suppresses chain-transfer and chain-termination
- Produces polymers with well-defined molecular weight and narrow molecular weight distribution
- Tolerant to many functional groups
- Wide range of monomers and solvents can be used
- Very robust technique and easy to perform
- Chain-end functionality is preserved leading to formation of block, graft , star, comb, and hyper-branched copolymers.

CONTROLLED SYNTHESIS OF DIOL FUNCTIONALIZED POLY(METHACRYLATE)S



Mn (VPO) ~5000
Mw/Mn = 1.18

NEARLY MONODISPERSE POLYURETHANE NANOPARTICLES - FUNCTIONAL POLY(LMA) AS STERIC SURFACTANTS



ATRP
CuBr, PPMI,
Toluene, 95°C

Mn (VPO) ~5000
Mw/Mn = 1.18

Stabilizer 5 wt %
DBTL 0.005%
Cyclohexane 20 parts

↓

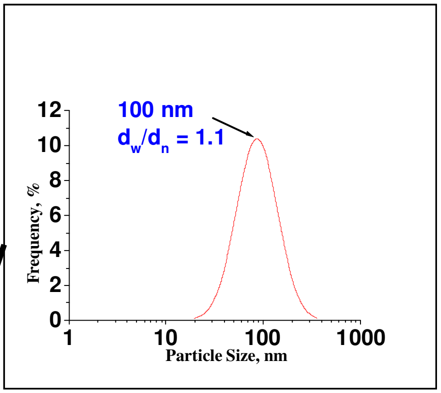
TDI
60°C, 4 h

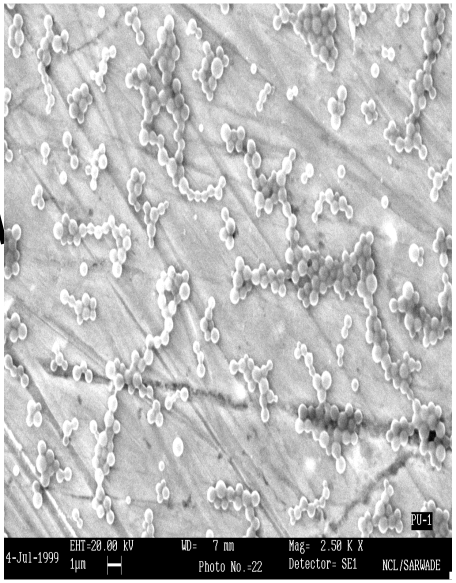
↓

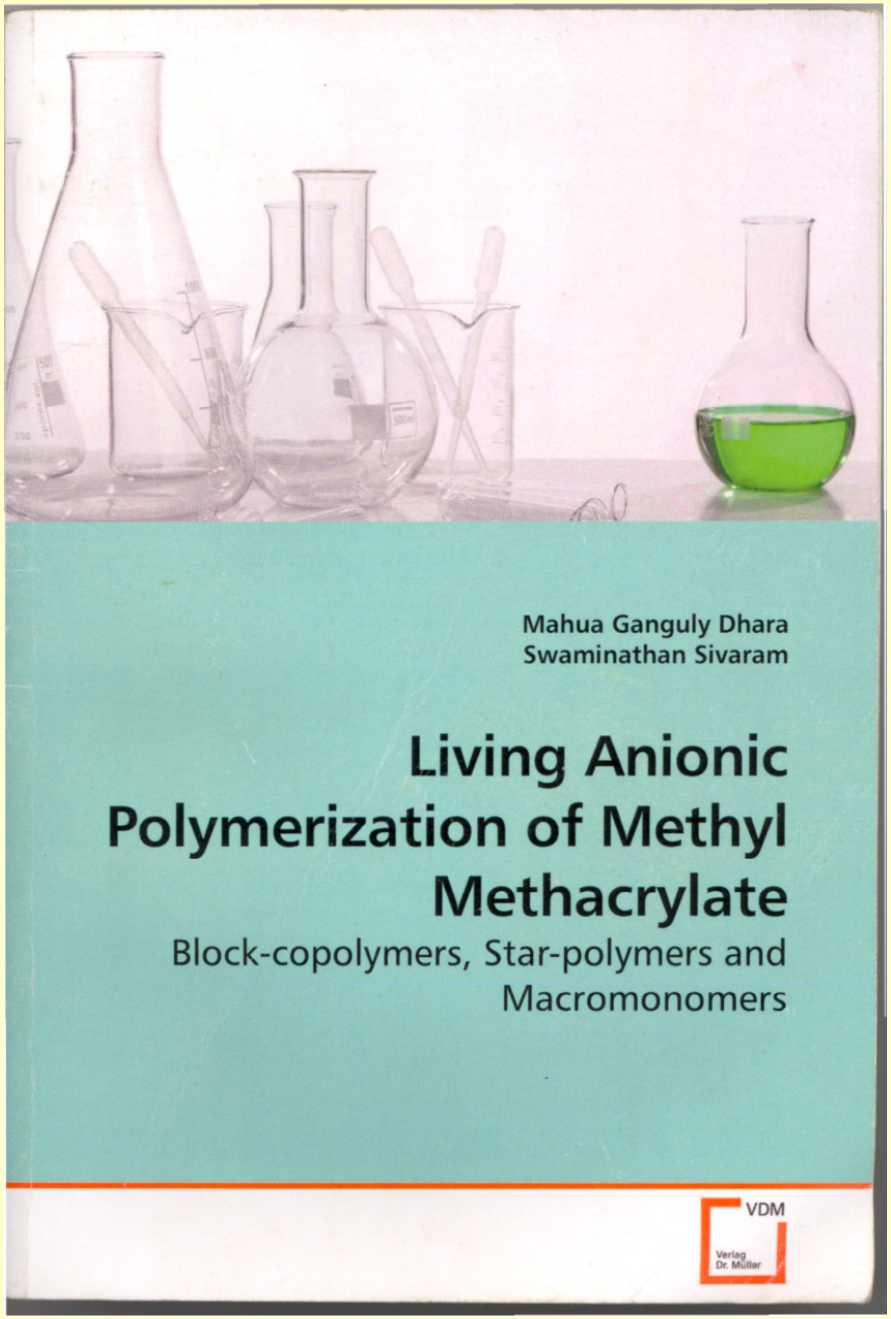
EHG
60°C, 4 h

↓

PU particles






Mahua Ganguly Dhara
Swaminathan Sivaram

Living Anionic Polymerization of Methyl Methacrylate
Block-copolymers, Star-polymers and Macromonomers

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THANK YOU

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