

CONTROLLED SYNTHESIS OF FUNCTIONAL POLYMERS



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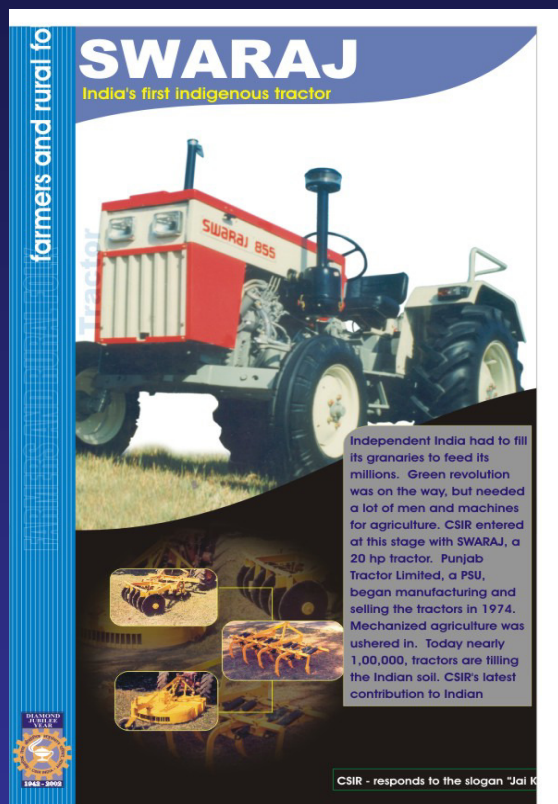
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Mission

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

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1942**



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

***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***

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

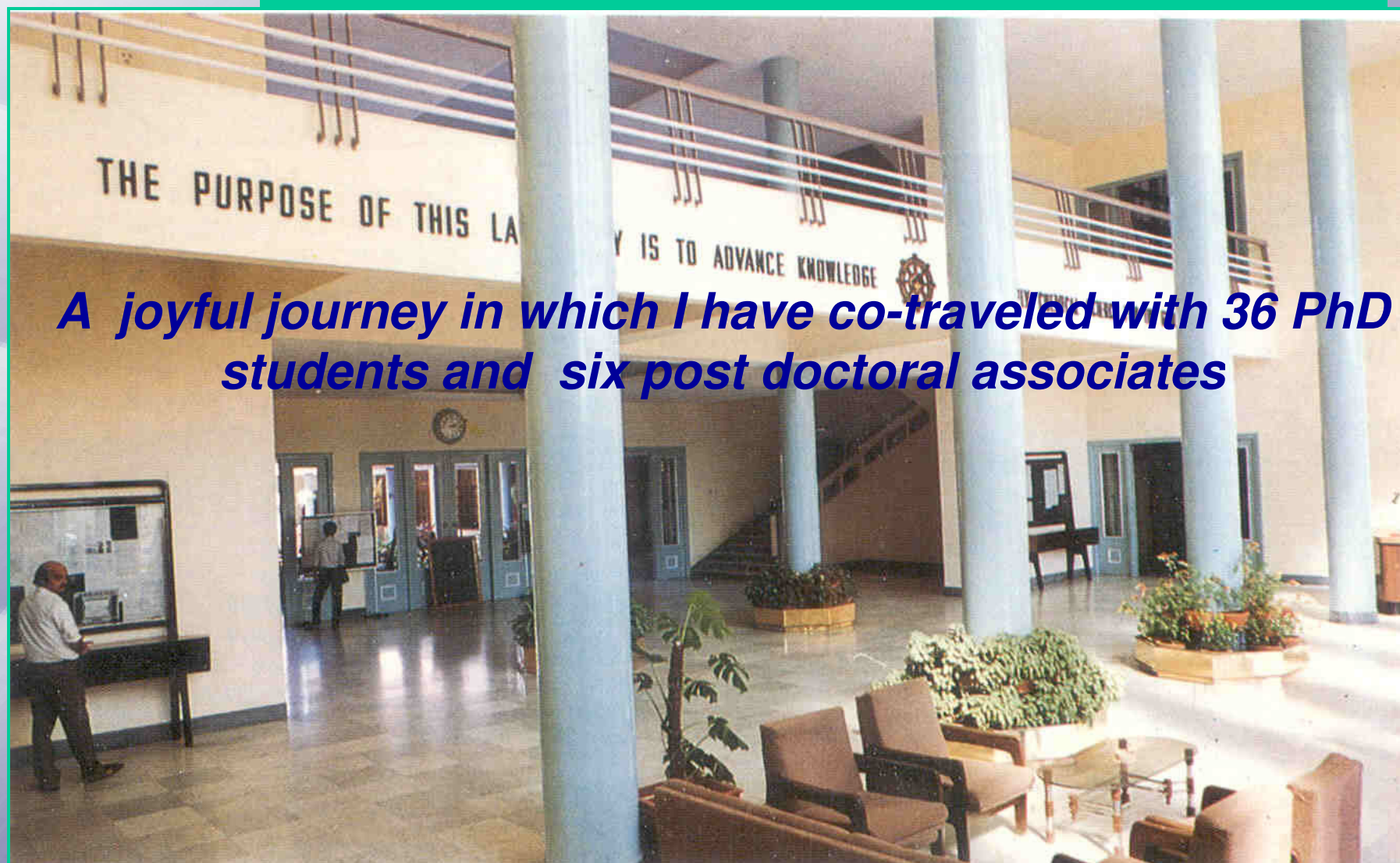


NCL AT A GLANCE

- 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)

A Recurrent Theme

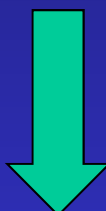
- **Introduction of functional groups in polymers**
 - *in the chain*
 - *at the terminal end of the chain*
- **Control of polymer structures**
 - *blocks, comb and branched*

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**

**Concepts and goals of
material science**



**Molecular scale
phenomena**

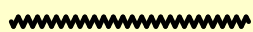


Macroscopic functions

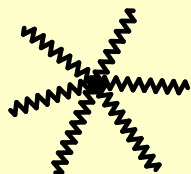


CONTROL OF STRUCTURES AND FUNCTIONALITIES

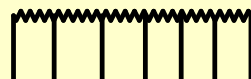
Topology



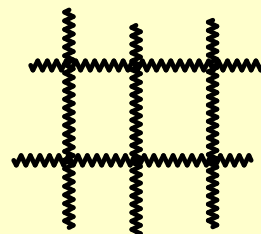
Linear



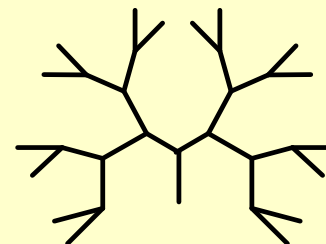
Star /
Multi-Armed



Comb Polymers



Networks



(Hyper) Branched

Composition



HomoPolymers



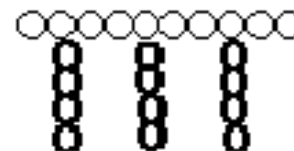
Block
Copolymers



Statistical
Copolymers

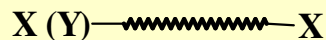


Tapered / Gradient
Copolymers

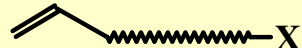


Graft

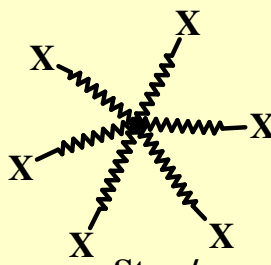
Functionality



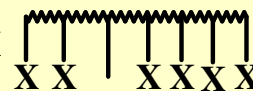
Homo / Hetero
Telechelic



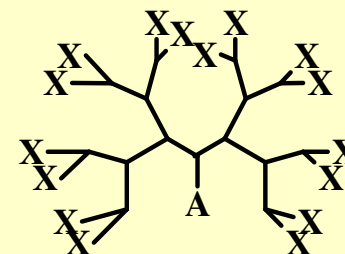
Macromonomers



Star /
Multi-Armed



Side Functional
Groups



Hyperbranched /
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

FUNCTIONAL 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 (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

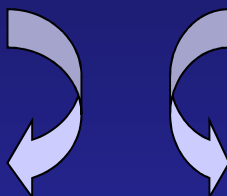


Excellent control over molecular weight, MWD, microstructure, functionality

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

Functional Polymers : Synthesis

Strategies for polymer functionalization



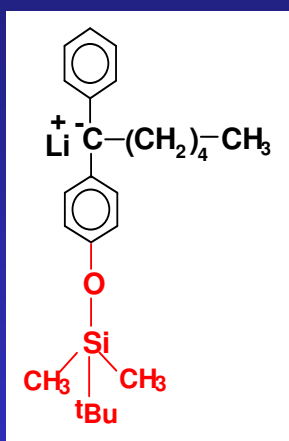
Electrophilic termination

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

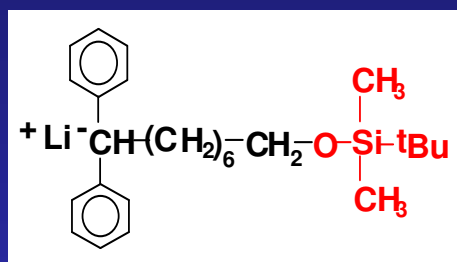
Functional initiation

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

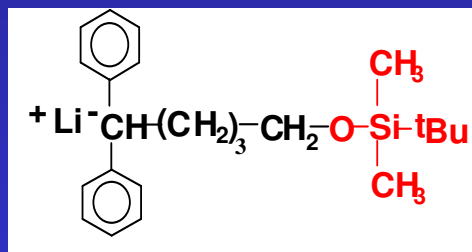
Synthesis of Hydroxyl End-functionalized PMMA Using Protected Hydroxyl-functionalized Initiators



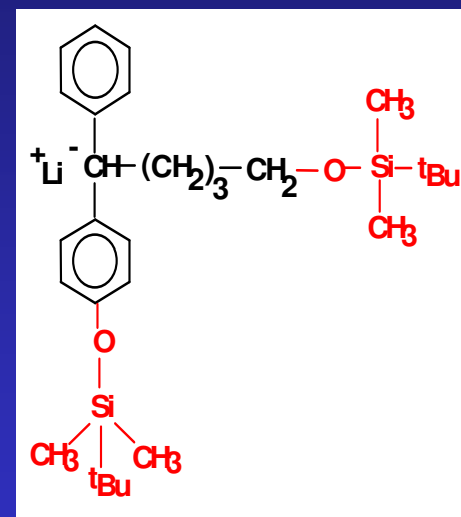
F1



F2



F3

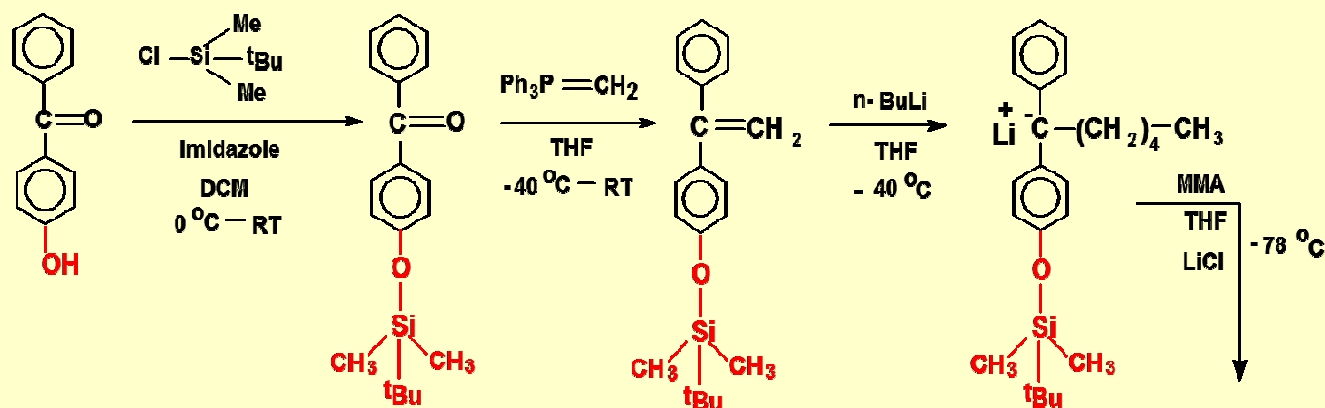


F4

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

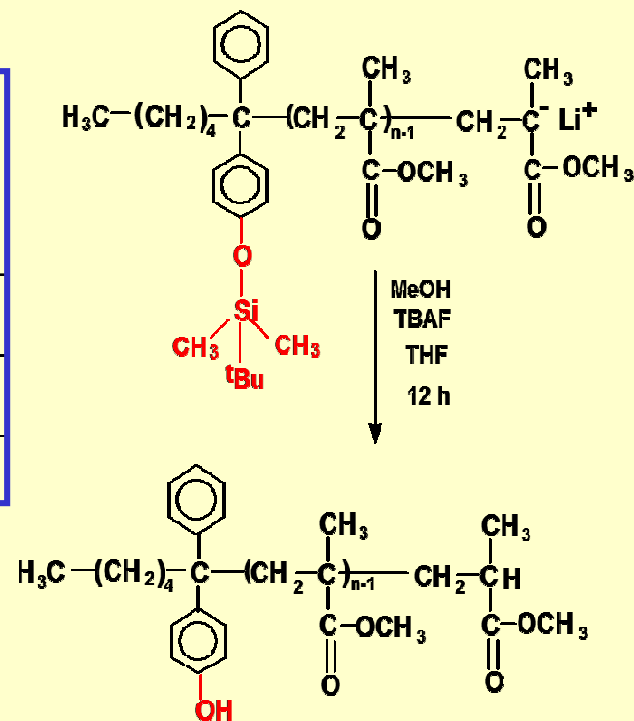
Synthesis of Hydroxyl End-functionalized PMMA Using F1

F1 \Rightarrow Adduct of 1-(p-hydroxyphenyl)-1'-phenyl ethylene and n-BuLi



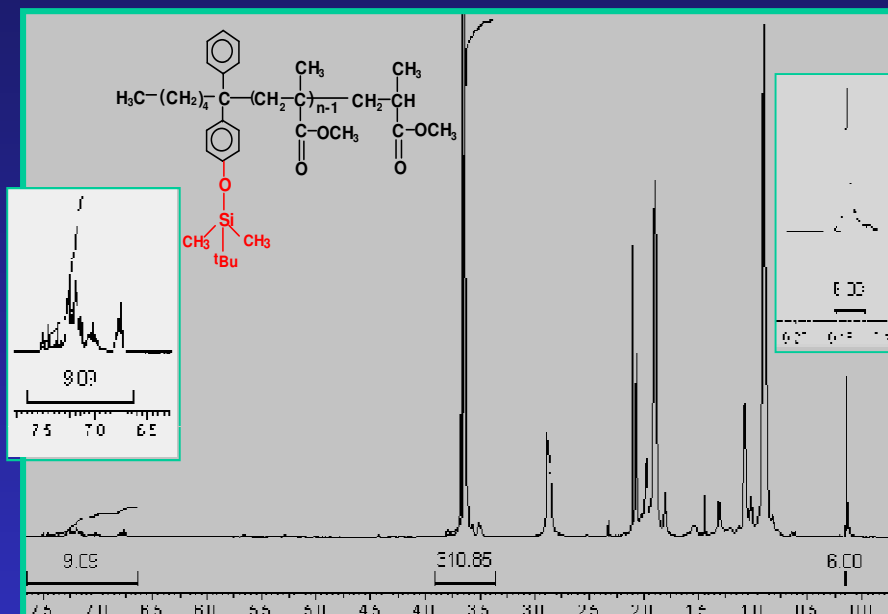
Run no.	$[I]_0 \times 10^{-3}$ m/L	$[M]_0$ m/L	Conv. %	$\bar{M}_{n,sec} \times 10^{-3}$	$\bar{M}_{n,calc} \times 10^{-3}$	MWD	$f = \bar{M}_{n,calc} / \bar{M}_{n,sec}$
1	3.67	0.12	~100	3.2	3.3	1.07	1.03
2	2.70	0.18	90	10.8	9.8	1.06	0.91
3	2.88	0.41	90	14.1	14.4	1.09	1.02

- ⊗ Well-controlled polymerization
- ⊗ Functionality confirmed by ^1H NMR, MALDI-TOF MS



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

^1H NMR (500 MHz, acetone- d_6) spectra of
silyl-protected hydroxy-PMMA
($M_{n, \text{sec}}=10800$)

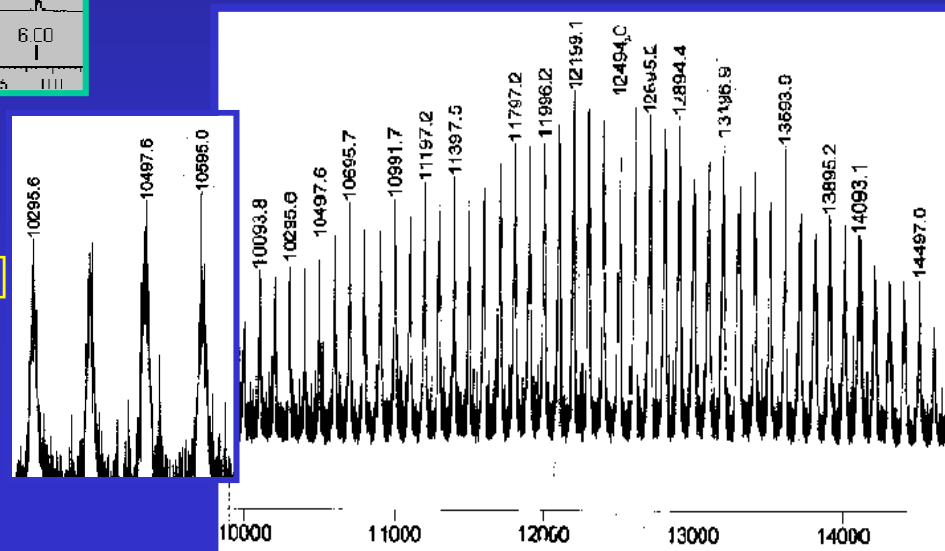


δ 0.0 6 H of $-\text{Si}(\text{CH}_3)_2$
 δ 6.7-7.6 9 H for 2 phenyl groups
 δ 3.58 310 H for $-\text{OCH}_3$ protons of PMMA



quantitative functionalization of PMMA chains

MALDI-TOF mass spectra of
hydroxy-PMMA (M_n ,
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 = $253 + 101 + 39 = 393$

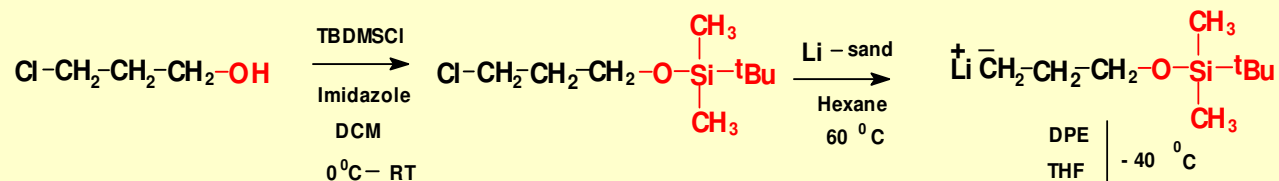
Also, single generation of polymers



Presence of protected $-\text{OH}$ at all chain-ends

Synthesis of Hydroxy End-functional PMMA Using F3

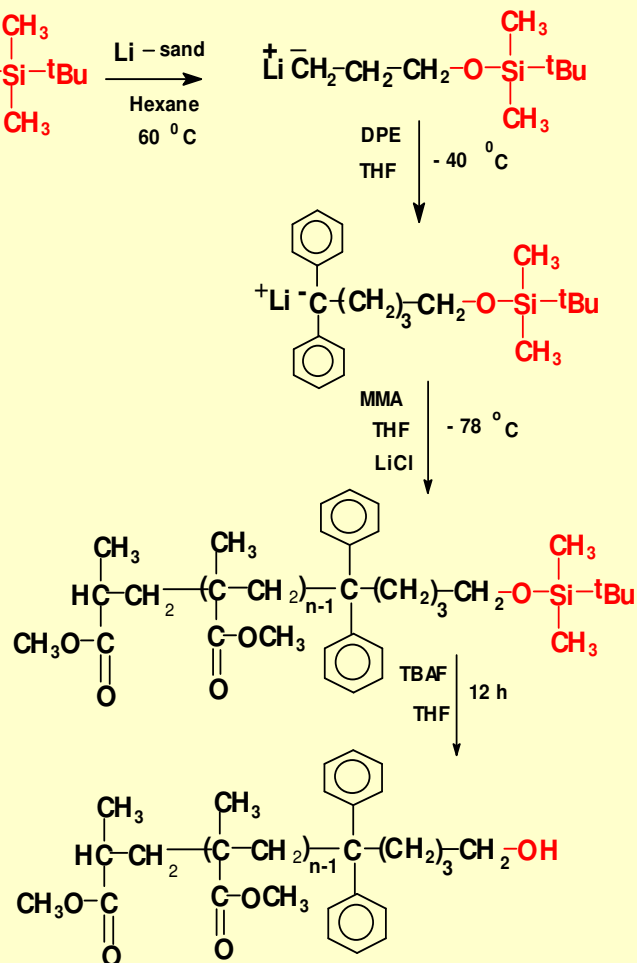
F3 : Adduct of 1,1'-diphenyl ethylene and protected hydroxy propyllithium



Run no.	[I] ₀ x10 ⁻³ m/L	[M] ₀	Conv. %	$\bar{M}_{n,\text{sec}}$	$\bar{M}_{n,\text{calc}}$	MWD	$f = \frac{\bar{M}_{n,\text{theo}}}{\bar{M}_{n,\text{sec}}}$
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

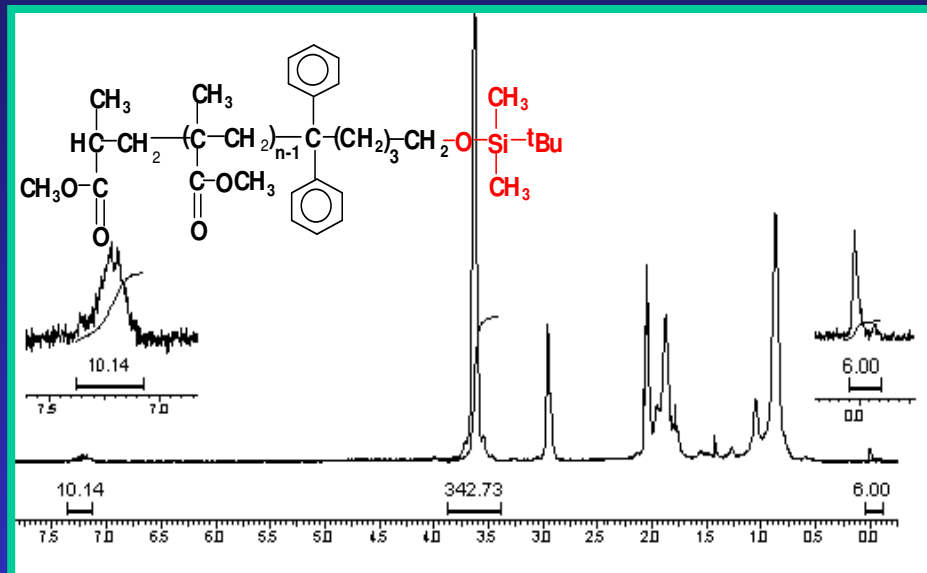


- ⊗ Well-controlled polymerization
- ⊗ Functionality confirmed by ¹H NMR, MALDI-TOF MS



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

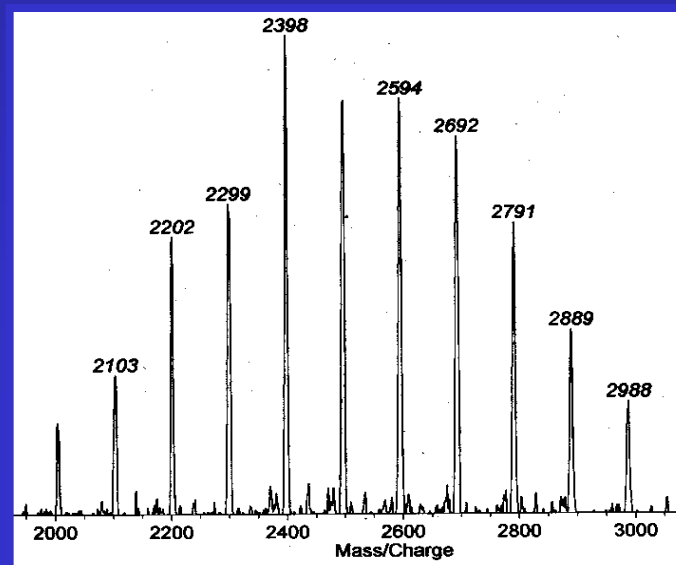
^1H NMR (500 MHz, acetone- d_6) spectra of silyl-protected hydroxy-PMMA ($M_n, \text{sec}=11500$)



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

quantitative functionalization of PMMA chains

MALDI-TOF mass spectra of hydroxy-PMMA ($M_n, \text{sec}=2300$)



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

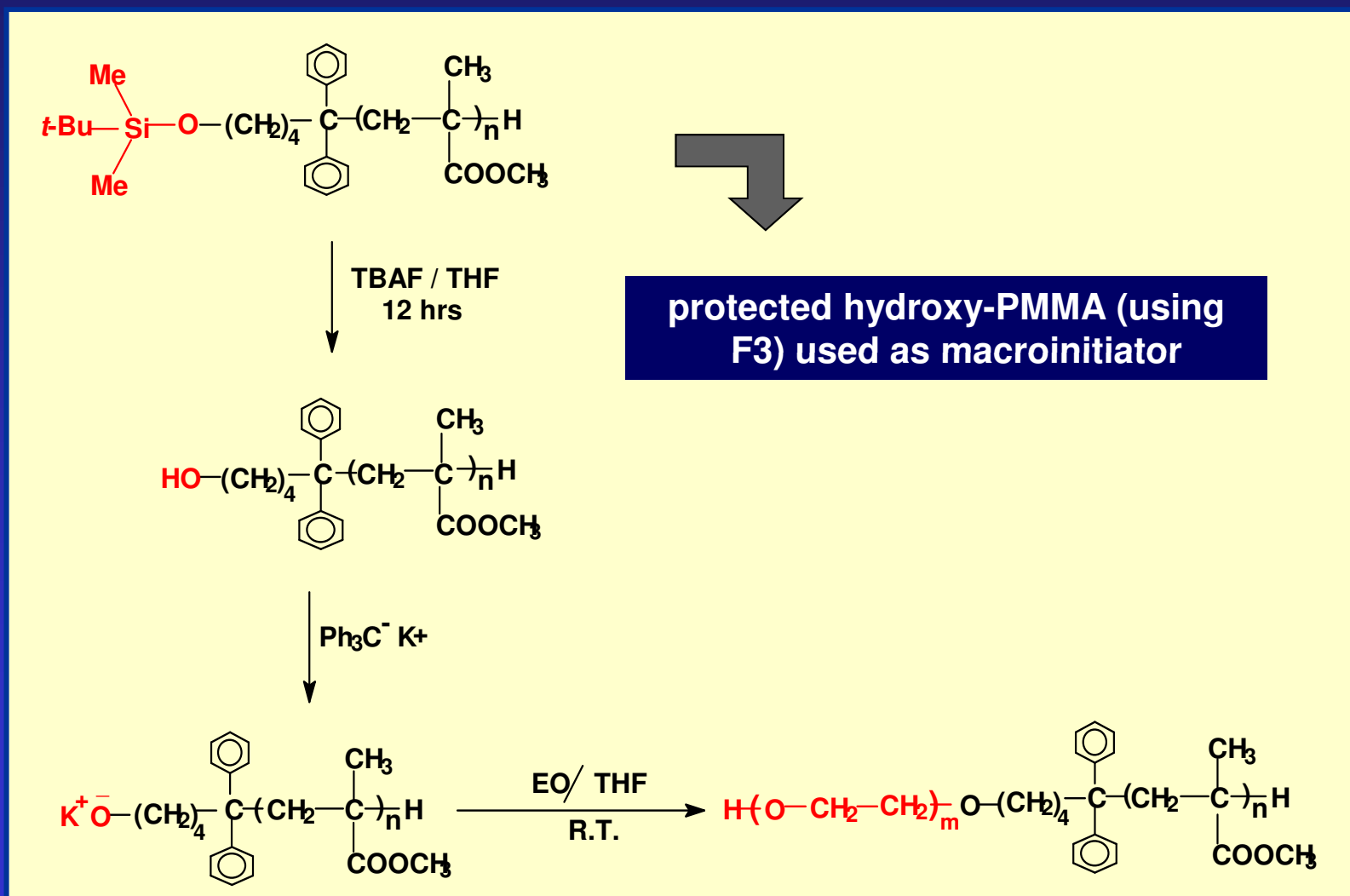
Theoretical end-group mass = $354 + 101 + 39 = 493$

Also, single generation of polymers

Presence of free $-\text{OH}$ at all chain-ends

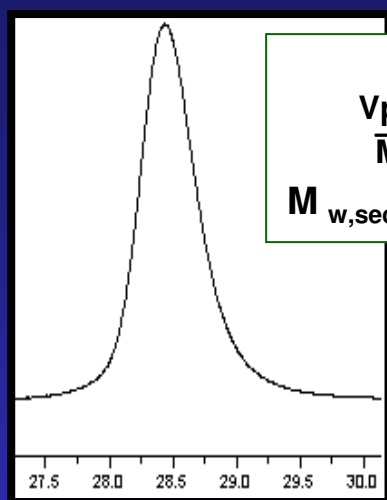
Synthesis of PMMA-*block*-PEO Copolymer

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

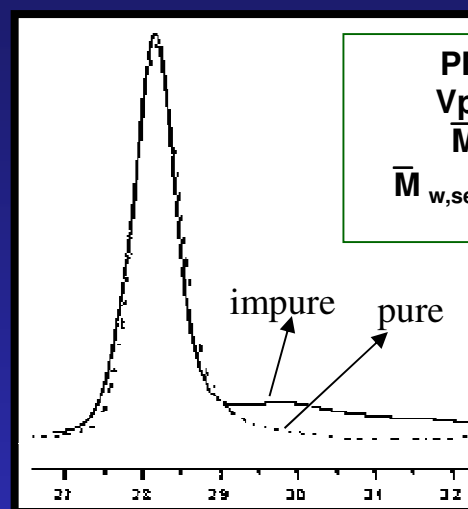


CHARACTERIZATION OF PMMA-BLOCK-PEO COPOLYMER

GPC Analysis



PMMA-OH
 $V_p = 28.43 \text{ mL}$
 $\bar{M}_{n,sec} = 11500$
 $\bar{M}_{w,sec} / \bar{M}_{n,sec} = 1.07$

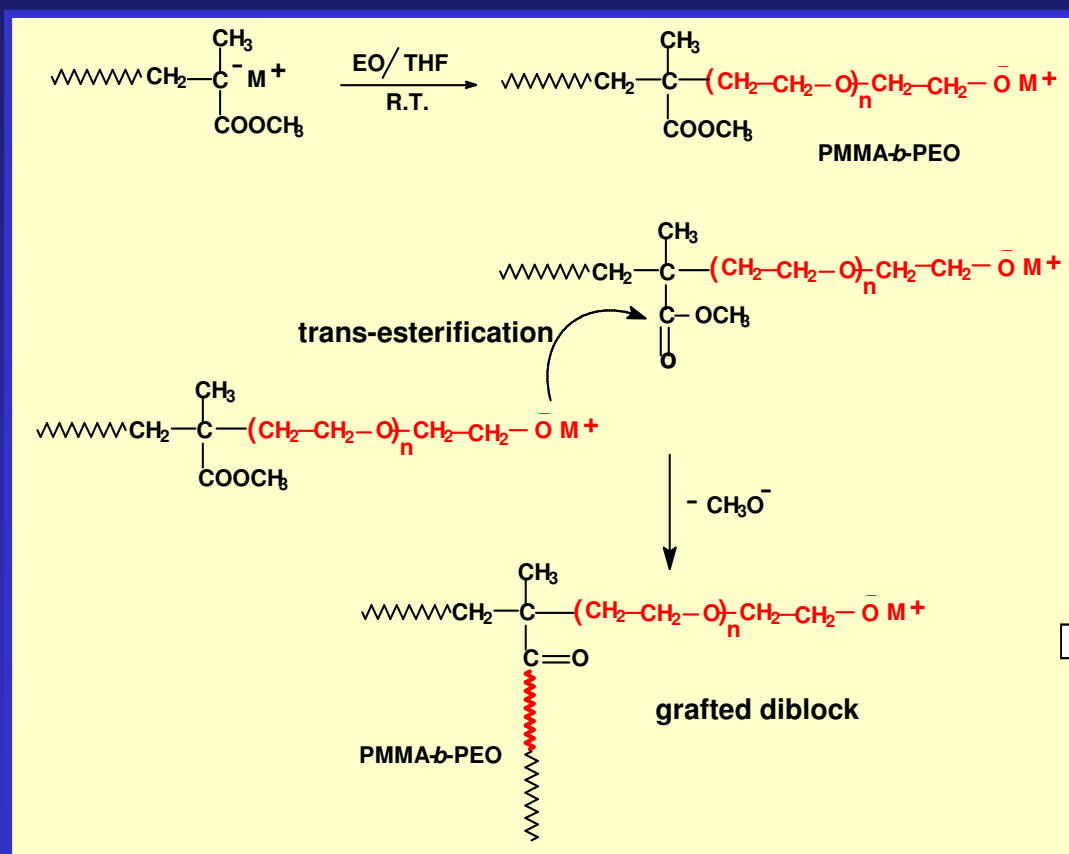


PMMA-b-PEO
 $V_p = 28.15 \text{ mL}$
 $\bar{M}_{n,sec} = 15500$
 $\bar{M}_{w,sec} / \bar{M}_{n,sec} = 1.20$

- 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

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

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

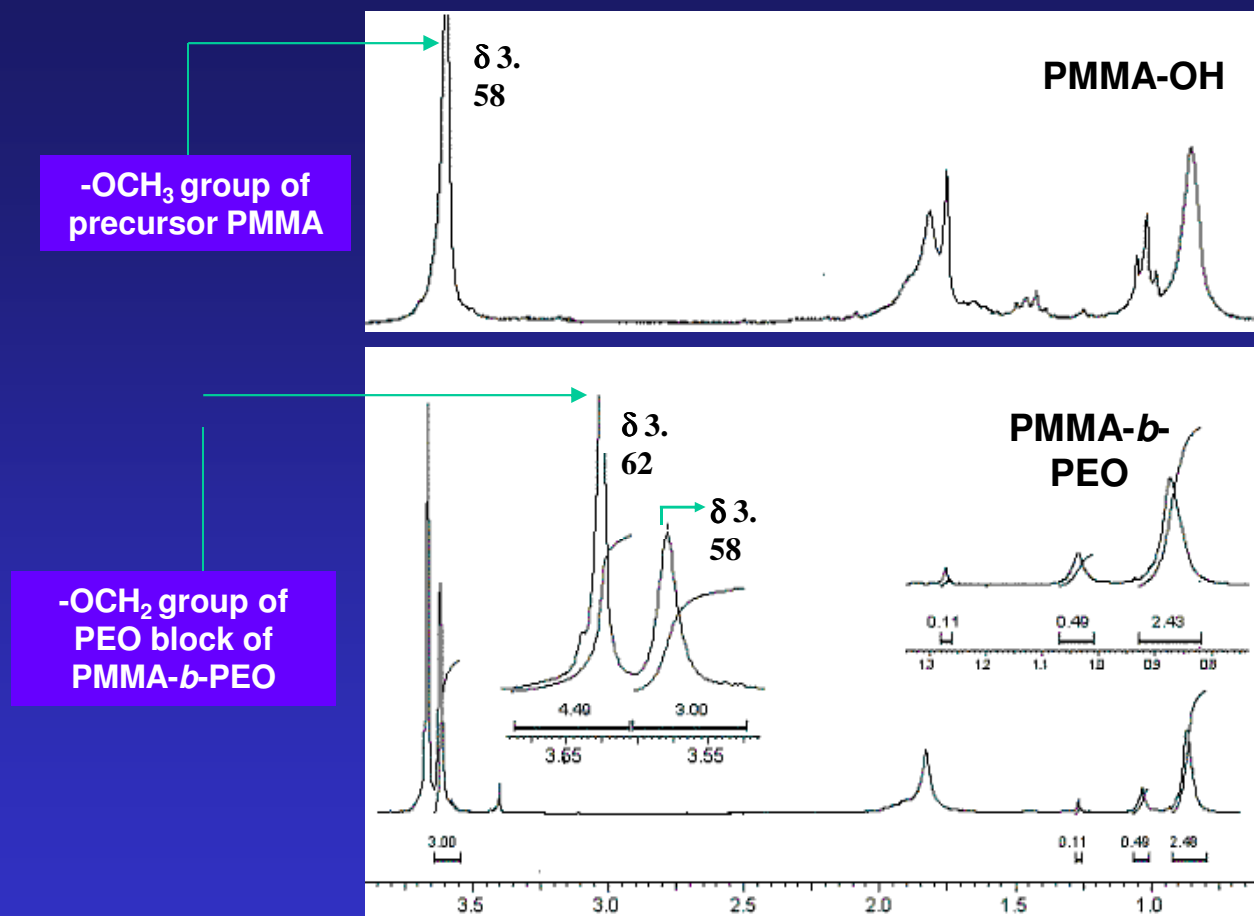


- GPC elugram of PMMA-*b*-PEO show broad multimodal MWD
- NMR of block copolymer show $-\text{OCH}_3$: $-\text{CH}_3$ proton ratio < 1.0

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

Characterization of PMMA-*block*-PEO Copolymer

^1H NMR (500 MHz) spectroscopic analysis



- Additional peak at δ 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

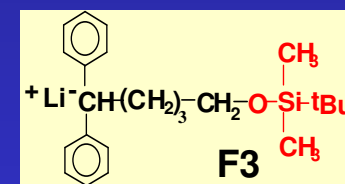
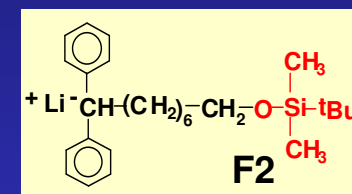
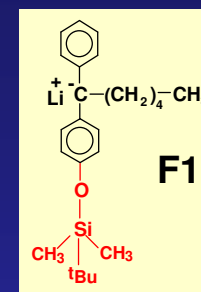
Appearance of new peak due to $-\text{OCH}_2$ protons confirm formation of the diblock
Presence of equal number of methyl and methoxy groups suggest insignificant amount of transesterification reaction

Characterization of PMMA-*block*-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



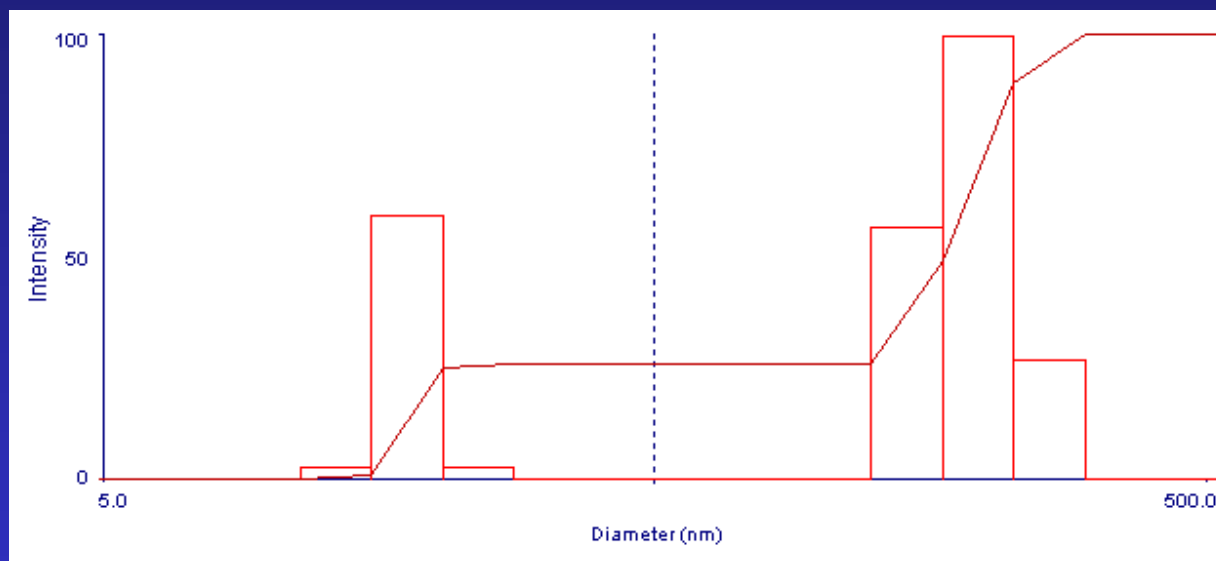
- NMR and GPC results prove the formation of PMMA-*b*-PEO from the precursor PMMA-OH
- Simple process of purification yields well-defined block copolymers with unimodal and fairly narrow MWD
- Run nos. 5 and 9 resulted in water-soluble PMMA-*b*-PEO copolymers



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

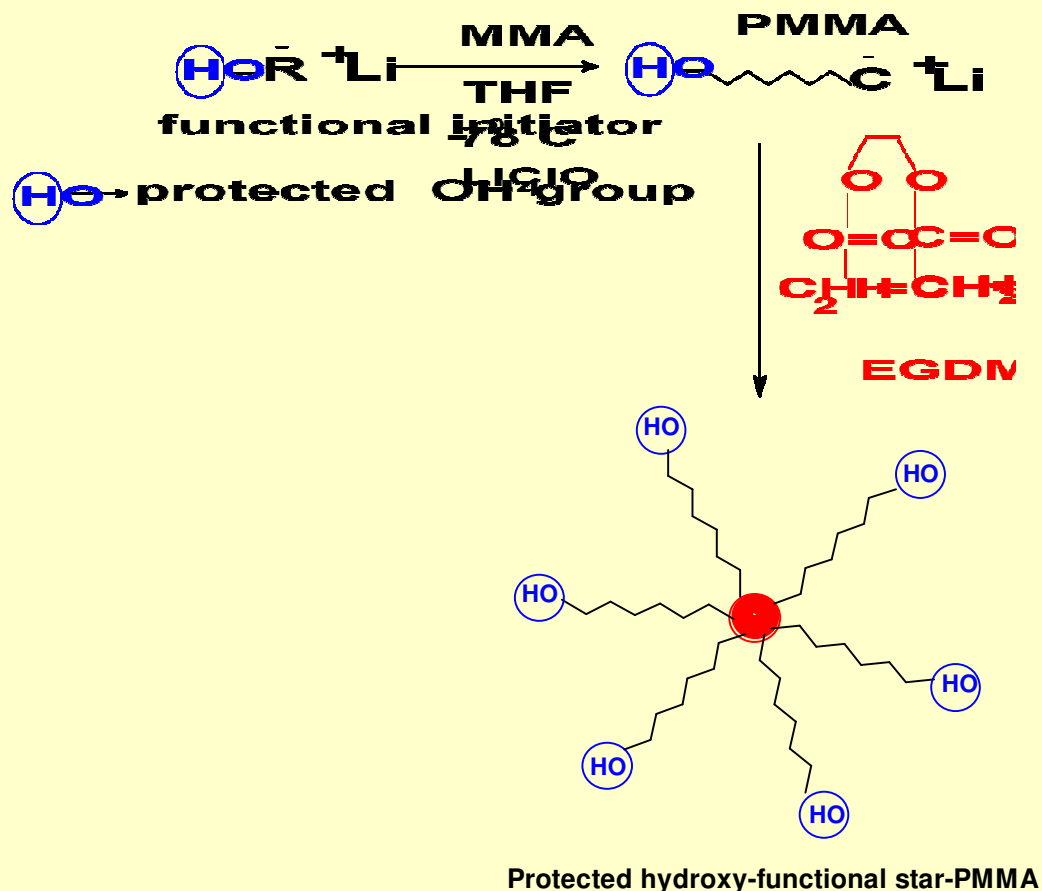
$[C] = 9.2 \times 10^{-4} \text{ g/mL}$ in water/THF (9:1 v/v)

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

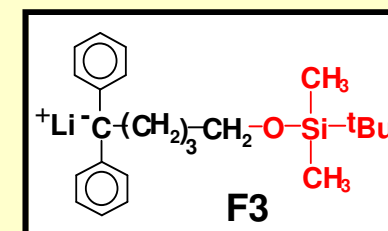
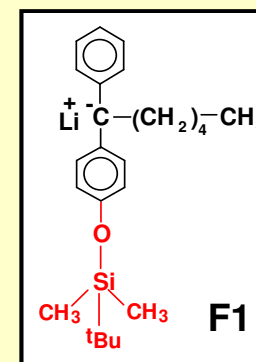
Step 2: Living chains coupled with bis-unsaturated monomer

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 (SEC)	\bar{M}_w (LS) $\times 10^{-3}$	\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



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



Degree of branching increases with

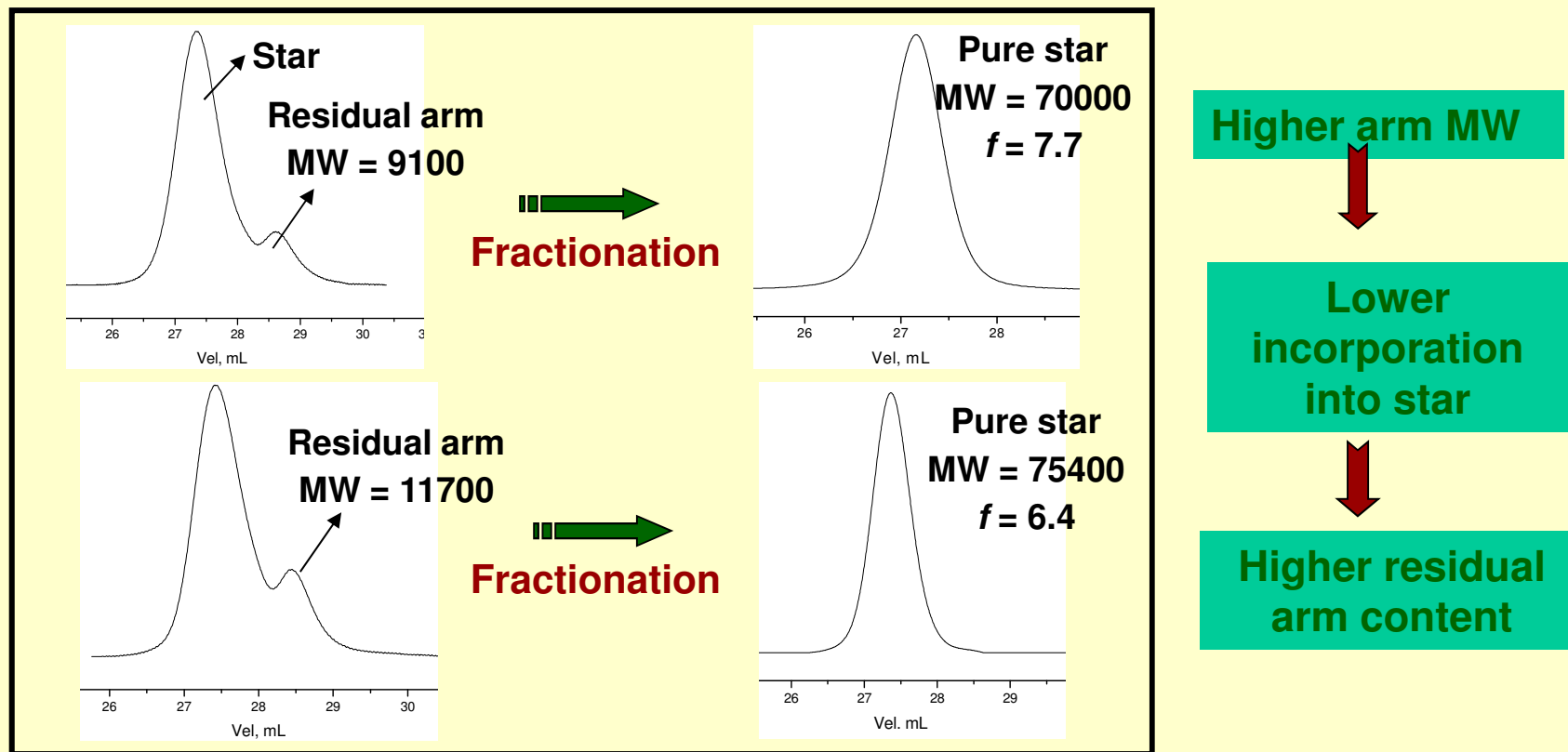


increase in EGDMA : initiator ratio

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

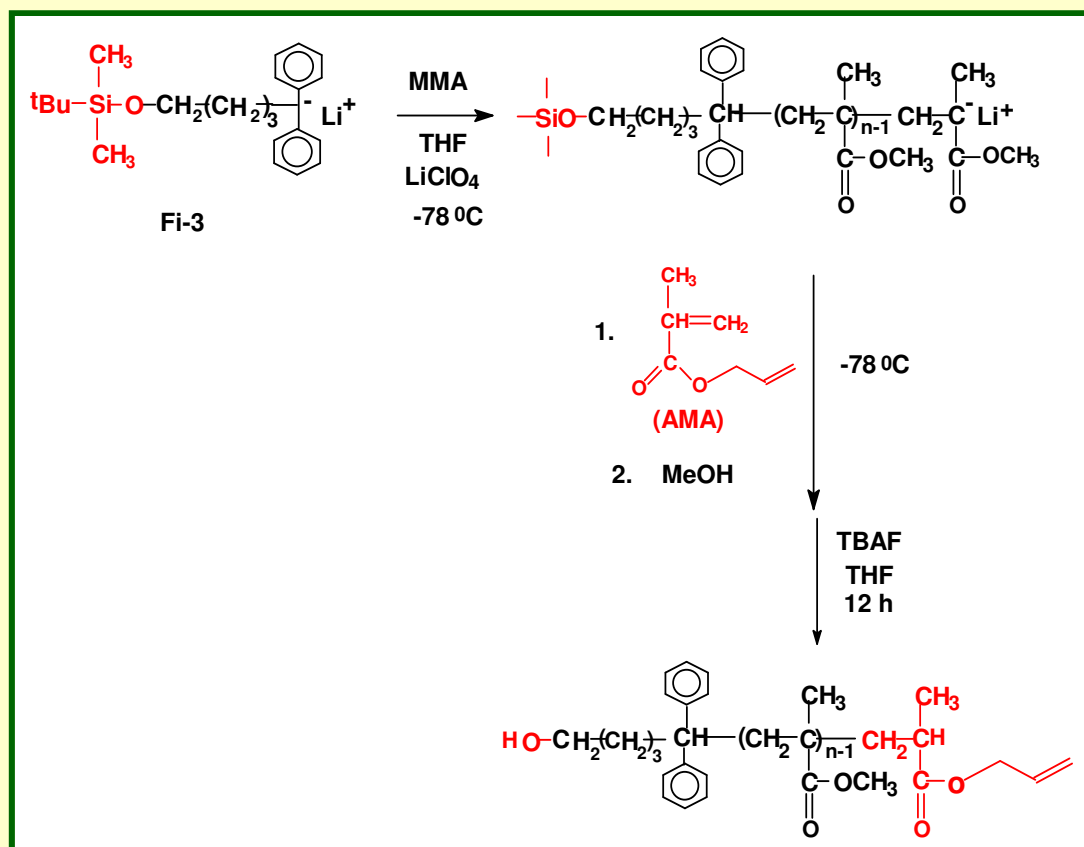


- Addition of dilute toluene solution of deprotected hydroxy-PMMA star to excess cold methanol causes the star to preferentially precipitate

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



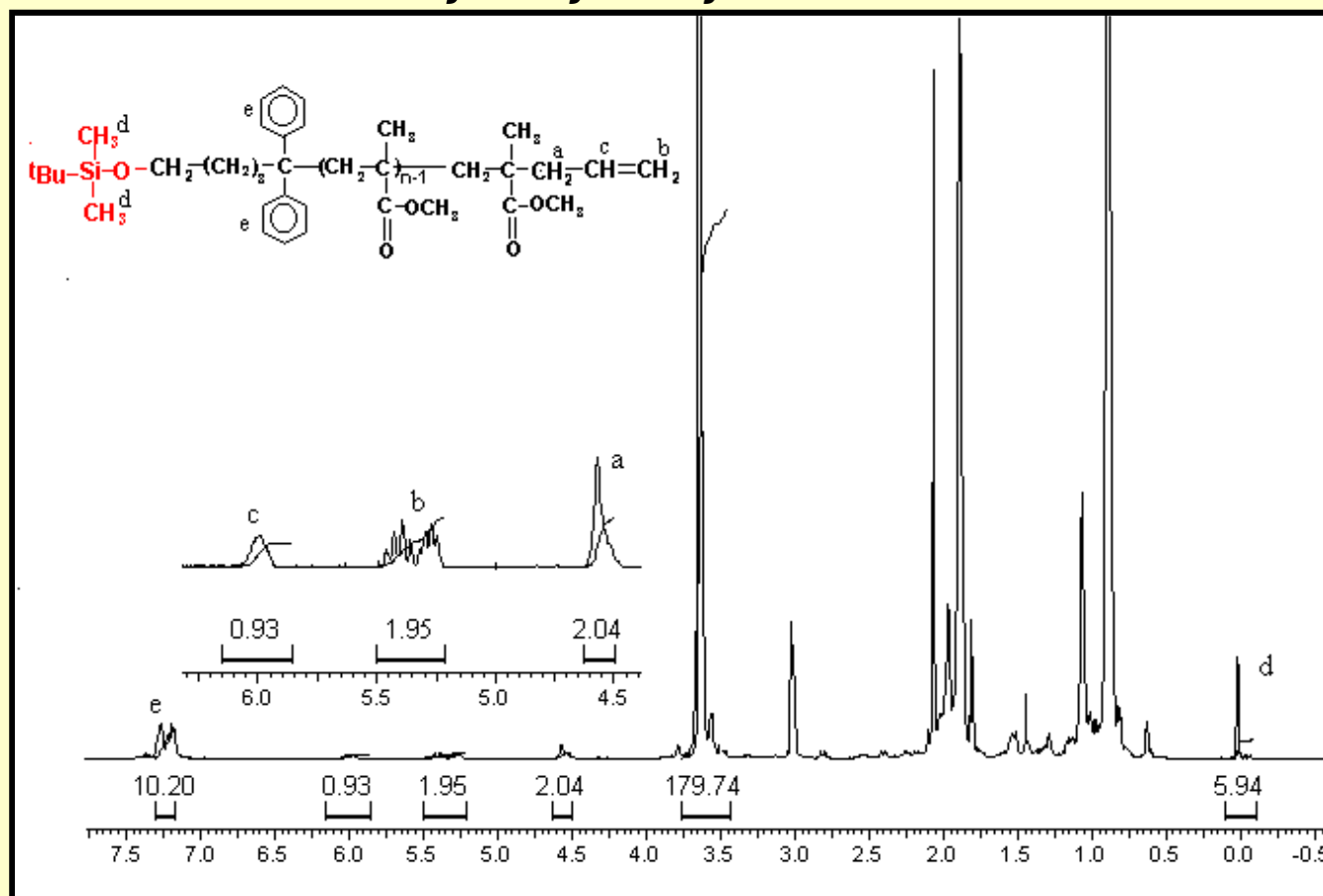
Step 1. Anionic polymerization of MMA using functional initiator F3

Step 2. Electrophilic termination of living chains by allyl methacrylate

Sample	$[\text{I}]_0$ $\times 10^{-3}$ m/L	$[\text{M}]_0$ $\times 10$ m/L	Temp. $^{\circ}\text{C}$	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 ^1H NMR

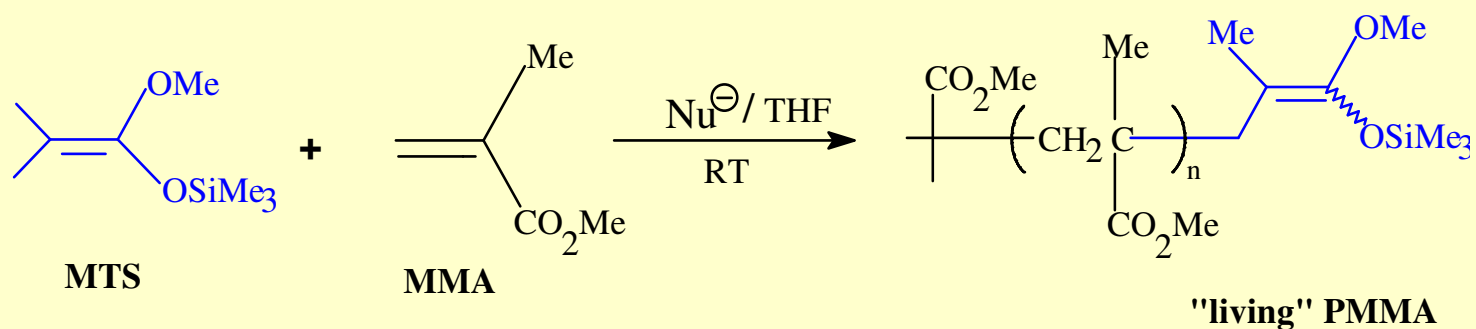
^1H NMR of α -hydroxy- ω -allyl PMMA



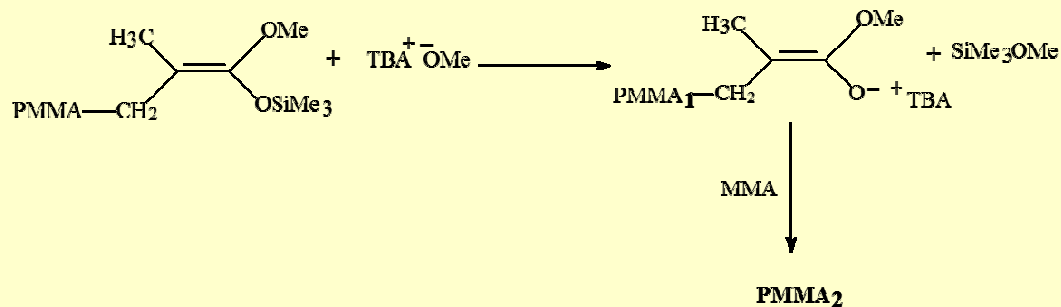
100 % end-functionalization of hydroxy-PMMA by allyl group

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

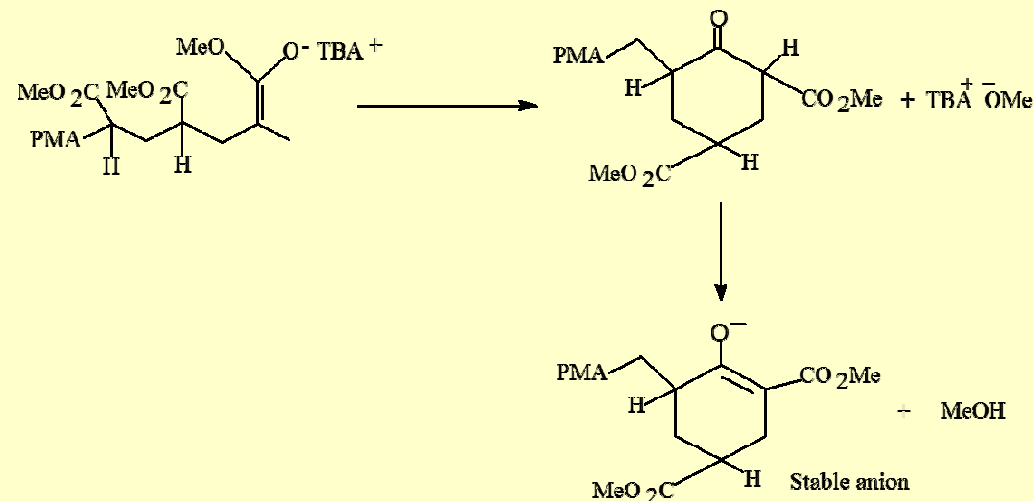
Termination of 'Living' chain end in GTP



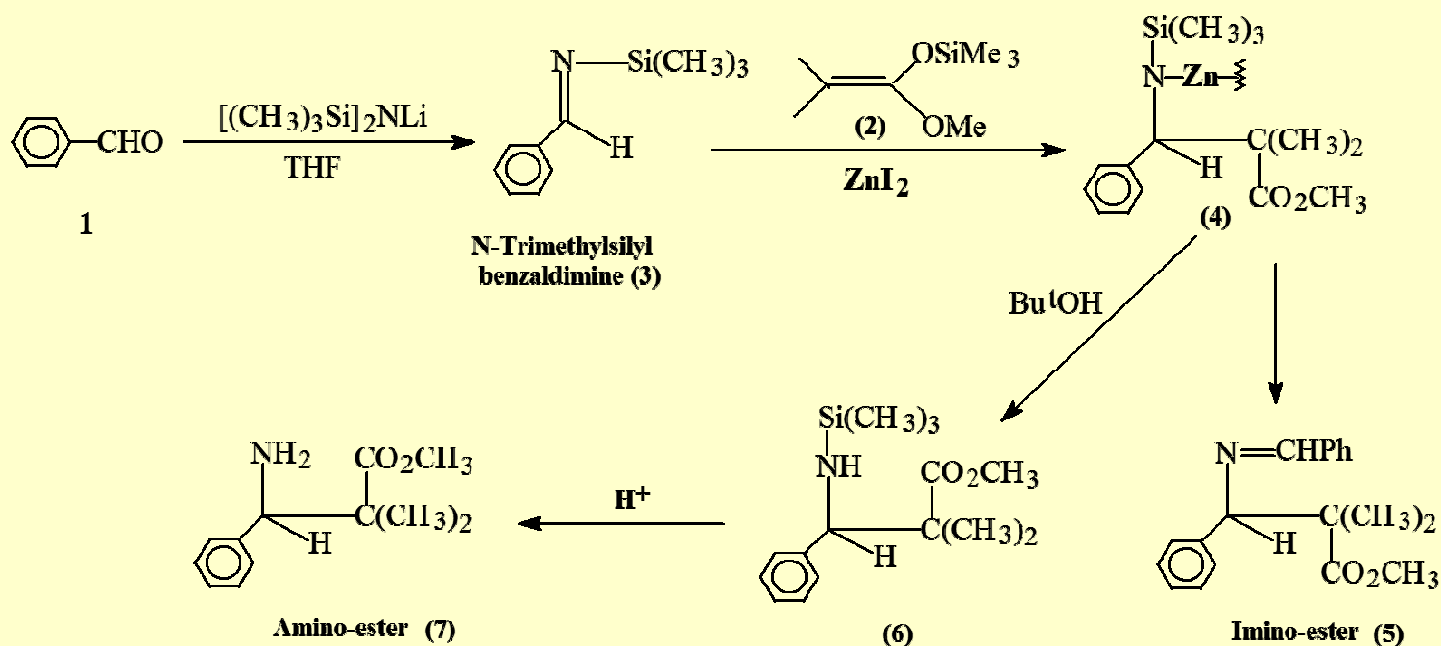
Ketene silyl acetal end group in the polymer chain end is in equilibrium with an ester enolate species. Under suitable conditions, the ester enolate can be trapped by a suitable electrophile



Backbiting termination reaction in MMA polymerization



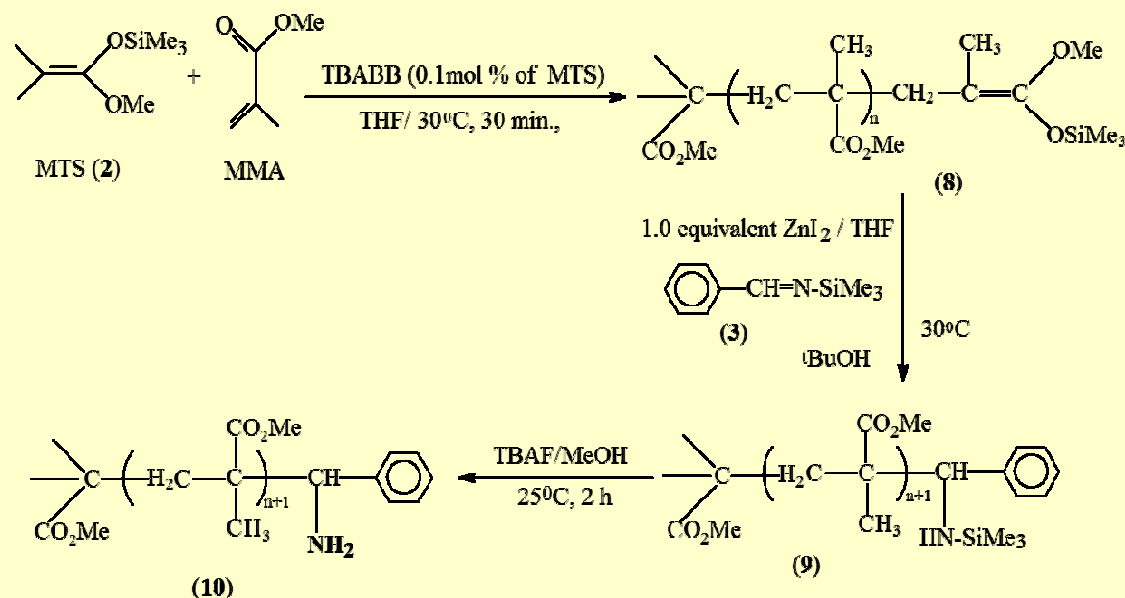
Termination reaction in acrylate polymerization via chain end cyclization



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 (β -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

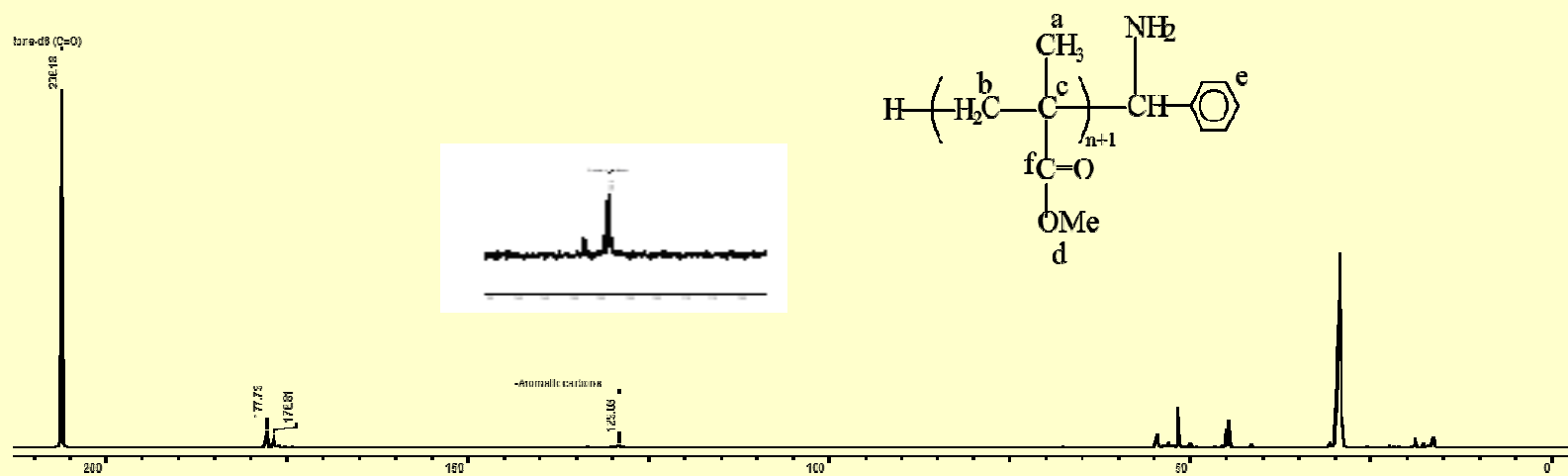
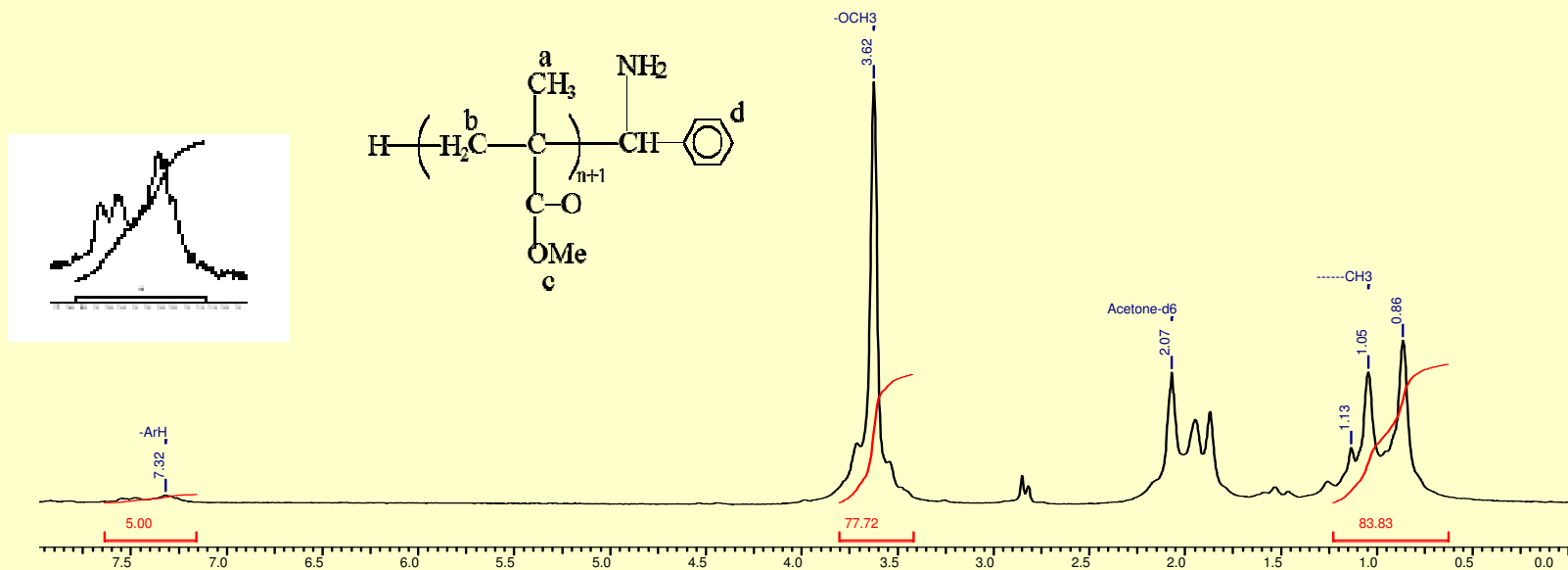
Table 5.2. Synthesis of amine end-functional poly (methyl methacrylate) s by GTP

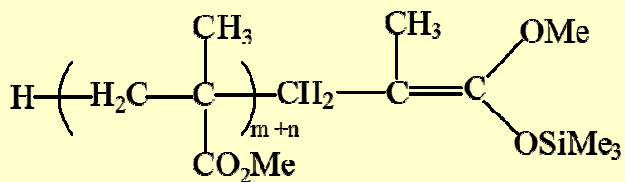
Entry	MMA ^a , mol	MTS, mol x 10 ³	THF, mL	TBABB, mol x 10 ⁶	N-TMS Benzaldimine, mol x 10 ³	ZnI ₂ , mol x 10 ³	^t BuOH, mol x 10 ³	M _n (theory), g/mol	M _n (SEC), g/mol	M _w /M _n (SEC)	M _n (VPO), g/mol	M _n (NMR) g/mol	I ^b _{efficiency}	F ^c _n
1	0.047	2.35	30	2.35	2.35	2.35	2.35	2100	2205	1.07	2400	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: [MMA]₀ = 1.56 mol/L

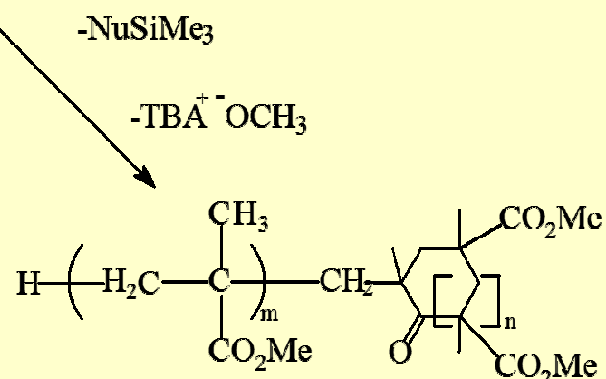
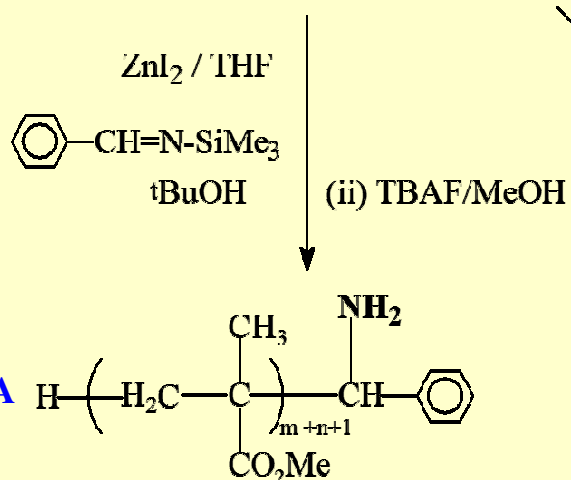
b: I_{efficiency} = M_n (theory)/M_n (SEC)

c: F_n = M_n (SEC)/ M_n (NMR)

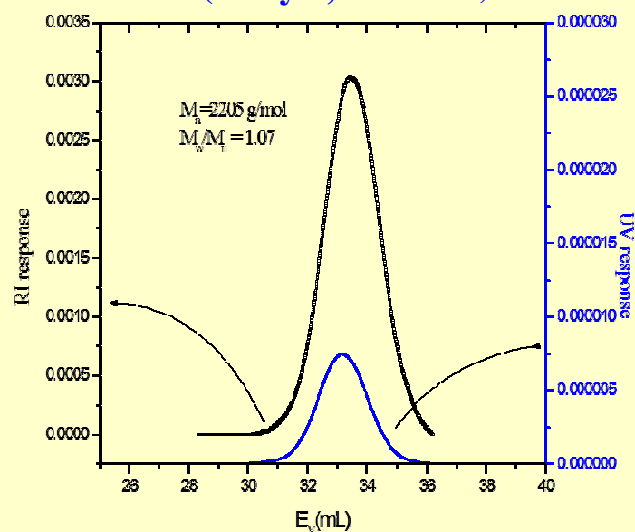




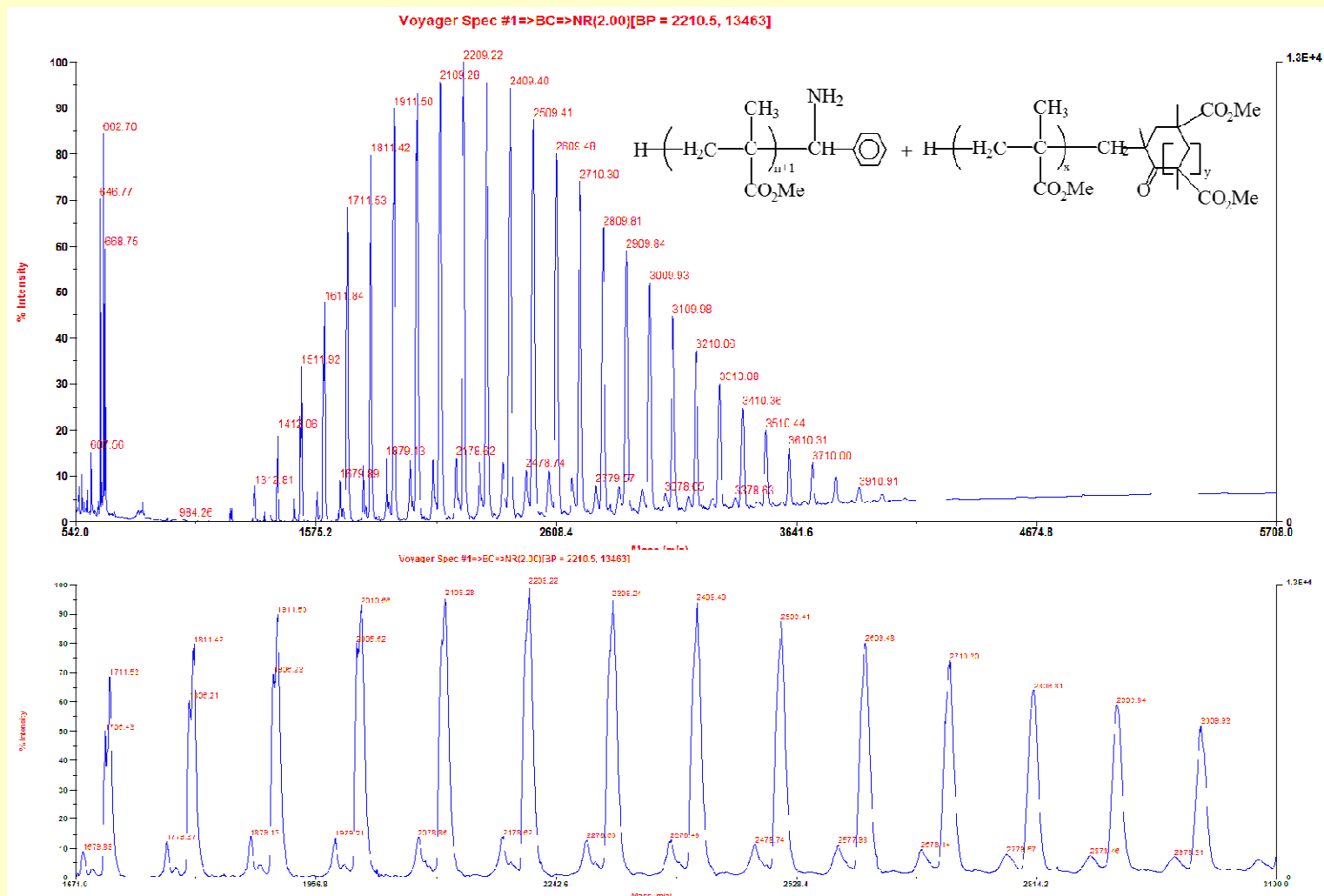
Silyl ketene acetal ended PMMA



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



Formation of cyclic fraction along with amine-terminated PMMA

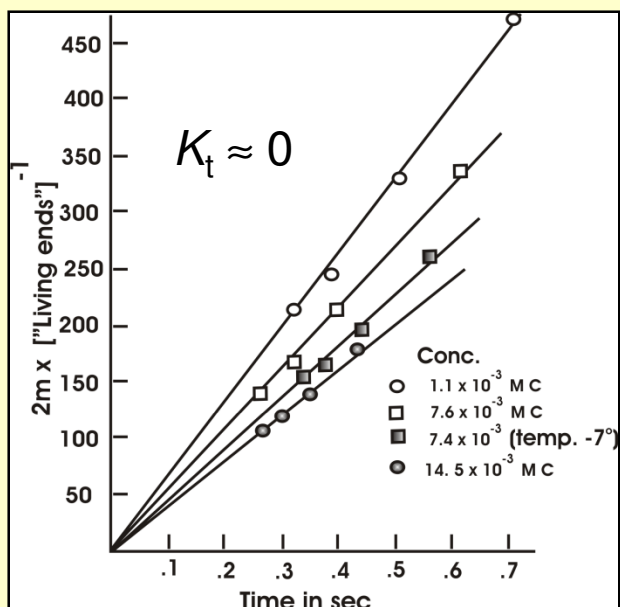


MALDI-ToF spectrum of amine-terminated PMMA prepared by GTP using TBABB catalyst for silyl ketene acetal ended PMMA and Lewis acid ZnI_2 for functionalization reaction at room temperature (entry 1, table 5.2). $[\text{M}+\text{Li}]^+ = 100.12 (\text{MMA}) * n (\text{DP}) + \text{H} (1.0079) + \text{Ar}-\text{CH}-\text{NH}_2 (106.1476) + \text{Li}^+ (6.941)$. (Matrix: Dihydroxybenzoic acid and LiCl for enhancement of ion formation) ($\Delta = 7 \text{ Da}$)

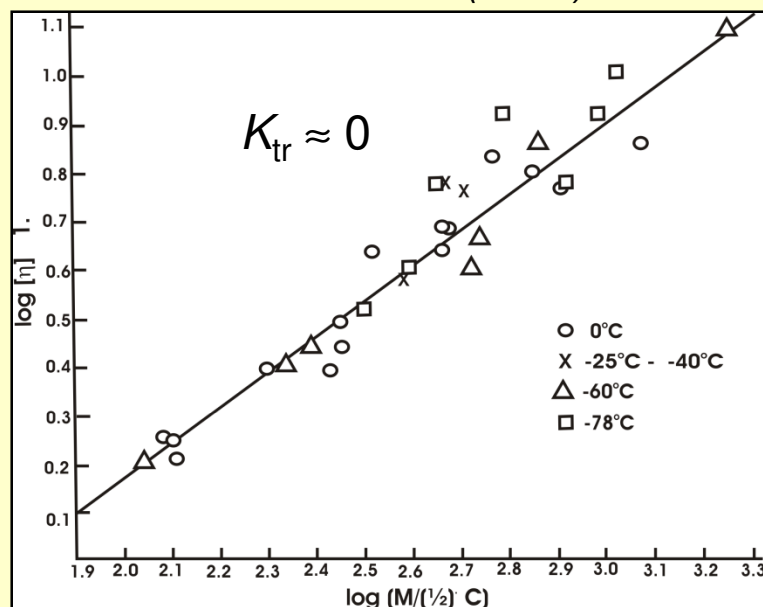
'Living' Polymerization

Anionic polymerization of styrene in THF at -78°C

- Michael Szwarc (1956)



First order time-conversion plot



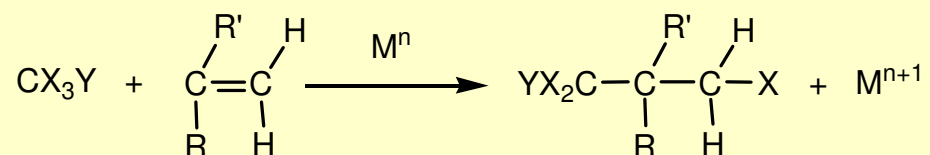
Viscosity vs. theoretical mol. wt.

Radical Polymerization Methods with Above Features:

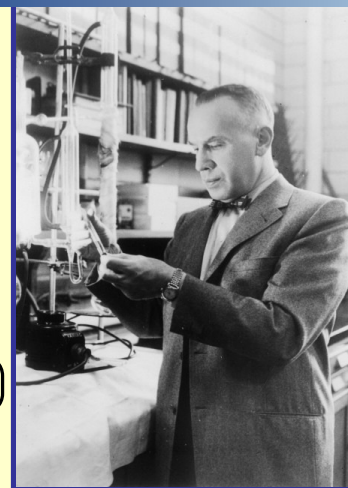
- Transition metal-mediated radical polymerization (ATRP)
- Nitroxide-mediated radical polymerization (NMP)
- Radical addition-fragmentation and transfer polymerization (RAFT)

Development of Atom-transfer Radical Polymerization (ATRP)

➤ Atom transfer radical addition

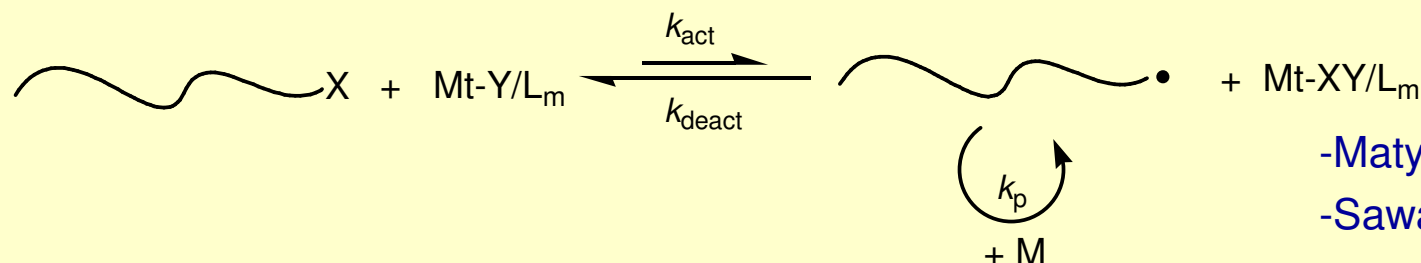


X = halogen; Y = H (or) electronegative group; M = Cu or Ni



Morris Kharash
(1938)

➤ Atom transfer radical polymerization

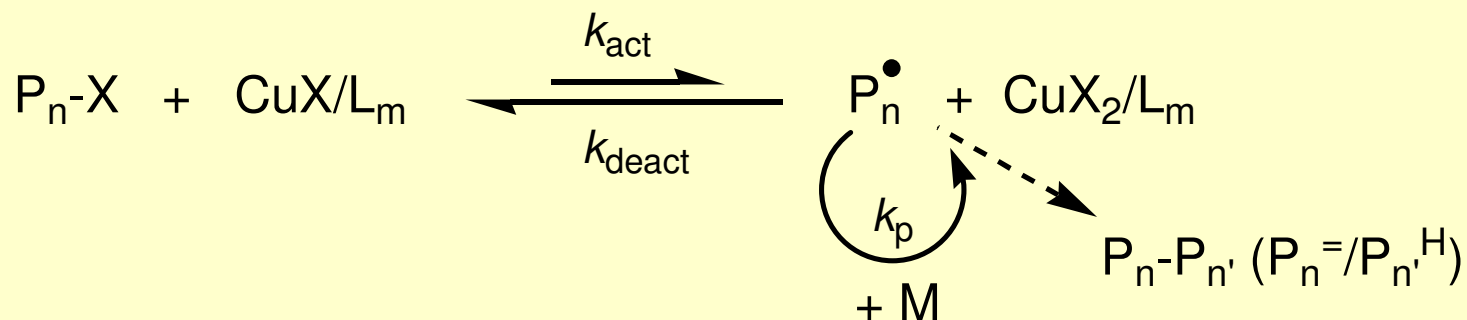


-Matyjaszewski (1995)

-Sawamoto (1995)

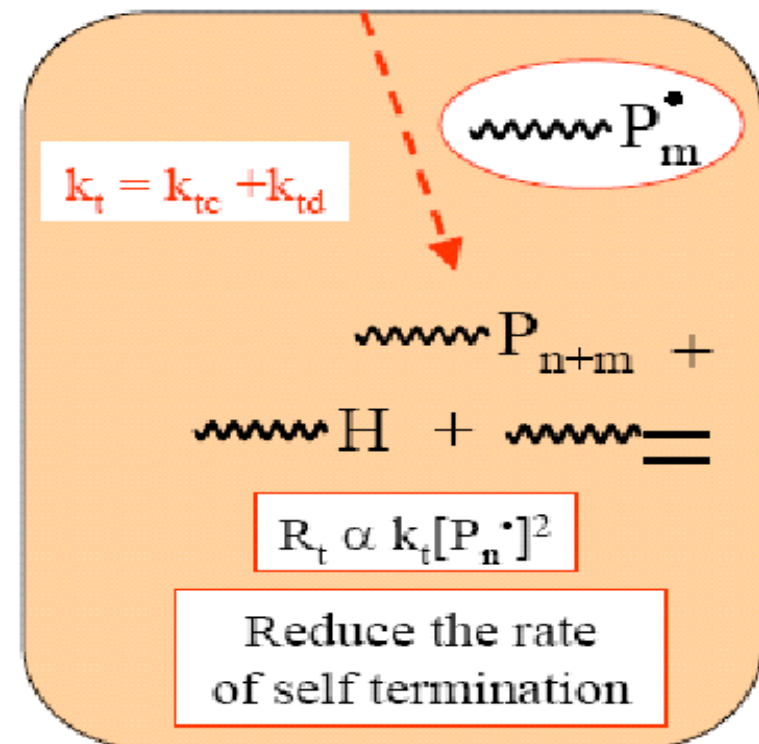
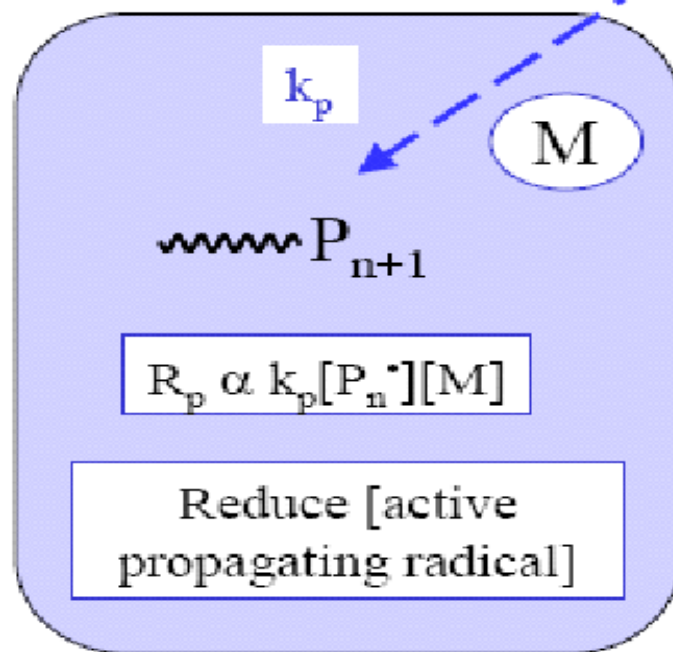
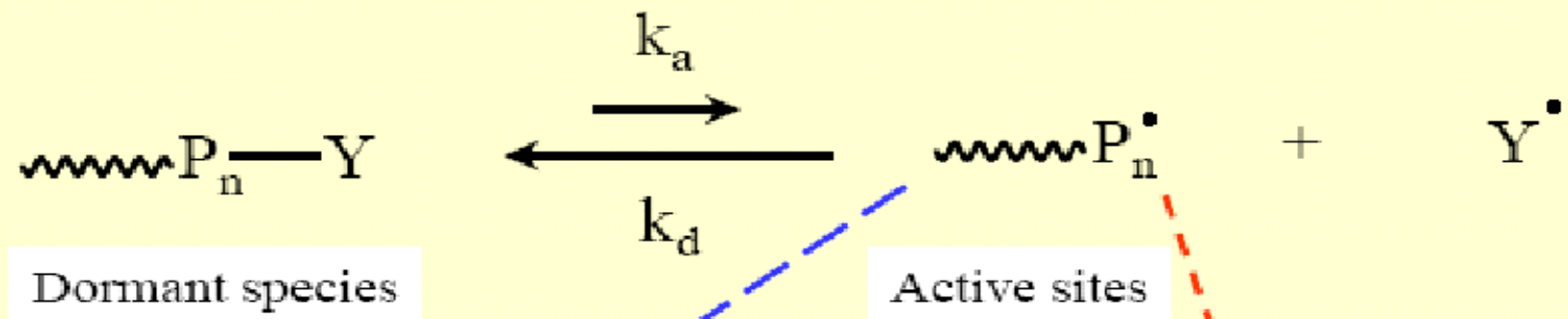
X and Y- halogen; Mt -Cu^I, Ru^{II}, Fe^{II}, Ni^{II}, etc; M- vinyl monomer, L-Ligand

Advantages of Copper-mediated ATRP

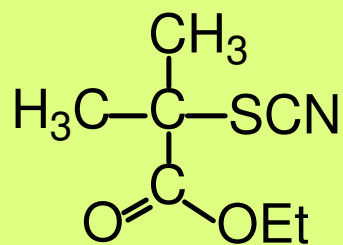


- Significantly suppresses chain-transfer and chain-termination
- Produces polymers with well-defined molecular weight and narrow molecular weight distribution
- Tolerant to many functional groups
- Wide range of monomers and solvents can be used
- Very robust technique and easy to perform
- Chain-end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

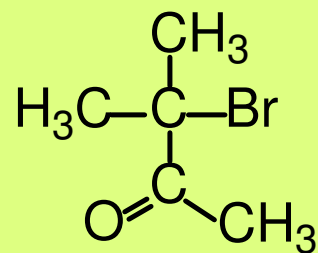
Controlled/ Living Radical Polymerization



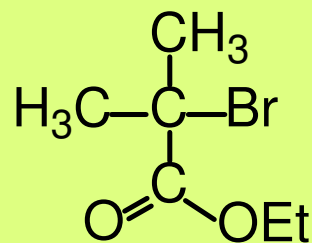
FUNCTIONAL INITIATORS



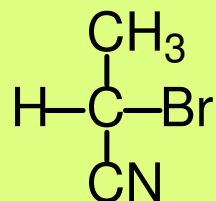
EMTP



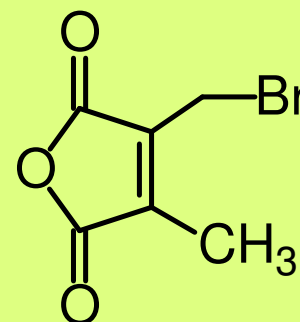
MBB



EB/B

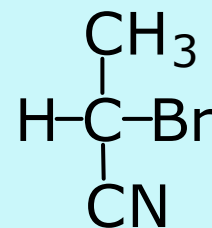
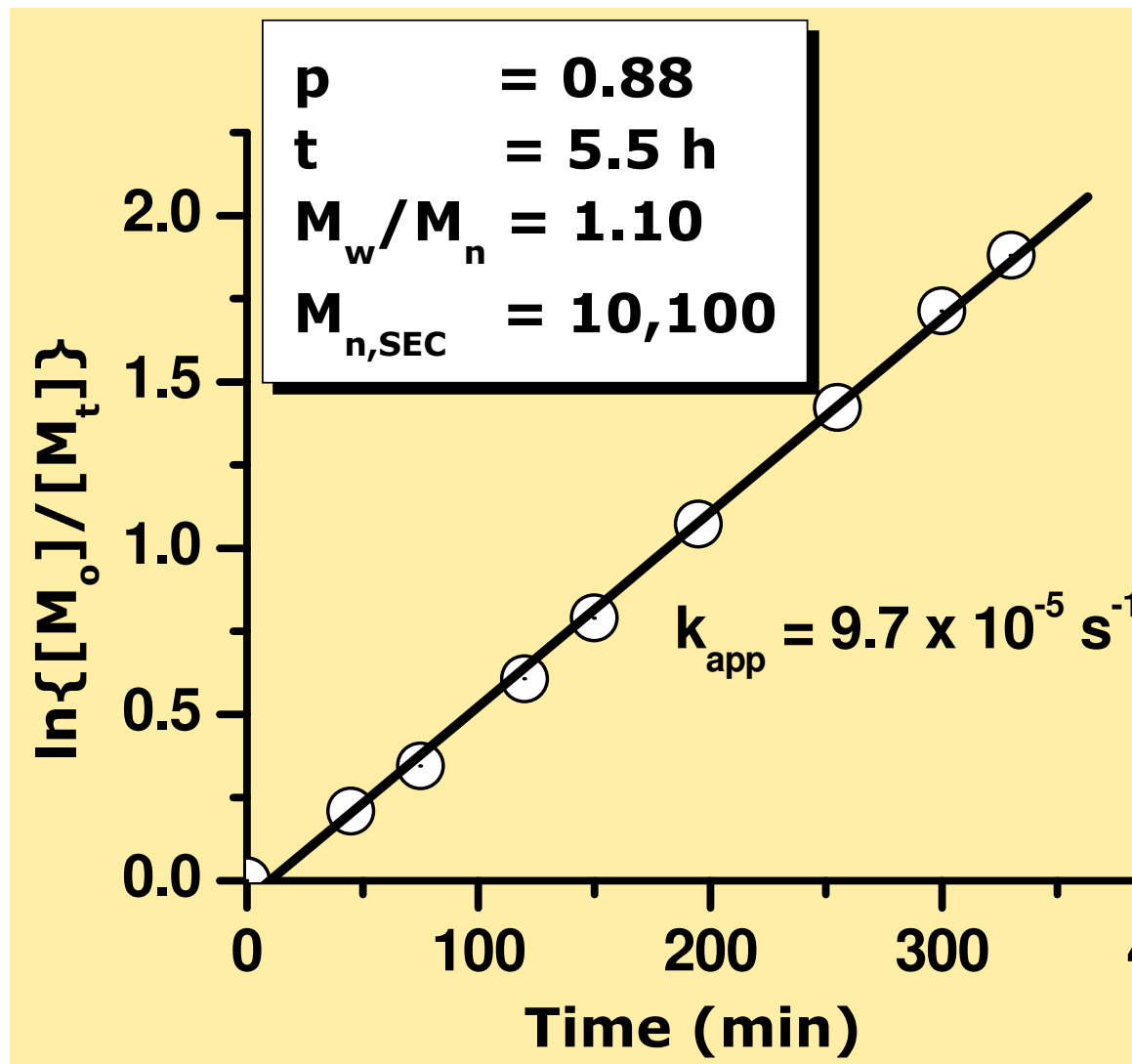


BPN



BMFD

ATRP Of MMA: Bromonitrile Initiator



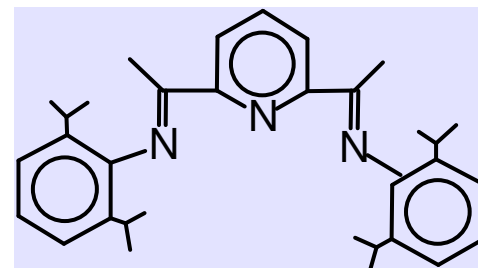
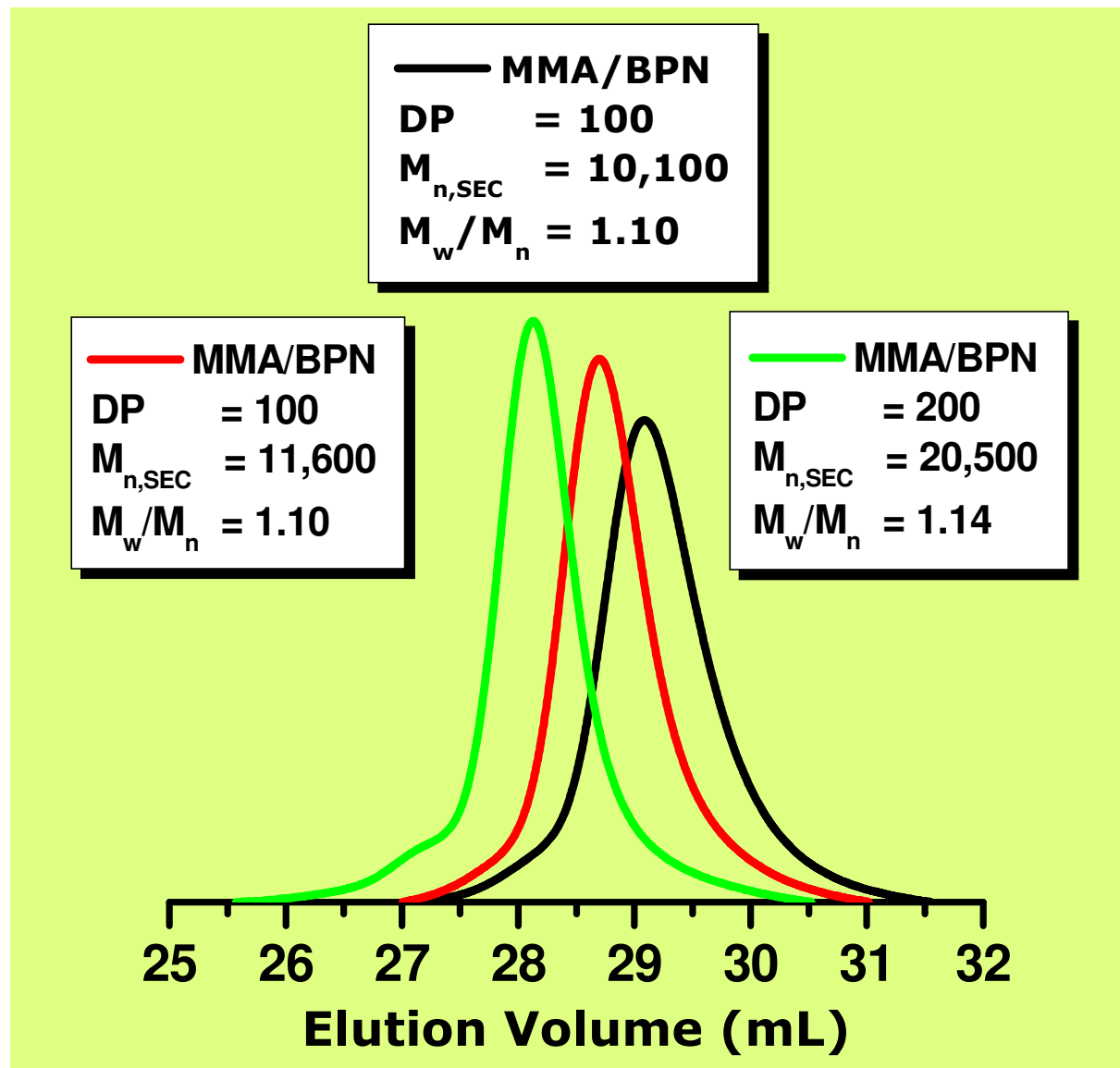
2-bromopropionitrile (BPN)

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 ^a	M _{n,Cal} (x 10 ³)	M _{n,SEC} (x 10 ³)	PDI	I _{eff}
1	85	8.5	7.5	1.15	0.90
2 ^b	90	9.0	9.5	1.16	0.90
3 ^c	55	5.5	6.0	1.12	0.90
4 ^d	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 M

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

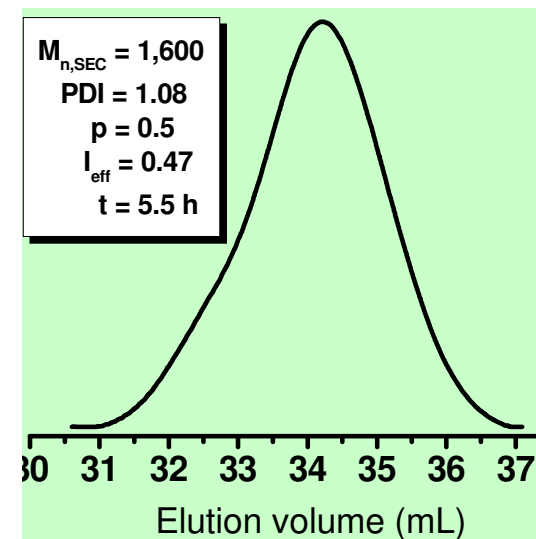
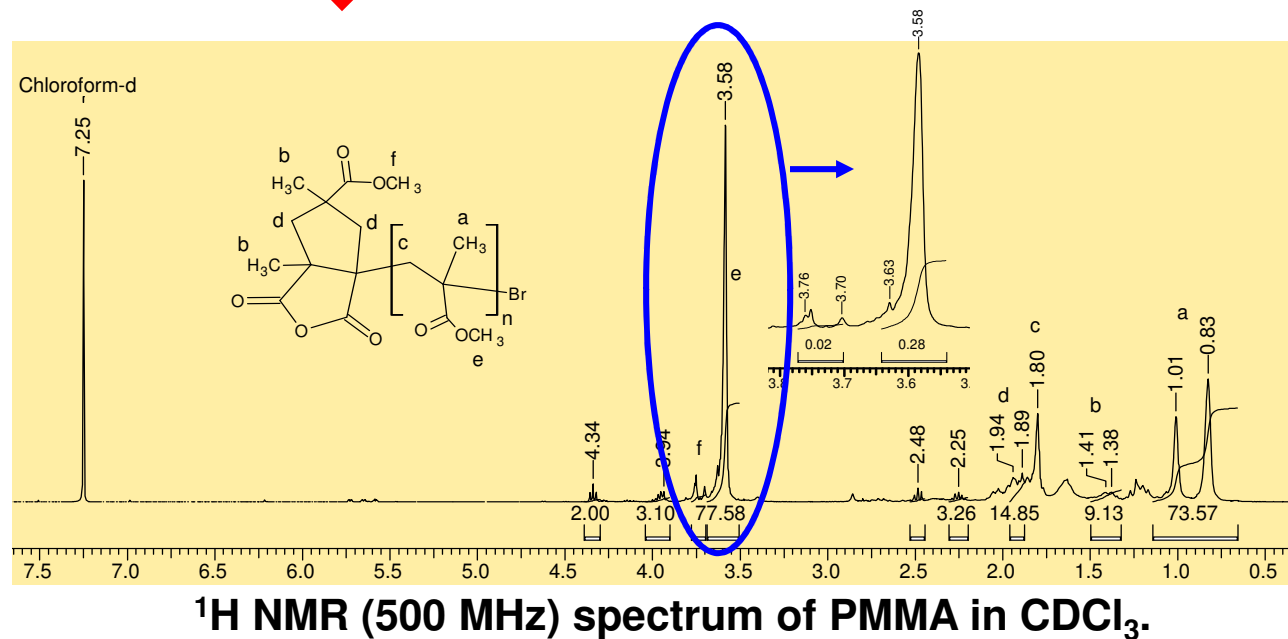
[MMA]: [BMFD]: [CuX]:
[BPIEP] = 100: 1: 1: 2,

← Polymerization reactions were homogeneous in nature. The addition of initiator changed the color of reaction even at RT.

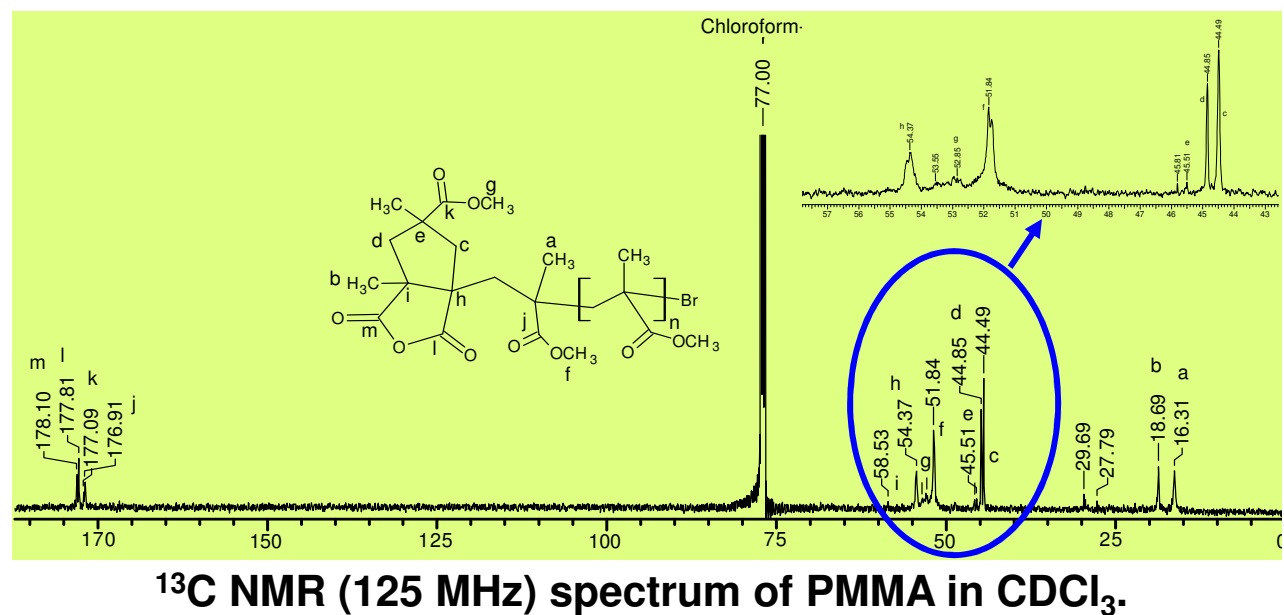
← High conversion and high I_{eff} were obtained with lower PDI.



Analysis Of PMMA-BMFD



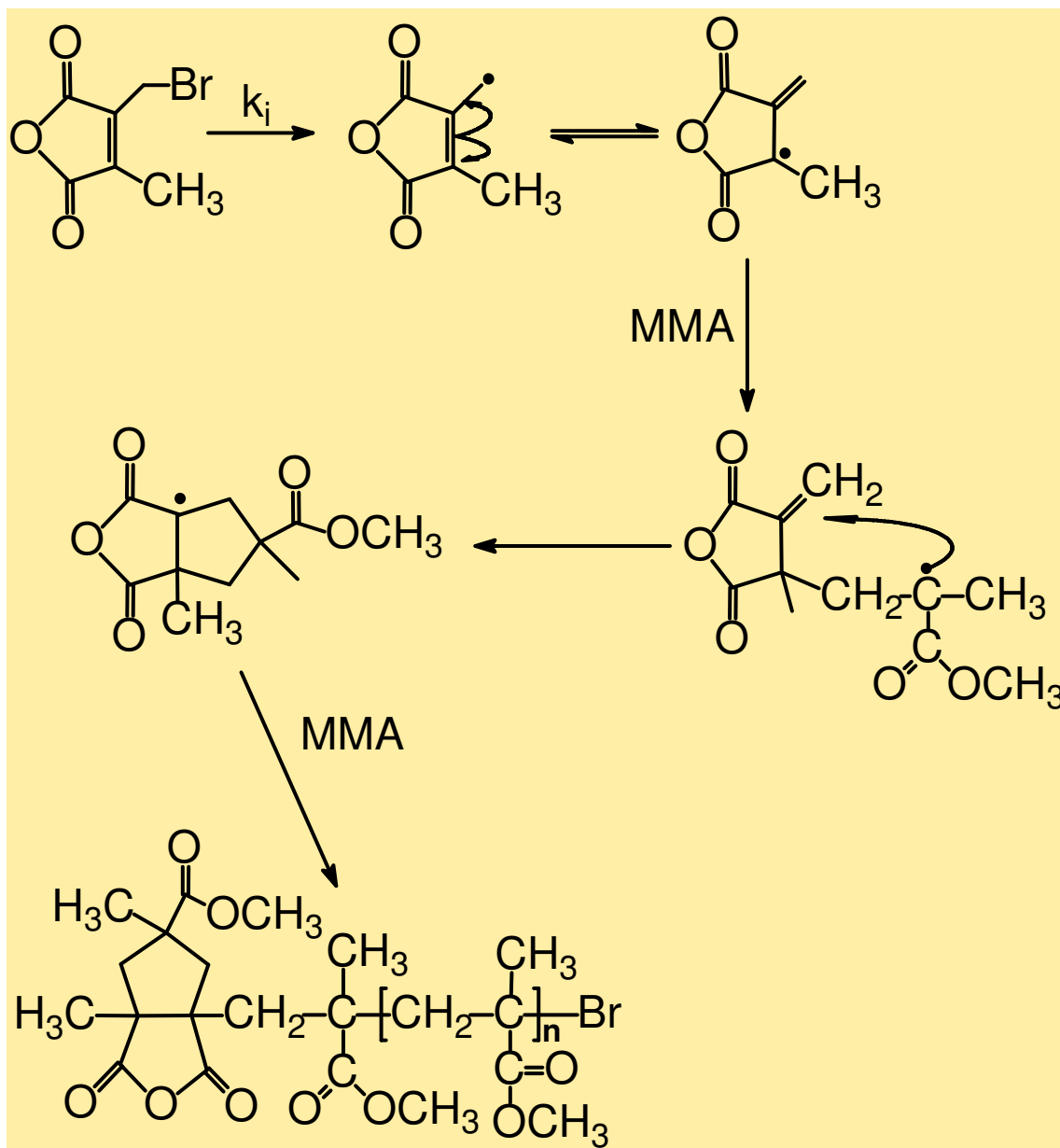
GPC eluogram



$$DP_{NMR}(\text{OCH}_3) = 14$$

$$DP_{SEC} = 15$$

Mechanism of Initiation: Head-group ?



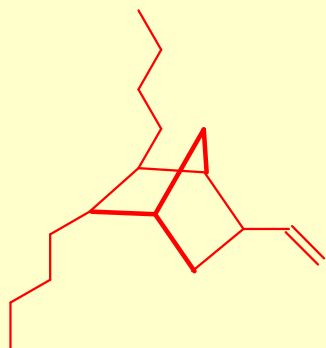
➤ Primary radical undergoes rearrangement

➤ Activation of $=CH_2$ due adjacent anhydride group favours ring closure rather than addition of monomer. \ leading to a new annular tertiary radical

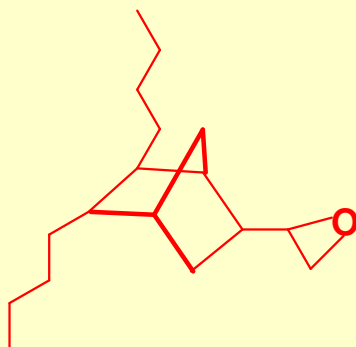
Controlled or “Living” polymerization of olefins

- **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**

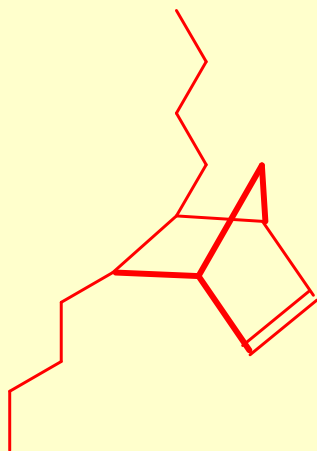
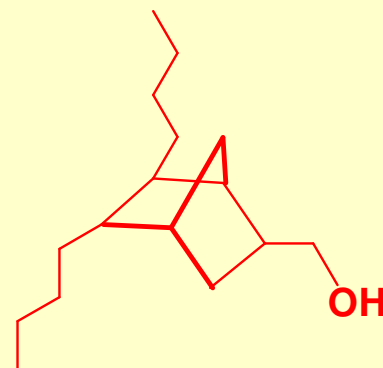
IN CHAIN FUNCTIONALIZATION OF POLY(OLEFIN)S



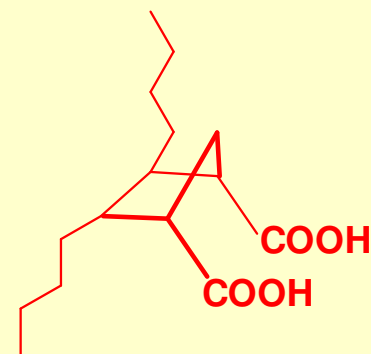
S. Marathe(1994)



K. Radhakrishnan (1998)

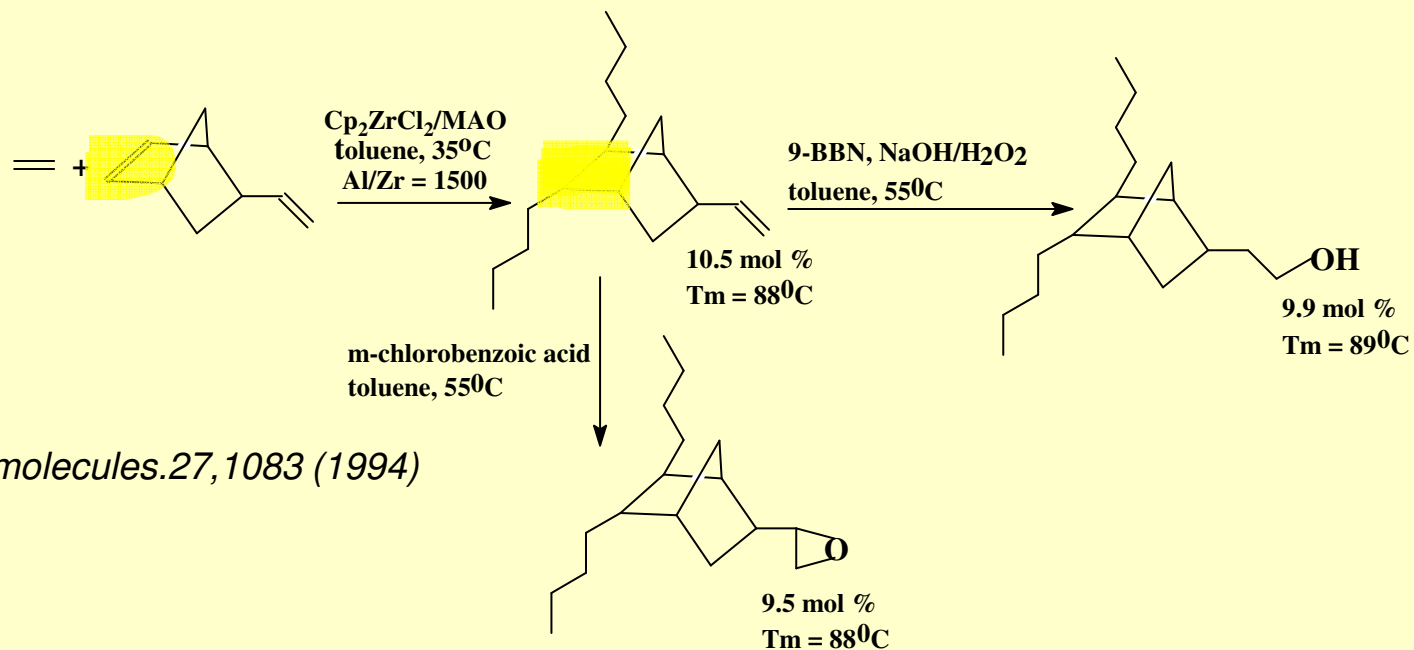


K. Radhakrishnan (1998)

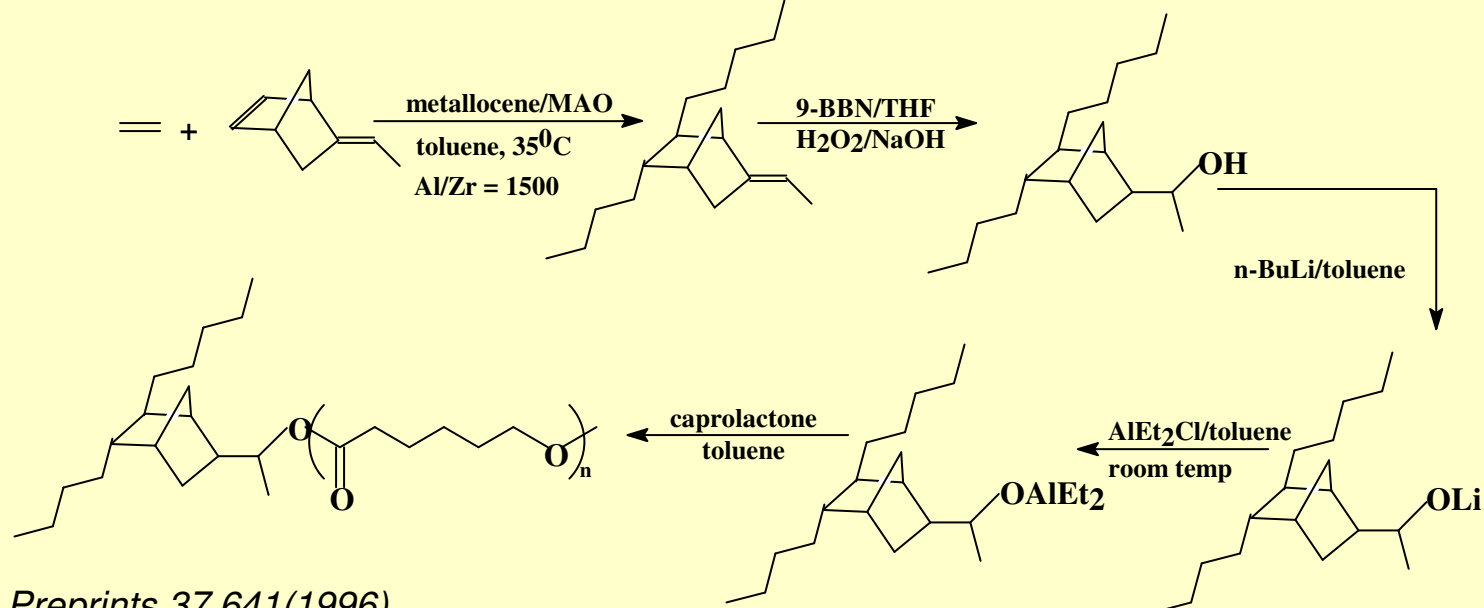


**K. Radhakrishnan, M.J. Yanjarappa
(2000)**

Post polymerization functionalization reactions



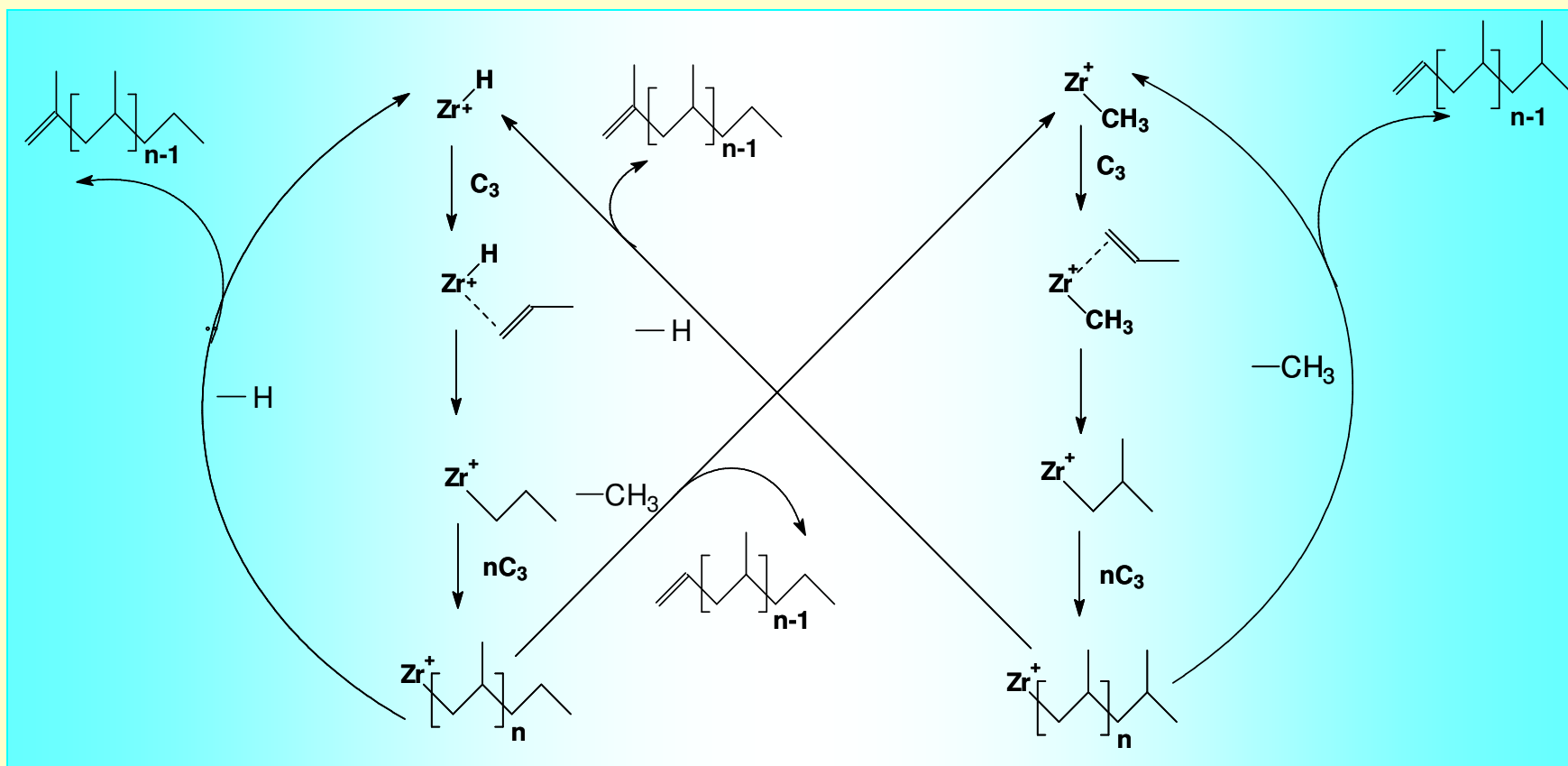
Macromolecules.27,1083 (1994)



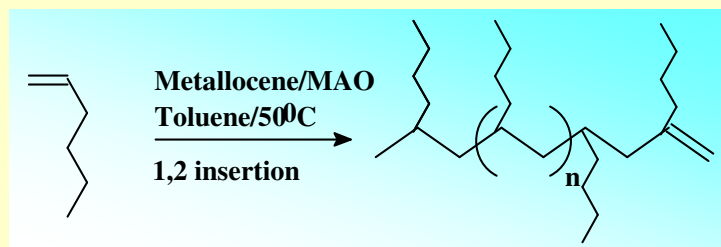
Polym Preprints,37,641(1996)

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)



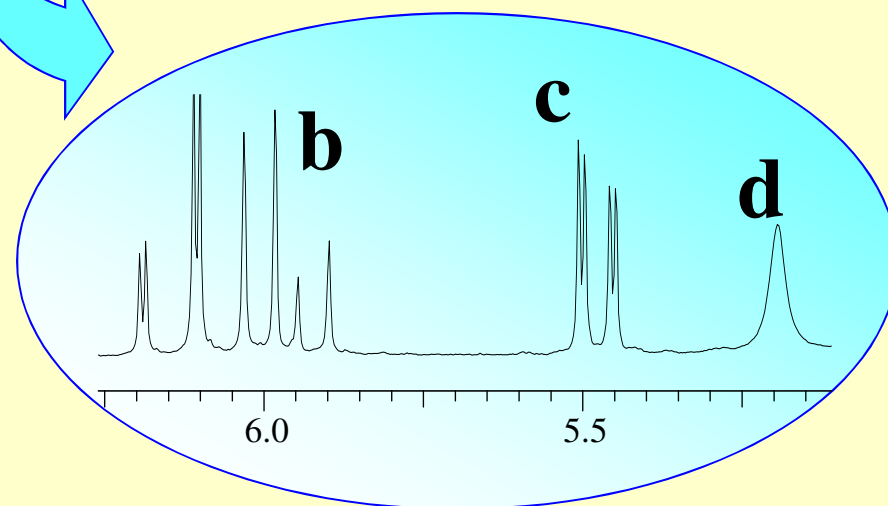
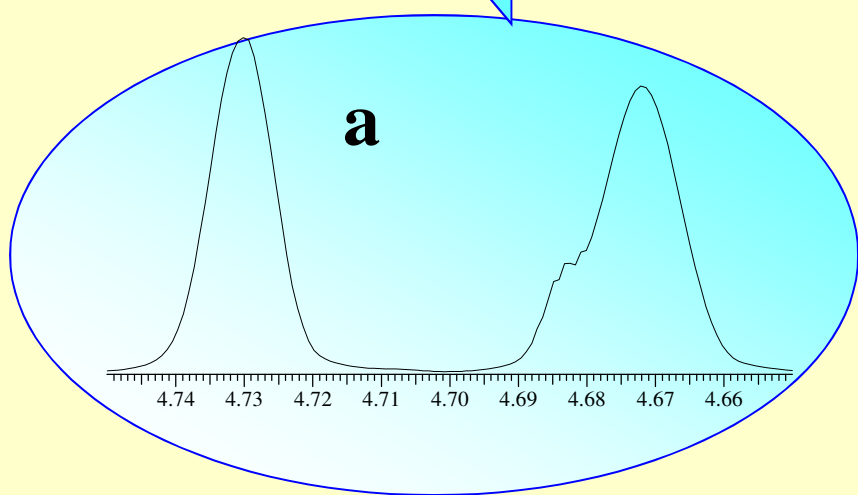
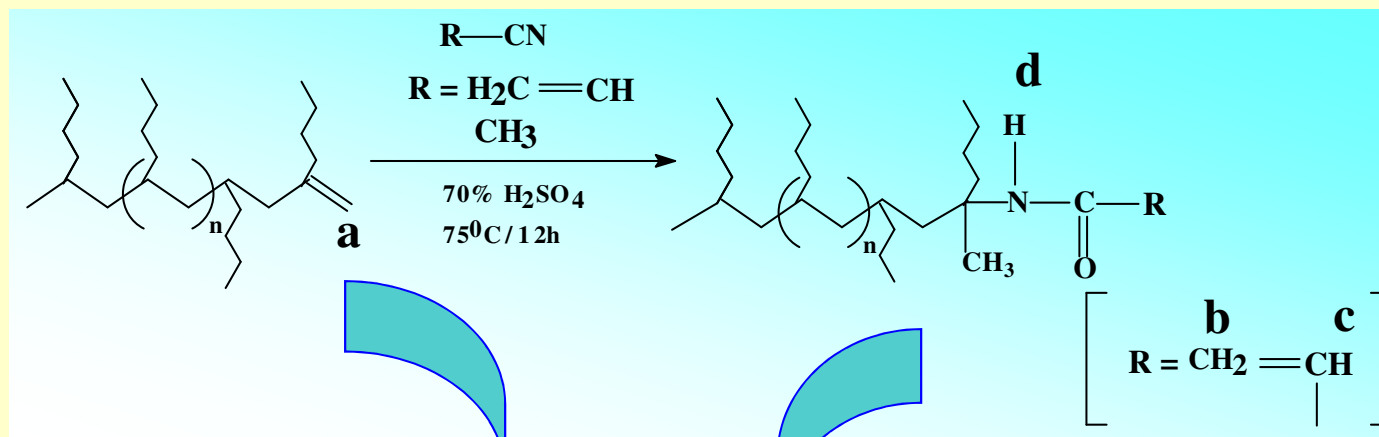
Mn = 300 - 2000

Fn > 95%, Mw/Mn = 2

n = 3-10

Metallocene	Temp (^oC)	Mn by VPO	Mn by ¹H NMR	mol% Vinylidene unsaturation
Cp₂ZrCl₂	50	370	380	98
	40	580	600	96
	30	860	900	95
n-BuCp₂ZrCl₂	50	440	460	98
	40	700	730	96
	30	1020	1100	93

RITTER REACTION USING VINYLIDENE TERMINATED OLIGO(HEXENE-1)



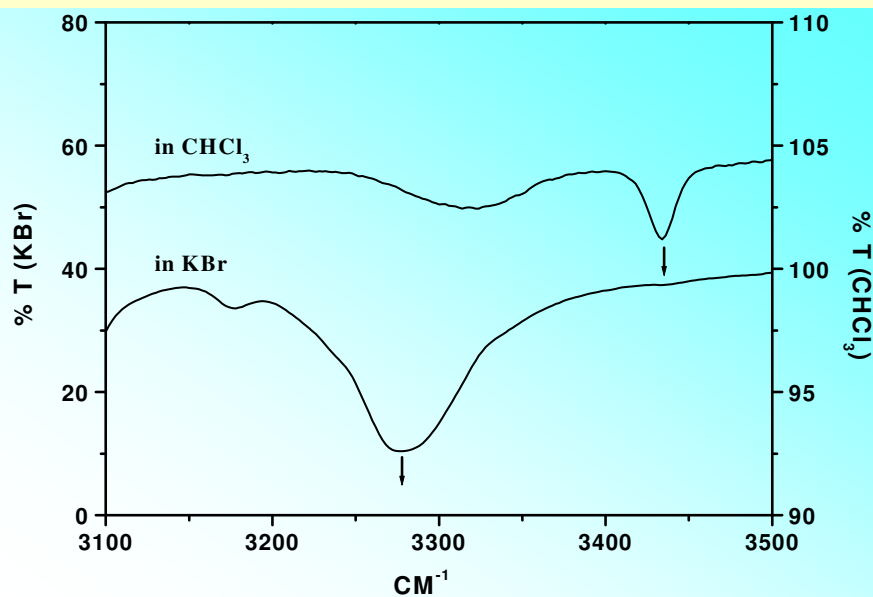
RITTER REACTION OF VINYLIDENE TERMINATED POLY(HEXENE-1) WITH ACRYLONITRILE

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% H₂SO₄ catalyst, Temperature = 70°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.

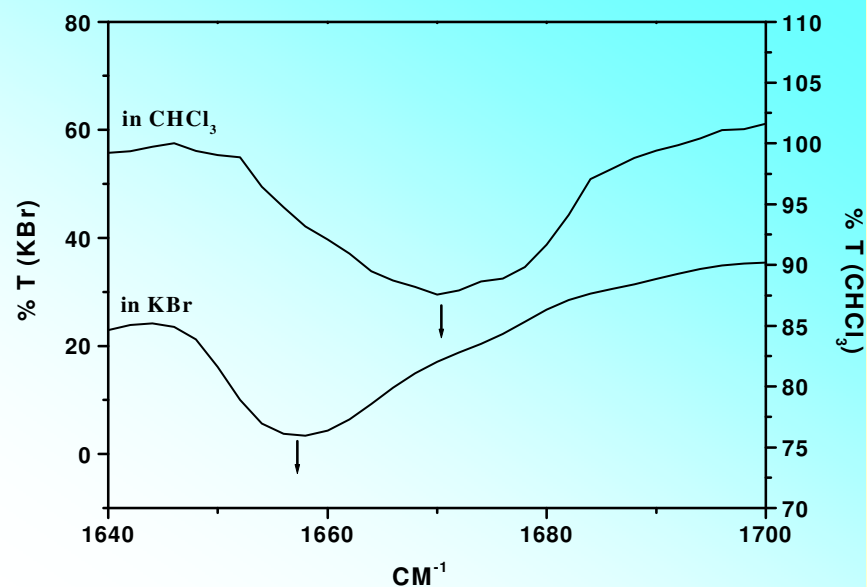
EVIDENCE OF INTERMOLECULAR HYDROGEN BONDING (FT-IR)



N-H stretch

KBr = 3278 cm^{-1}

CHCl_3 = 3434 cm^{-1}

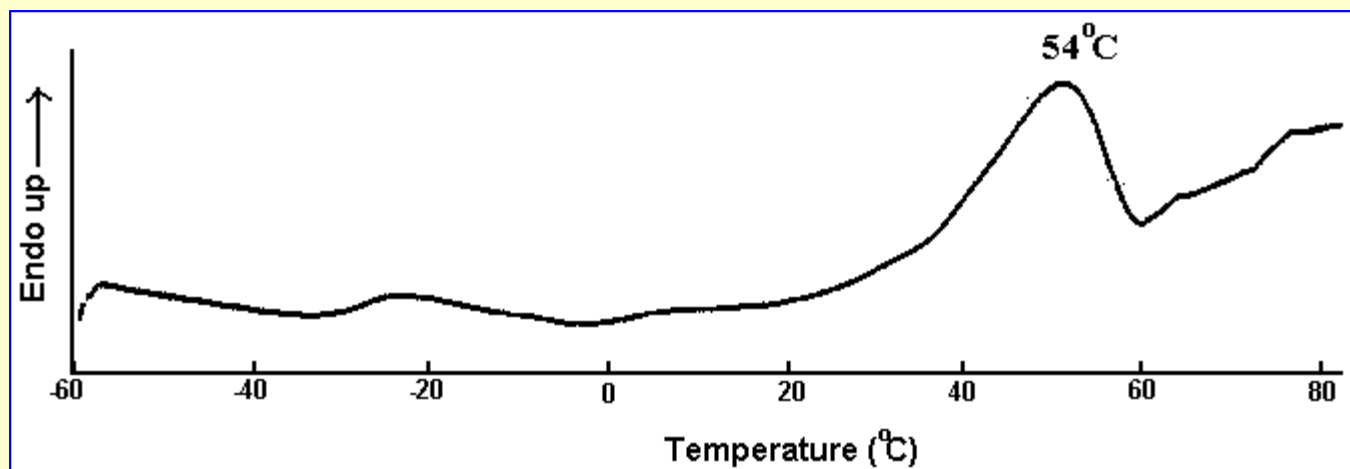


C=O stretch

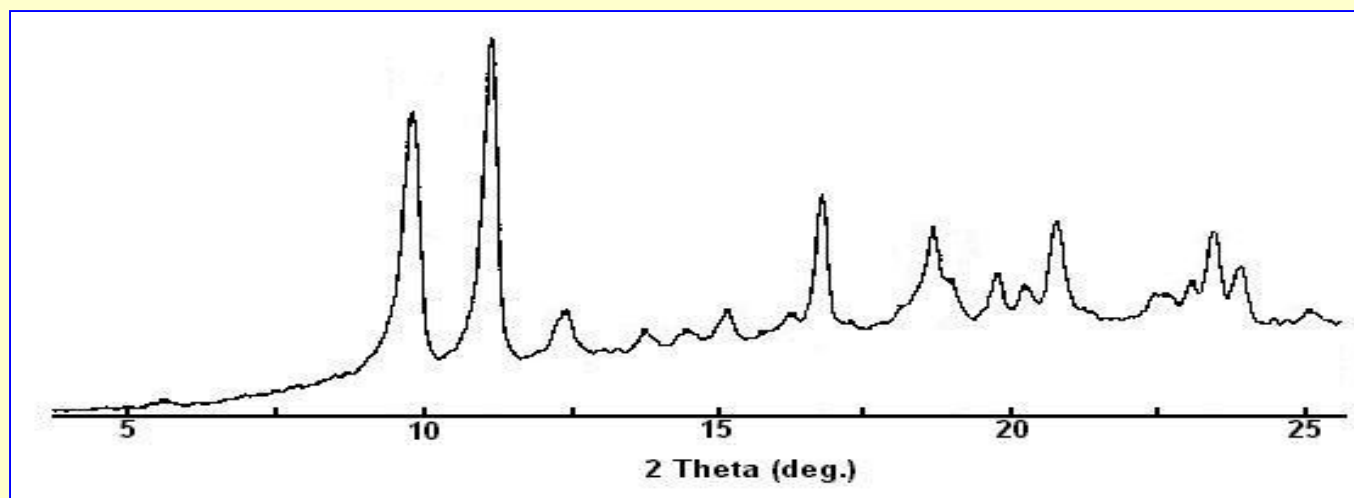
KBr = 1658 cm^{-1}

CHCl_3 = 1670 cm^{-1}

CRYSTALLINITY DUE TO AMIDE FUNCTIONALITY

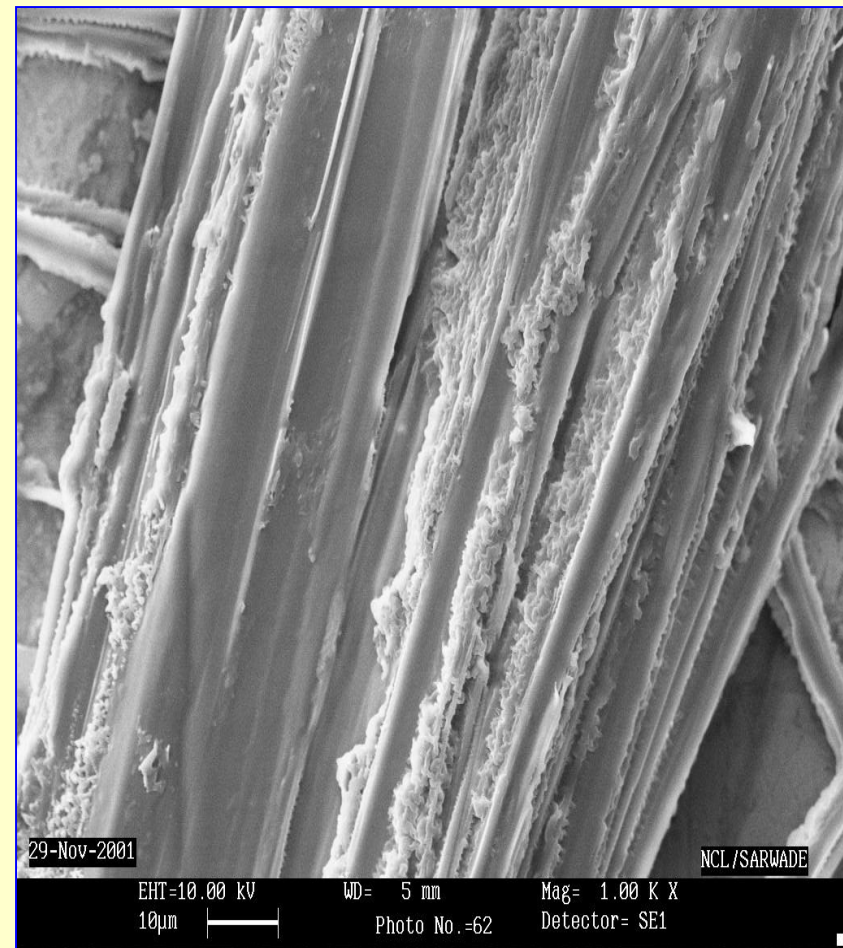
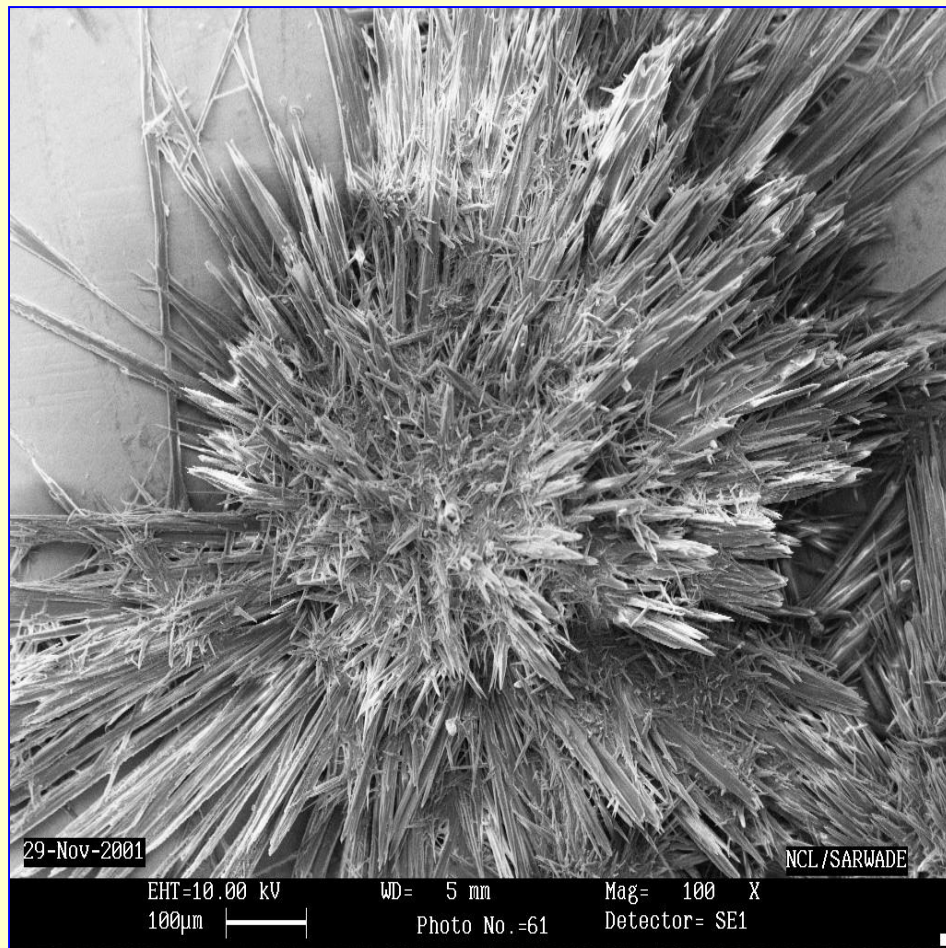


DSC of N-poly(alkenyl) acrylamide.



WAXD of N-poly(alkenyl) acrylamide

SCANNING ELECTRON MICROSCOPY



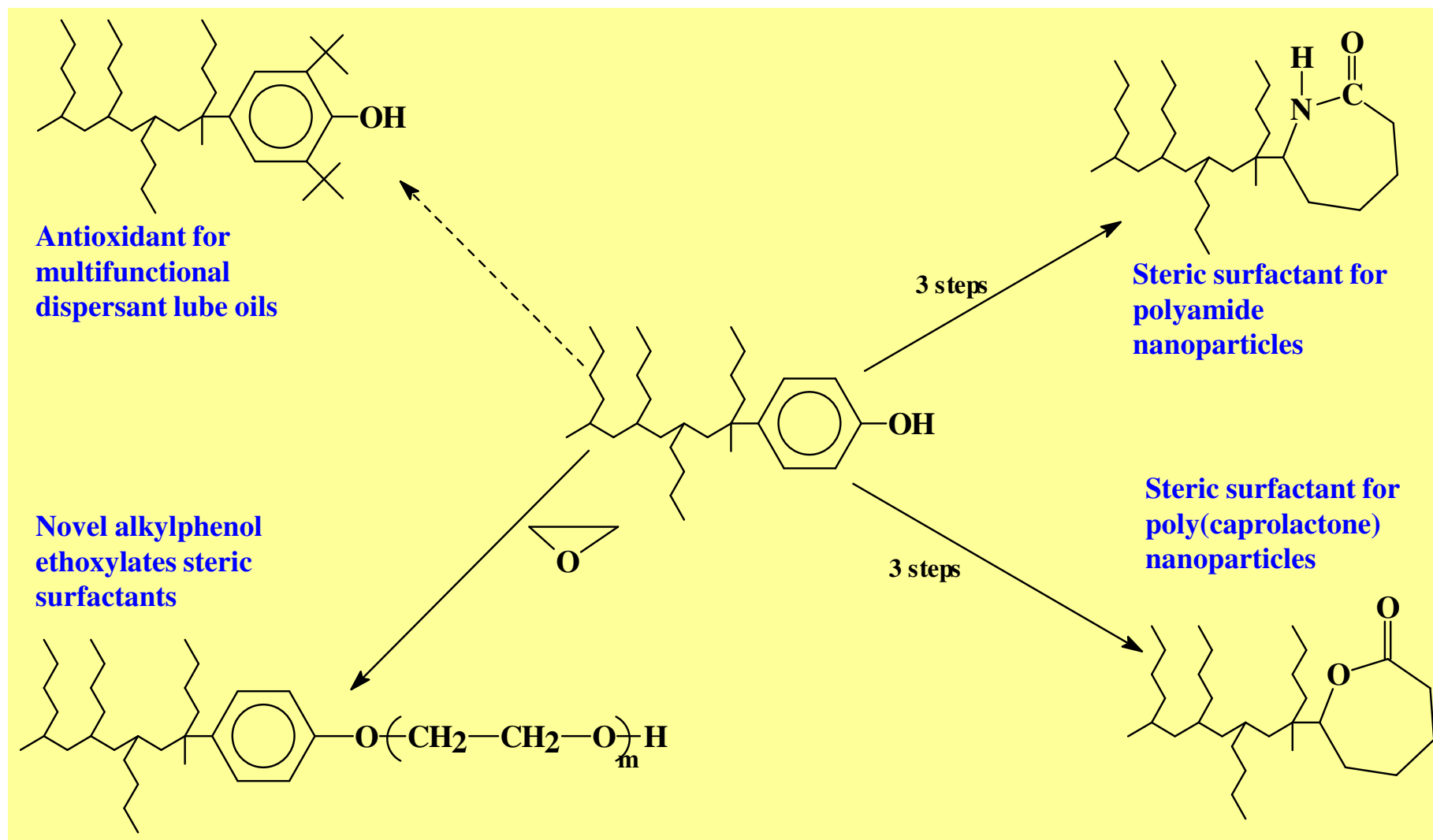
CONCLUSIONS

N-poly(alkenyl) acrylamides were found to be

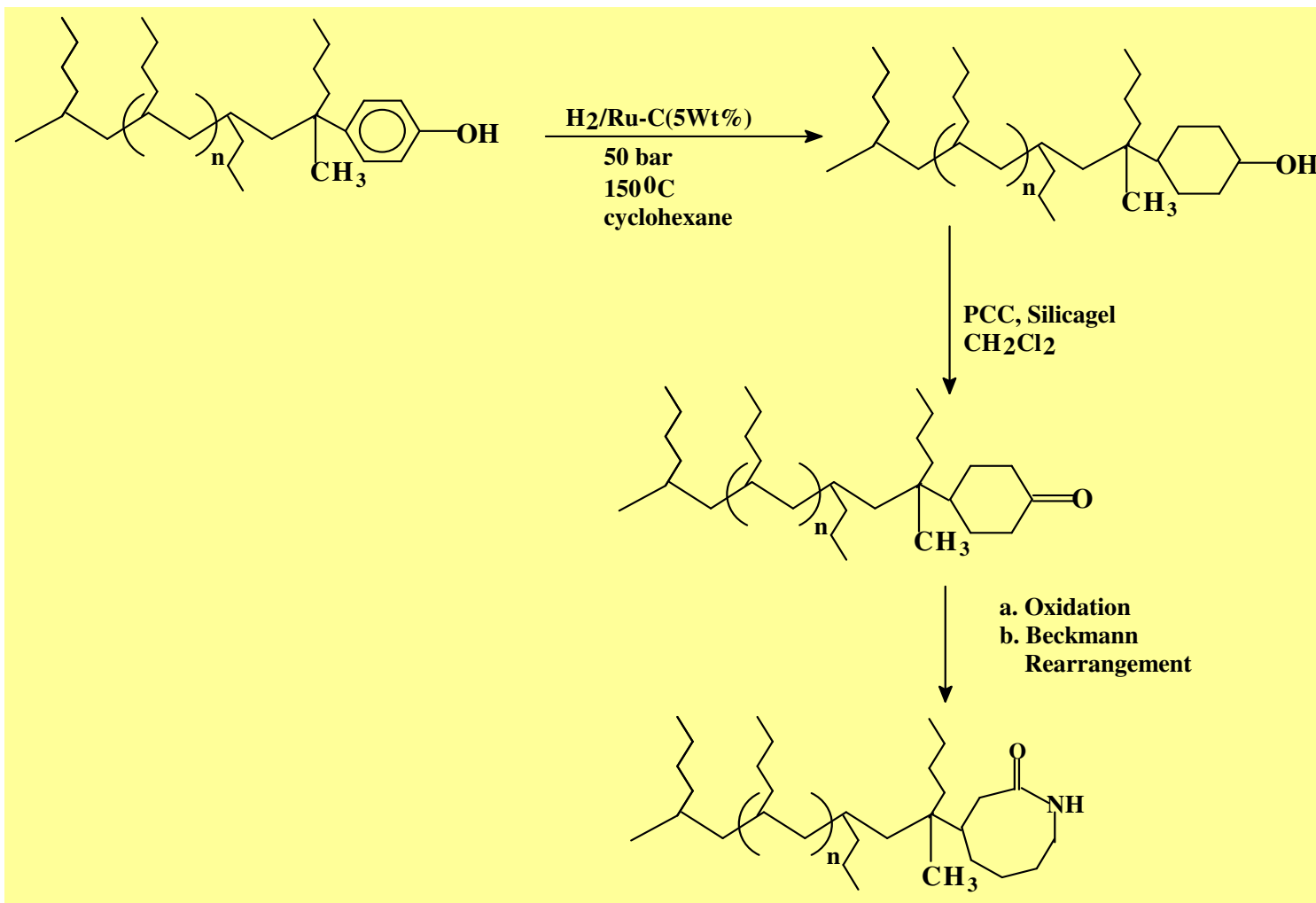
- Ampiphilic in nature.**
- Amide groups were found to be intermolecularly hydrogen bonded.**
- DSC exhibits a melting endotherm arising due to the dissociation of hydrogen bonds**
- The oligomer crystallizes to form rod like dendritic structure from n-pentane solution**

[illegible]

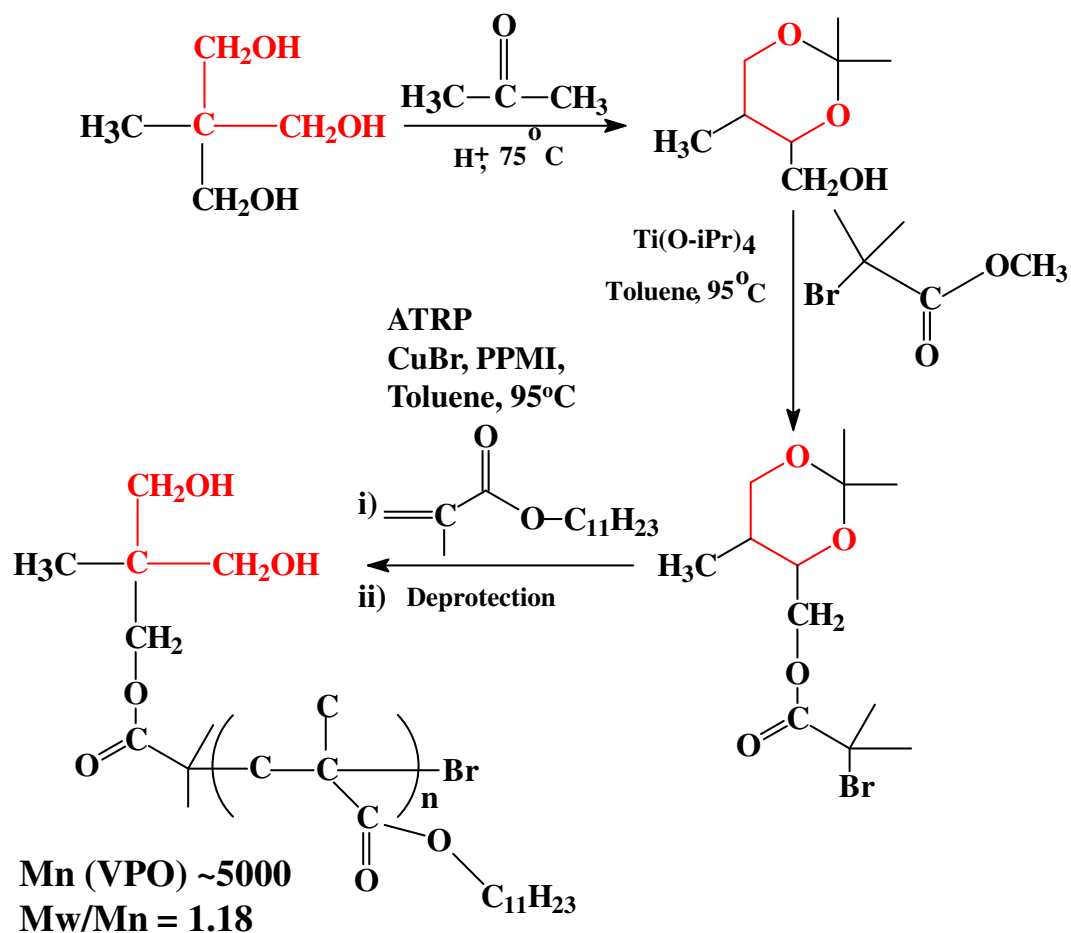
TERMINAL PHENOL FUNCTIONAL POLY(1-HEXENE) : TRANSFORMATIONS OF FUNCTIONAL GROUP



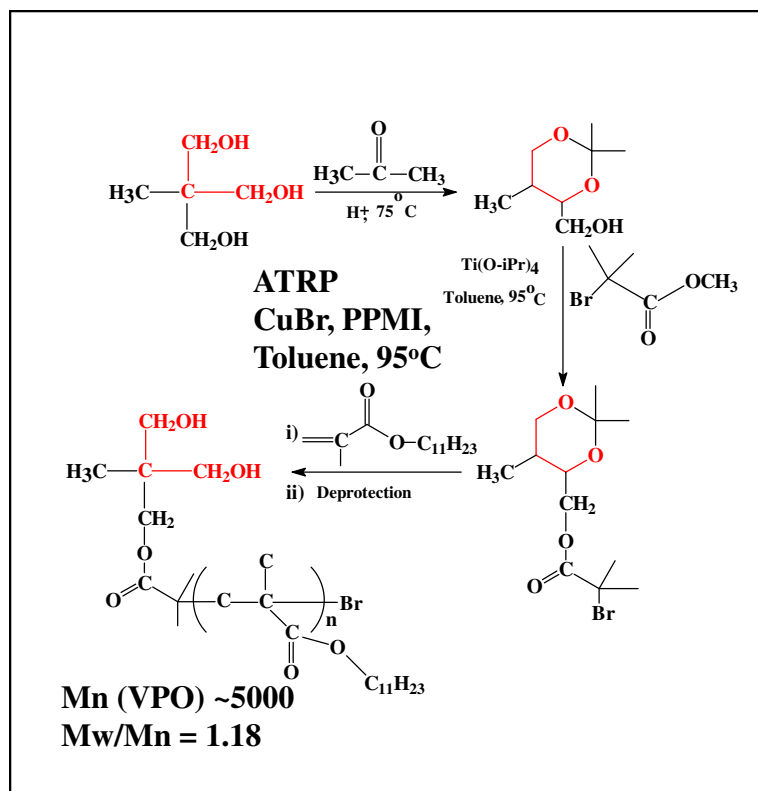
STERIC STABILIZER FOR RING OPENING POLYMERIZATION OF ϵ -CAPROLACTAM



CONTROLLED SYNTHESIS OF DIOL FUNCTIONALIZED POLY(METHACRYLATE)S



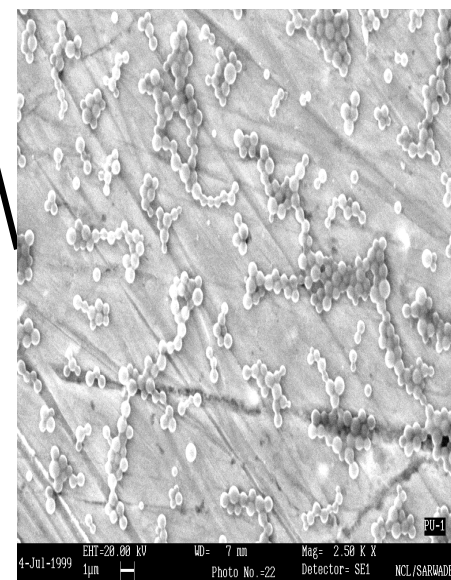
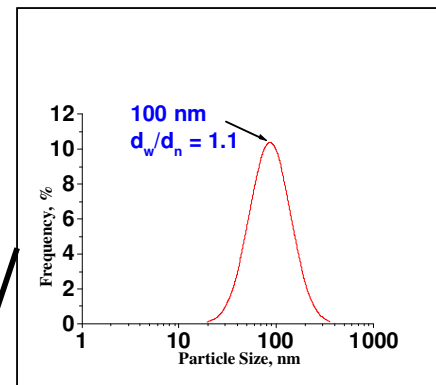
NEARLY MONODISPERSE POLYURETHANE NANOPARTICLES - FUNCTIONAL POLY(LMA) AS STERIC SURFACTANTS

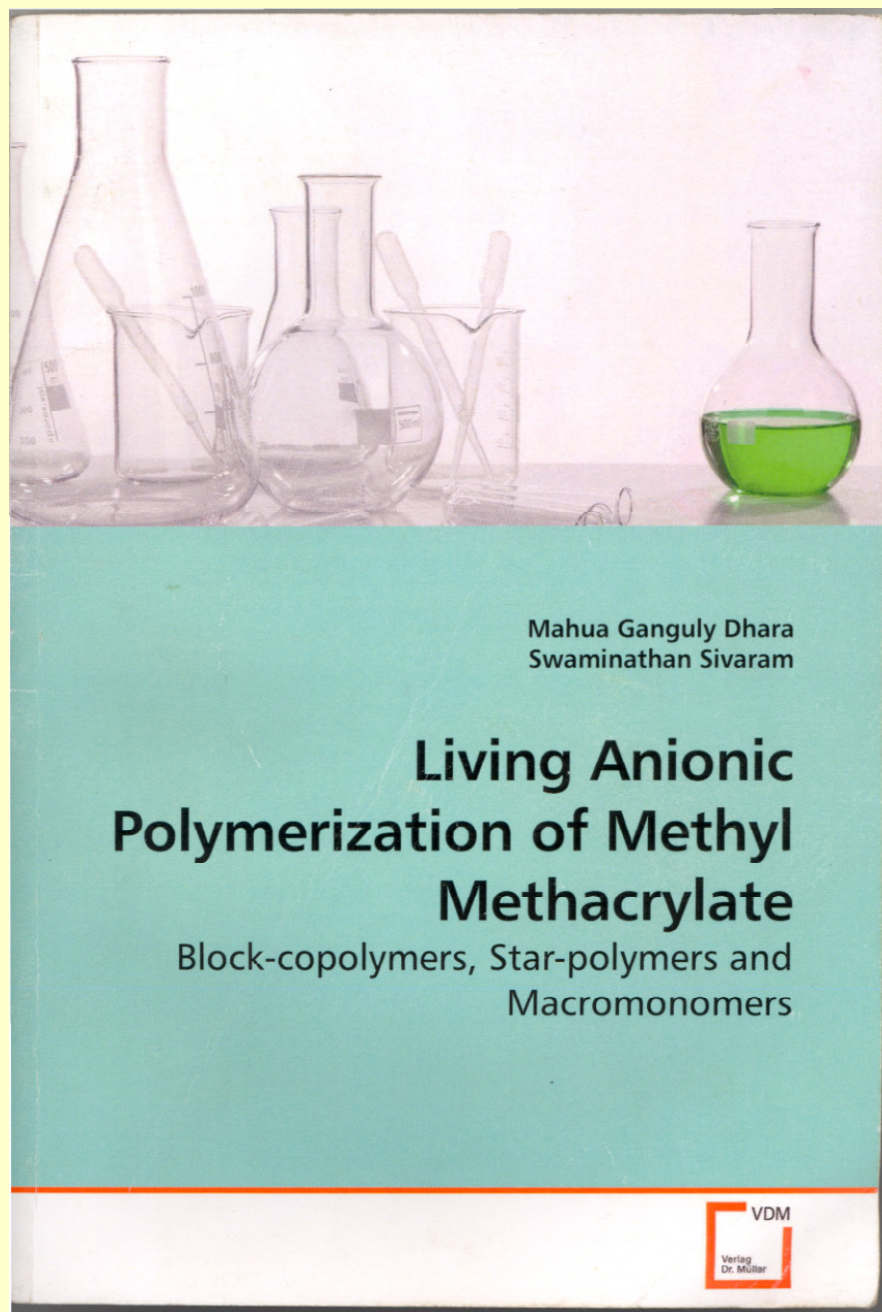


Stabilizer 5 wt %
DBTL 0.005%
Cyclohexane 20 parts

TDI
60°C, 4 h
EHG
60°C, 4 h

PU particles





ACKNOWLEDGMENTS

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

THANK YOU

