

# **CONTROLLED SYNTHESIS OF FUNCTIONAL POLYMERS**



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May 14, 2010**





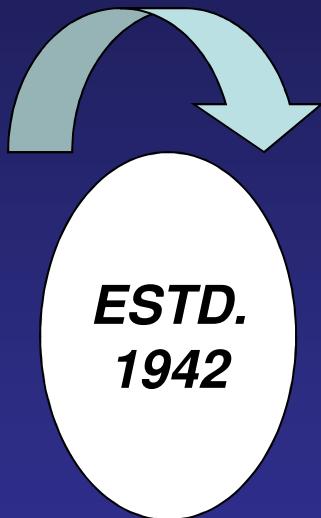
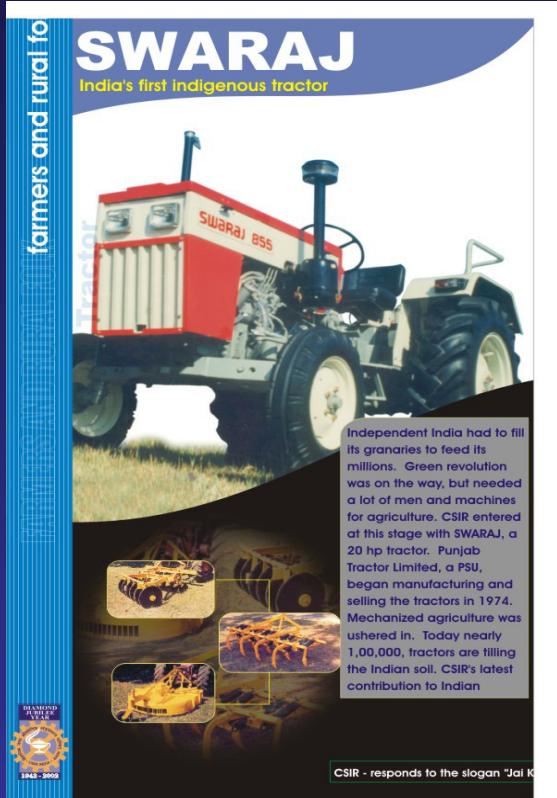
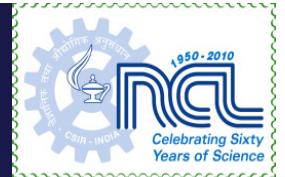
# **COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH**



## ***Mission***

**To provide scientific industrial research & development that maximizes the economic, environmental & societal benefits for the people**

# COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH (CSIR)



**Multi-disciplinary multi-location chain of 37 research laboratories**  
**Largest chain of publicly funded laboratories**  
**Total staff strength of 18000 ; scientific and technical staff : 13000**

**Aerospace**  
**Life and Plant Sciences**  
**Chemical Sciences**  
**Drugs & Pharmaceuticals**  
**Material Science**  
**Leather Science**  
**Engineering Sciences**  
**Food Science**  
**Earth , Ocean & Physical Sciences....**

## ***NCL : A SNAP SHOT***



- **Established** : 1950
- **Location** : Pune, India
- **Total personnel**
  - **Permanent Staff** : 730
    - Scientific** : 206
    - Technical** : 330
    - Administrative** : 194
  - **Research Fellows (CSIR, UGC)** : 440
  - **Project Staff (M.Sc's)** : 382
  - **Post doctoral fellows** : 24

***One of the largest publicly funded research institution in India***  
***One of the oldest research institutions of independent India***



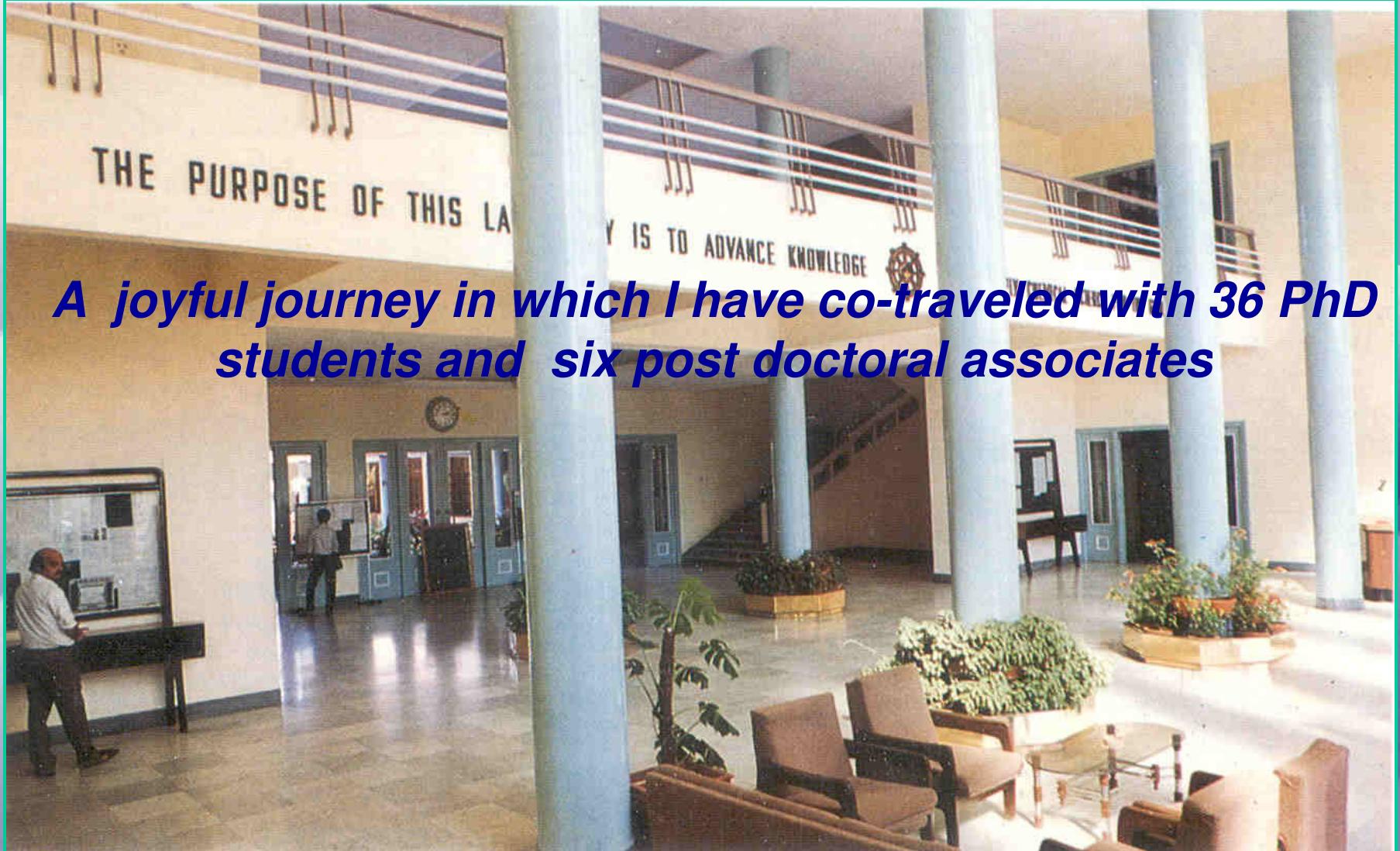
## **NCL AT A GLANCE**

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- Over 220 scientific staff with PhD
- Interdisciplinary research with interests in polymer science, organic chemistry, catalysis, materials chemistry, chemical engineering, biochemical sciences and process development
- Excellent infrastructure for measurement science and chemical information
- 400 + graduate students pursuing research towards doctoral degree; about 80 students awarded Ph.D. degree by the University of Pune every year; a strong and young talent pool which renews every few years
- Publish the second largest number of peer reviewed papers in chemical sciences (> 450), file the largest number of patents, both in India and overseas (> 50) and produce the largest number of Ph.Ds in chemical sciences in India

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

**J W McBain**



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

## ***TWENTY YEARS OF RESEARCH AT NCL (1989-2009)***

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### **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.....***

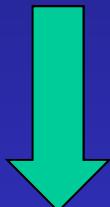
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**Techniques of controlled polymer synthesis**

**Concepts and goals of material science**

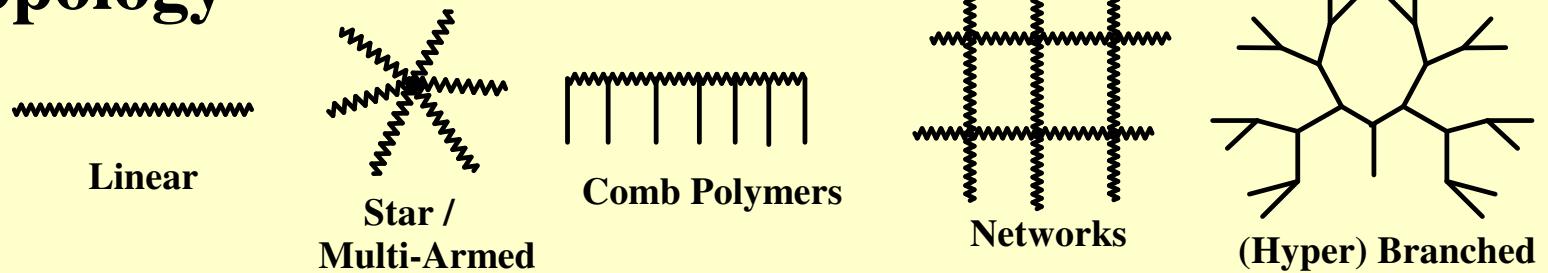
**Molecular scale phenomena**

**Macroscopic functions**



# CONTROL OF STRUCTURES AND FUNCTIONALITIES

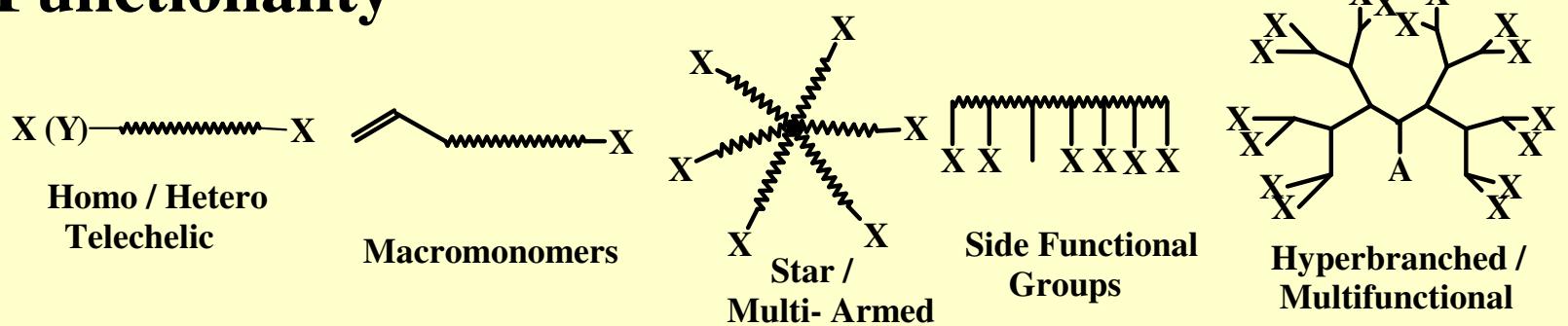
## Topology



## Composition



## Functionality



## ***WHY FUNCTIONAL POLYMERS?***

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- 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***

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- 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

# ***FUNCTIONAL POLYMERS THROUGH CONTROLLED CHAIN GROWTH POLYMERIZATION***

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- 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***

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- **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***

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- 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 ( $F_n$ ) 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

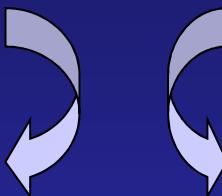
Living anionic polymerization enables synthesis of functional polymers with well-defined structures

## Functional Polymers : Synthesis

### Strategies for polymer functionalization

#### Electrophilic termination

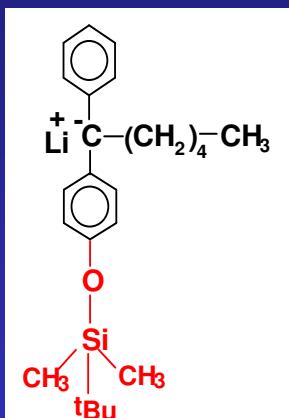
- Method more general
- Functionalization usually not quantitative  $\Rightarrow$  Unfunctionalized chains
- Undesirable side-reaction  $\Rightarrow$  Polymeric side-products



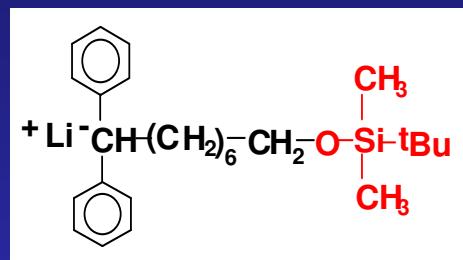
#### Functional initiation

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

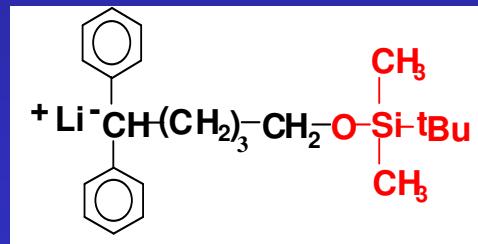
## Synthesis of Hydroxyl End-functionalized PMMA Using Protected Hydroxyl-functionalized Initiators



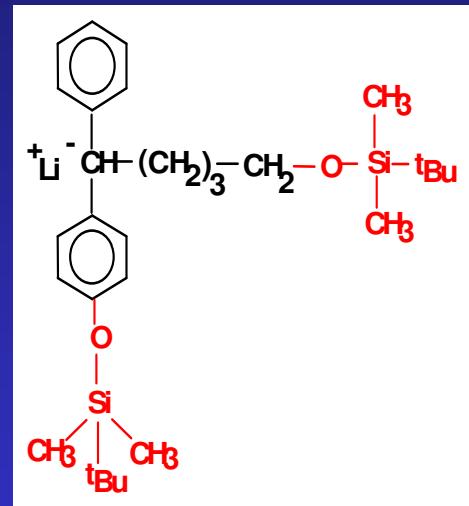
F1



F2



F3

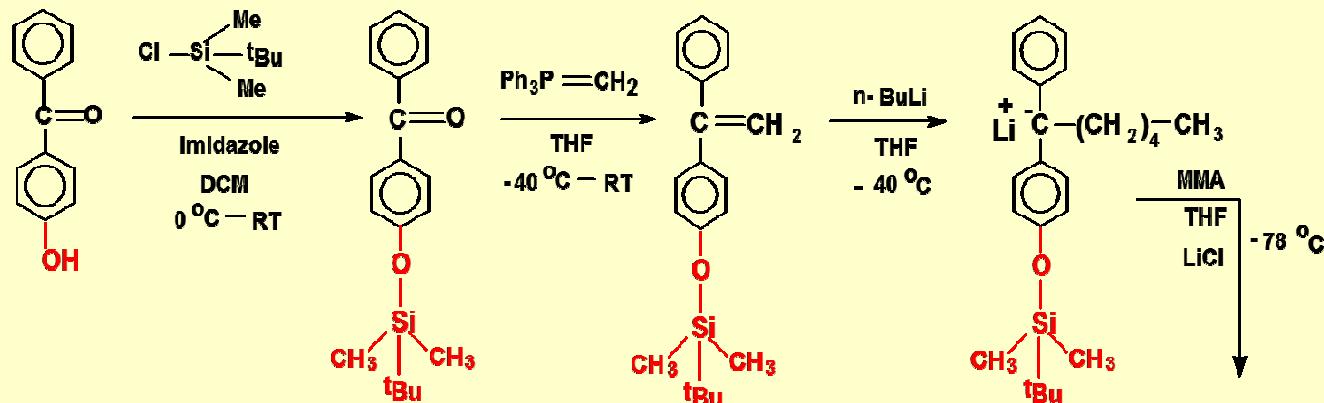


F4

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

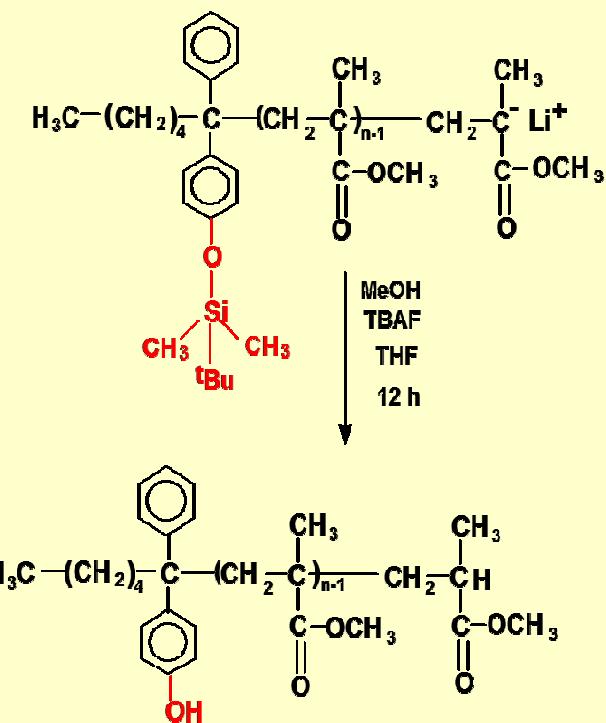
# Synthesis of Hydroxyl End-functionalized PMMA Using F1

## F1 $\rightleftharpoons$ Adduct of 1-(*p*-hydroxyphenyl)-1'-phenyl ethylene and *n*-BuLi



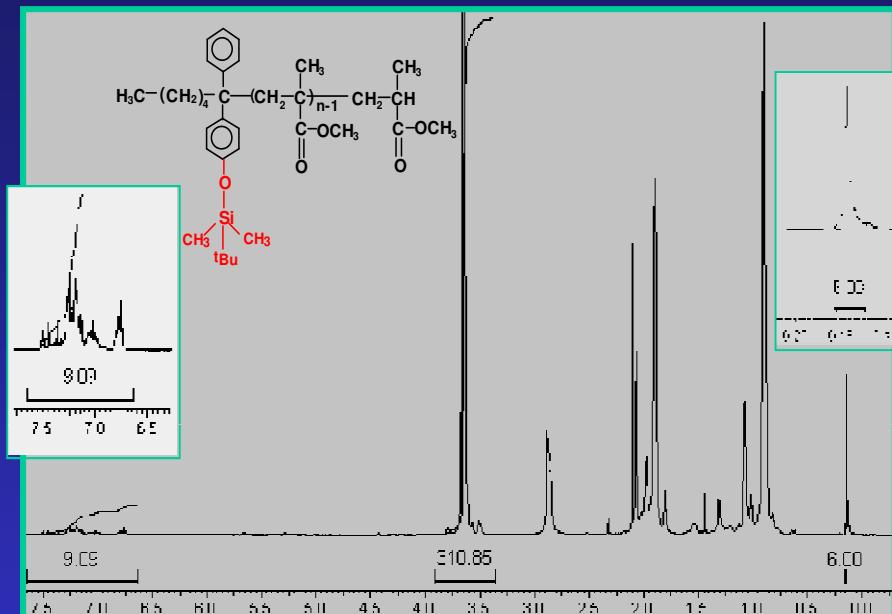
Run no.	$[I]_0 \times 10^{-3}$ m/L	$[M]_0$ m/L	Conv. %	$\bar{M}_{n,sec} \times 10^{-3}$	$\bar{M}_{n,calc} \times 10^{-3}$	MWD	$f = \bar{M}_{n,calc} / \bar{M}_{n,sec}$
1	3.67	0.12	~100	3.2	3.3	1.07	1.03
2	2.70	0.18	90	10.8	9.8	1.06	0.91
3	2.88	0.41	90	14.1	14.4	1.09	1.02

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



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

<sup>1</sup>H NMR (500 MHz, acetone-d6) spectra of silyl-protected hydroxy-PMMA (M<sub>n</sub>,sec=10800)



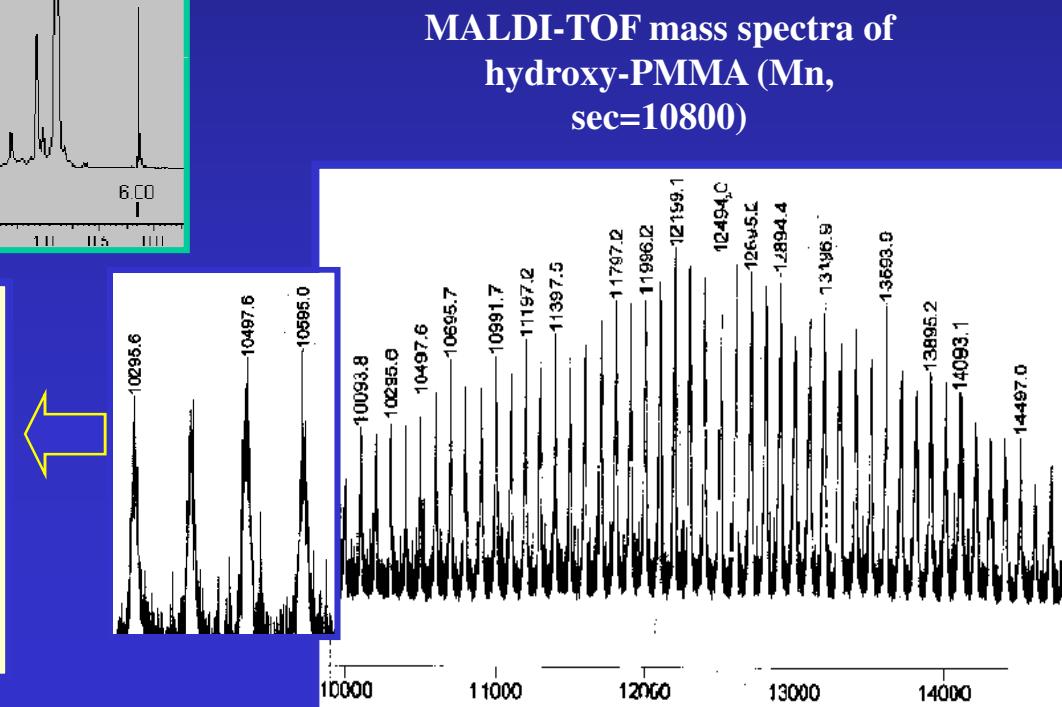
$\delta$  0.0 6 H of -Si(CH<sub>3</sub>)<sub>2</sub>  
 $\delta$  6.7-7.6 9 H for 2 phenyl groups  
 $\delta$  3.58 310 H for -OCH<sub>3</sub> protons of PMMA  
  
 quantitative functionalization of PMMA chains

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



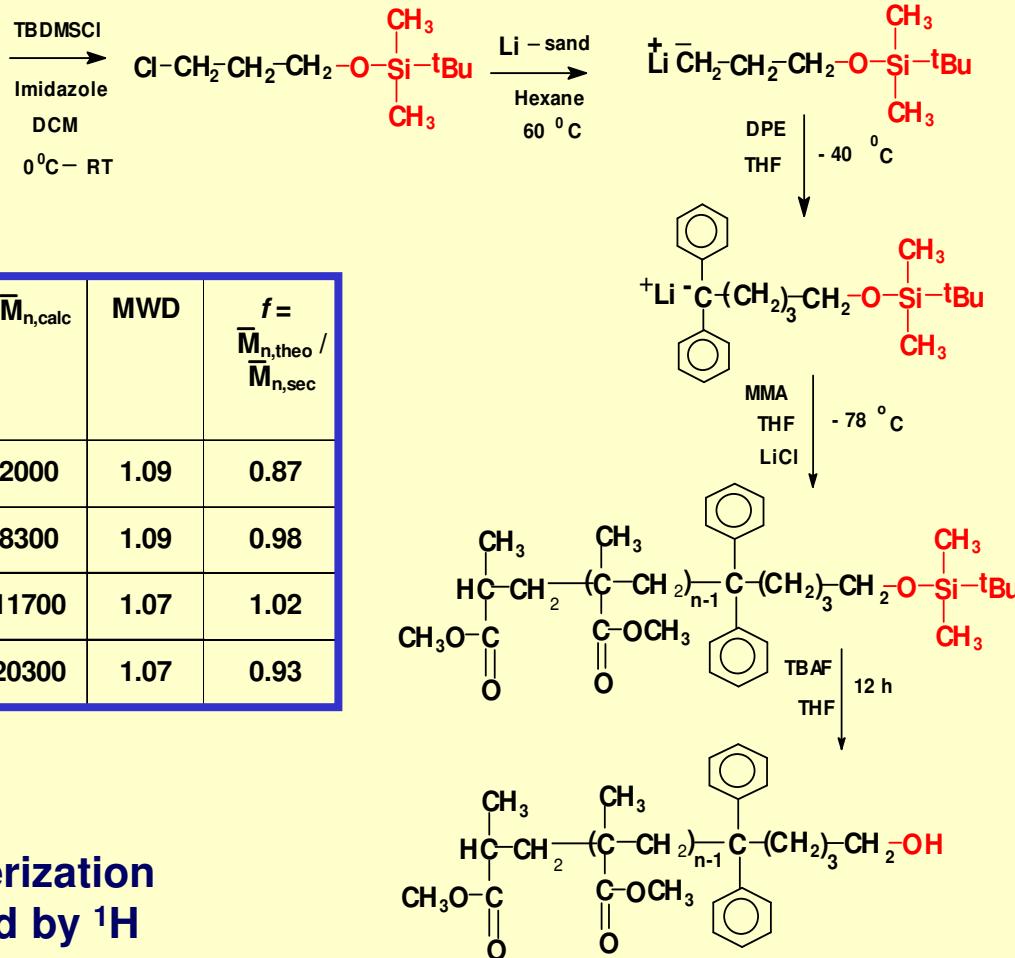
# Synthesis of Hydroxy End-functional PMMA Using F3

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

Run no.	$[I]_0 \times 10^{-3}$ m/L	$[M]_0$	Conv. %	$\bar{M}_{n,sec}$	$\bar{M}_{n,calc}$	MWD	$f = \bar{M}_{n,theo} / \bar{M}_{n,sec}$
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

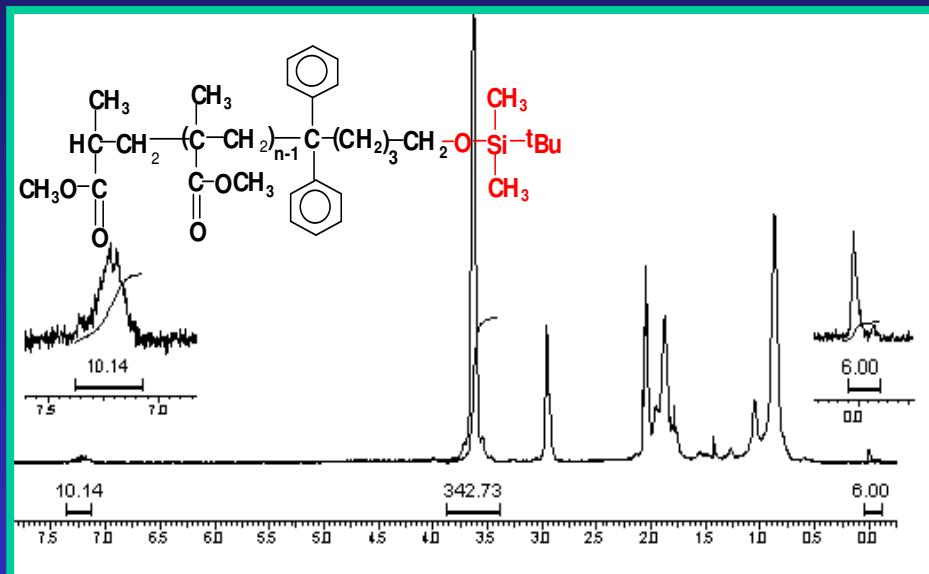


- ⊗ Well-controlled polymerization
- ⊗ Functionality confirmed by  $^1\text{H}$  NMR, MALDI-TOF MS



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

## **<sup>1</sup>H NMR (500 MHz, acetone-d6) spectra of silyl-protected hydroxy-PMMA (M<sub>n</sub>,sec=11500)**



$\delta$  0.0      6 H of  $-\text{Si}(\text{CH}_3)_2$   
 $\delta$  6.7-7.6    10 H for 2 phenyl groups  
 $\delta$  3.58       342 H for  $-\text{OCH}_3$  protons of

## quantitative functionalization of PMMA chains

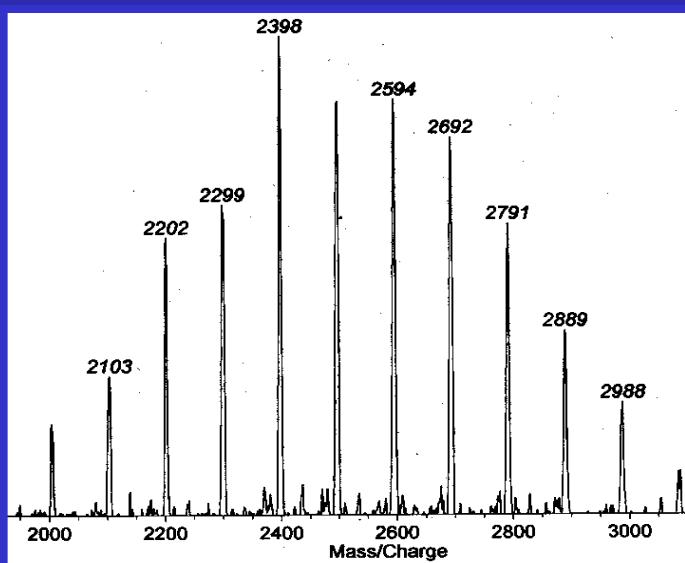
End-group. mass from any say, m/z = 2597 and 2791 are 494 and 491 respectively

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

## Also, single generation of polymers

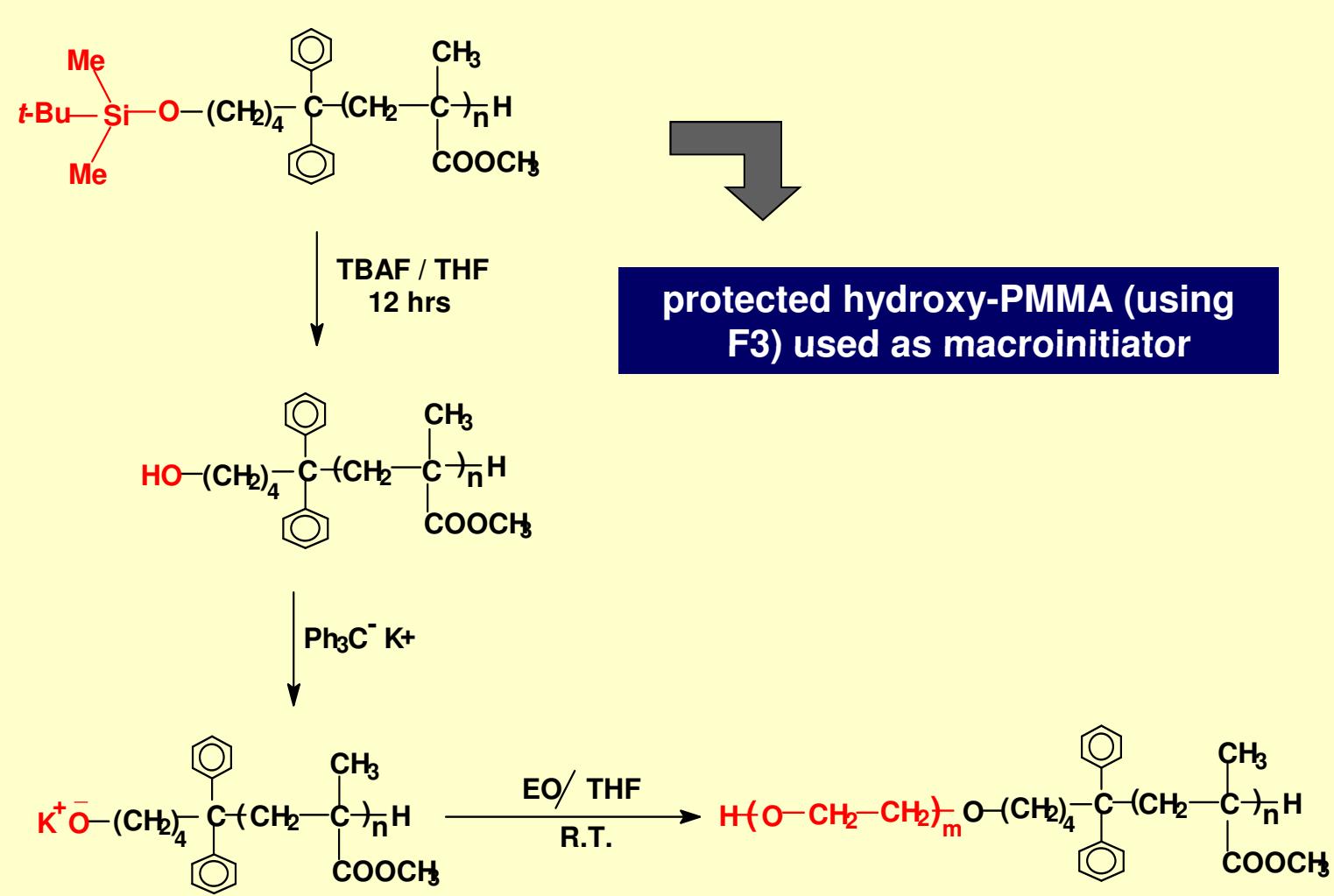
## Presence of free –OH at all chain-ends

## MALDI-TOF mass spectra of hydroxy-PMMA (M<sub>n</sub>, sec=2300)



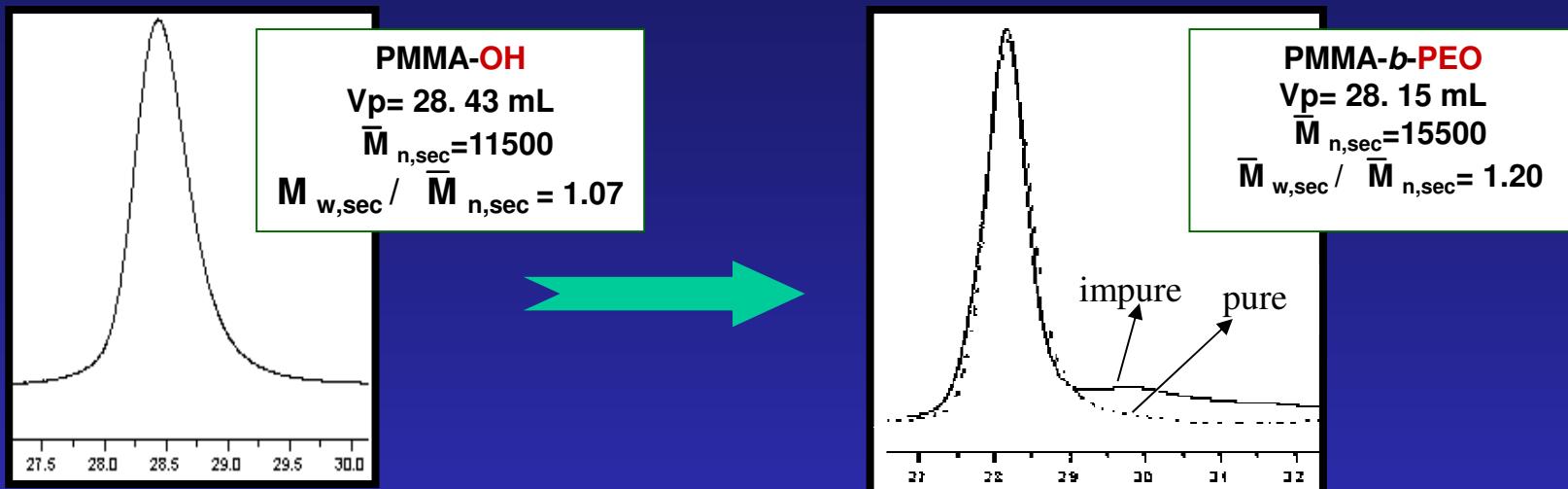
## Synthesis of PMMA-*block*-PEO Copolymer

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



## CHARACTERIZATION OF PMMA-BLOCK-PEO COPOLYMER

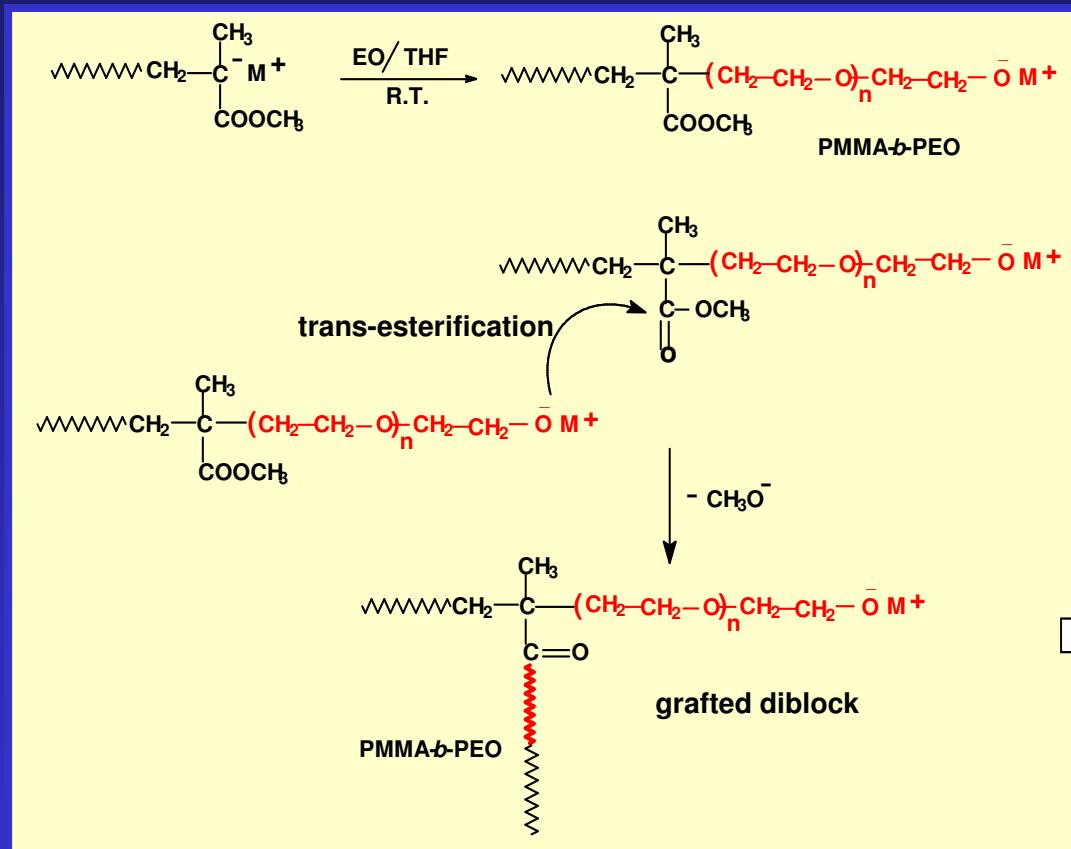
### GPC Analysis



- 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

## PMMA-*b*-PEO Synthesis: Complication due to Trans-esterification Reactions

*Trans-esterification*       $\Rightarrow$       *Attack of living diblock on ester group of PMMA*

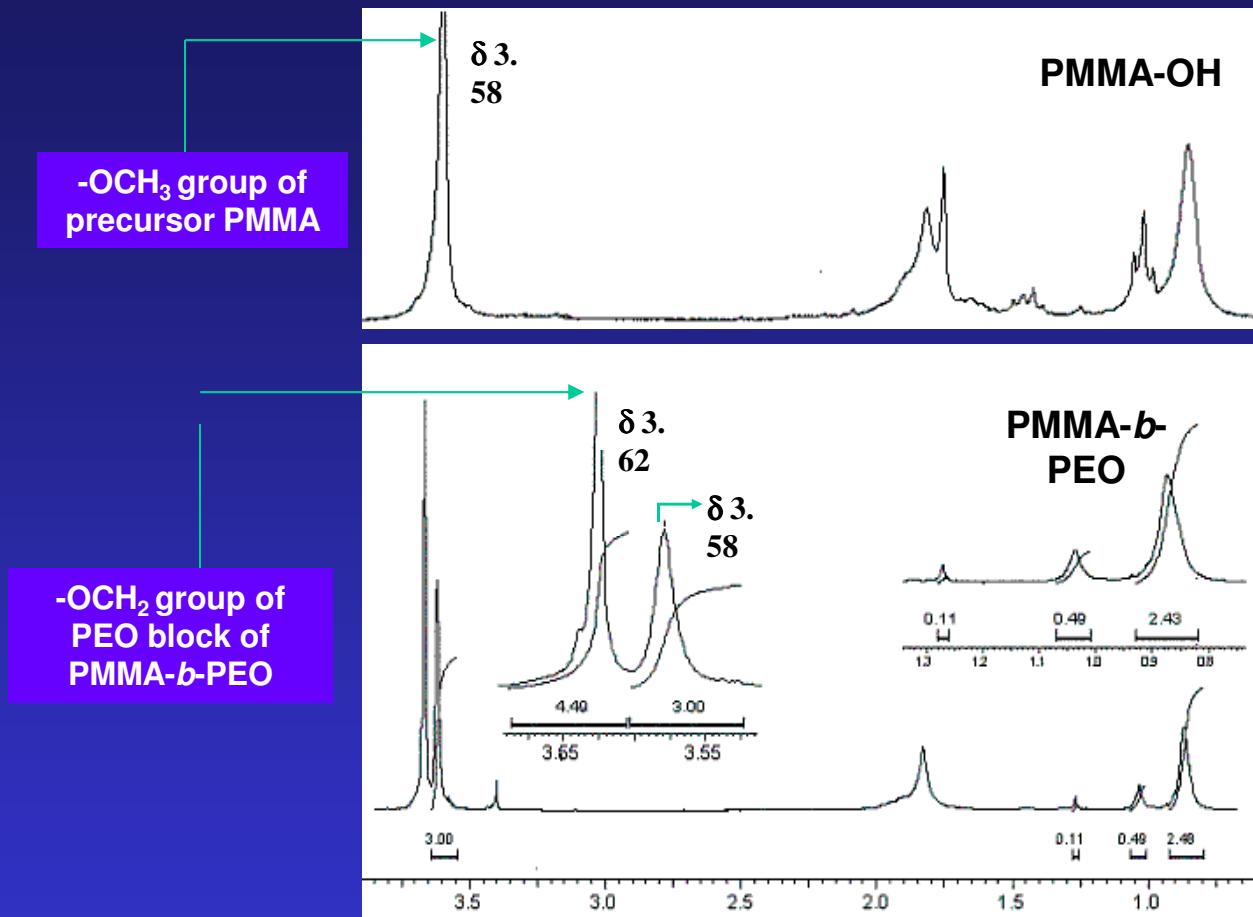


- GPC elugram of PMMA-*b*-PEO show broad multimodal MWD
- NMR of block copolymer show  $-\text{OCH}_3 : -\text{CH}_3$  proton ratio  $< 1.0$

All prior reported synthesis of PMMA-*b*-PEO are complicated due to significant occurrence of trans-esterification reaction

## Characterization of PMMA-*block*-PEO Copolymer

<sup>1</sup>H NMR (500 MHz) spectroscopic analysis

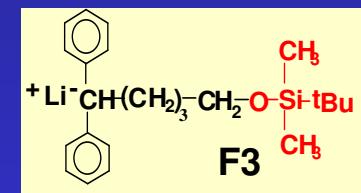
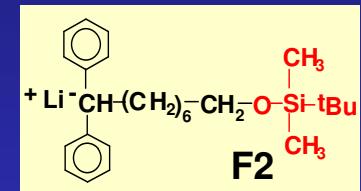
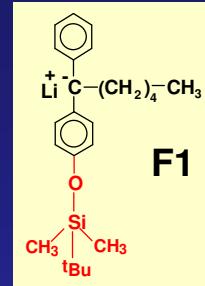


- Additional peak at  $\delta$  3.62 due to  $-\text{OCH}_2$  protons in PMMA-*b*-PEO
- Ratio of peak intensities due to  $-\text{CH}_3$  and  $-\text{OCH}_3$  protons is 1:1

Appearance of new peak due to  $-\text{OCH}_2$  protons confirm formation of the diblock  
Presence of equal number of methyl and methoxy groups suggest insignificant amount of transesterification reaction

## Characterization of PMMA-*b*-PEO Copolymers : GPC & NMR

Run no.	PMMA-OH			[MMA]:[EO] in feed	PMMA- <i>b</i> -PEO			
	Sample no.	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$ (SEC)		Conv.	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$ (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

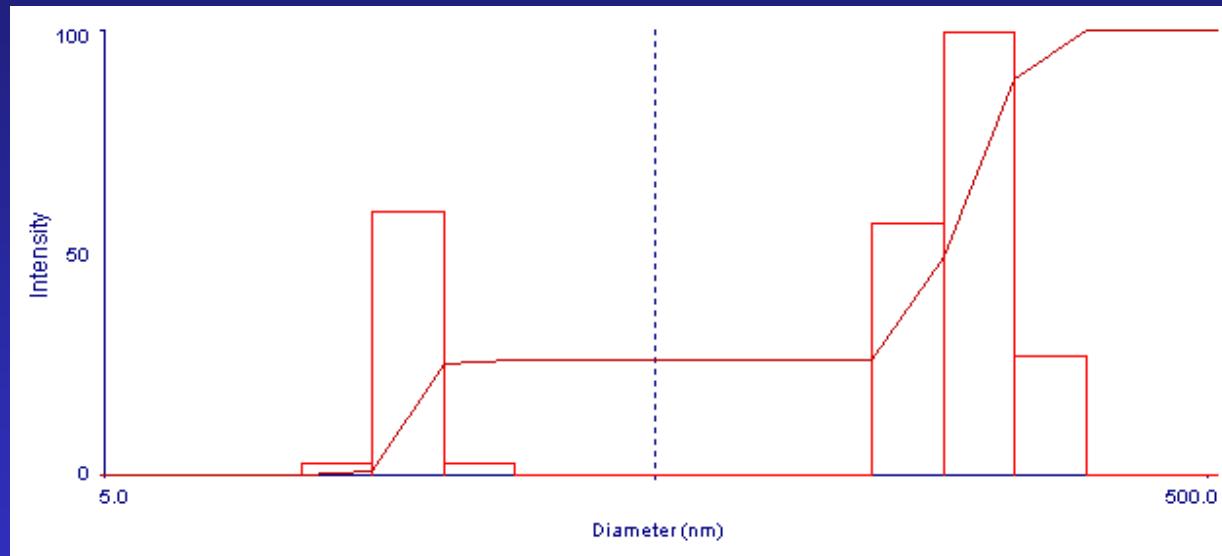


- NMR and GPC results prove the formation of PMMA-*b*-PEO from the precursor PMMA-OH
- Simple process of purification yields well-defined block copolymers with unimodal and fairly narrow MWD
- Run nos. 5 and 9 resulted in water-soluble PMMA-*b*-PEO copolymers

# DLS Results of micelles of PMMA-*b*-PEO copolymer

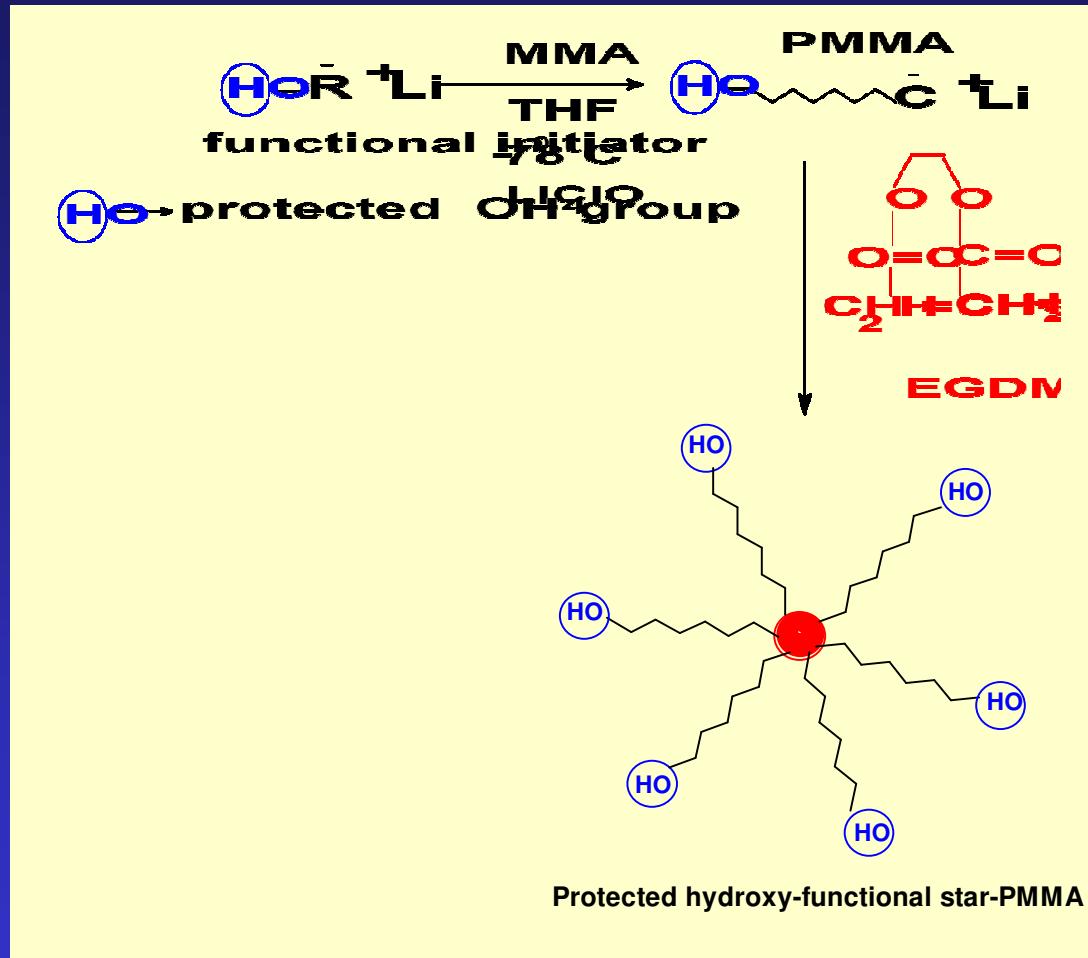
$[C] = 9.2 \times 10^{-4}$  g/mL in water/THF (9:1 v/v)

Run 2: 10 ms/5 s-100 pin



- **Micelles with effective diameter ( $2 \times R_{h,app}$ ) = 83.3 nm were evident**
- **Very broad polydispersity (0.37)**
- **Presence of two populations with average effective diameter of 17 nm and 190 nm**

## Synthesis of Hydroxyl-functionalized PMMA Star polymer



### 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 & [EGDMA]:[I] on no. of branches*

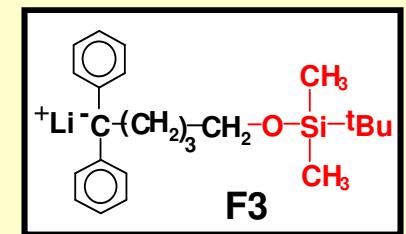
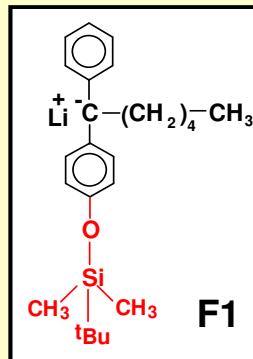
Sample	EGDMA/ initiator	Arm			Star				No. of arms (by -OH titrn.)
		$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$ (SEC) $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$ (LS) $\times 10^{-3}$	$f_w$	
F3-S1	3:1	7000	7600	1.09	55.0	1.11	74.6	9.8	9.3
F3-S2	3:1	8500	9100	1.07	54.5	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

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

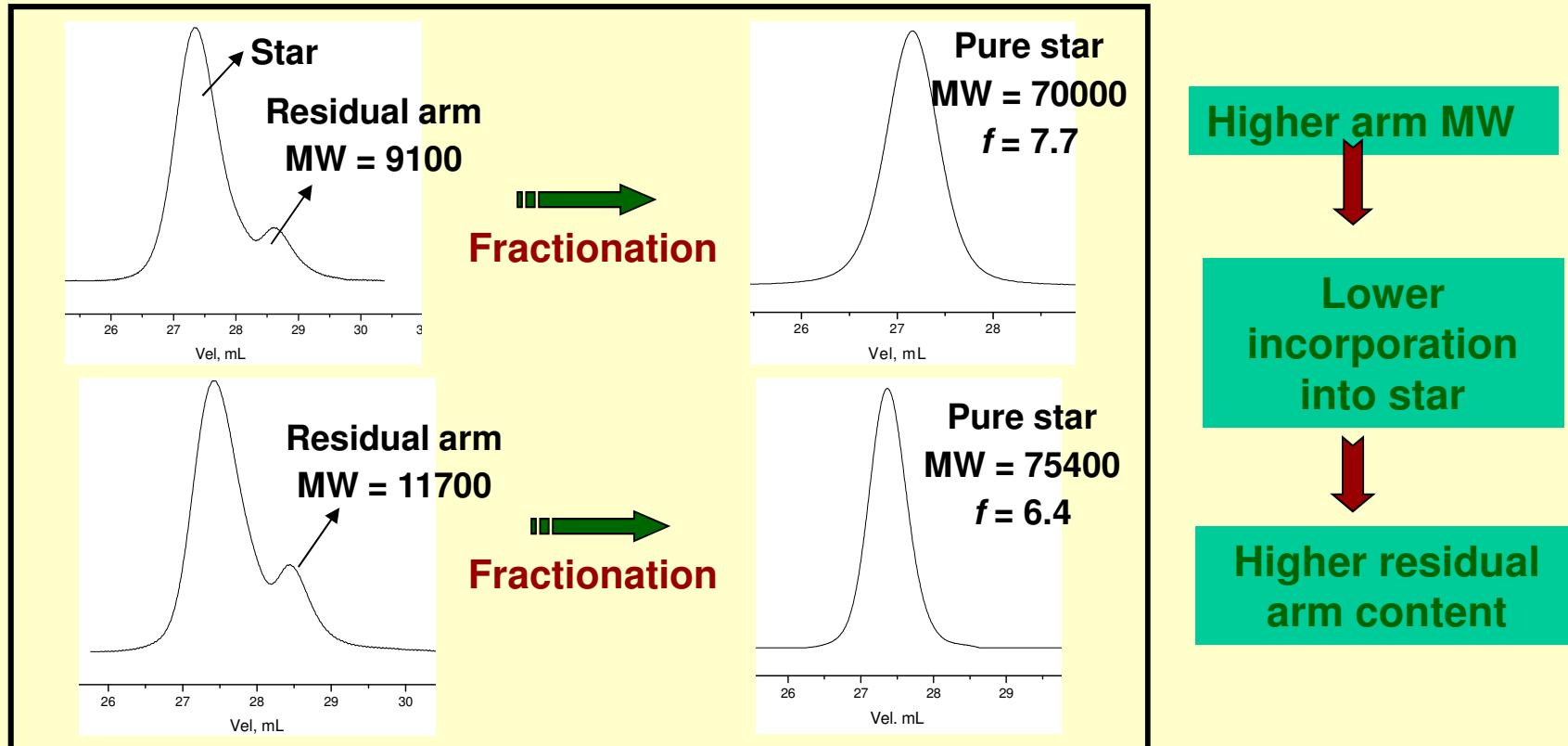
☞ Degree of branching increases with

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

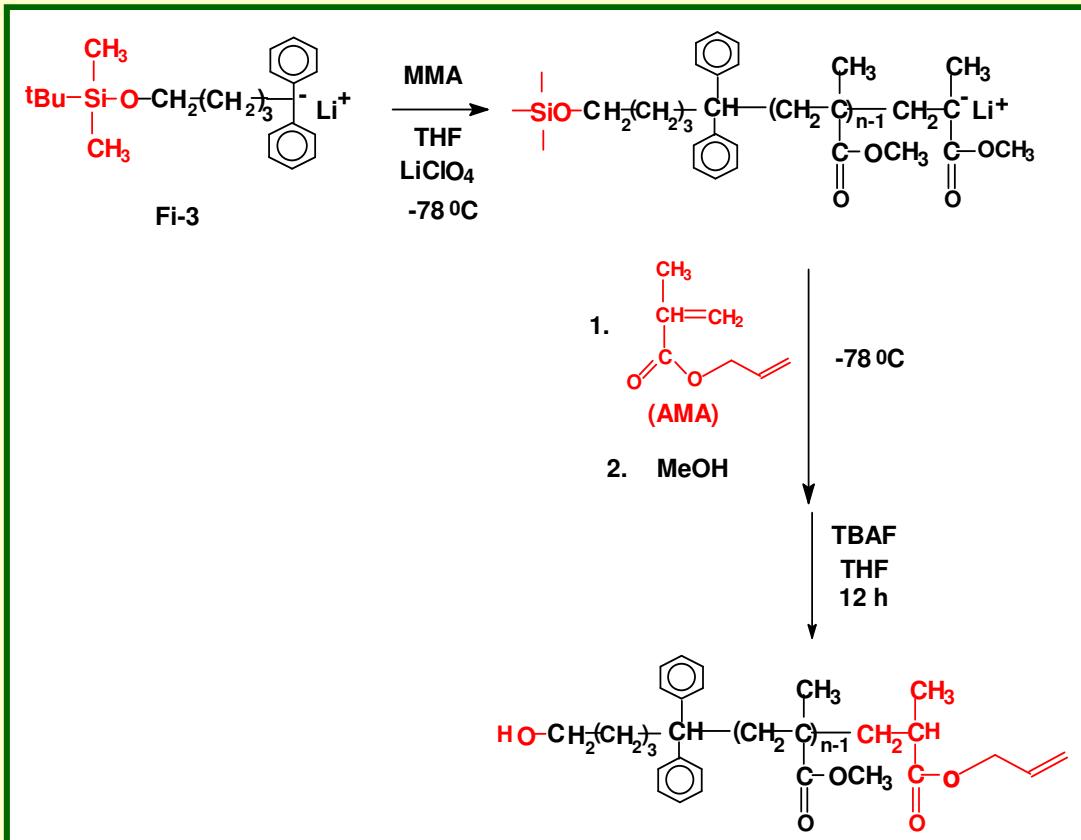


- Addition of dilute toluene solution of deprotected hydroxy-PMMA star to excess cold methanol causes the star to preferentially precipitate

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

# Controlled Synthesis of Functional PMMA-macromonomers

## **Synthesis of $\alpha$ -hydroxy- $\omega$ -allyl PMMA in THF at $-78$ °C using F3 as initiator and allyl methacrylate as end-capper**



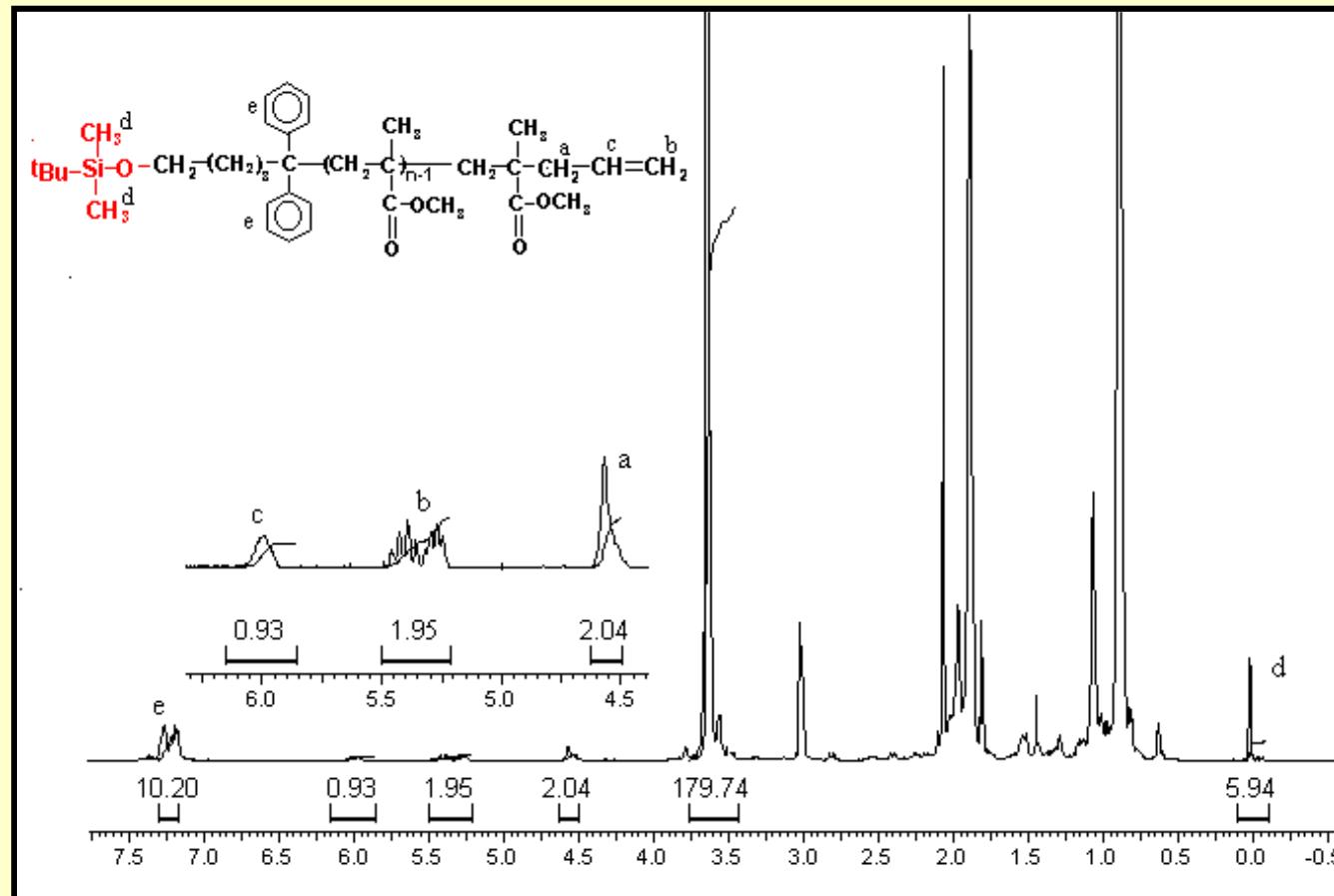
## Step 1. Anionic polymerization of MMA using functional initiator F3

## Step 2. Electrophilic termination of living chains by allyl methacrylate

Sample	$[\Pi]_0$ $\times 10^{-3}$ m/L	$[M]_0$ $\times 10$ m/L	Temp. °C	Time of rxn. (mins)	Yield %	$M_{n,\text{theo}}$	$M_{n,\text{sec}}$	MWD	$f$
F3-PMAM-1	3.0	1.75	-78 °C	30	100	5800	6000	1.09	0.96

## Characterization of hydroxy-functional PMMA-macromonomers by $^1\text{H}$ NMR

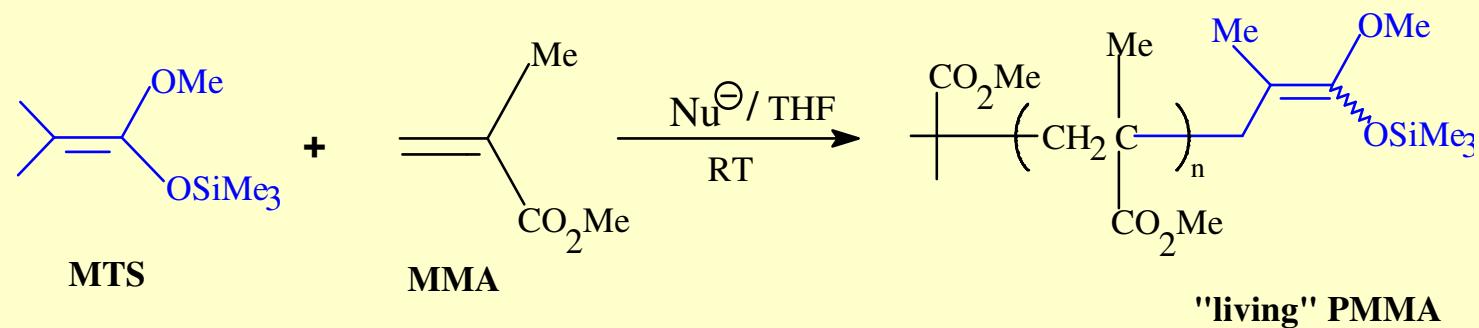
### $^1\text{H}$ NMR of $\alpha$ -hydroxy- $\omega$ -allyl PMMA



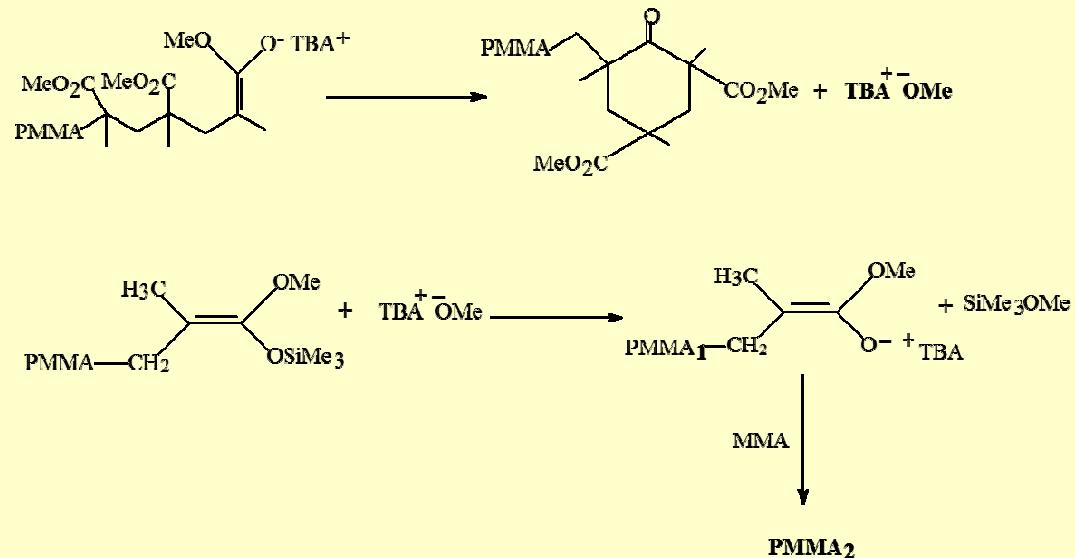
100 % end-functionalization of hydroxy-PMMA by allyl group

Hydroxy-PMMA living chains react efficiently with AMA to give quantitative allyl functionality

## *Termination of 'Living' chain end in GTP*

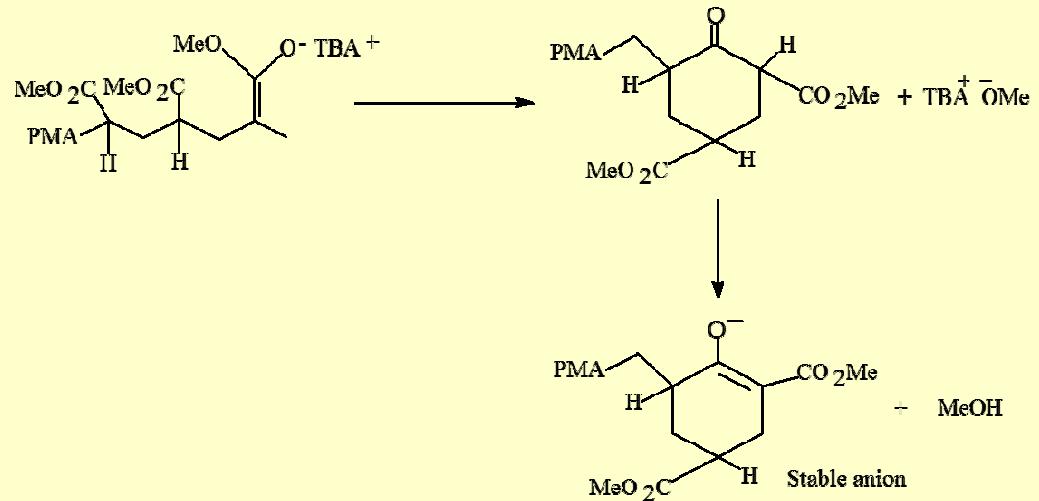


**Ketene silyl acetal end group in the polymer chain end is in equilibrium with an ester enolate species. Under suitable conditions , the ester enolate can be trapped by a suitable electrophile**

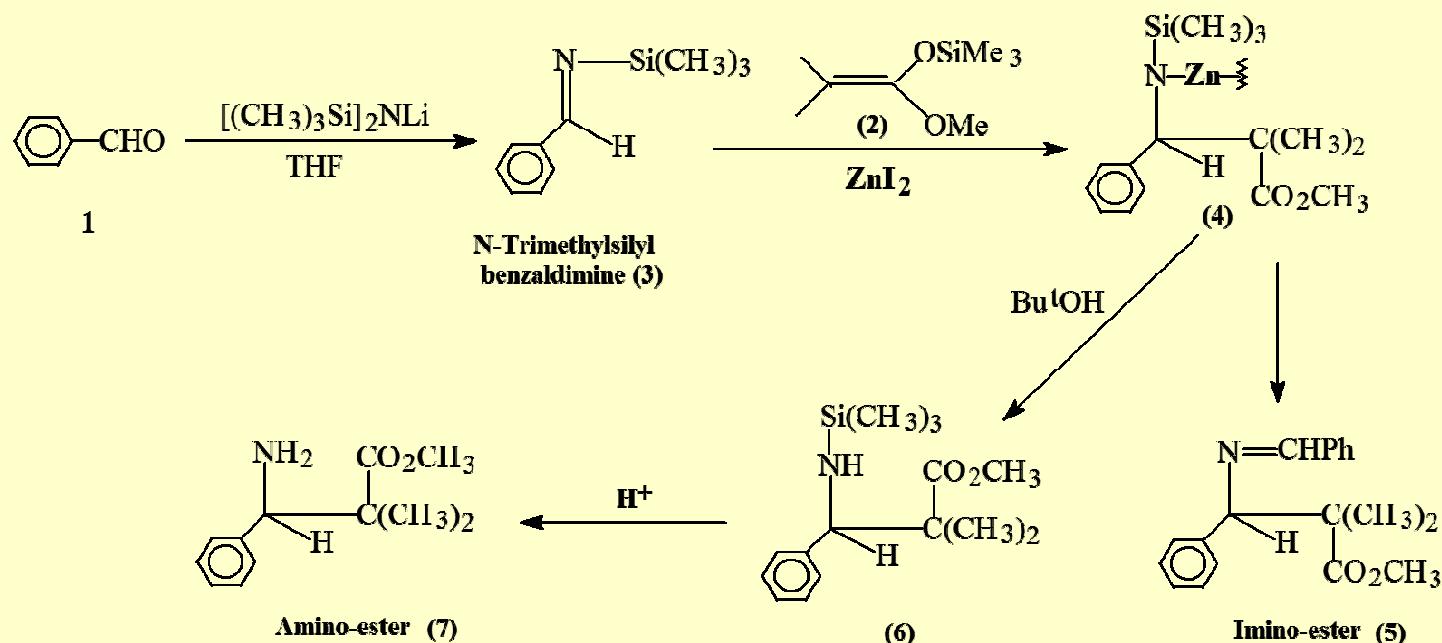


## Backbiting termination reaction in MMA polymerization

Webster, O. W. *Adv. Polym. Sci.* 2004, 167, 1



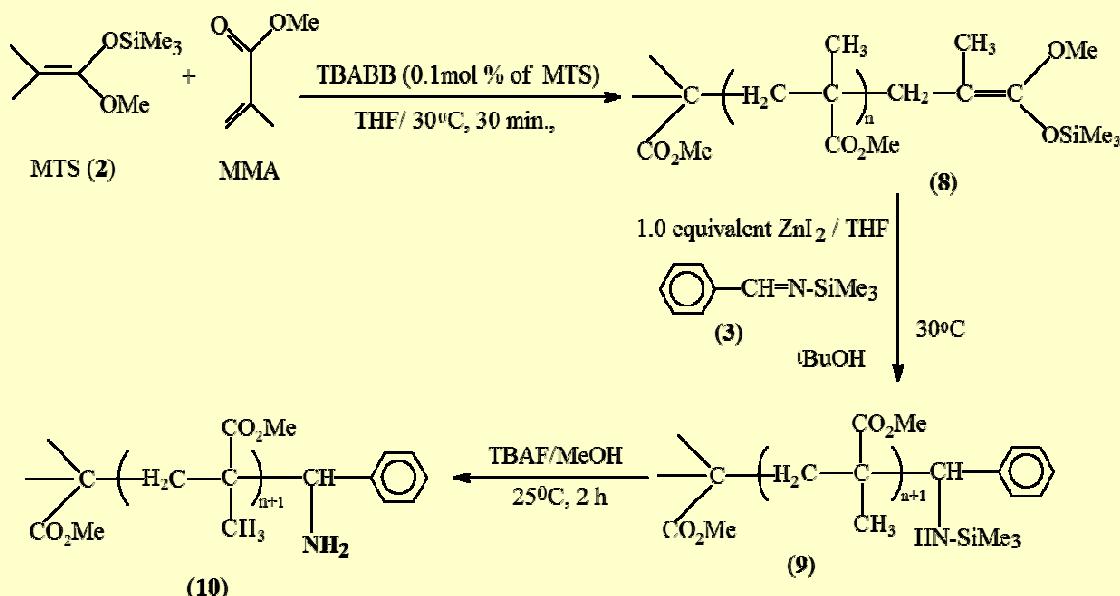
## Termination reaction in acrylate polymerization via chain end cyclization



### Reaction between MTS and N-trimethylsilyl benzaldimine

Table 5.1. Reaction between MTS and N-TMS benzaldimine at 25 °C

Entry	N-TMS benzaldimine, mmol	$ZnI_2$ , mmol	$t\text{-}BuOH$ , mmol	MTS, mmol	Solvent, mL	Time, h	Isolated Yield ( $\beta$ -amino ester) %
1	1.15	1.15	1.15	1.15	Diethyl ether, 10	3	98
2	1.15	1.15	1.15	1.15	THF, 10	3	93



## Amine-terminated PMMA's via GTP

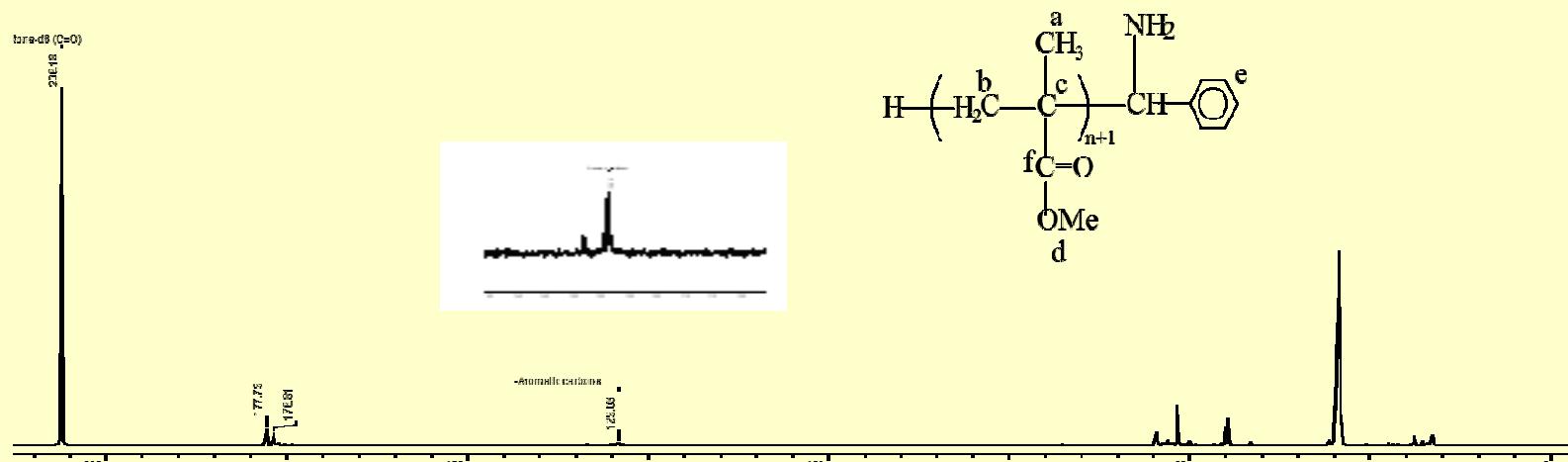
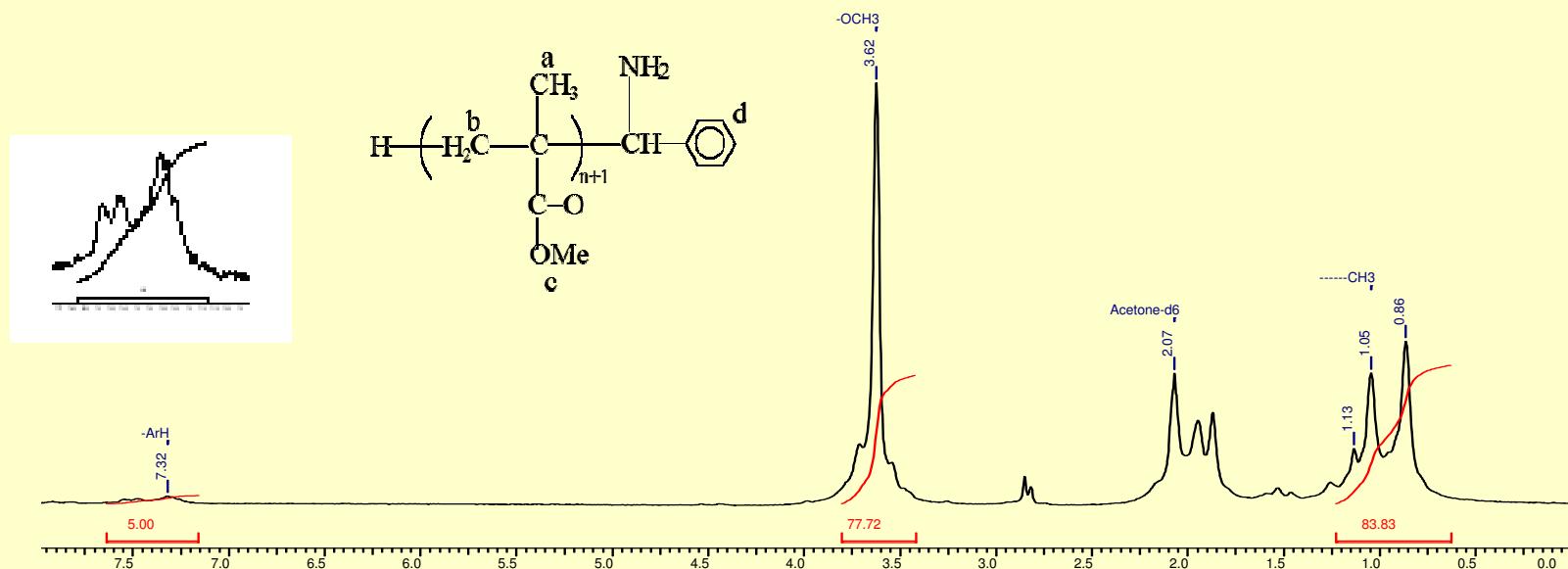
Table 5.2. Synthesis of amine end-functional poly (methyl methacrylate)s by GTP

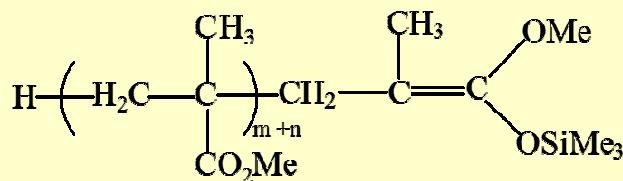
Entry	MMA <sup>a</sup> , mol	MTS, mol $\times 10^3$	THF, mL	TBABB, mol $\times 10^6$	N-TMS Benzaldimine, mol $\times 10^3$	ZnI <sub>2</sub> , mol $\times 10^3$	<sup>t</sup> BuOH, mol $\times 10^3$	$M_n$ (theory), g/mol	$M_n$ (SEC), g/mol	$M_w/M_n$ (SEC)	$M_n$ (VPO), g/mol	$M_n$ (NMR), g/mol	$I^b$ efficiency	$F_n^c$
1	0.047	2.35	30	2.35	2.35	2.35	2.35	2100	2205	1.07	2400	2600	0.95	0.85
2	0.047	1.56	30	1.56	1.56	1.56	1.56	3100	3200	1.11	2800	4000	0.97	0.80
3	0.047	2.35	30	2.35	2.35	2.35	2.35	2100	2525	1.09	2800	3155	0.84	0.80
4	0.047	1.56	30	1.56	1.56	1.56	1.56	3100	2905	1.09	3200	3418	1.06	0.85

a:  $[\text{MMA}]_0 = 1.56 \text{ mol/L}$

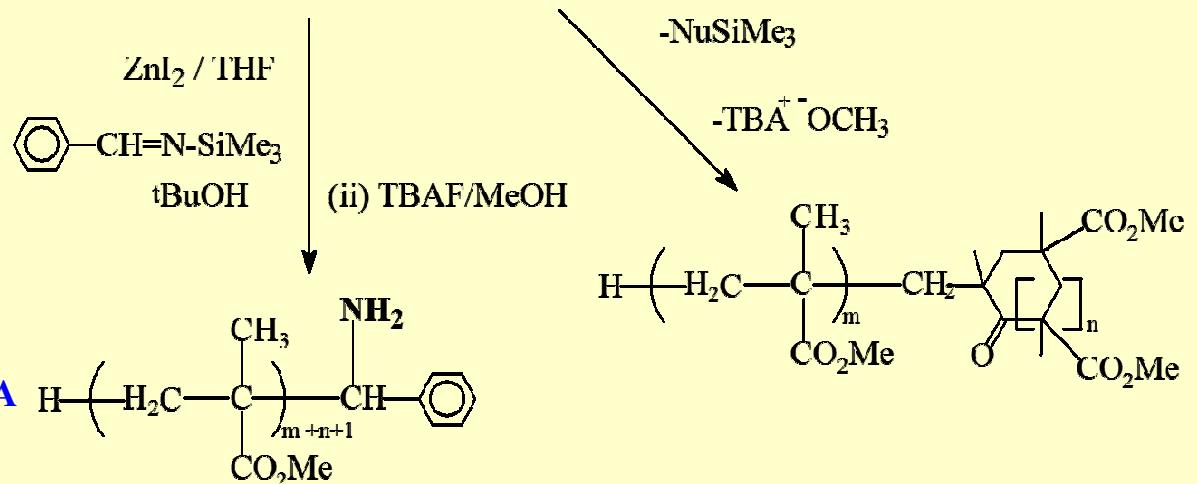
b:  $I_{\text{efficiency}} = M_n \text{ (theory)}/M_n \text{ (SEC)}$

c:  $F_n = M_n \text{ (SEC)}/M_n \text{ (NMR)}$

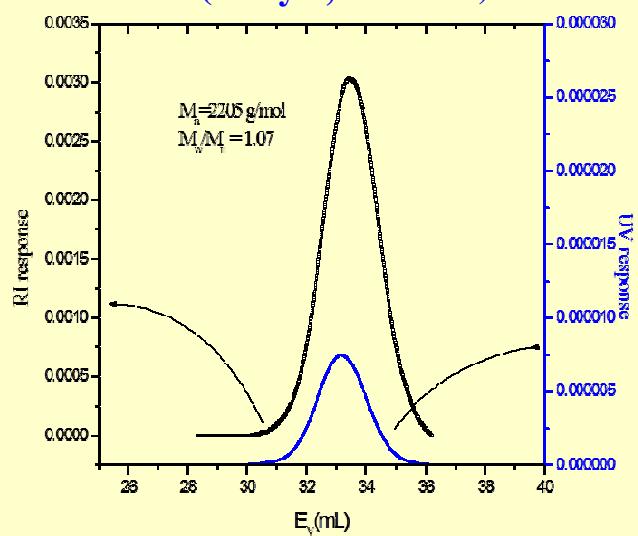




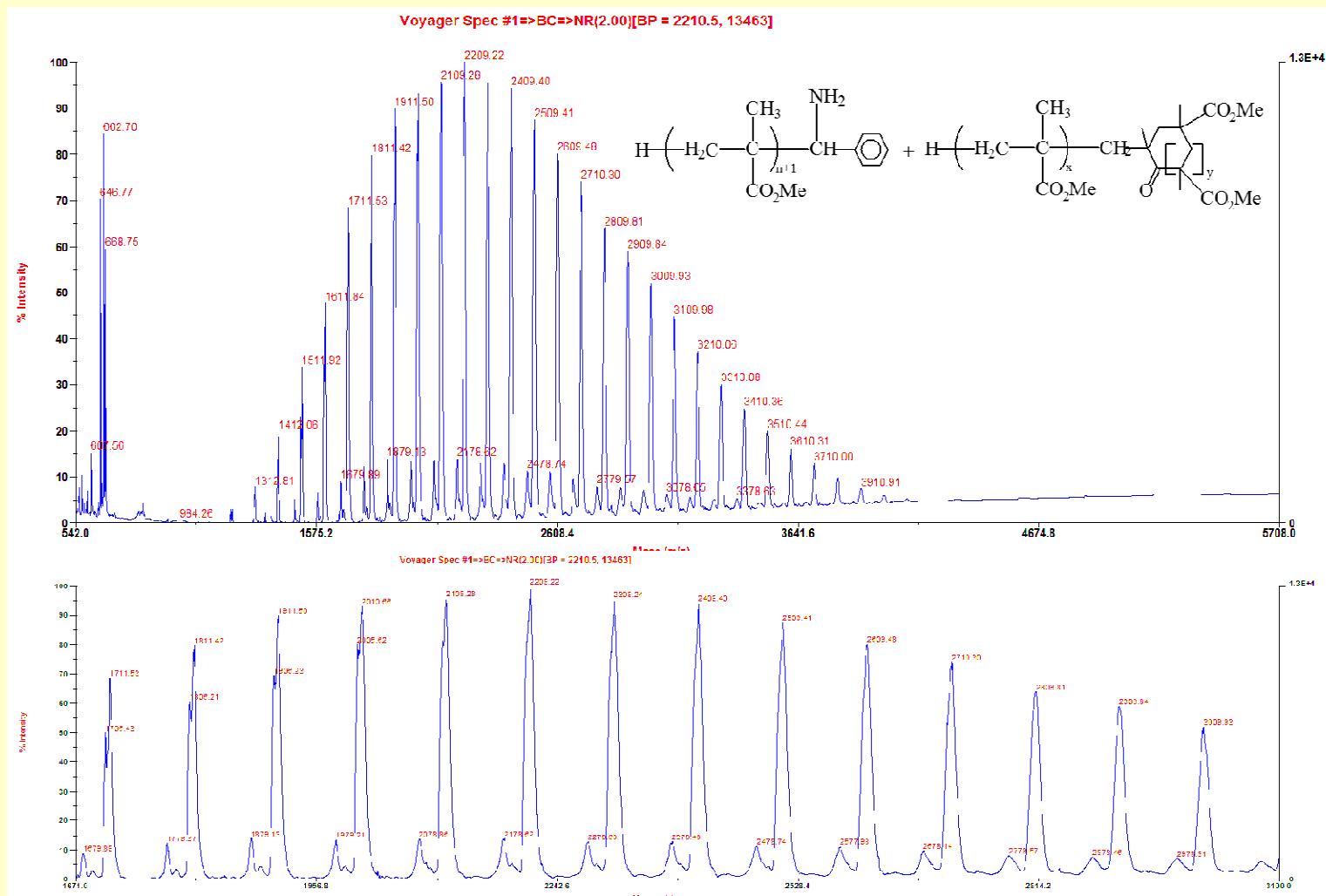
**Silyl ketene acetal ended PMMA**



**SEC trace of amine-terminated PMMA  
(entry 1, table 5.2)**



**Formation of cyclic fraction along with amine-terminated PMMA**

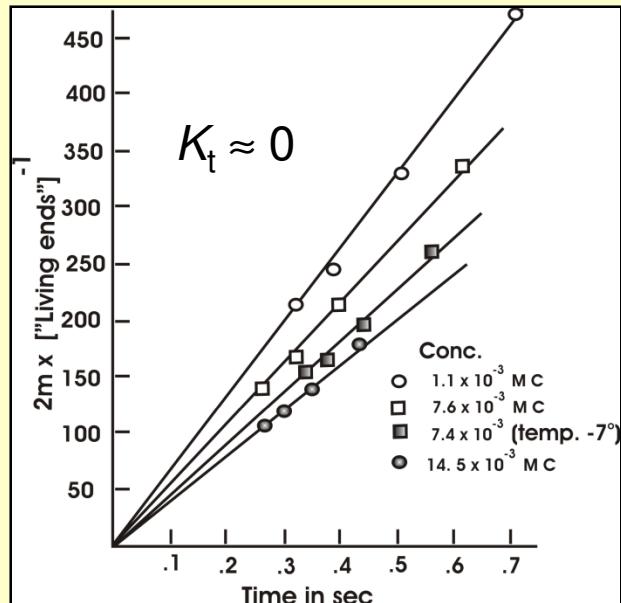


MALDI-ToF spectrum of amine-terminated PMMA prepared by GTP using TBABB catalyst for silyl ketene acetal ended PMMA and Lewis acid  $ZnI_2$  for functionalization reaction at room temperature (entry 1, table 5.2).  $[M+Li]^+ = 100.12 \text{ (MMA)} * n \text{ (DP)} + H \text{ (1.0079)} + Ar-CH-NH_2 \text{ (106.1476)} + Li^+ \text{ (6.941)}$ . (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) ( $\Delta = 7 \text{ Da}$ )

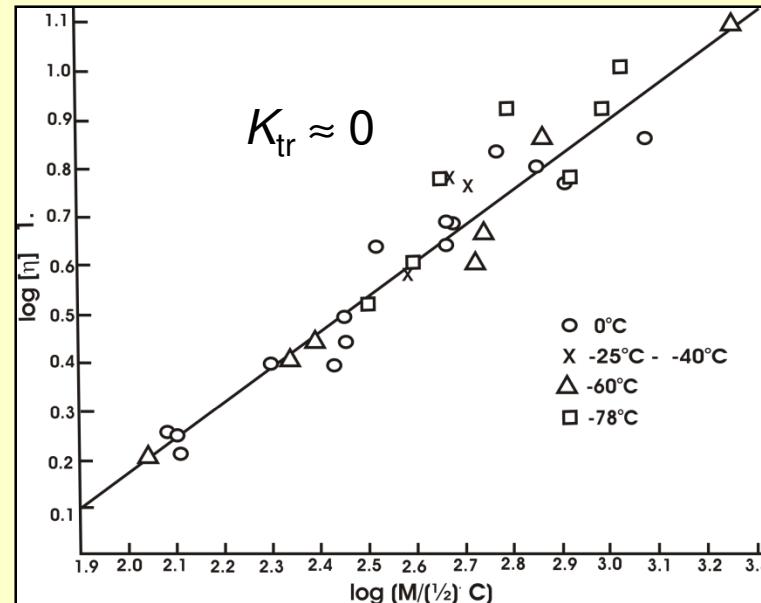
# ‘Living’ Polymerization

Anionic polymerization of styrene in THF at -78°C

- Michael Szwarc (1956)



First order time-conversion plot



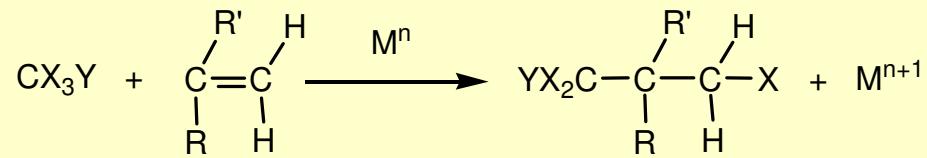
Viscosity vs. theoretical mol. wt.

## Radical Polymerization Methods with Above Features:

- Transition metal-mediated radical polymerization (ATRP)
- Nitroxide-mediated radical polymerization (NMP)
- Radical addition-fragmentation and transfer polymerization (RAFT)

# Development of Atom-transfer Radical Polymerization (ATRP)

## ➤ Atom transfer radical addition

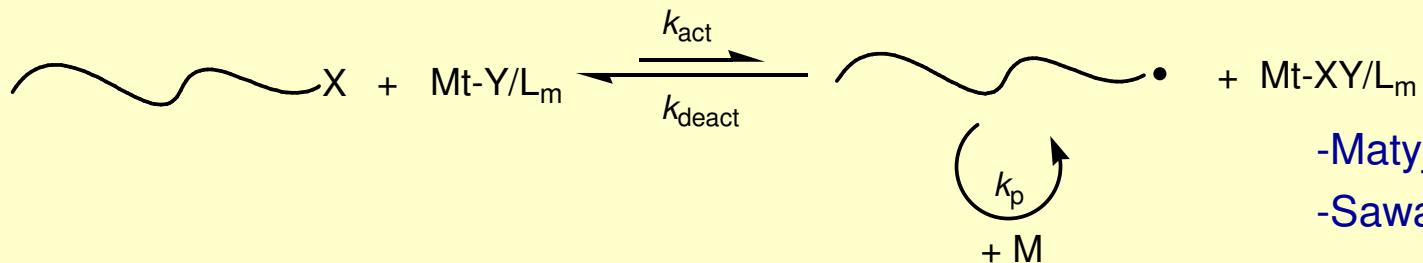


X = halogen; Y = H (or) electronegative group; M = Cu or Ni



Morris Kharash  
(1938)

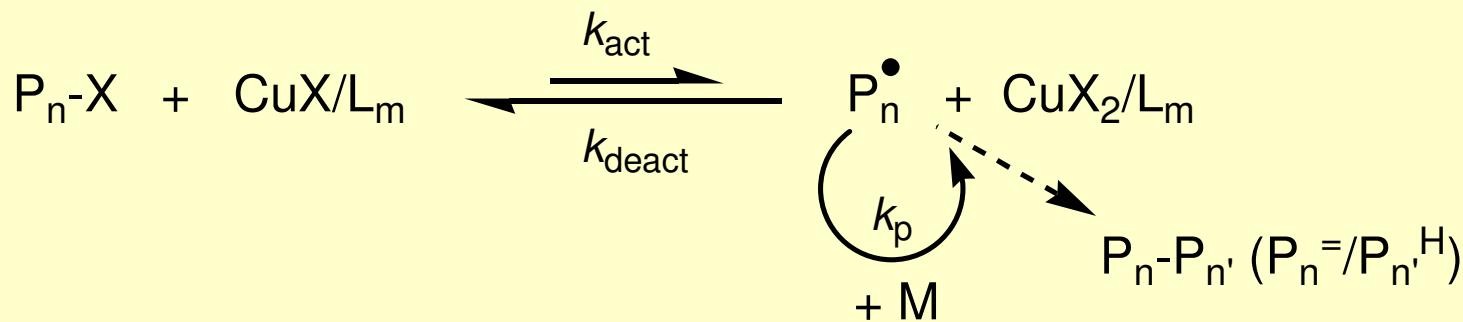
## ➤ Atom transfer radical polymerization



-Matyjaszewski (1995)  
-Sawamoto (1995)

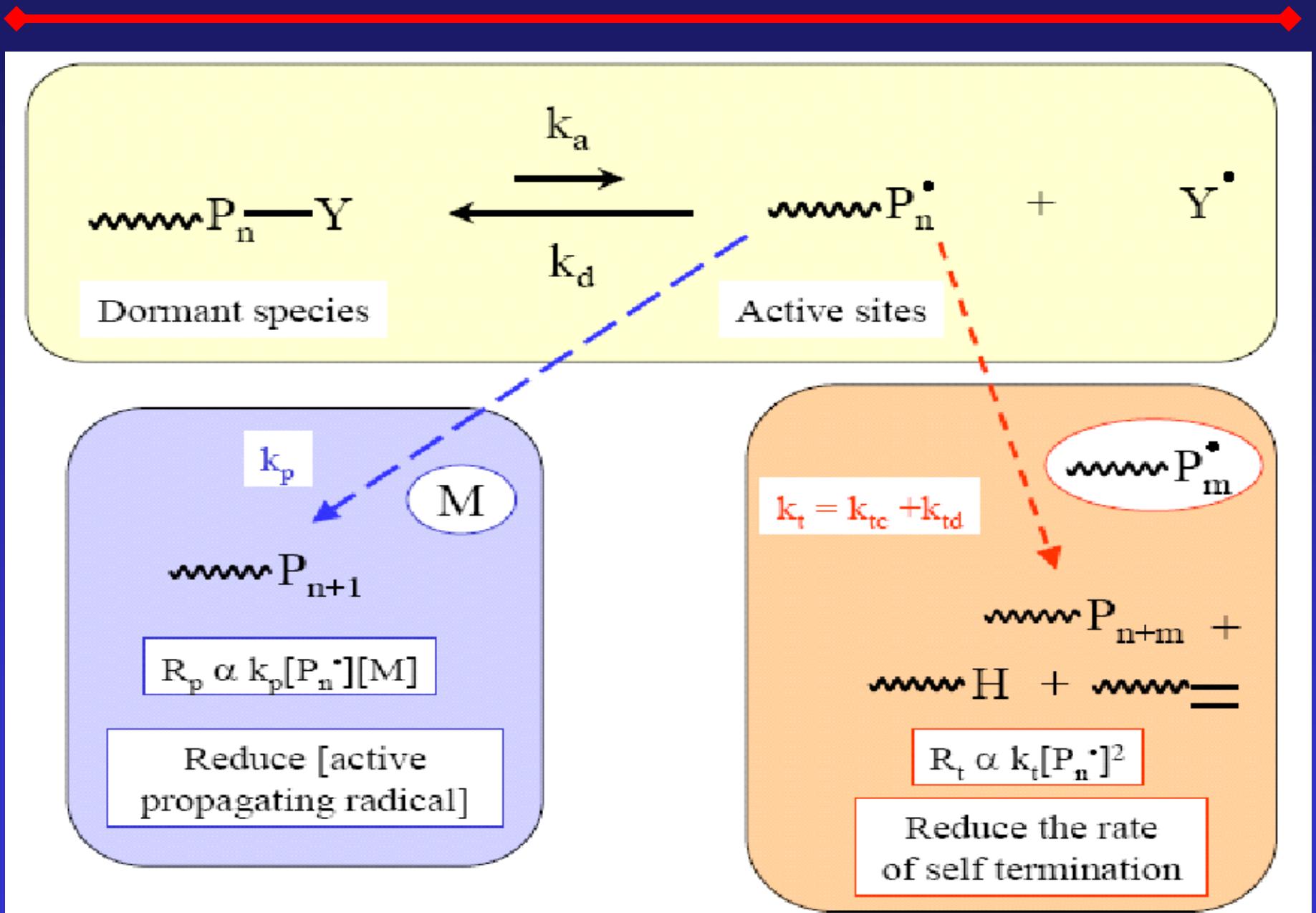
X and Y- halogen; Mt -Cu<sup>I</sup>, Ru<sup>II</sup>, Fe<sup>II</sup>, Ni<sup>II</sup>, etc; M- vinyl monomer, L-Ligand

# Advantages of Copper-mediated ATRP

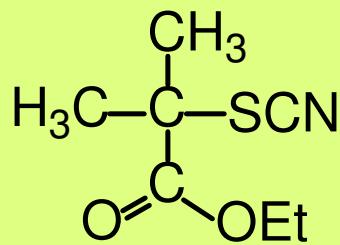


- Significantly suppresses chain-transfer and chain-termination
- Produces polymers with well-defined molecular weight and narrow molecular weight distribution
- Tolerant to many functional groups
- Wide range of monomers and solvents can be used
- Very robust technique and easy to perform
- Chain-end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

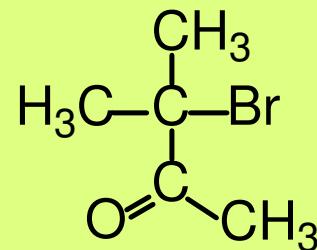
# Controlled/ Living Radical Polymerization



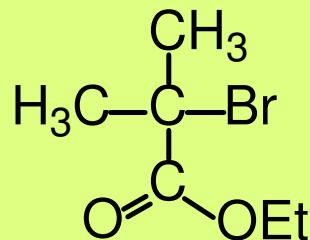
## ***FUNCTIONAL INITIATORS***



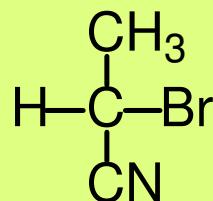
**EMTP**



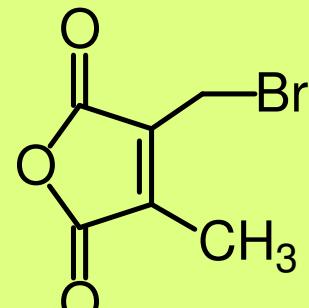
**MBB**



**EB*i*B**

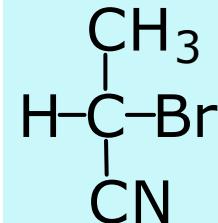
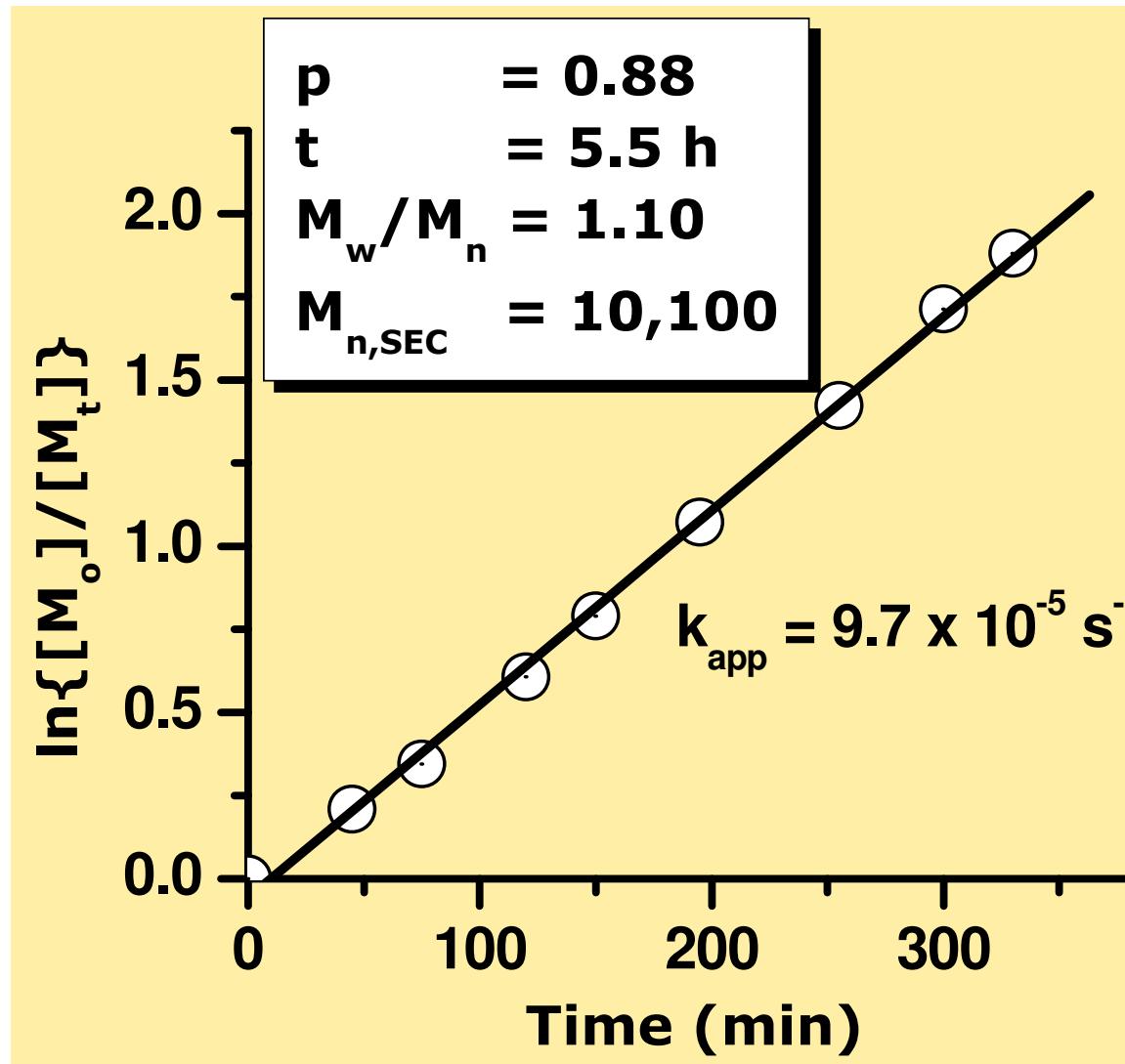


**BPN**



**BMFD**

# ATRP Of MMA: Bromonitrile Initiator



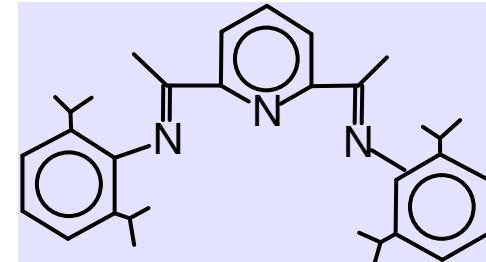
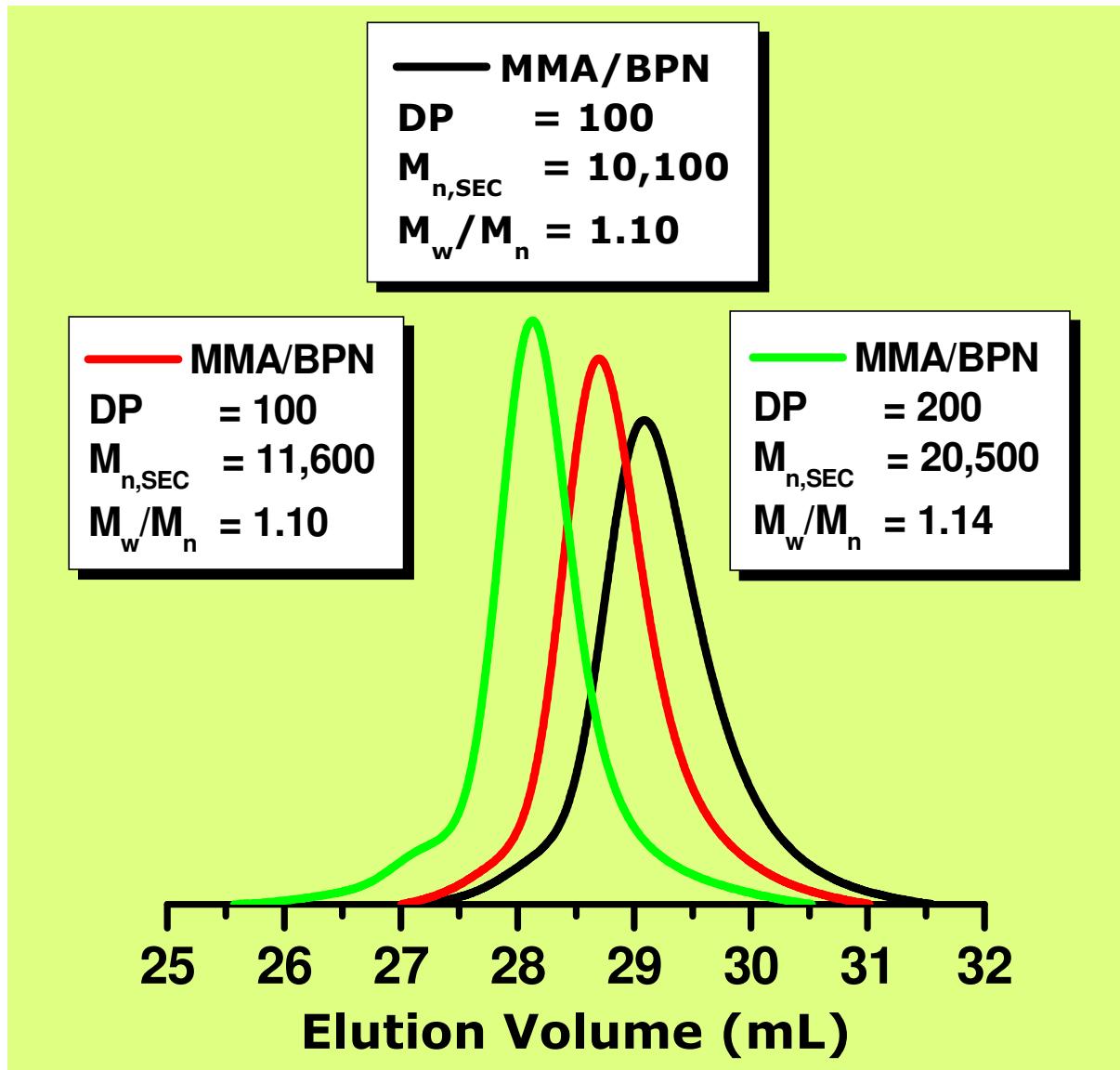
2-bromopropionitrile (BPN)

Semi logarithmic kinetic plot of ATRP of MMA using MBB as initiator in toluene (50%, v/v) at 90 °C, [MMA] = 3.12 M.

[MMA]: [BPN]: [CuBr]: [BPIEP] = 100: 1: 1: 2.

→ Concentration of stationary radicals is constant

# GPC Eluograms: Different [M]/[I] Ratios

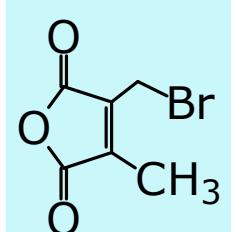


GPC eluograms for ATRP of MMA in toluene at different [M]/[I] ratios by varying [Ini] at 90 °C, [MMA] = 3.12 M.

[MMA]: [X]: [CuBr]: [BPIEP] = 100: 1: 1: 2.

# ATRP Of MMA: BMFD Initiator

Run	Conv <sup>a</sup>	$M_{n,Cal}$ (x 10 <sup>3</sup> )	$M_{n,SEC}$ (x 10 <sup>3</sup> )	PDI	$I_{eff}$
1	85	8.5	7.5	1.15	0.90
2 <sup>b</sup>	90	9.0	9.5	1.16	0.90
3 <sup>c</sup>	55	5.5	6.0	1.12	0.90
4 <sup>d</sup>	26	2.6	3.5	1.15	0.80



3-(bromo methyl)-4-methylfuran-2,5-dione (BMFD)

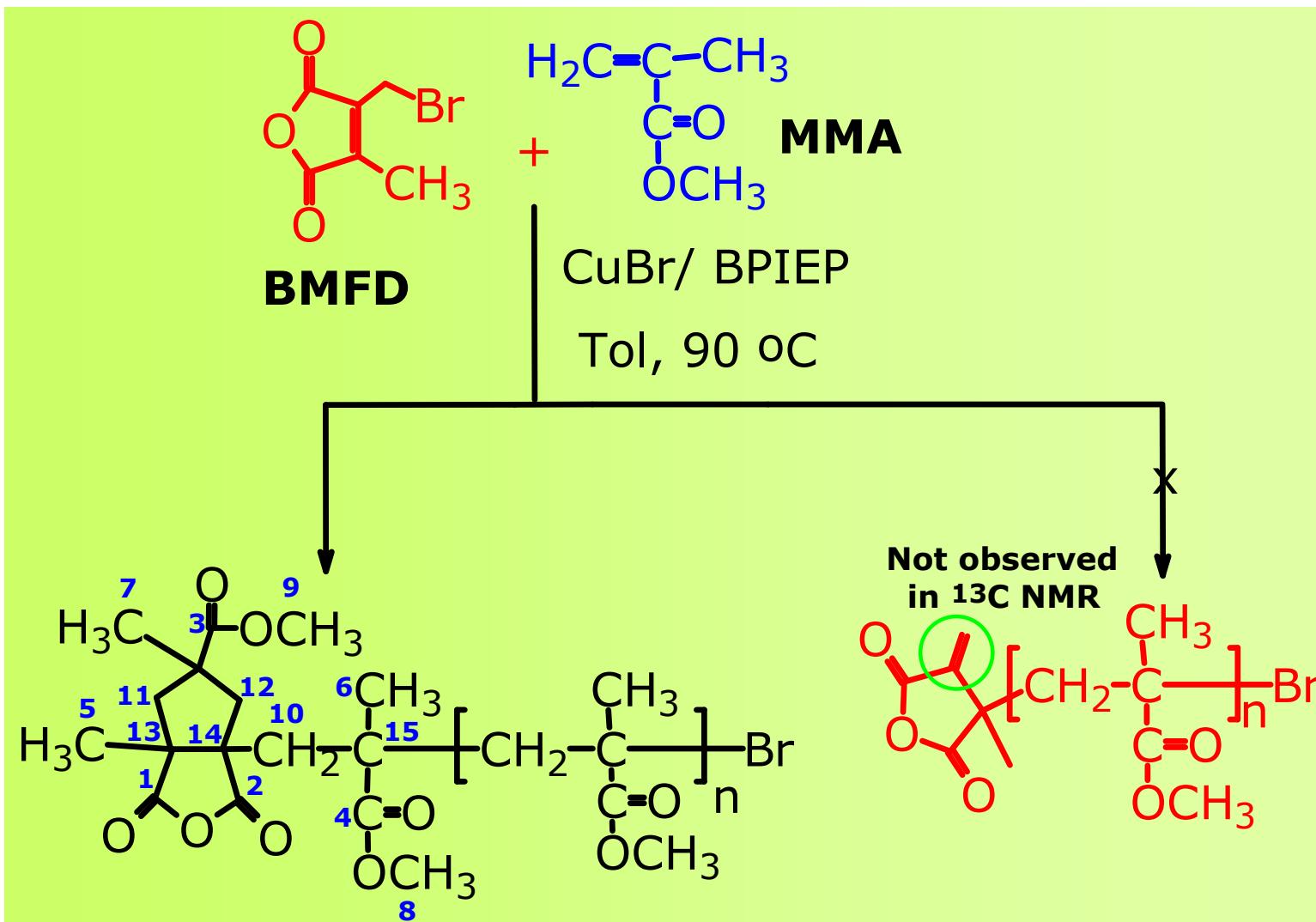
ATRP of MMA at 90 °C in toluene (50 %, v/v) for 5.5 h using BMFD as initiator.  
 $[MMA]_0 = 3.12 \text{ M}$

<sup>a</sup> gravimetric, <sup>b</sup> toluene (66 %, v/v), <sup>c</sup> CuCl in toluene (66%, v/v) at 90 °C, <sup>d</sup> CuCl at 27 °C.

$[MMA]: [BMFD]: [CuX]: [BPIEP] = 100: 1: 1: 2$ ,

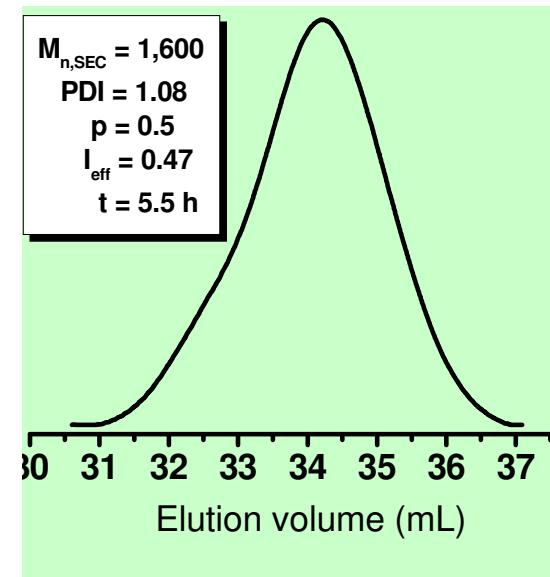
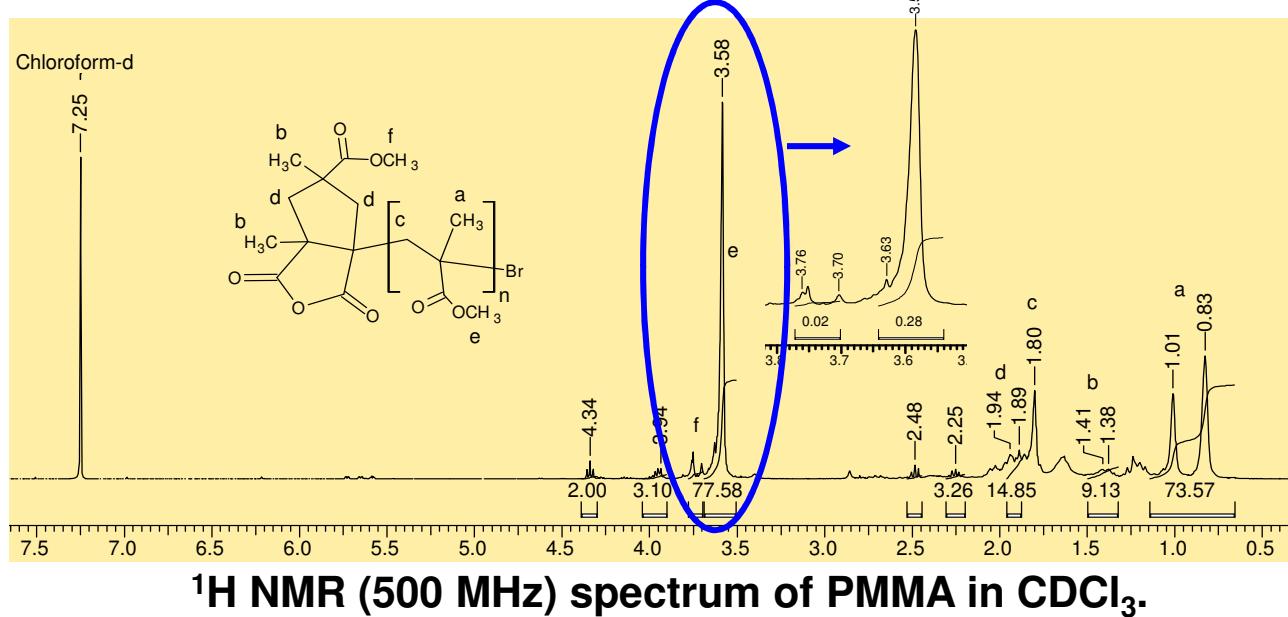
- **Polymerization reactions were homogeneous in nature. The addition of initiator changed the color of reaction even at RT.**
- **High conversion and high  $I_{eff}$  were obtained with lower PDI.**

# ATRP Of MMA Using BMFD

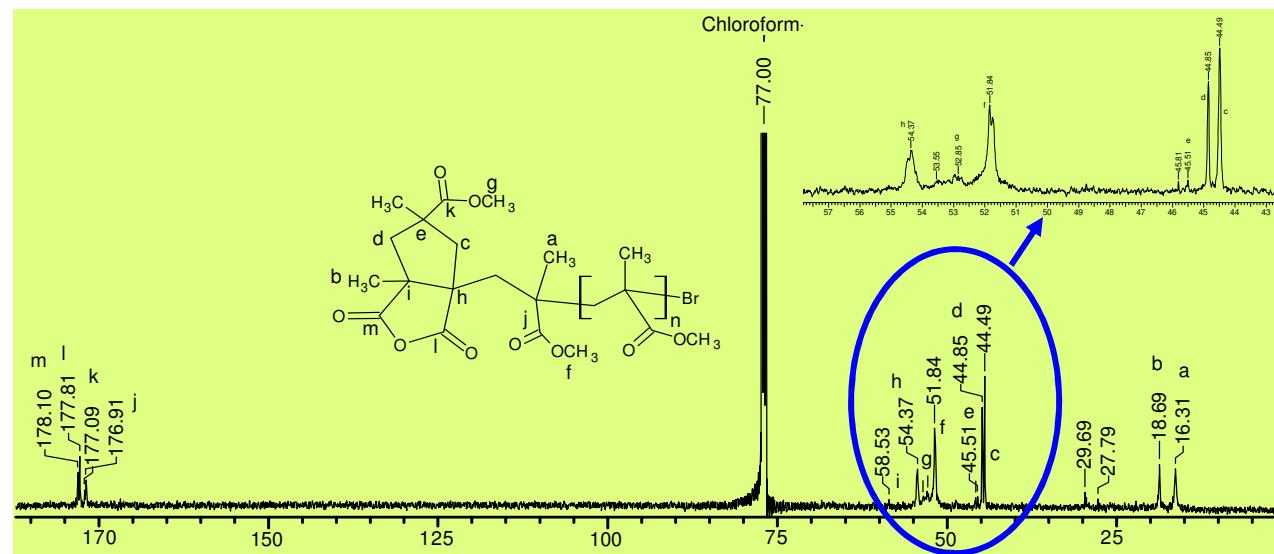


✓ An unexpected head group was obtained, revealed from  $^{13}\text{C}$ -NMR and FT-IR spectrum.

# Analysis Of PMMA-BMFD



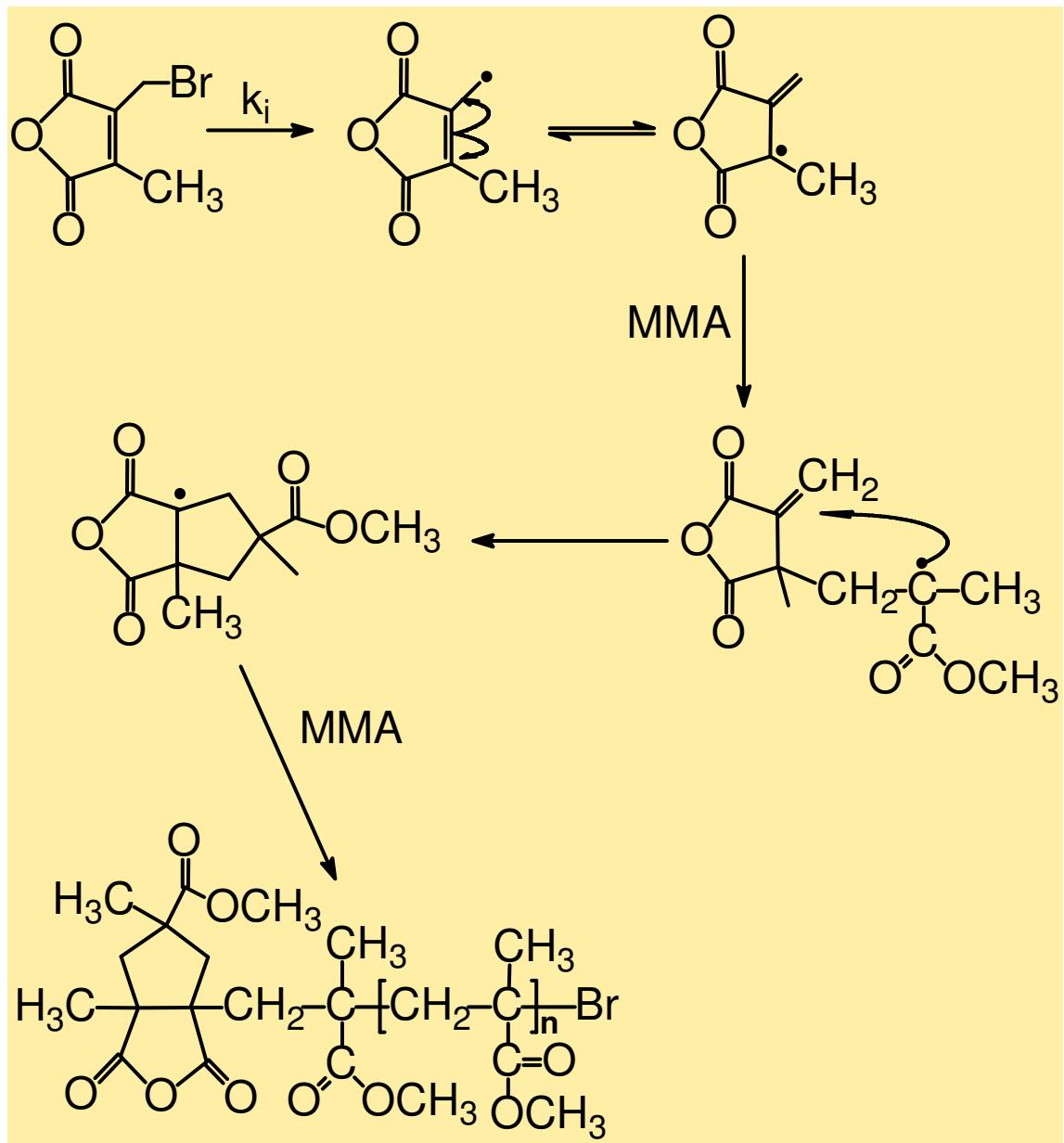
GPC eluogram



$$DP_{NMR} (OCH_3) = 14$$

$$DP_{SEC} = 15$$

# Mechanism of Initiation: Head-group ?

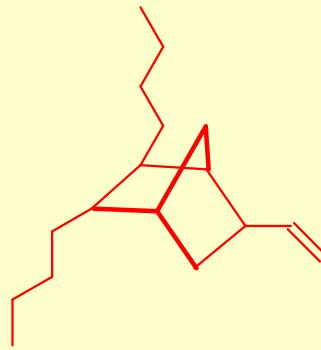


- Primary radical undergoes rearrangement
- Activation of  $=\text{CH}_2$  due adjacent anhydride group favours ring closure rather than addition of monomer. \ leading to a new annular tertiary radical

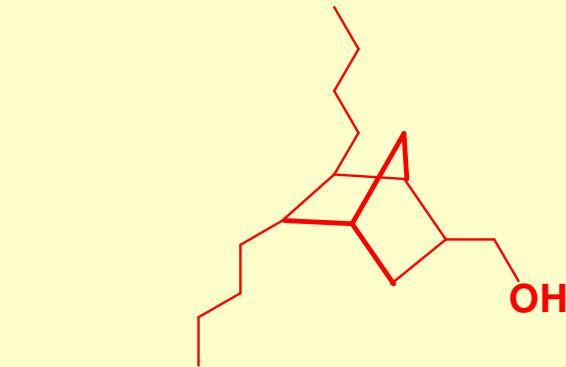
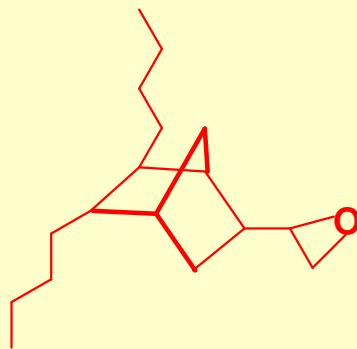
## **Controlled or “Living” polymerization of olefins**

- **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**

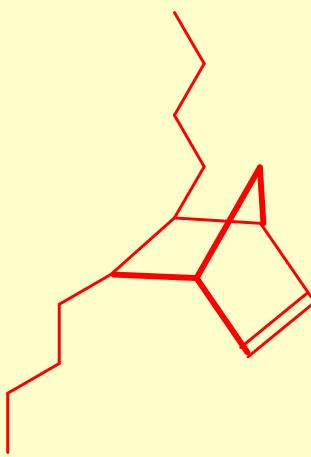
## ***IN CHAIN FUNCTIONALIZATION OF POLY(OLEFIN)S***



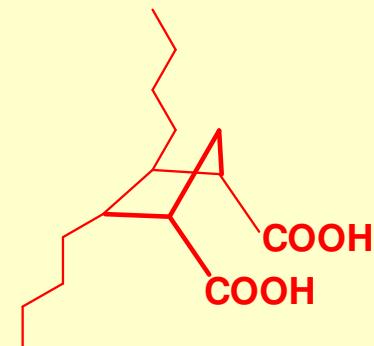
**S. Marathe(1994)**



**K. Radhakrishnan (1998)**

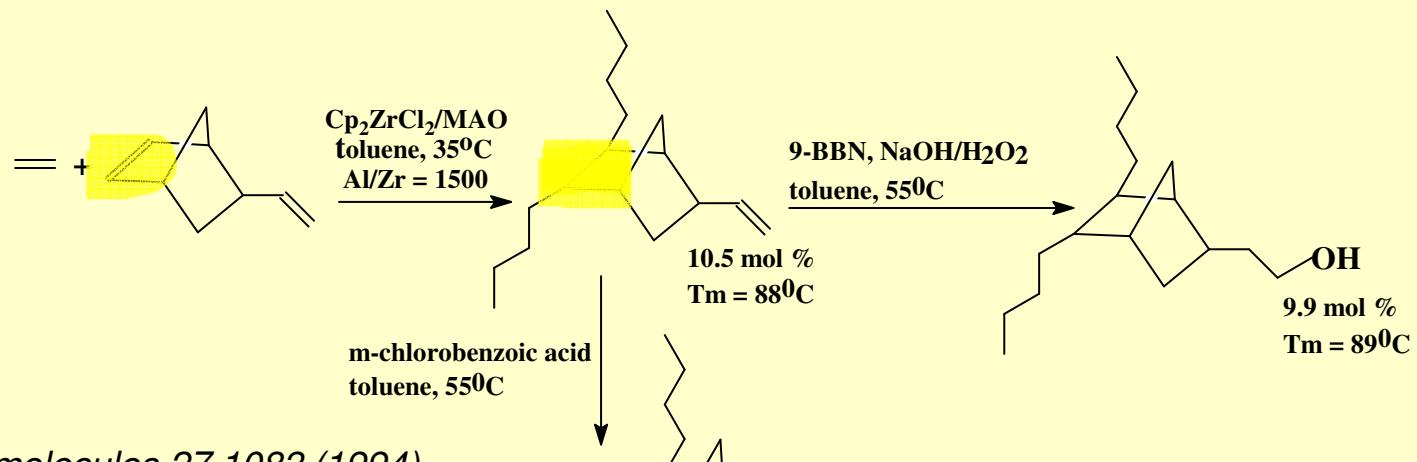


**K. Radhakrishnan (1998)**

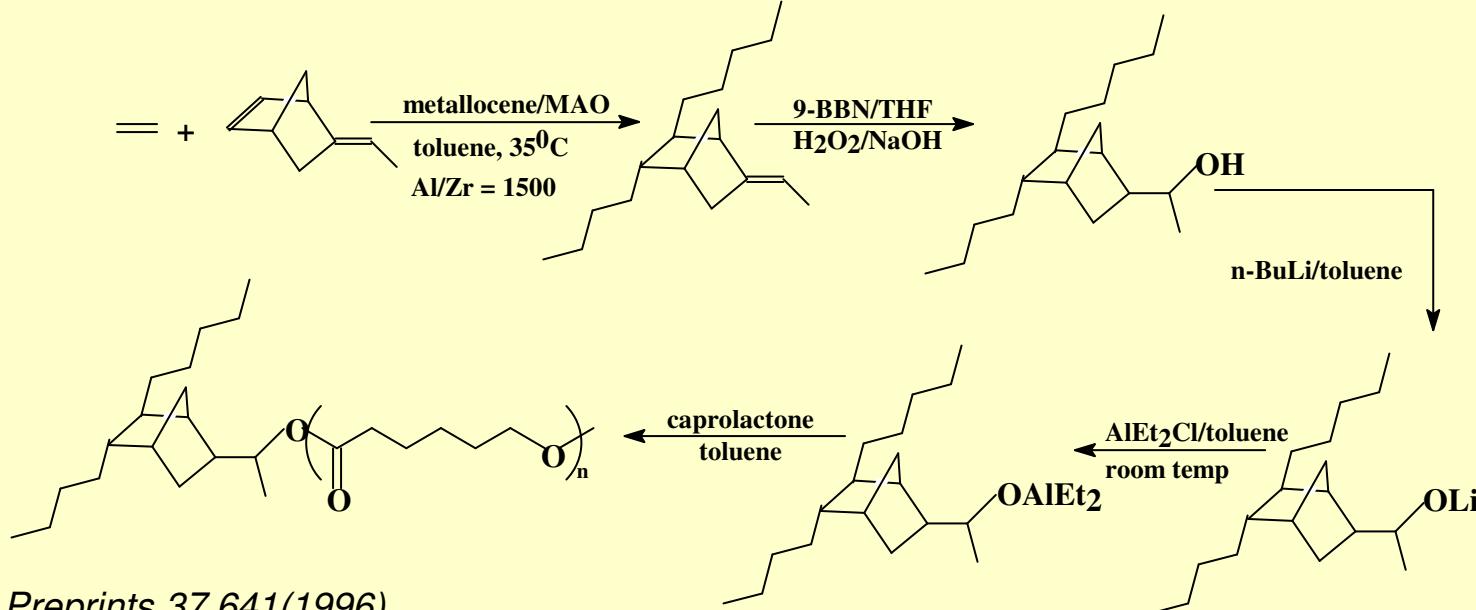


**K. Radhakrishnan, M.J. Yanjarappa (2000)**

## Post polymerization functionalization reactions



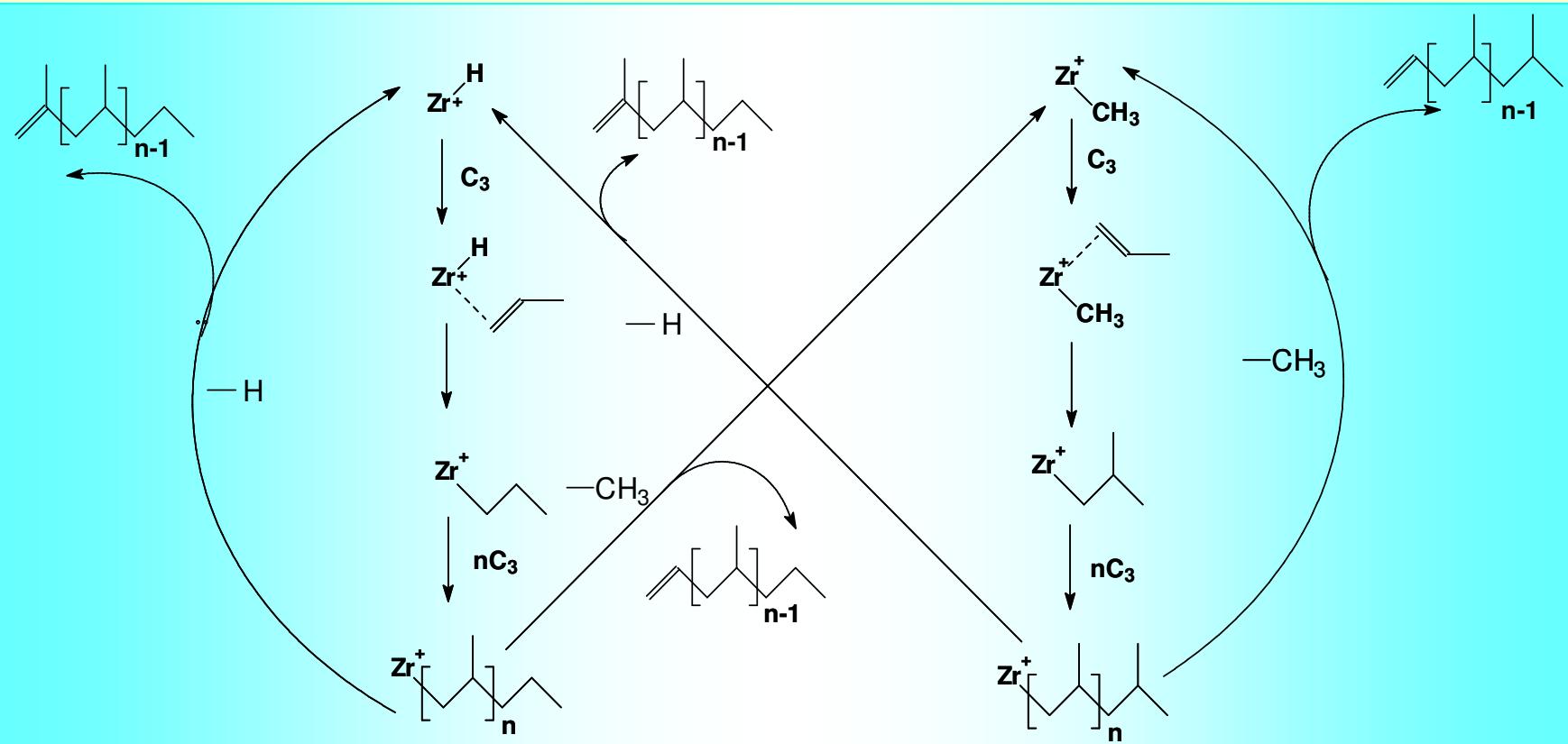
Macromolecules.27,1083 (1994)



Polym Preprints,37,641(1996)

## 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)*



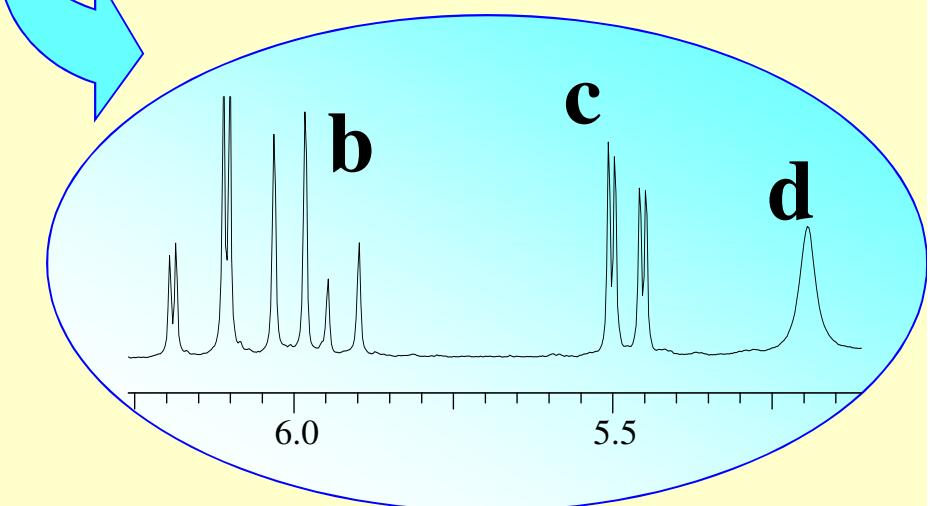
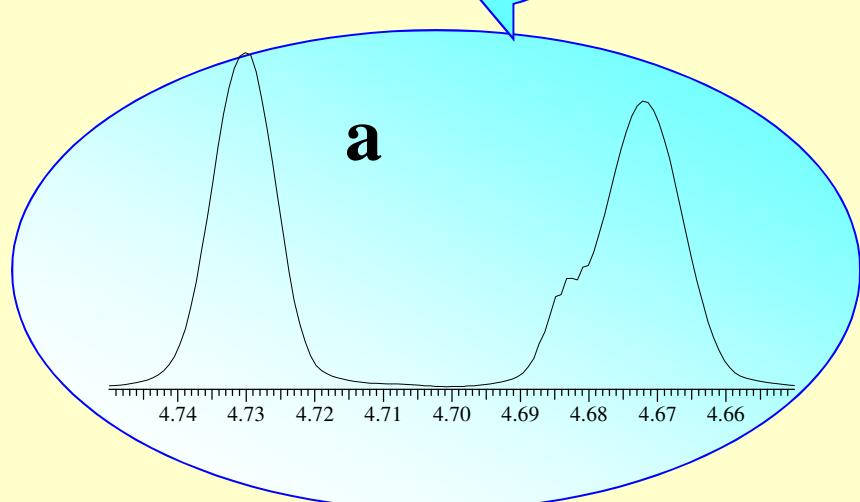
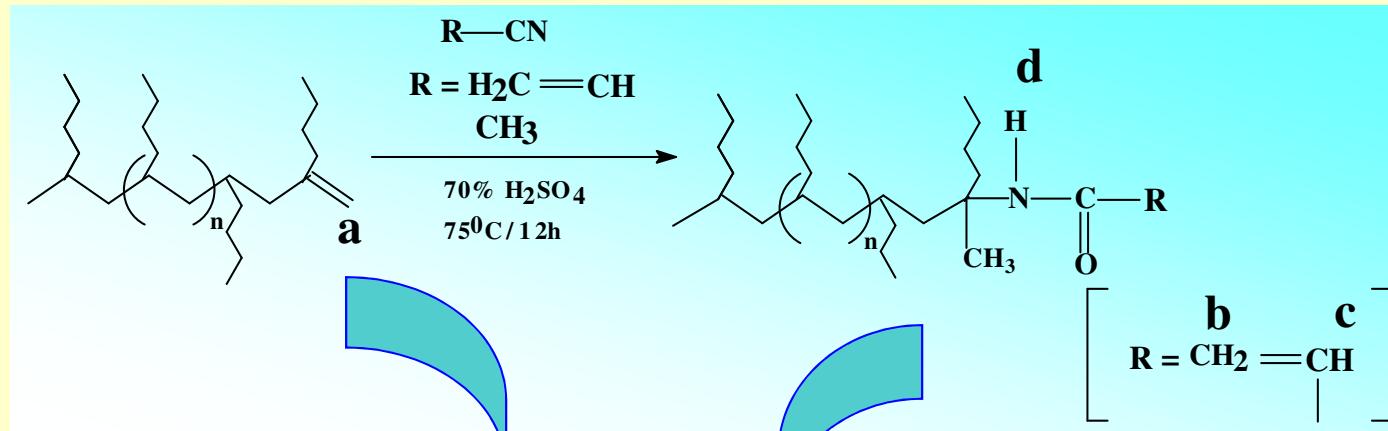
**Mn = 300 - 2000**

**F<sub>n</sub> > 95%, M<sub>w</sub>/M<sub>n</sub> = 2**

**n = 3-10**

<b>Metallocene</b>	<b>Temp (°C)</b>	<b>Mn by VPO</b>	<b>Mn by <sup>1</sup>H NMR</b>	<b>mol % Vinylidene unsaturation</b>
<b>Cp<sub>2</sub>ZrCl<sub>2</sub></b>	<b>50</b>	<b>370</b>	<b>380</b>	<b>98</b>
	<b>40</b>	<b>580</b>	<b>600</b>	<b>96</b>
	<b>30</b>	<b>860</b>	<b>900</b>	<b>95</b>
<b>n-BuCp<sub>2</sub>ZrCl<sub>2</sub></b>	<b>50</b>	<b>440</b>	<b>460</b>	<b>98</b>
	<b>40</b>	<b>700</b>	<b>730</b>	<b>96</b>
	<b>30</b>	<b>1020</b>	<b>1100</b>	<b>93</b>

## RITTER REACTION USING VINYLIDENE TERMINATED OLIGO(HEXENE-1)

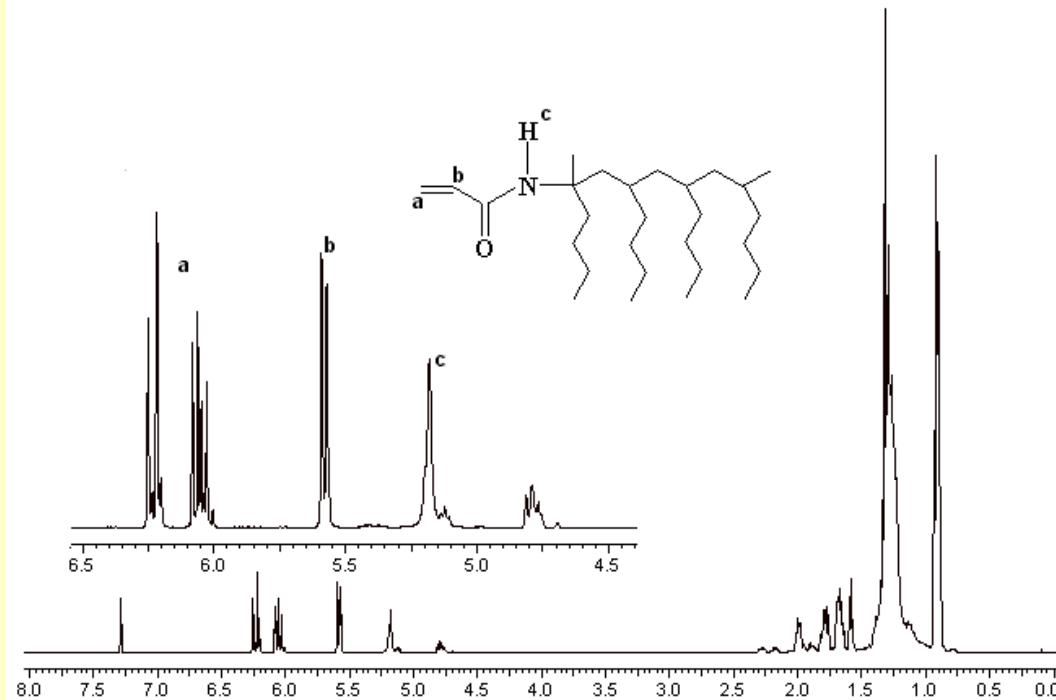


## **RITTER REACTION OF VINYLIDENE TERMINATED POLY(HEXENE-1) WITH ACRYLONITRILE**

Run no.	Poly(hexene-1)				Mn after functionalization		$F_n$ (mol%) <i>a / b</i>	
	Mn	mol	End groups (mol%)		VPO <i>a</i>	$^1H$ NMR <i>b</i>		
			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	

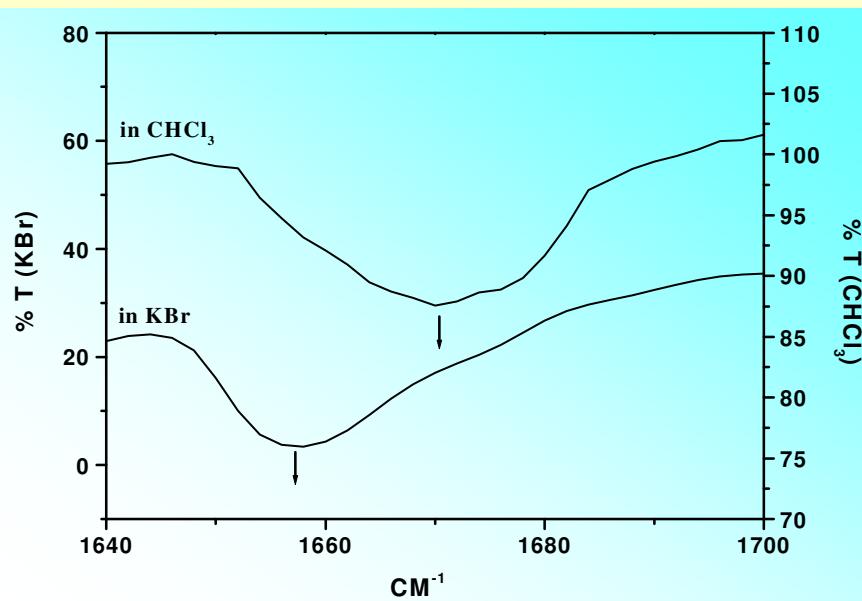
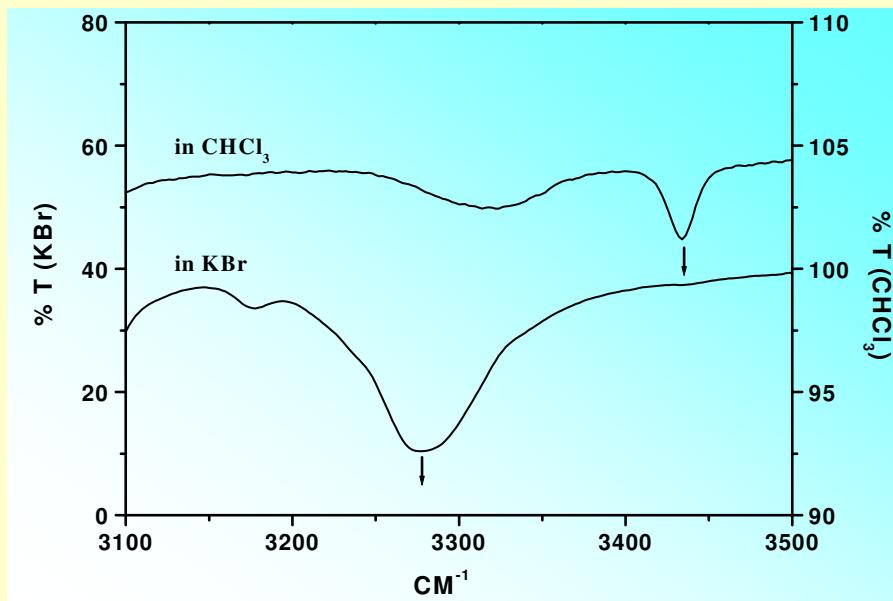
*Reaction conditions: 2 mL of 70%  $H_2SO_4$  catalyst, Temperature = 70°C, Nitrile/Olefin = 5 mol/mol,*

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



## $^1\text{H}$ NMR OF N-POLY(ALKENYL)ACRYLAMIDE

## **EVIDENCE OF INTERMOLECULAR HYDROGEN BONDING (FT-IR)**



**N-H strech**

$\text{KBr} = 3278 \text{ cm}^{-1}$

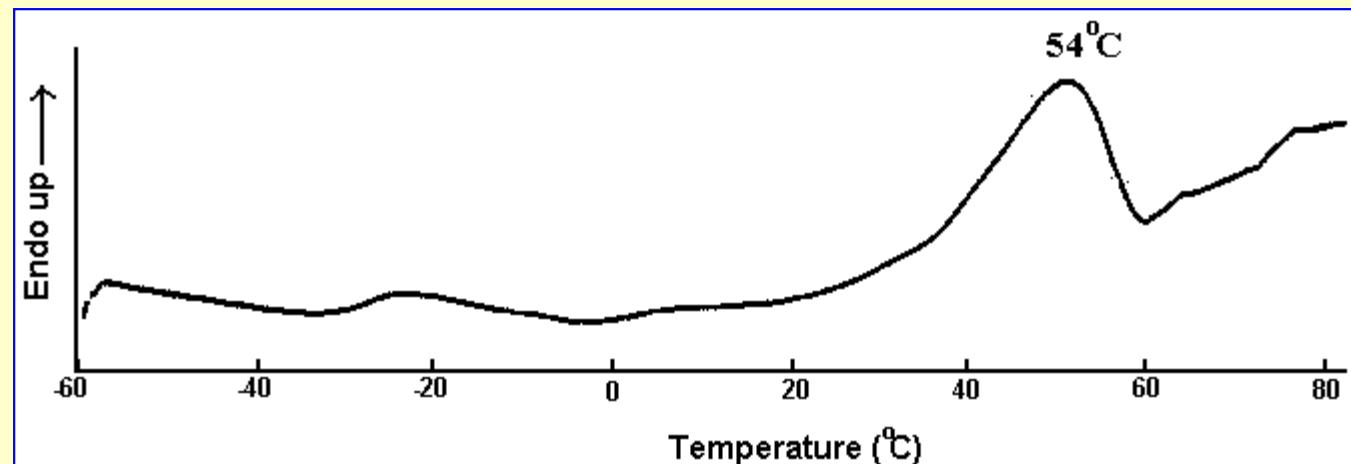
$\text{CHCl}_3 = 3434 \text{ cm}^{-1}$

**C=O strech**

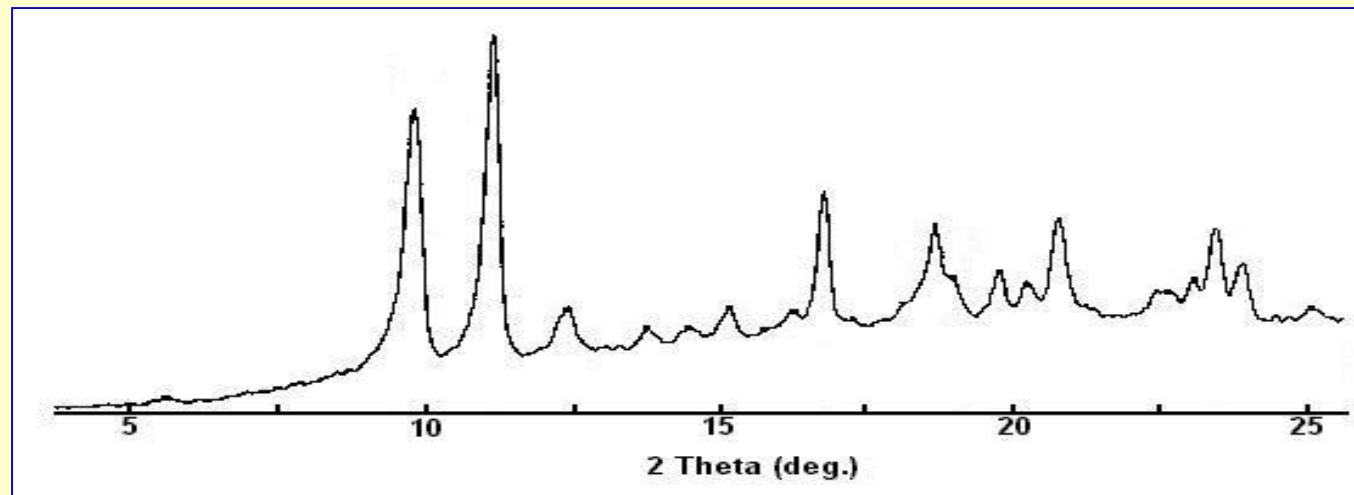
$\text{KBr} = 1658 \text{ cm}^{-1}$

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

## CRYSTALLINITY DUE TO AMIDE FUNCTIONALITY

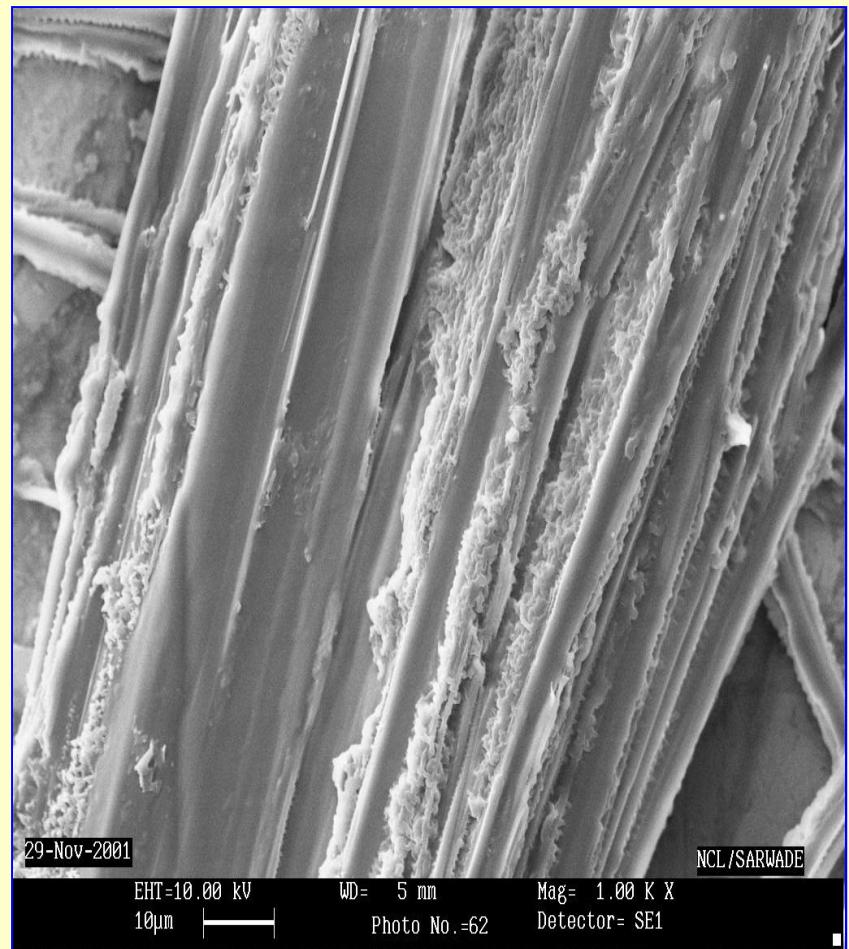
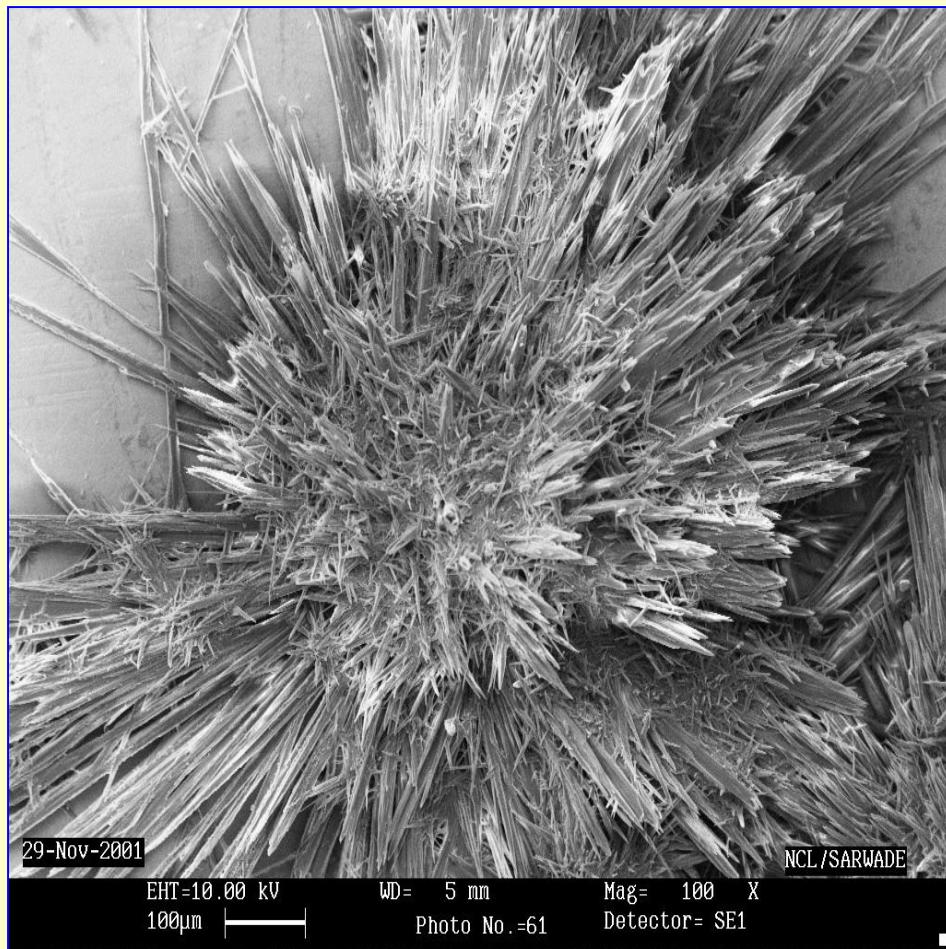


DSC of N-poly(alkenyl) acrylamide.



WAXD of N-poly(alkenyl) acrylamide

# SCANNING ELECTRON MICROSCOPY

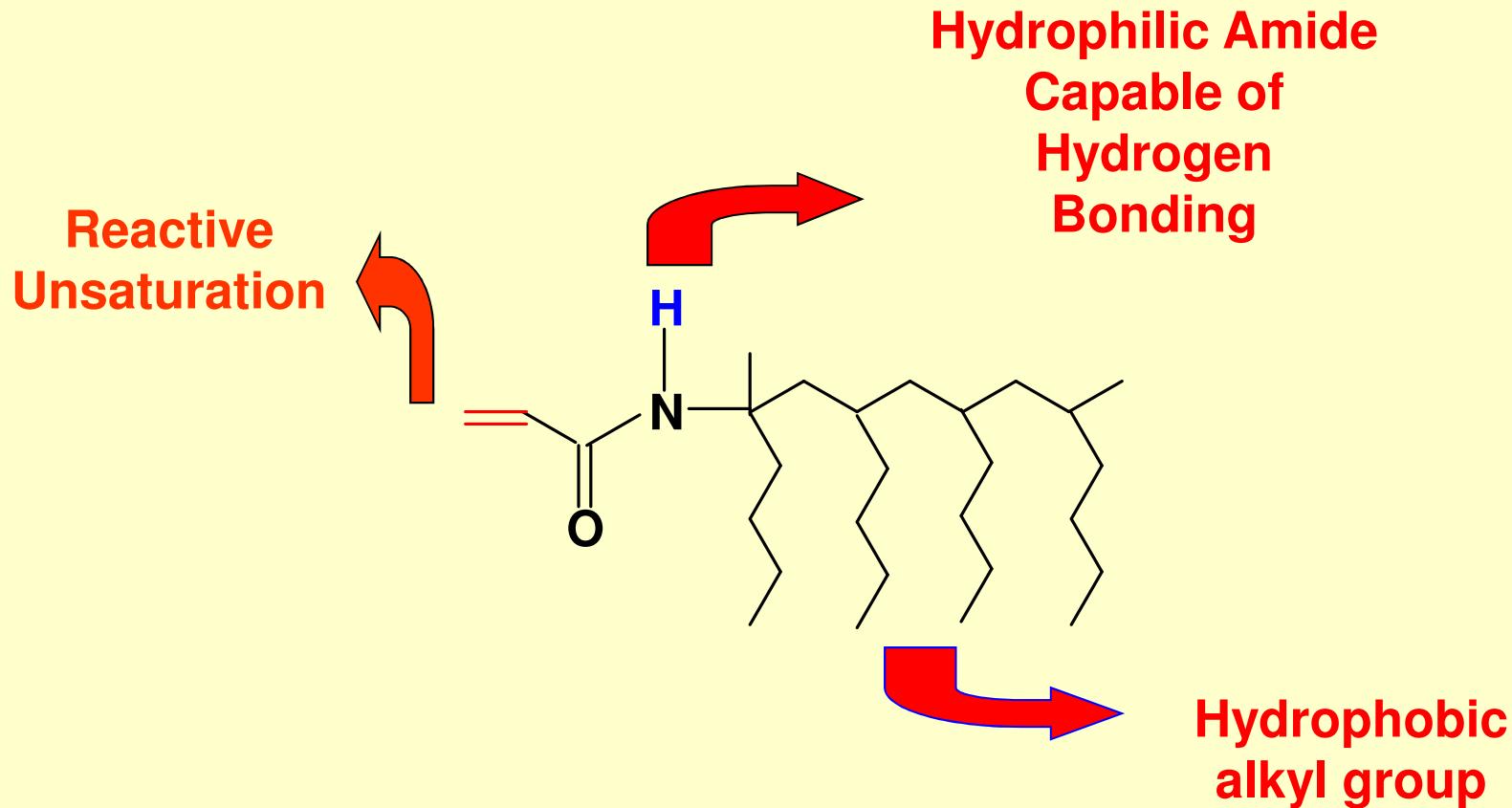


## CONCLUSIONS

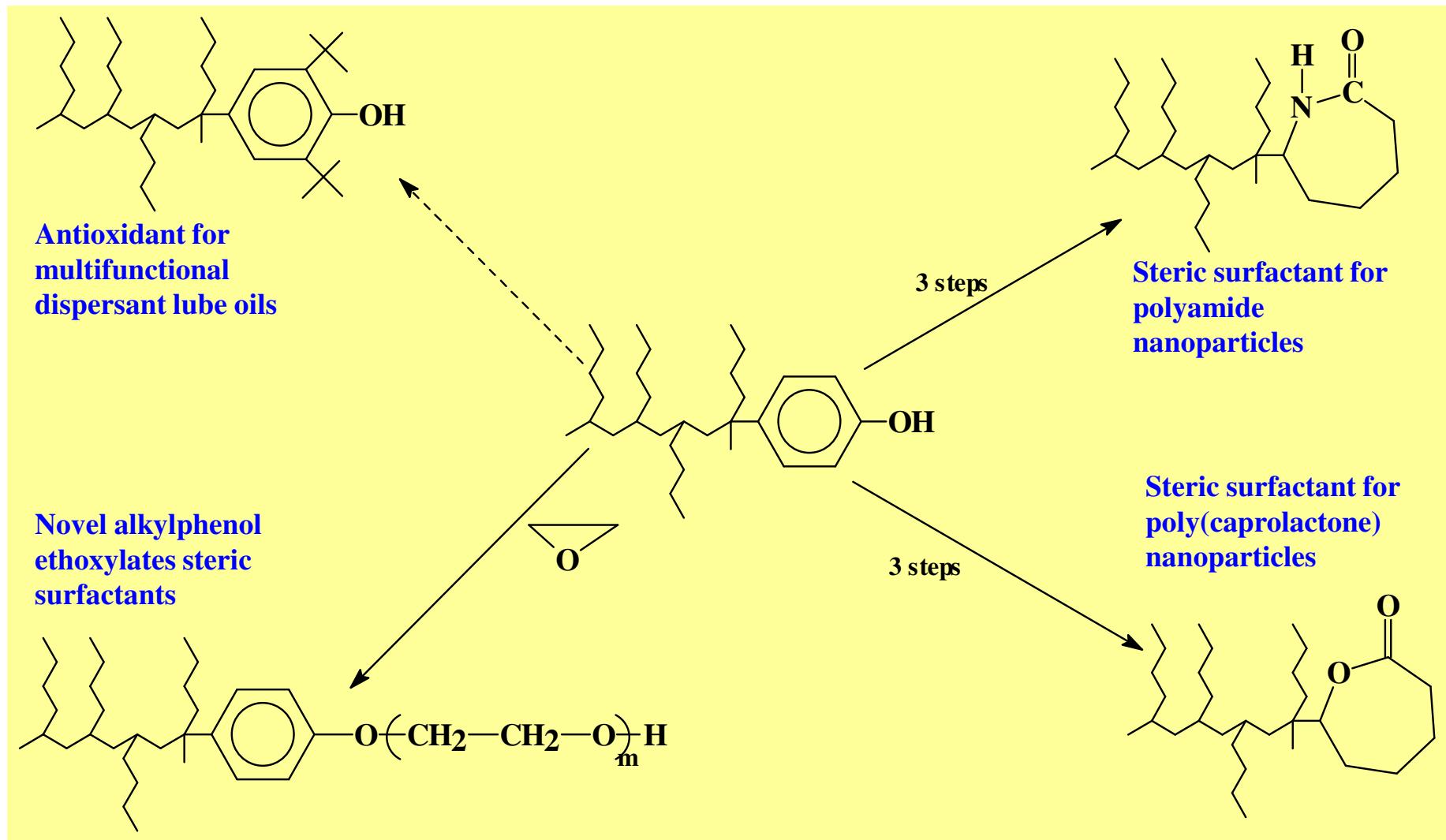
**N-poly(alkenyl) acrylamides were found to be**

- **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**

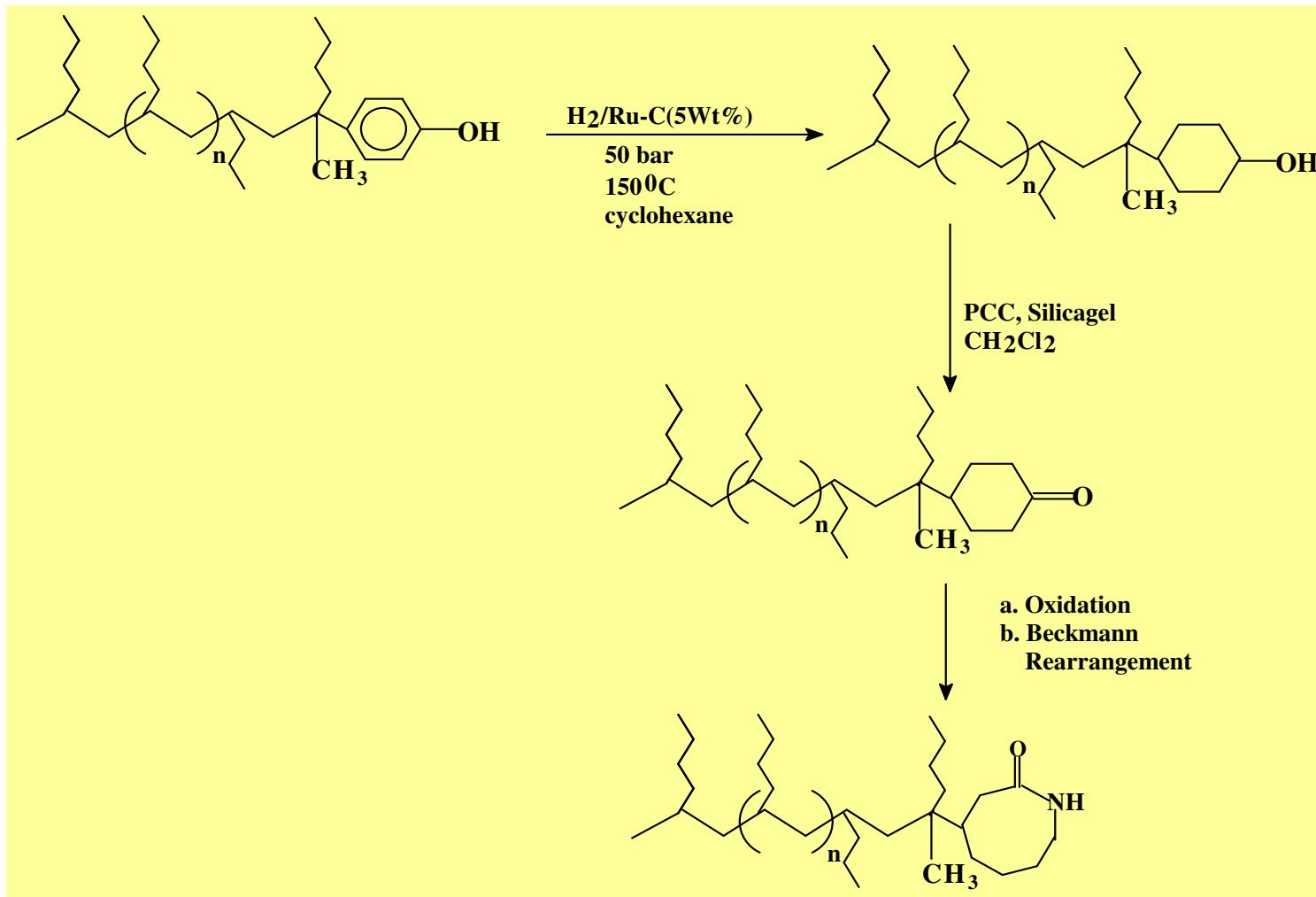
# **N-POLY(ALKENYL) ACRYLAMIDES : NOVEL AMPHIPHILIC MACROMONOMERS**



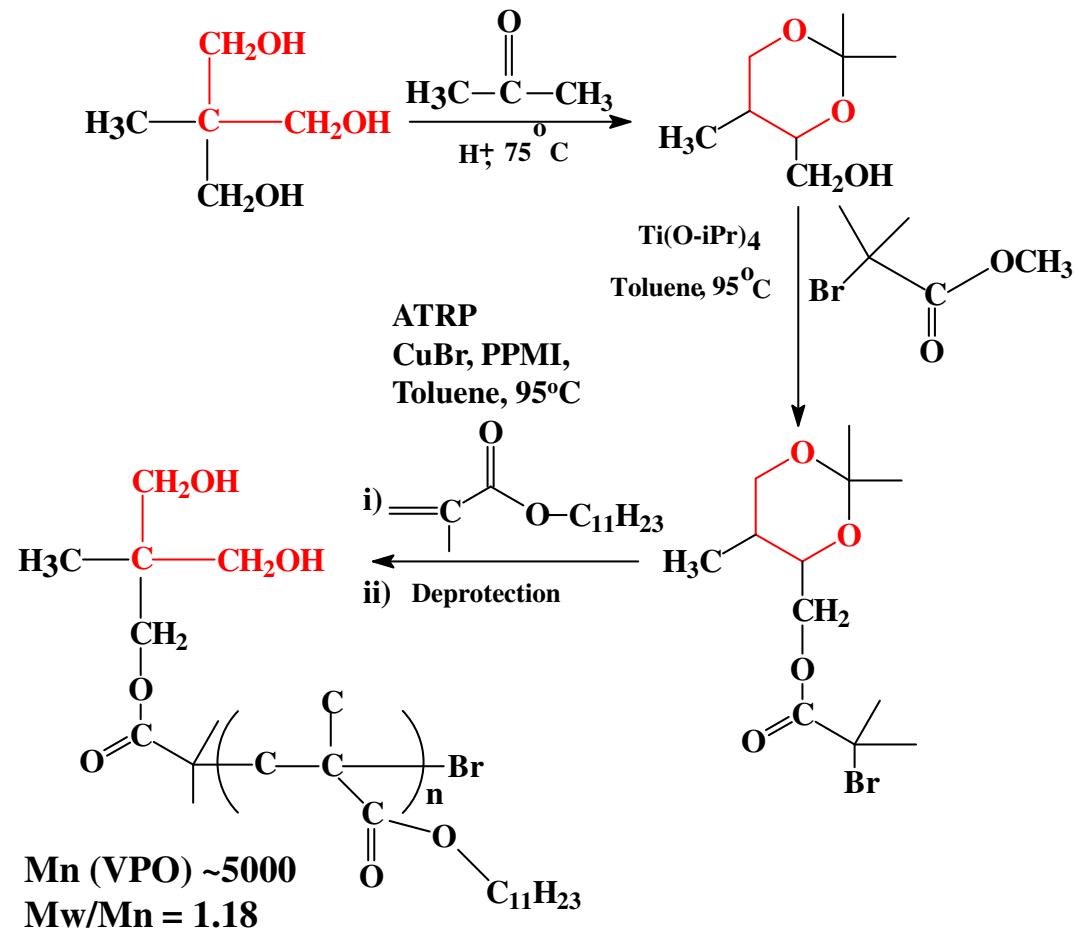
## TERMINAL PHENOL FUNCTIONAL POLY(1-HEXENE) : TRANSFORMATIONS OF FUNCTIONAL GROUP



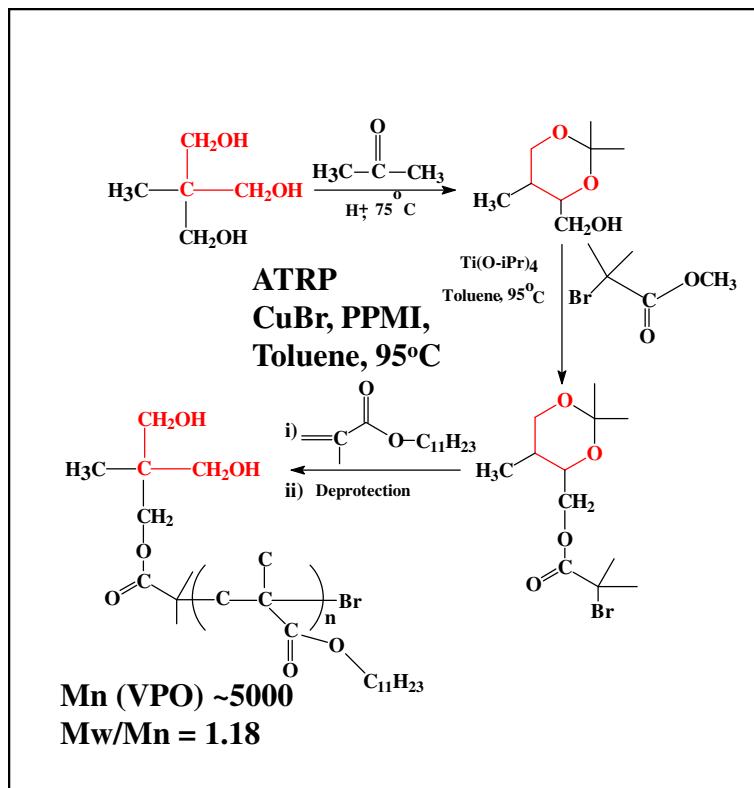
# **STERIC STABILIZER FOR RING OPENING POLYMERIZATION OF $\epsilon$ -CAPROLACTAM**



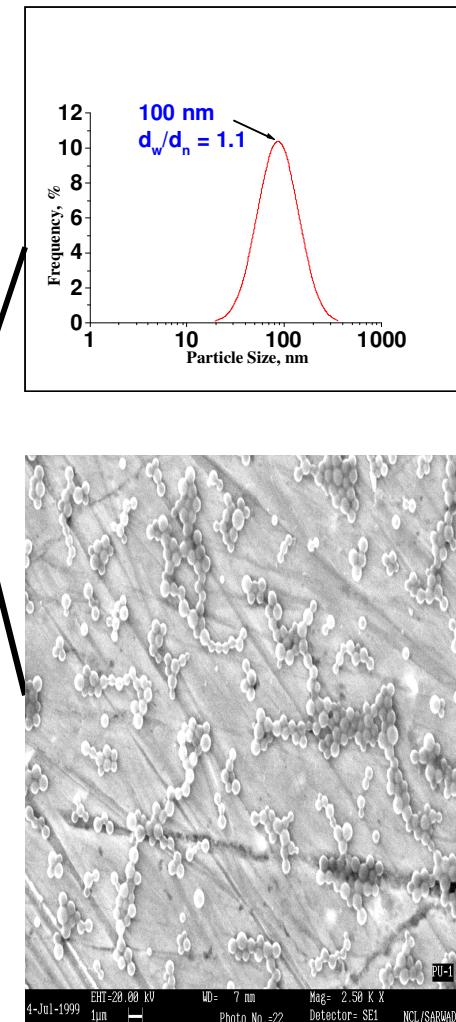
# CONTROLLED SYNTHESIS OF DIOL FUNCTIONALIZED POLY(METHACRYLATE)S



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



**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



## **ACKNOWLEDGMENTS**

***Dr. Ms. Mahua Dhara  
Dr R.Gnaneshwar  
Dr Anuj Mittal  
Dr M J Yanjarappa  
and  
Dr D. Baskaran***

**THANK YOU**

