SCIENCE FOR PLEASURE AND PROFIT: MY EXCURSIONS IN POLYMER CHEMISTRY

Dr. S. Sivaram,
National Chemical Laboratory,
Pune-411 008, INDIA

Tel : 0091 20 2590 2614
Fax : 0091 20 2590 2615
Email : s.sivaram@ncl.res.in
Visit us at : http://www.ncl-india.org

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH, KOLKATTA

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Science : Is it for

- Pleasure ?
- Profit ?, or
- Pleasure and Profit ?

Does it benefit anybody ?
Is it worth the money spent on it ?
Is it directed at the right objectives ?
Is there too much or too little?
Is it too pure or applied ?
What are the rewards of research ?

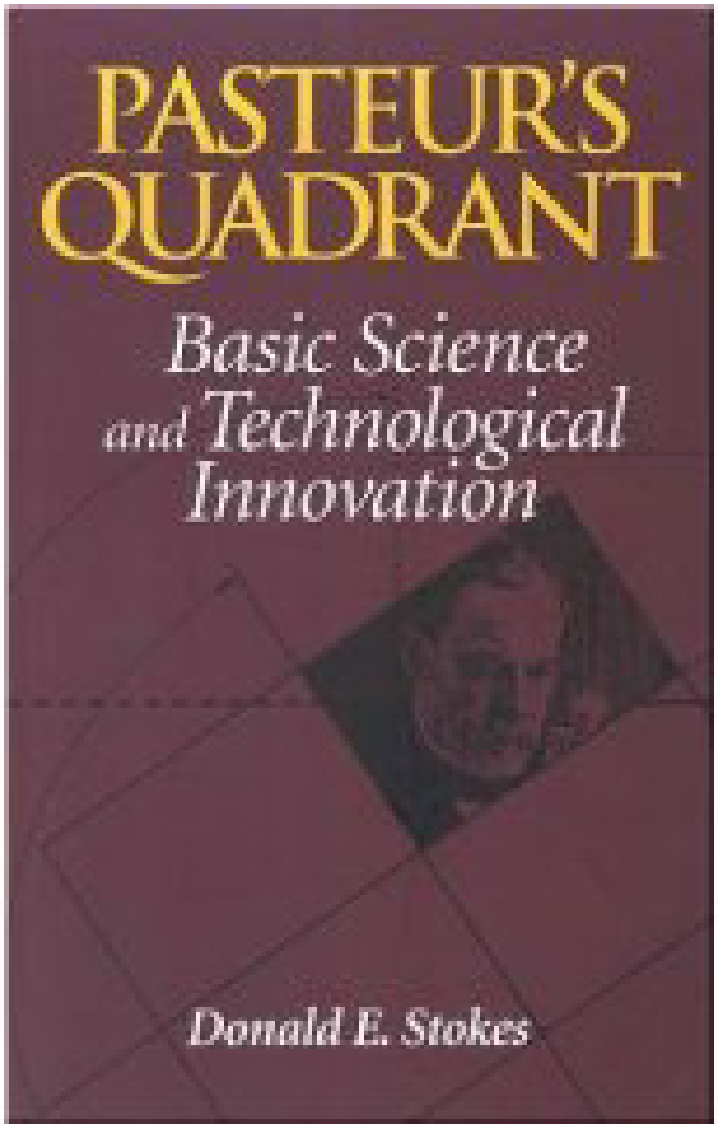
As the world attains prosperity, science is taken for granted and is increasingly being questioned

WHY DO YOU WANT TO BE A SCIENTIST?

- **To be famous and be known**
- **To become rich**
- **To be useful to society and help humanity**
- **To invent and create new products for consumers**
- **To teach, excite, inspire and communicate science**

SCIENCE IN THE 21st CENTURY

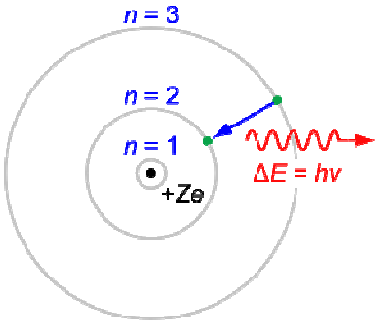
- **Blue skies vs Directed Science**
- **Small vs Big Science**
- **Individual vs Team Science**
- **Curiosity driven vs Grand Challenges or Utilitarian Science**
- **Open access vs Intellectual Property**

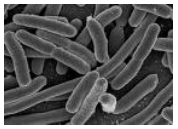

PASTEUR'S
QUADRANT
Basic Science
and Technological
Innovation
Donald E. Stokes

1997

Pasteur's Quadrant

Bohr





Pasteur

Average
Academic
and
Industrial
R & D

Edison

Fundamental Research

Use Inspired Research

TWENTY YEARS OF RESEARCH AT NCL (1989-2009)

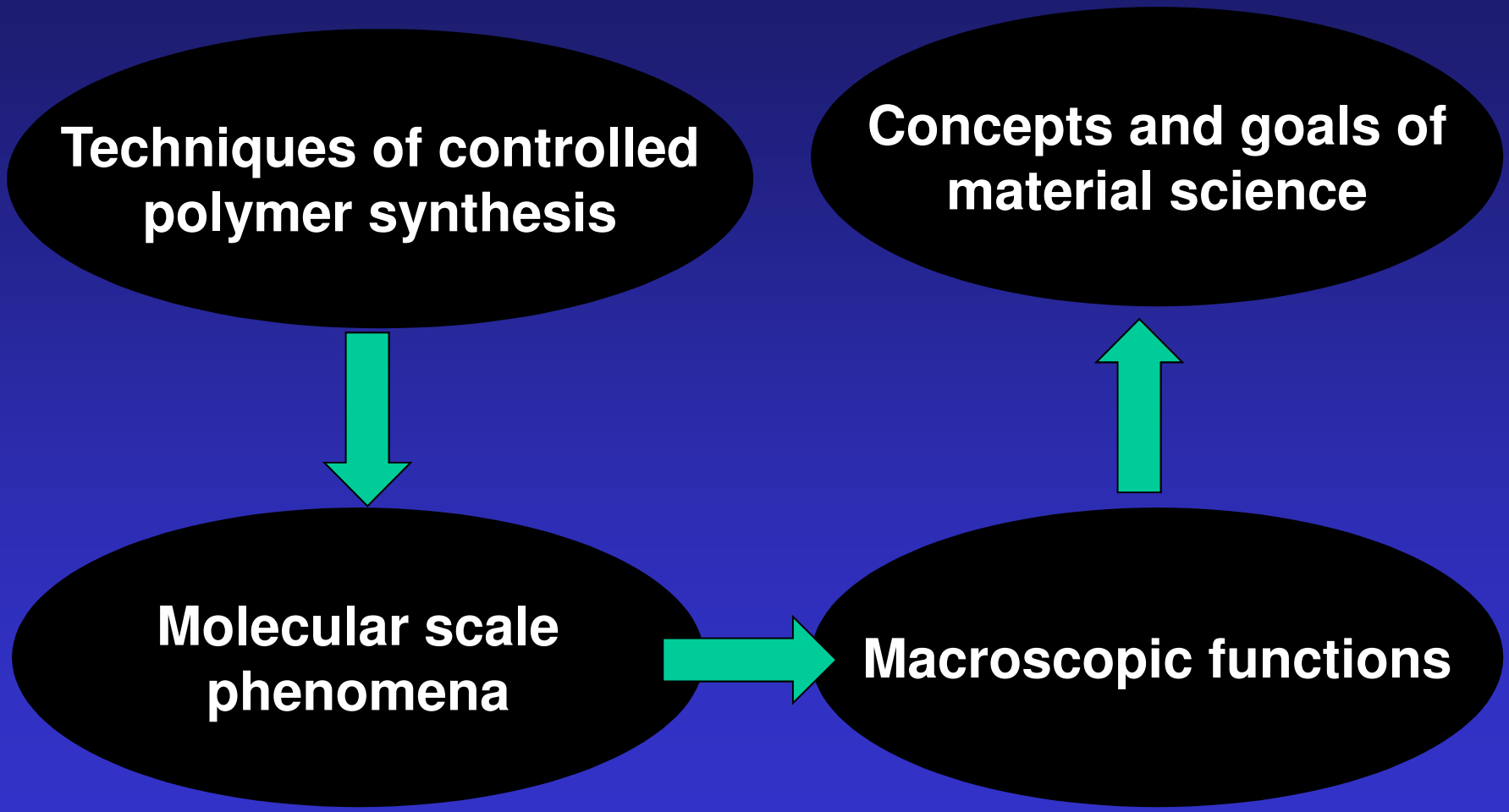
A Recurrent Theme

- **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……



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

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 (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

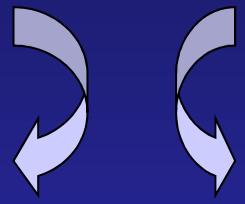
Absence of termination and transfer

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



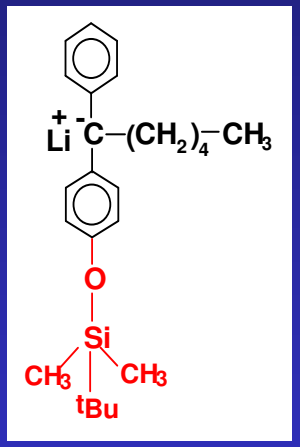
Electrophilic termination

- 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



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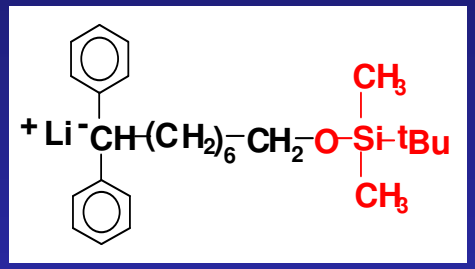

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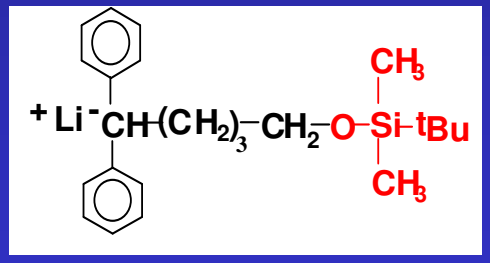
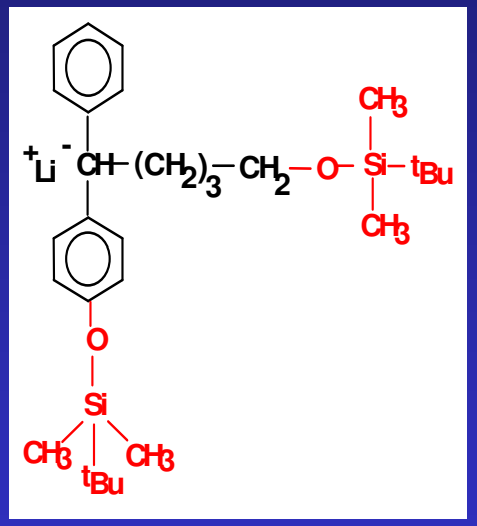


F3

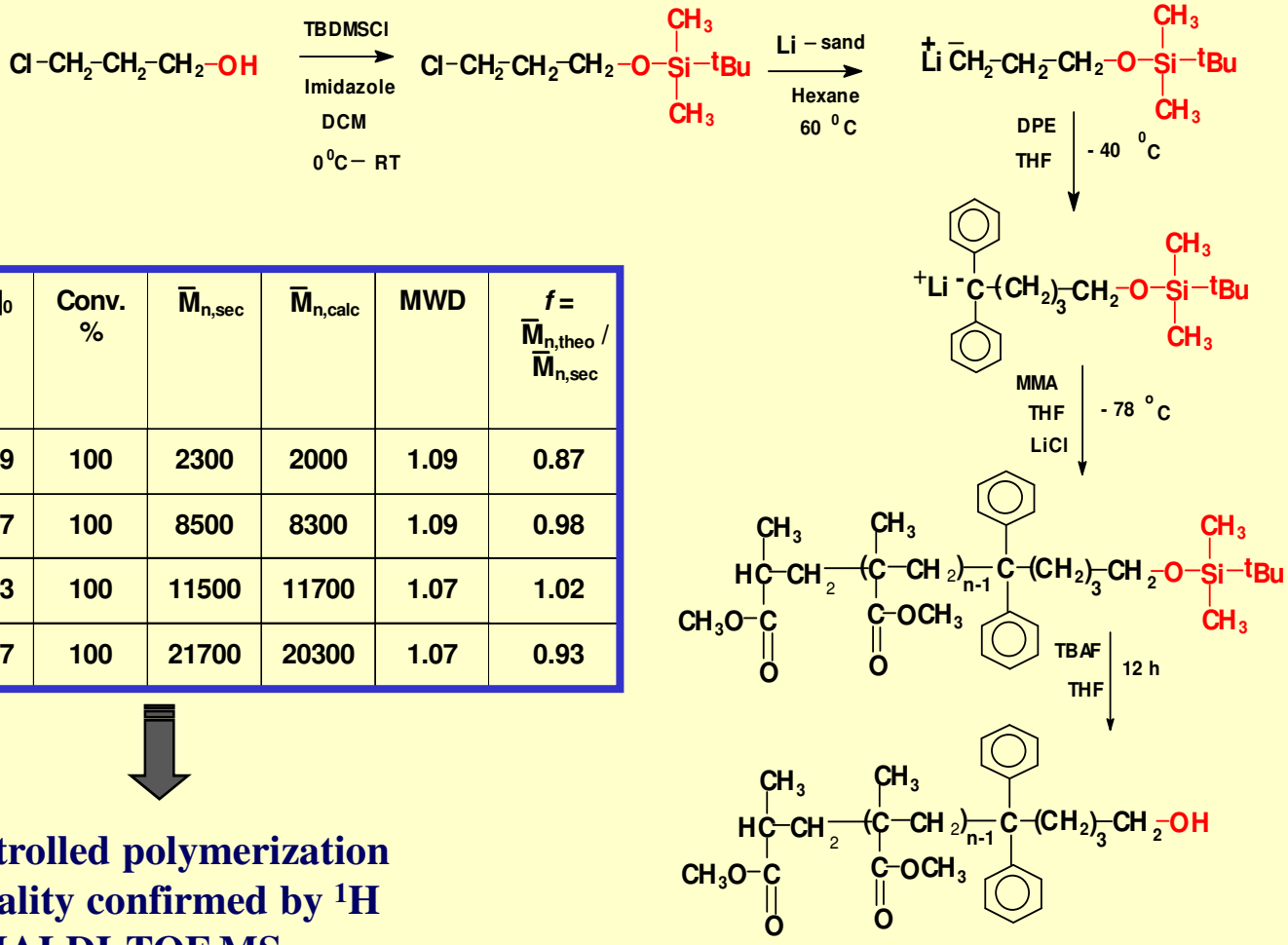


F4

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

Synthesis of Hydroxy End-functional PMMA Using F3

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

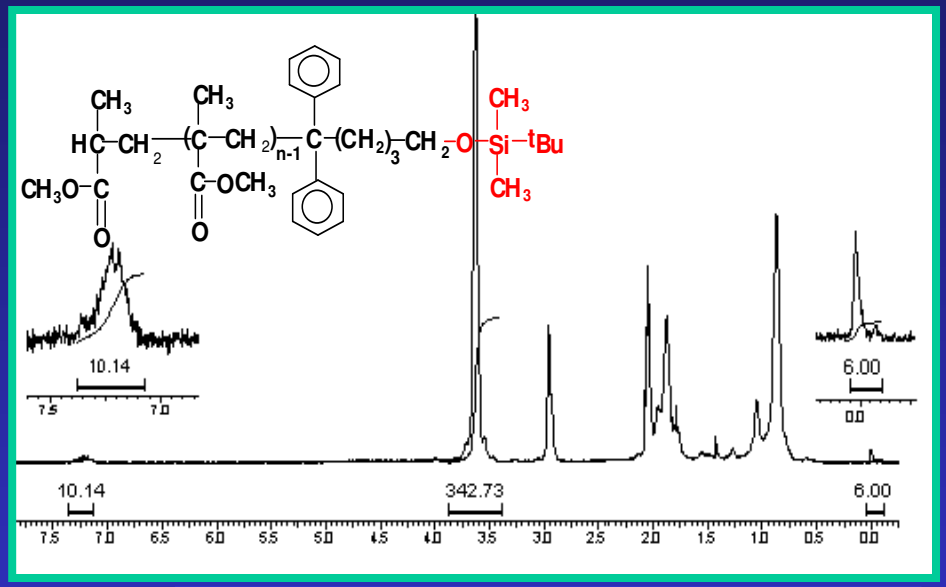


Run no.	$[I]_0$ x10^{-3} m/L	$[M]_0$	Conv. %	$\bar{M}_{n,sec}$	$\bar{M}_{n,calc}$	MWD	$f = \bar{M}_{n,theo} / \bar{M}_{n,sec}$
1	4.45	0.09	100	2300	2000	1.09	0.87
2	3.22	0.27	100	8500	8300	1.09	0.98
3	2.79	0.33	100	11500	11700	1.07	1.02
4	1.84	0.37	100	21700	20300	1.07	0.93

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

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

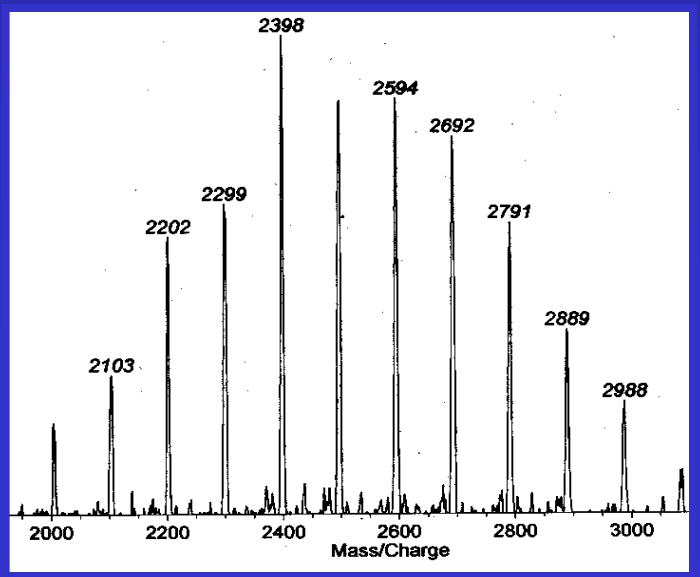
^{1}H NMR (500 MHz, acetone-d6) spectra of silyl-protected hydroxy-PMMA (Mn,sec=11500)



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

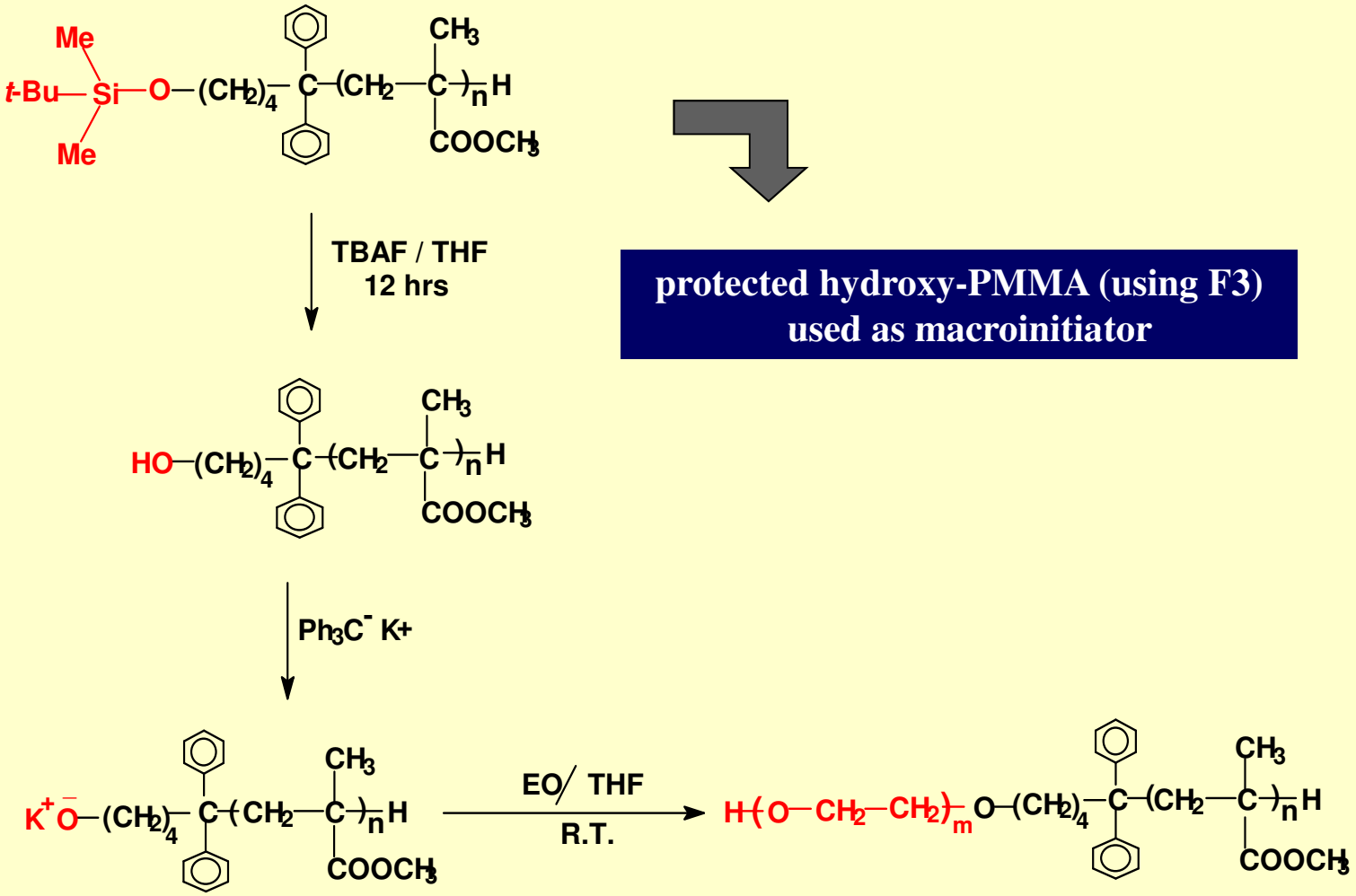
Theoretical end-group mass = 354+101+39= 493

Also, single generation of polymers

Presence of free –OH at all chain-ends

Synthesis of PMMA-*block*-PEO Copolymer

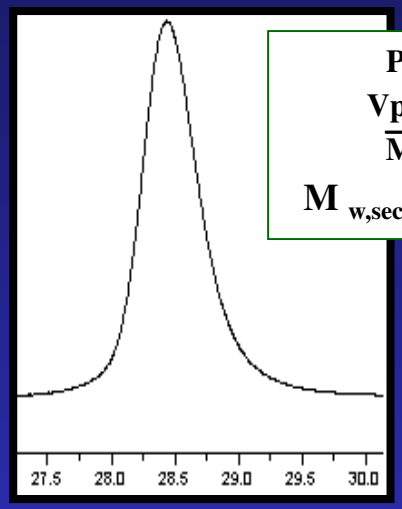
Hydroxy-PMMA prepared using F1, F2 and F3 were used as macro-initiators for the synthesis of PMMA-*block*-PEO



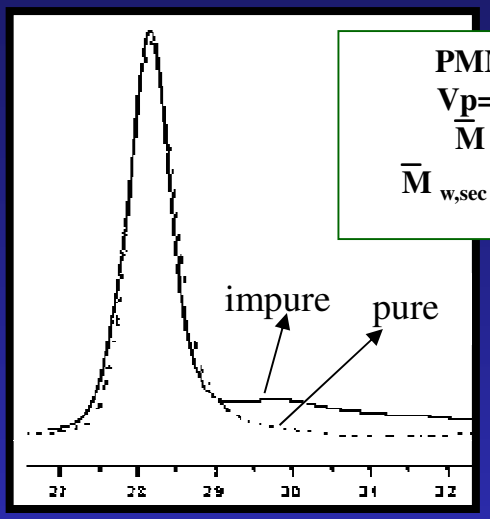
protected hydroxy-PMMA (using F3) used as macroinitiator

CHARACTERIZATION OF PMMA-BLOCK-PEO COPOLYMER

GPC Analysis



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



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

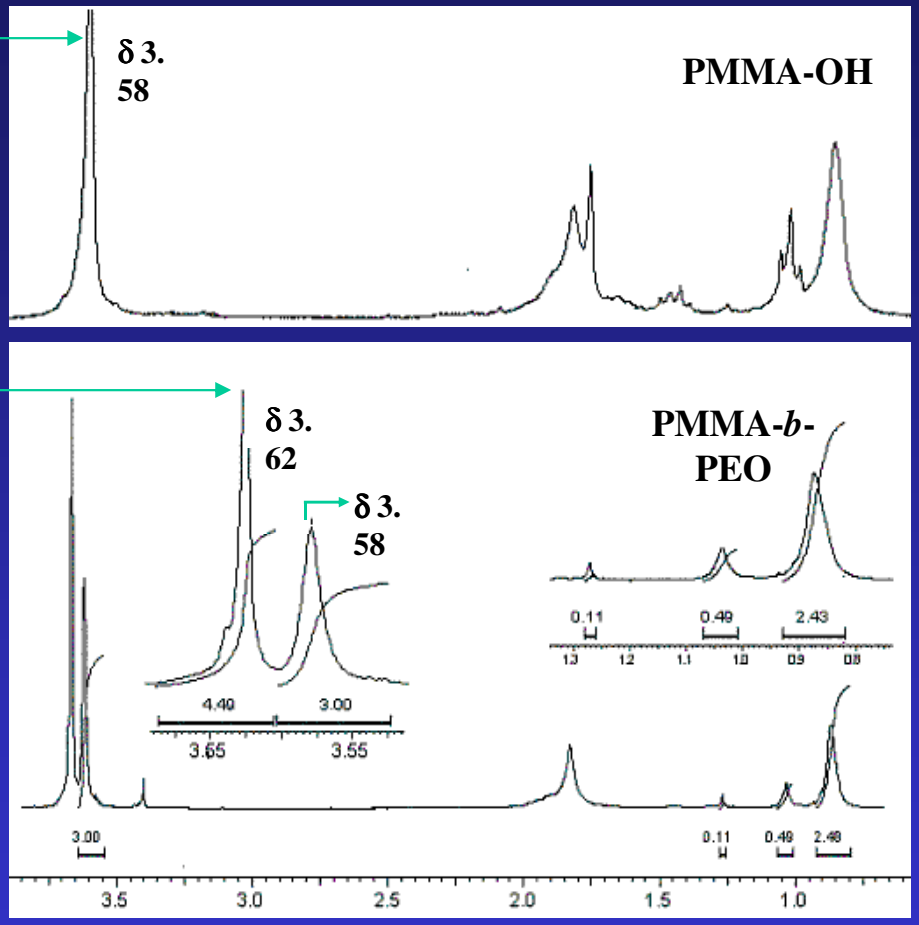
- **Increase in molecular weight**
- **Elugram of block copolymer show tailing in low molecular weight region**
- **Tailing disappears on washing the copolymers with water**
- **Water-soluble portion (~3.0 % by wt.) was found to be PEO homopolymer**

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



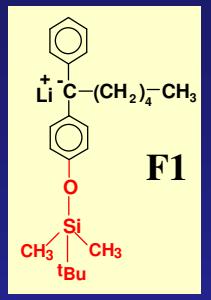
- Additional peak at δ 3.62 due to –OCH_2 protons in PMMA-*b*-PEO
- Ratio of peak intensities due to –CH_3 and –OCH_3 protons is 1:1

Appearance of new peak due to –OCH_2 protons confirm formation of the diblock

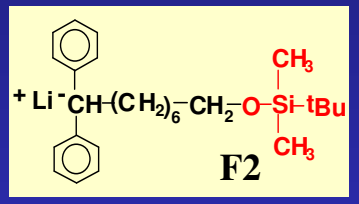
Presence of equal number of methyl and methoxy groups suggest insignificant amount of transesterification reaction

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

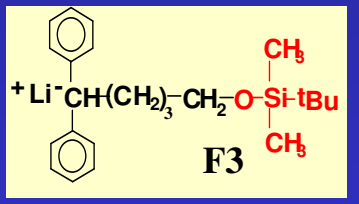
Run no.	PMMA-OH			[MMA]:[EO] in feed	PMMA-*b*-PEO			
	Sample no.	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$ (SEC)		Conv.	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$ (SEC)	[MMA]: [EO] (by NMR)
1	F3	11500	1.07	3.3:6.7	0.51	15400	1.20	3.9:6.1
2	F3	11500	1.07	2.7:7.3	0.53	15900	1.20	3.1:6.9
3	F3	14000	1.08	4.1:5.9	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



F1



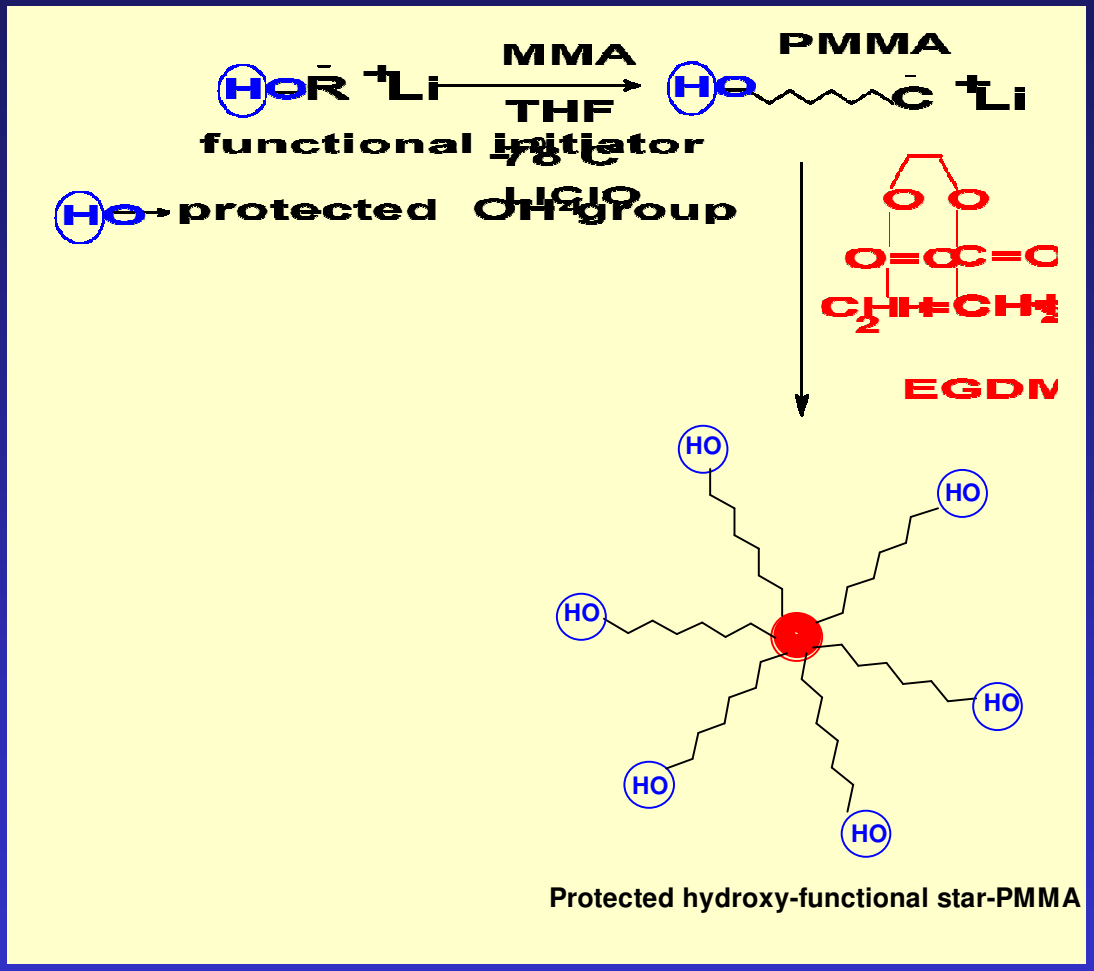
F2



F3

- 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



Synthetic procedure

Step 1: Anionic polymerization of MMA using functional initiators

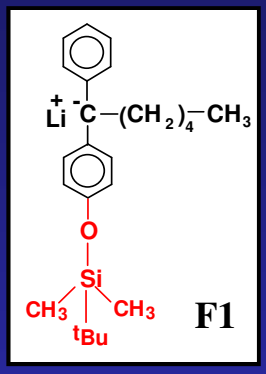
Step 2: Living chains coupled with bis-unsaturated monomer

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

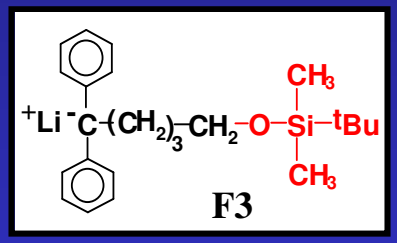
Controlled synthesis of hydroxyl-functional PMMA-star

Effect of arm length & [EGDMA] on number 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

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

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**

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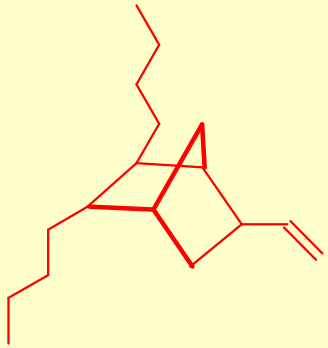
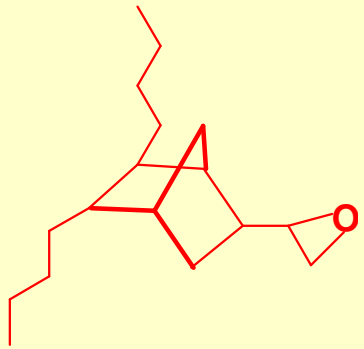
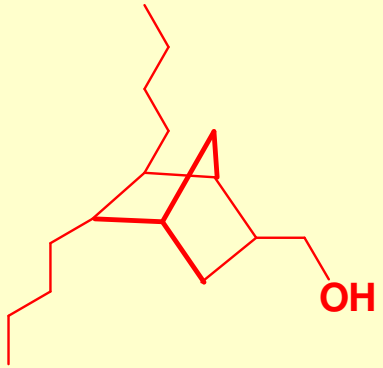
IN CHAIN FUNCTIONALIZATION OF POLY(OLEFIN)S

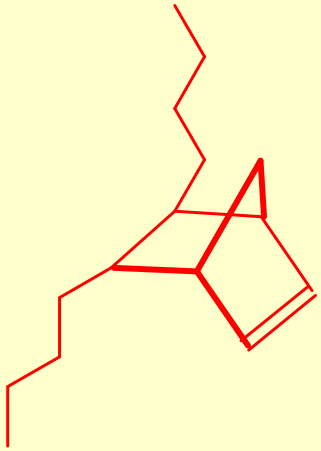




S. Marathe(1994)



K. Radhakrishnan (1998)



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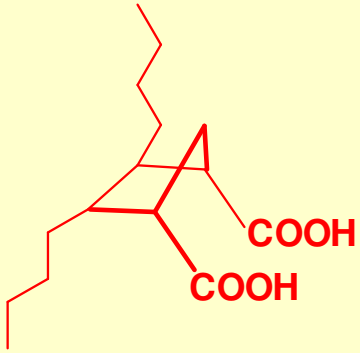
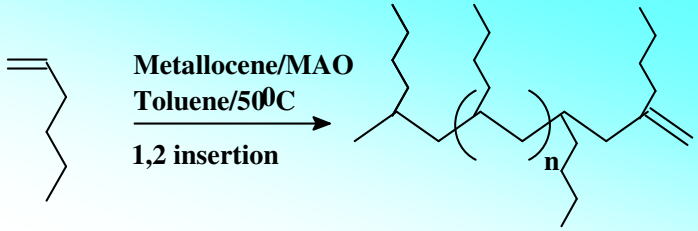


K. Radhakrishnan, M.J. Yanjarappa (2000)

SYNTHESIS OF VINYLIDENE TERMINATED OLIGO(1-HEXENE)



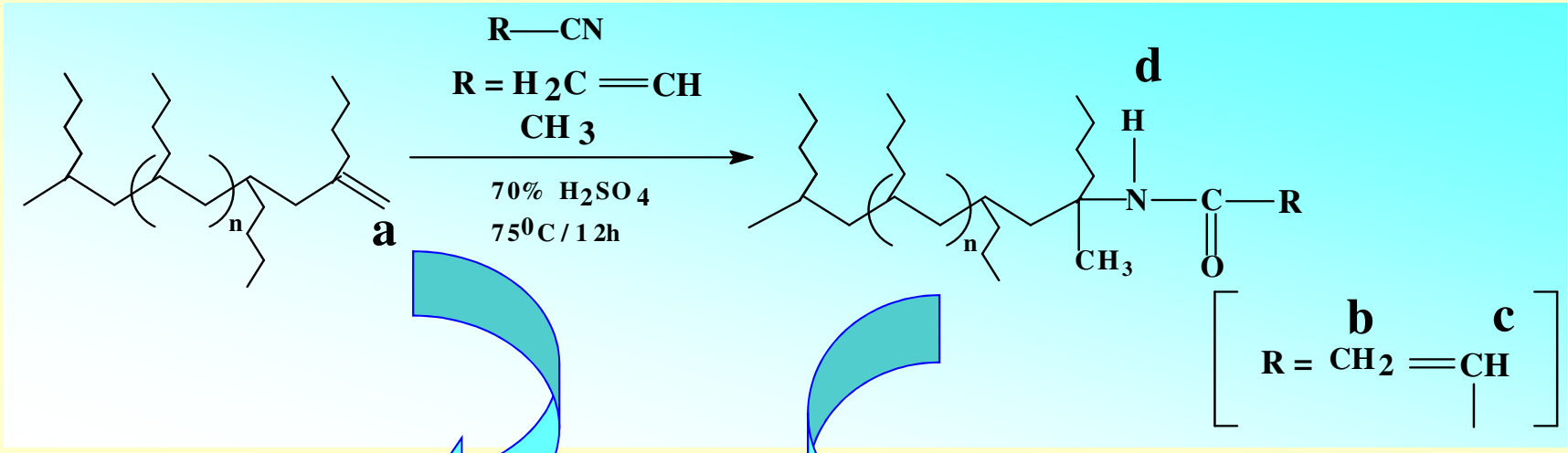
Mn = 300 - 2000

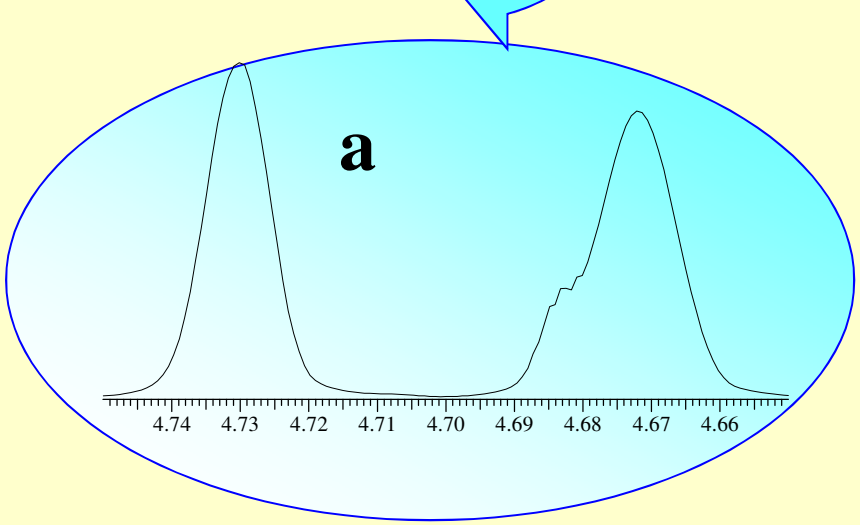
Fn > 95%, Mw/Mn = 2

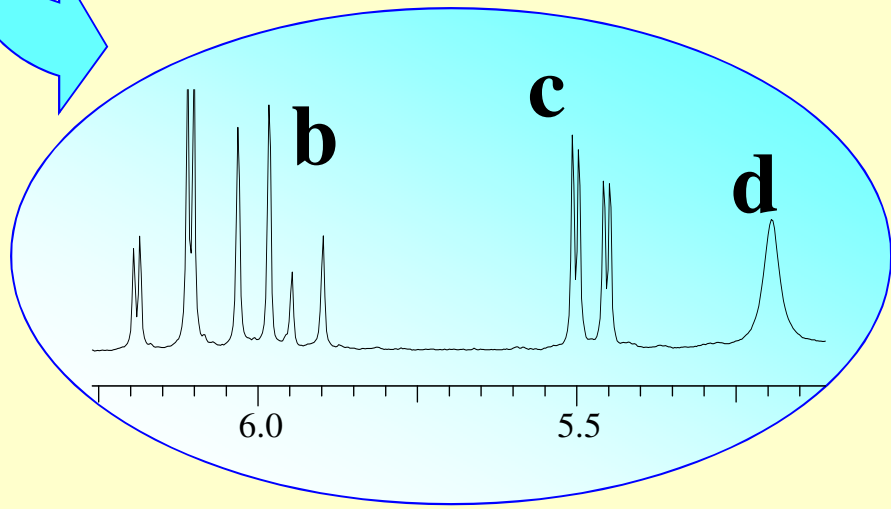
n = 3-10

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

RITTER REACTION USING VINYLIDENE TERMINATED OLIGO(HEXENE-1)



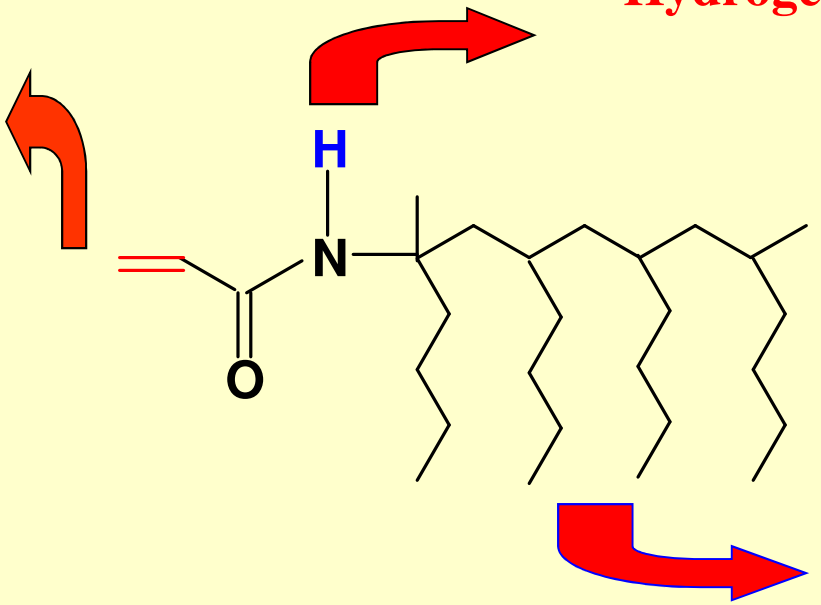




N-POLY(ALKENYL) ACRYLAMIDES : NOVEL AMPIPHILIC MACROMONOMERS

Hydrophilic Amide Capable of Hydrogen Bonding

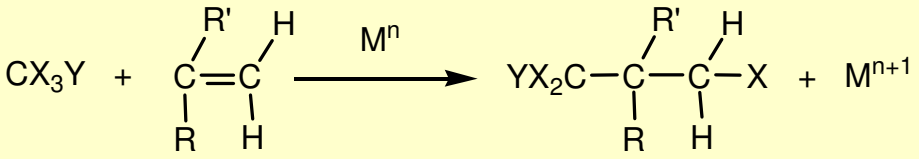
Reactive Unsaturation



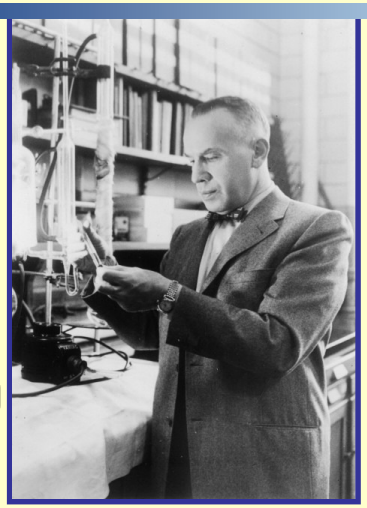
Hydrophobic alkyl group

Atom-transfer Radical Polymerization (ATRP)

➢ Atom transfer radical addition



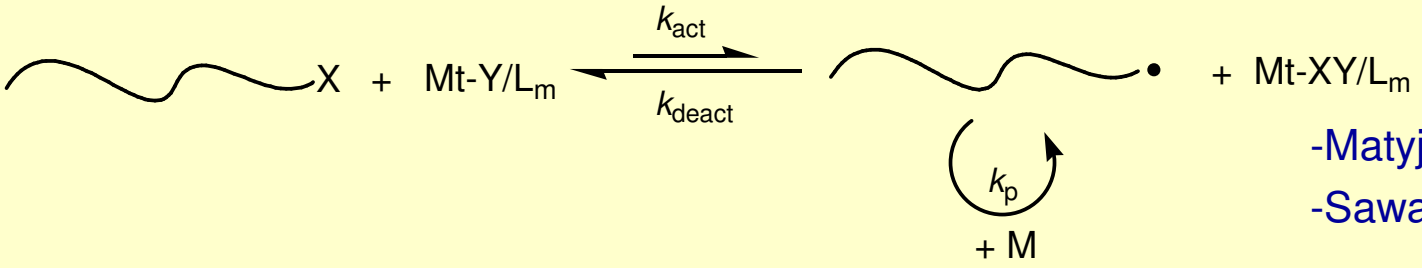
X = halogen; Y = H (or) electronegative group; M = Cu or Ni



Morris Kharash

(1938)

➢ Atom transfer radical polymerization

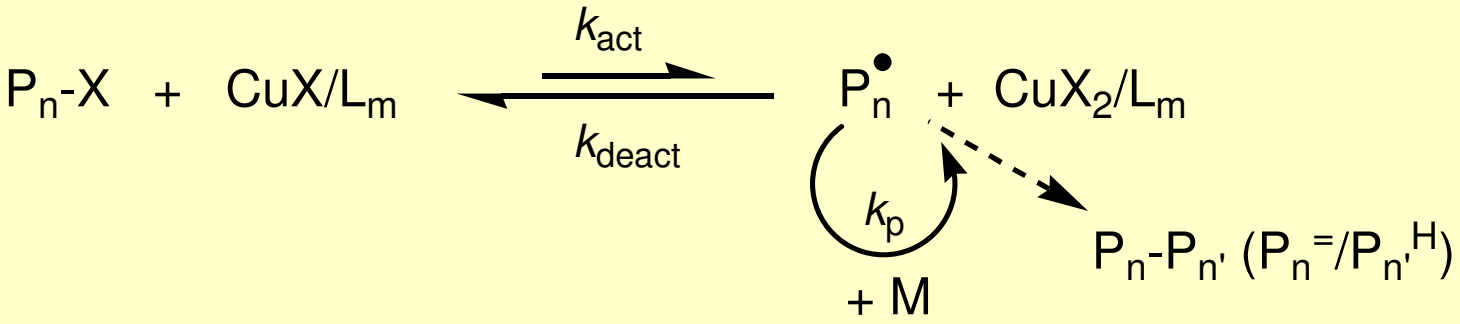


-Matyjaszewski (1995)

-Sawamoto (1995)

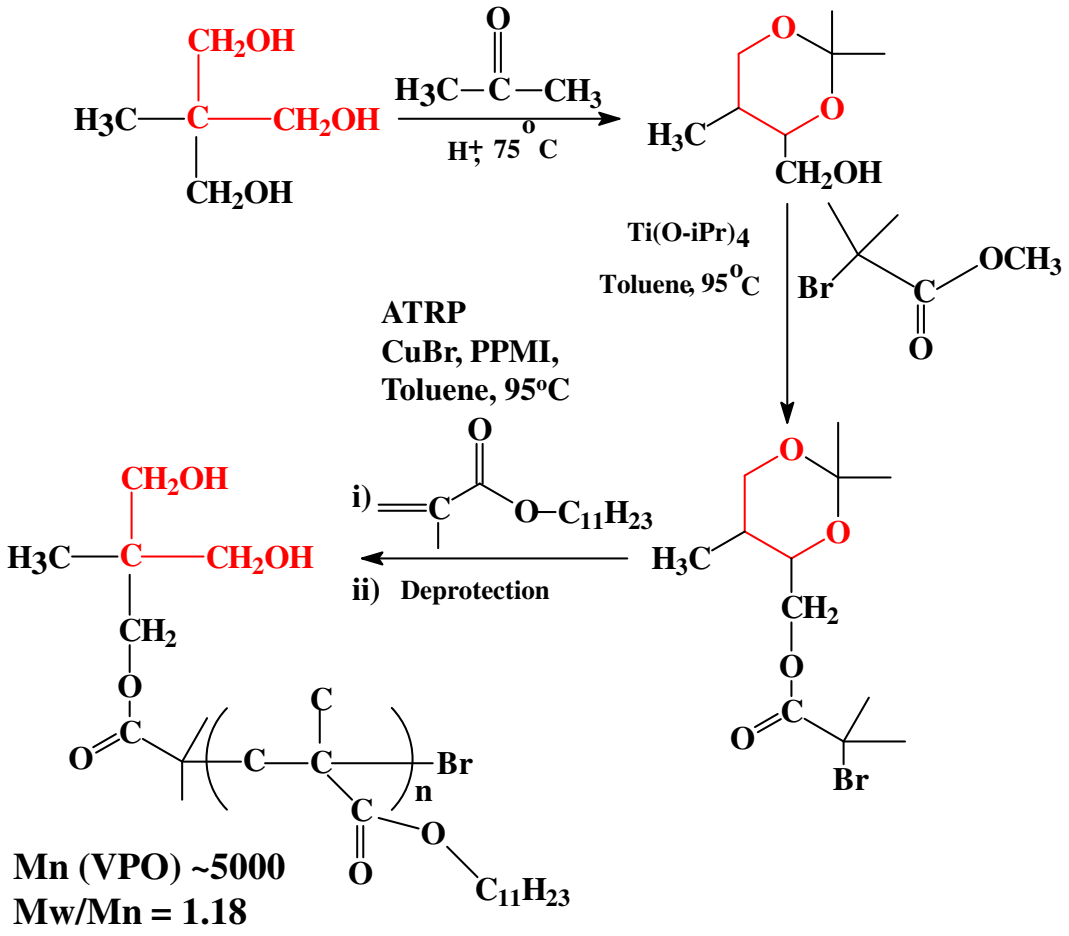
X and Y- halogen; Mt -Cu^{I}, Ru^{II}, Fe^{II}, Ni^{II}, etc; M- vinyl monomer, L-Ligand

Advantages of Copper-mediated ATRP

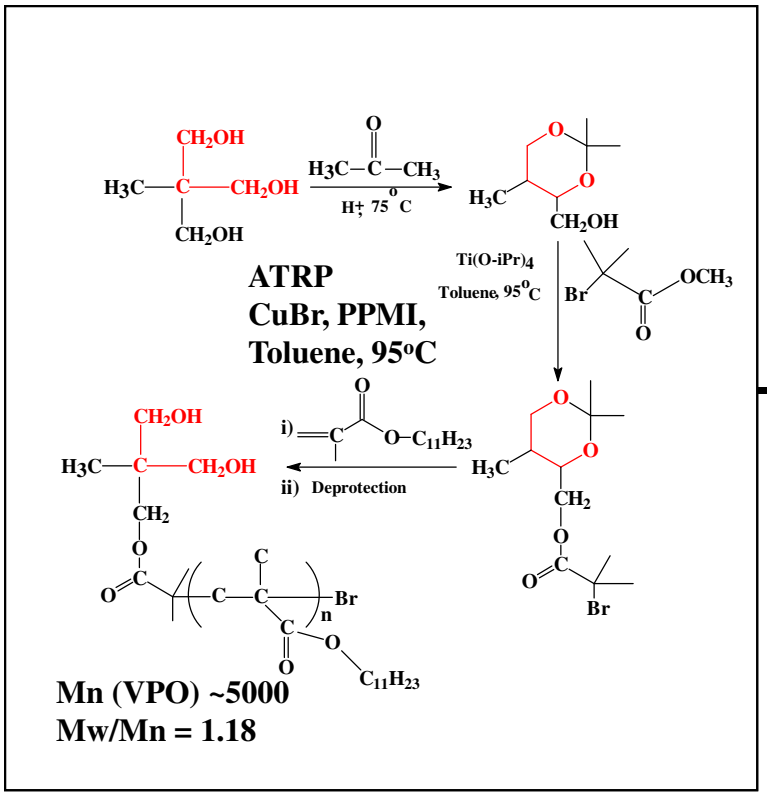


- **Significantly suppresses chain-transfer and chain-termination**
- **Produces polymers with well-defined molecular weight and narrow molecular weight distribution**
- **Tolerant to many functional groups**
- **Wide range of monomers and solvents can be used**
- **Very robust technique and easy to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

CONTROLLED SYNTHESIS OF DIOL FUNCTIONALIZED POLY(METHACRYLATE)S



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

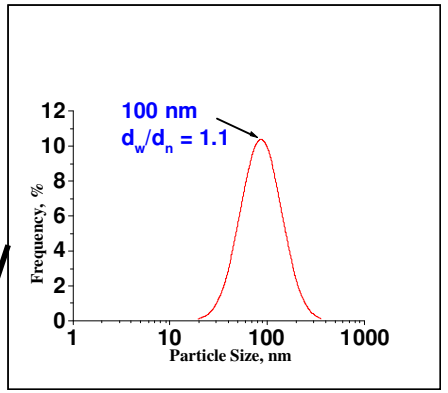


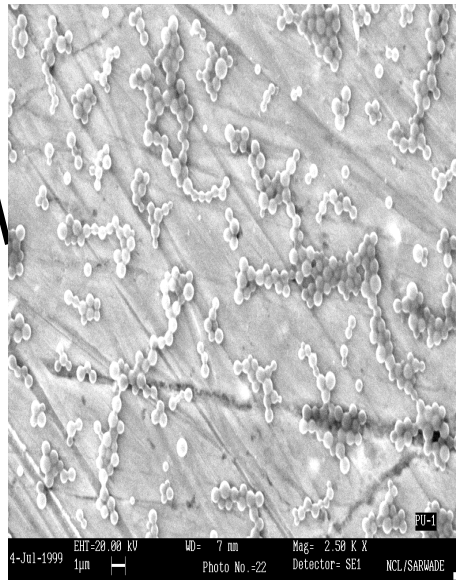
Stabilizer 5 wt %
DBTL 0.005%
Cyclohexane 20 parts

↓ TDI 60°C, 4 h

↓ EHG 60°C, 4 h

PU particles



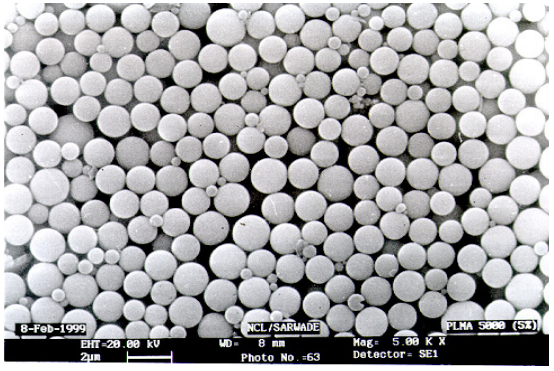


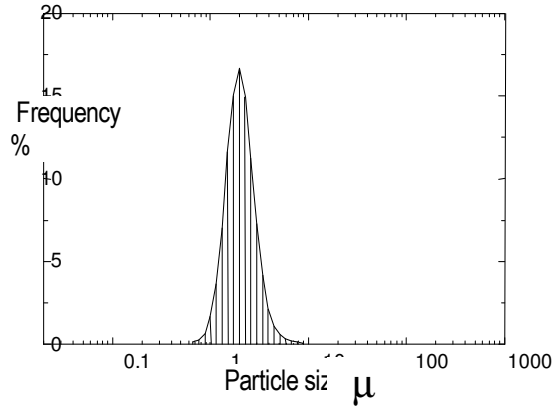
POLYURETHANE- MICROSPHERES

METHODS DEVELOPLED

- **ARE SIMPLE AND APPLICABLE TO WIDE VARIETY OF DIOLS AND ISOCYANATES**
- **PRODUCE FREE FLOWING PU SPHERICAL PARTICLES WITH ALMOST UNIFORM SIZE RANGE**
- **0.1 TO 100 MICRON RANGE BY CHOOSING APPROPRIATE EXPERIMENTAL PARAMETERS**

SEM AND PARTICLE SIZE DISTRIBUTION OF PU MICROSPHERES (NCL)





P.G.Shukla, S.Sivaram, US Patents 5,814,675 (1998), 5,859,075 (1999)

CONTROLLED RELEASE

Controlled Release (CR) can be defined as a method or technique by which an active agent is delivered to an intended target through a polymeric device at a concentration and for a duration designed to accomplish the desired effect while avoiding other responses or side effects this agent may cause.

Concept of CR is applied in many areas viz.

Pharmaceuticals Flavors Curing agents
Pesticides Perfumes Viruses
Electronic ink

MICROCAPSULES:

The most desired form in Controlled Release

- Microcapsules are small particles that contain an active agent or core material surrounded by a shell or coating.
- Microcapsule Size : 1 to 1000 microns
- Different types of microcapsules having a variety of structures

Spheres or particles with a continuous core region surrounded by a continuous shell

Active agent uniformly dispersed in a polymer matrix

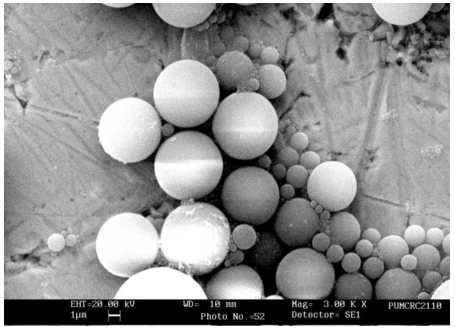
POLYURETHANE MICROCAPSULES:MONOCROTOPHOS

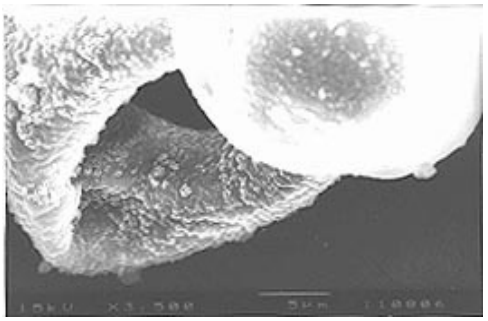
PESTICDE MONOCROTOPHOS

- **THERMALLY UNSTABLE AT TEMP ABOVE 40^{o}C**
- **FREELY SOLUBLE IN WATER AND MANY ORGANIC SOLVENTS EXCEPT ALIPHATIC HYDROCARBONS**
- **DECOMPOSES IN MOIST CONDITION**

CONVENTIONAL MICROENCAPSULATION METHODS CAN NOT BE EMPLOYED

- **A NEW PROCESS WAS SUCCESSFULY DEVELOPED TO PREPARE PU MICROCAPSULES OF MCR WITHOUT ANY DELETERIOUS EFFECT**





P.G.Shukla, N. Rajgopalan and S.Sivaram, US Patent 5,962,003 (1999)
P.G.Shukla and S.Sivaram, J. Microencapn., 16, 517 (1999)
P.G.Shukla, B. Kalidhass, A.Shah and D.V.Palaskar, J. Microencapn, 19, 293 (2002)

MICROCAPSULES: PERFUME

" Getting fragrance onto clothes presents a challenge for detergent companies and their suppliers"

Cover story: Chem. & Engg. News, Jan. 29,2007

Customer perceptions

Nice fragrance while taking out the fabric from washing machine

Fragrance persists when washed fabric is being used i.e. superior "tenacity " is desired.

Far better "tenacity" fragrance should have good "substantivity"

To protect the perfume from different chemicals present in detergent composition i.e. perfume should have good storage stability in the product.

High values of these parameters can be obtained by using microencapsulated perfumes.

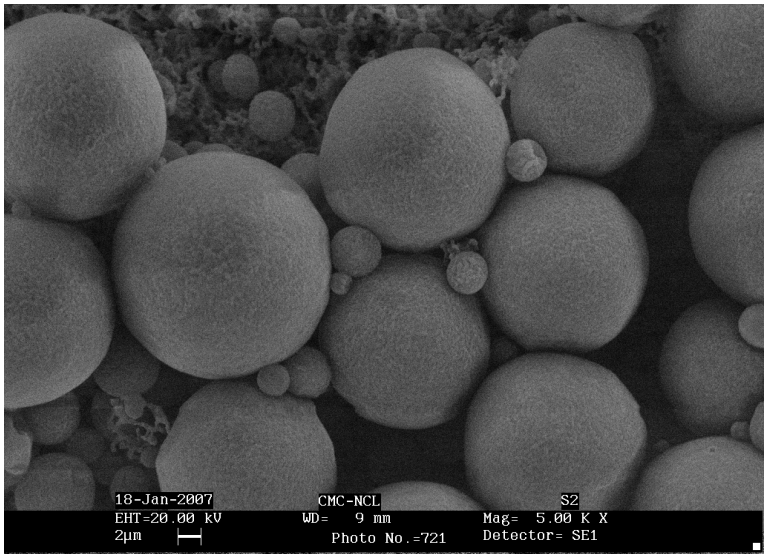
PERFUME MICROCAPSULES: SUCCESS CRITERIA

Develop microcapsules containing perfume:

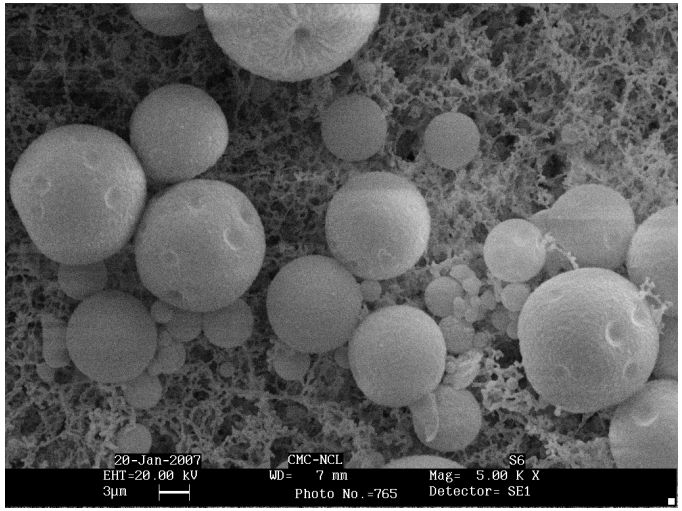
- **Particle size : < 50 µ**
- **Stability : leakage <30% , 2 weeks / 35 C**
- **Release triggers : loss of water (dehydration of the capsule), pressure and/or temperature**

Microcapsules with Non-formaldehyde wall chemistry

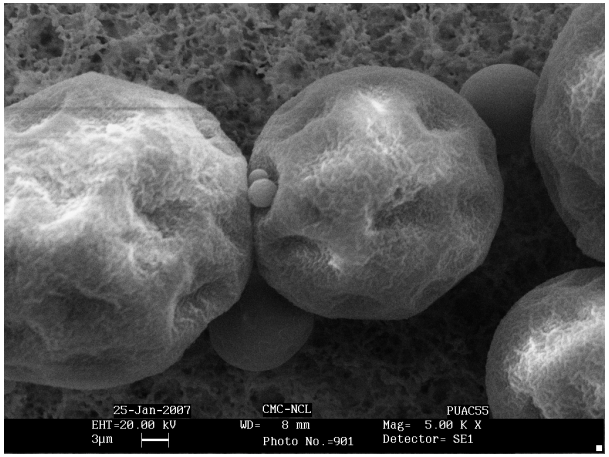
Microcapsules containing perfume



PUAC, 70% Loading



PUAC 60% Loading



PUAC, 50% Loading

STABILITY OF PU CAPSULES

Microcapsule	% Leakage at 35C					
	In LFE After 1day	2 Wks	4Wks	In HDL After 1day	2Wks	4Wks
PUAC , 50% Loading	27	51	58	11	26	39
PUAC , 50% Loading Surfactant PVP removed	22	34	55	31	27	53

Hindustan Times 17th Sept. 2010

Procter's gamble

How much force do you need to twist the cap off a bottle? How do you keep clothes smelling nice even a week after they've been washed? Just some of the questions that allow one of the world's largest consumer goods giants to take its Indian brains global

Seema Singh
seema.s@livemint.com

Stepping inside the innovation centre of the world's largest consumer goods company in suburban Bangalore, anticipation runs high: how does the $78.9 billion Procter & Gamble Co., maker of Tide detergent and Pampers diapers, come up with its next blockbuster product? How big is the innovation funnel that has spewed out products ranging from paper towels to dentifrice to boatloads of over-the-counter brands?

Inside the fifth floor of Neil Rao Towers at Whitefield, a thin veil of disappointment descends when all that comes to view is a bunch of P&G products neatly displayed in the hallway, and later, deliberately arranged in the conference room.

But as Ashish Chatterjee, head of the Bangalore Innovation Centre (BLIC), starts talking about some of the 200 brands that the company sells, and how it immerses itself into the lives of consumers, it dawns that the consumer business is far from being a pedestrian affair.

What should be the optimum force needed for twisting open a bottle cap?

What's the right pressure for the plunger on a bottle of skincare cream?

Why should the black box that a lotion comes in be replaced with transparent packaging, as with Olay products?

These and many such questions dominate researchers' work as they drive "purpose-inspired innovation" at P&G. "It's certainly not an aircraft engine; we don't always go for the big bang," says Chatterjee. "Our innovation is driven by consumer inspiration."

He sums it up as two moments of truth — one, when the consumer browses in a store and ends up buying a P&G product; second, when the person returns to buy either the same or any other item made by the company.

Defined by these moments of truth, BLIC was set up in July 2008 as one of the 28 innovation centres within P&G. It is a capability hub, smaller than some of P&G's mega centres, and provides modelling and open innovation resources for the global enterprise.

It was in 2000 that the Connect and Develop, or C+D, concept of open innovation was mooted by the then chief executive Alan G. Lafley. It wasn't the best of times for P&G: the stock had just lost half its value amid an aggressive growth plan and Lafley decided to shed bricks and mortar R&D infrastructure for open innovation. He directed that ideas and innovations sourced from outside should go up from 10 per cent to 50 per cent in the next five years.

A decade later, the company has far exceeded that limit. It has also changed tack — from getting the world to its lab to taking its labs to the world. For each of its 100 engineers and scientists working in Bangalore, the centre collaborates with five researchers outside.

Now, at two-year-old BLIC, there are a few tangible results, says Chatterjee, who is also director, Asia C+D and Bangalore Beauty Care.

Using computer modelling, this centre has screened millions of molecules to identify a new molecule in the area of skin improvement. While it's into clinical studies now, Chatterjee emphasises that in such studies, knowing "how it works", rather than "why it works" is more important so that the active can be used in other skin applications as well. The computing expertise of BLIC, which Chatterjee likens to "Intel Inside", powers the P&G innovation engine but isn't visible from outside.

From simulating entire packaging lines to complete plant production units, modelling is used to reduce the start-up cost, eliminate waste in the system and to optimise existing operations. A new multi-category production system, designed at BLIC, has just been rolled out which Chatterjee says will save "several millions of dollars for P&G". In this industry, there's no such thing as a cost that can't be cut.

As economic recovery has been slow in many parts of world and consumers are still hurting, premium brands continue to struggle. Meanwhile, in India, where the $24 billion consumer packaged-goods industry is growing at 12 per cent per year according to Nielsen Co., P&G lags behind its closest rival, Unilever, in market share.

Historically, says Ramesh Srinivas, executive director, consumer business practice, KPMG Advisory Services India, P&G has placed its products globally; it won't be looking at just regional benefits arising out of these innovation centres. He is right.

Though some of the BLIC-designed packaging, such as of Olay Total Effects and Olay Regenerist, have been selling in global stores, one of the earliest examples of open innovation from here has gone into products that have not yet entered the Indian market.

For instance, BLIC and the National Chemical Laboratory, a Council of Scientific and Industrial Research laboratory in Pune, have developed a new micro-encapsulating technology that has gone into its fabric softener Downy. Yet to hit Indian stores, the company says its fragrance lasts for a week after the wash, longer than rival products.

The key lies in the technology that allows the perfume-containing micro capsules to open up when the dehydration process kicks in. The end product, says Chatterjee, is "cheaper and better". The laundry science groups in Newcastle and Brussels were also involved in the development of the product.

P&G, like many other consumer goods companies, is trying hard to boost sales in the US and Europe.

While sales growth in emerging markets is easier to come by, in mature markets the company needs to rely on lowering prices or come up with innovative products, says Jack P. Russo, an analyst with the Edward Jones, a retail brokerage in St Louis, US.

"P&G is relying on both of these measures but it appears the emphasis on innovation has been more pronounced since (Robert) McDonald has taken over as CEO (in June 2009)."

Consumers definitely want innovative products but because they are also seeking value P&G won't be able to charge a premium on these as it would have done in the past, added Russo.

The Cincinnati giant is already treading that path. C+D 2.0, which has been effective since 2008, is all about "value creation for the company and its partners", Chatterjee says.

P&G's products touch about four billion lives today. The company intends to add another billion to this in the next five years, spurred by its well-oiled innovation machine. To the two Asian 'mega' centres in China and Japan, a third one is being added in Singapore. "It's no secret Asia is a battleground," says Chatterjee, who is firming up plans to add more products as well as processes to BLIC's modelling capabilities.

yeswecan

- **Bangalore Innovation Centre Started: 2008**
- **Made in India: New 'holistic' designs of Head & Shoulder shampoo and conditioner bottles; a new molecule/active for skin improvement; transparent packaging of Olay products; microencapsulating technology that has gone into its fabric softener Downy**

BLIC head Ashish Chatterjee poses with P&G's products at its Bangalore centre.

Laboratories at P&G's innovation centre in Bangalore support computer modelling. HEMANT MISHRA / MINT PHOTOS

Every Friday, this series chronicles technological innovation and India's rise as a global R&D hub. Read previous stories at www.hindustantimes.com/innovation

" Though some of the BLIC-designed packaging, such as of Olay Total Effects and Olay Regenerist, have been selling in global stores, one of the earliest examples of open innovation from here has gone into products that have not yet entered the Indian market.

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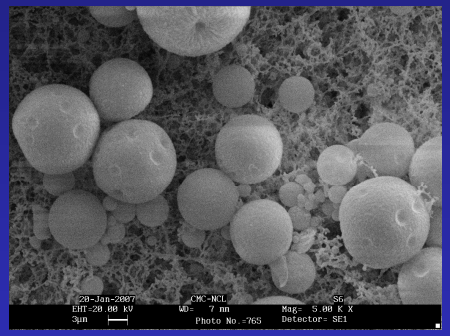
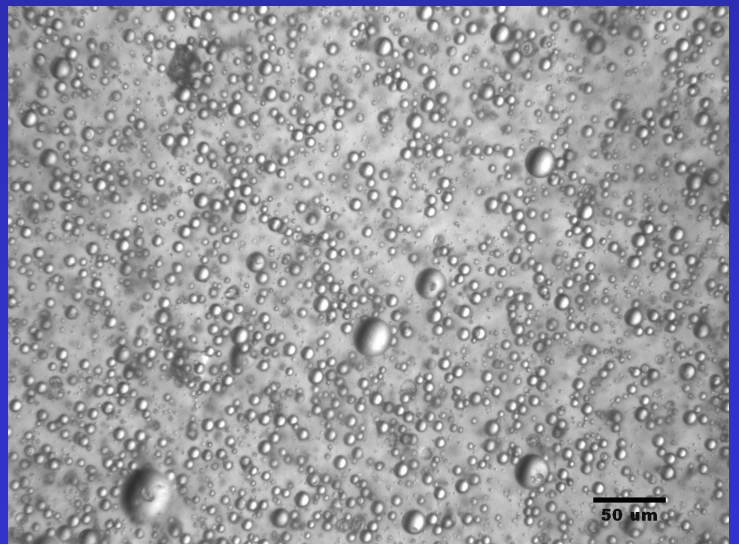
Patent applications filed US 2010/0119679 and WO 2010/053940

1950-2010 Celebrating Sixty Years of Science

Polymer microcapsules for fabric care





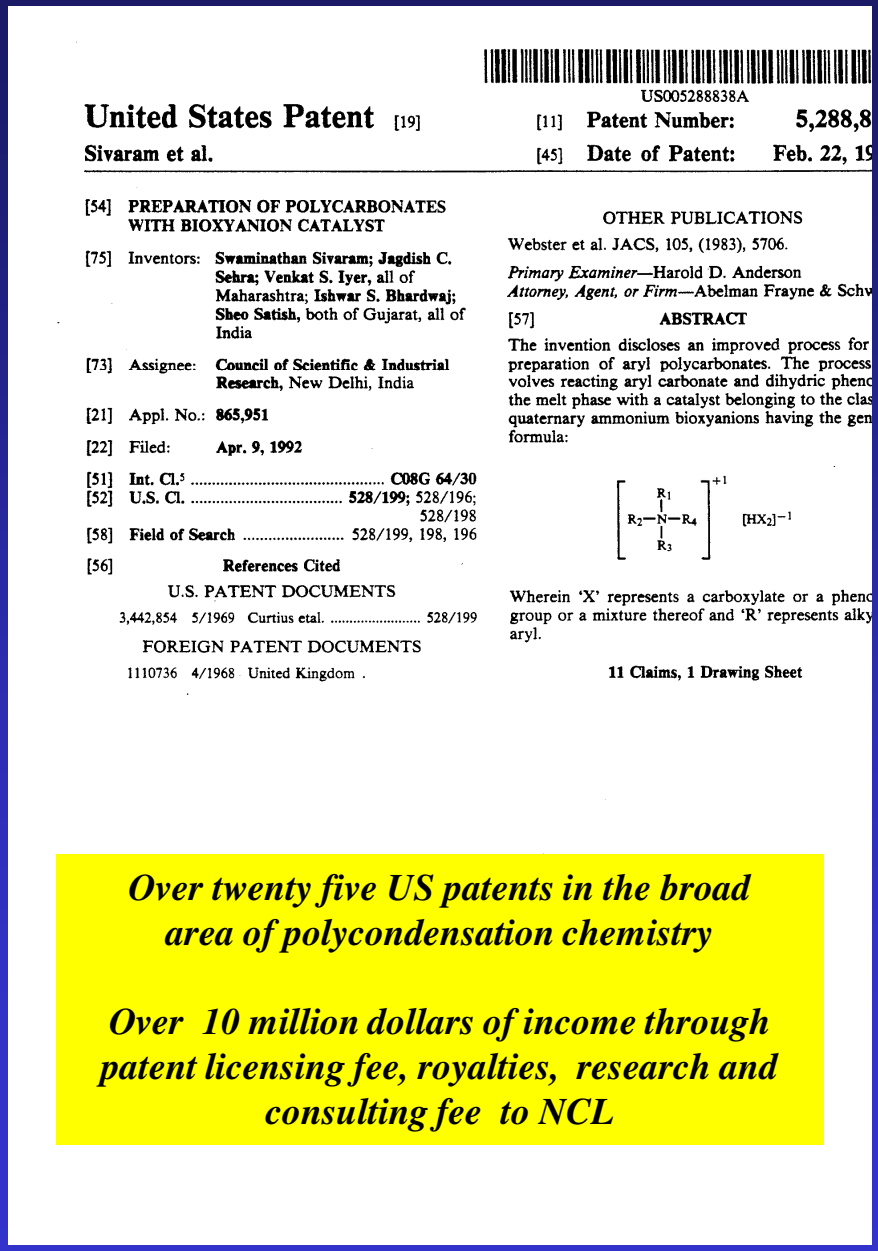
EARLY LESSONS IN PATENTS : UNIVERSITY OF AKRON (1972-73)

- **A course (1 semester) on "Patenting for chemists" by Professor J.P. Kennedy (JPK)**
- **Professor Kennedy came to academia after a distinguished industrial career of over 20 years at Exxon Research and Engineering**
- **JPK (80 years) obtained his 100th US Patent in 2009**

Lesson : Excellence in science and applications are not mutually exclusive

Mere exploration without exploitation of knowledge is sterile. In an environment where research is predominantly publicly funded, this situation leads to loss of credibility amongst stakeholders

EARLY YEARS AT NCL : THE THRILL OF PATENTING



US005288838A

United States Patent [19]
Sivaram et al.

[11] **Patent Number:** 5,288,8
[45] **Date of Patent:** Feb. 22, 19

[54] **PREPARATION OF POLYCARBONATES WITH BIOXYANION CATALYST**

[75] Inventors: **Swaminathan Sivaram; Jagdish C. Sehra; Venkat S. Iyer,** all of Maharashtra; **Ishwar S. Bhardwaj; Sheo Satish,** both of Gujarat, all of India

[73] Assignee: **Council of Scientific & Industrial Research,** New Delhi, India

[21] Appl. No.: **865,951**

[22] Filed: **Apr. 9, 1992**

[51] **Int. Cl.**[5] **C08G 64/30**
[52] **U.S. Cl.** **528/199**; 528/196; 528/198
[58] **Field of Search** 528/199, 198, 196

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,442,854 5/1969 Curtius etal. 528/199

FOREIGN PATENT DOCUMENTS

1110736 4/1968 United Kingdom .

OTHER PUBLICATIONS

Webster et al. JACS, 105, (1983), 5706.

Primary Examiner—Harold D. Anderson
Attorney, Agent, or Firm—Abelman Frayne & Schv

[57] **ABSTRACT**

The invention discloses an improved process for preparation of aryl polycarbonates. The process volves reacting aryl carbonate and dihydric phenc the melt phase with a catalyst belonging to the clas quaternary ammonium bioxyanions having the gen formula:

Wherein 'X' represents a carboxylate or a phenc group or a mixture thereof and 'R' represents alky aryl.

11 Claims, 1 Drawing Sheet

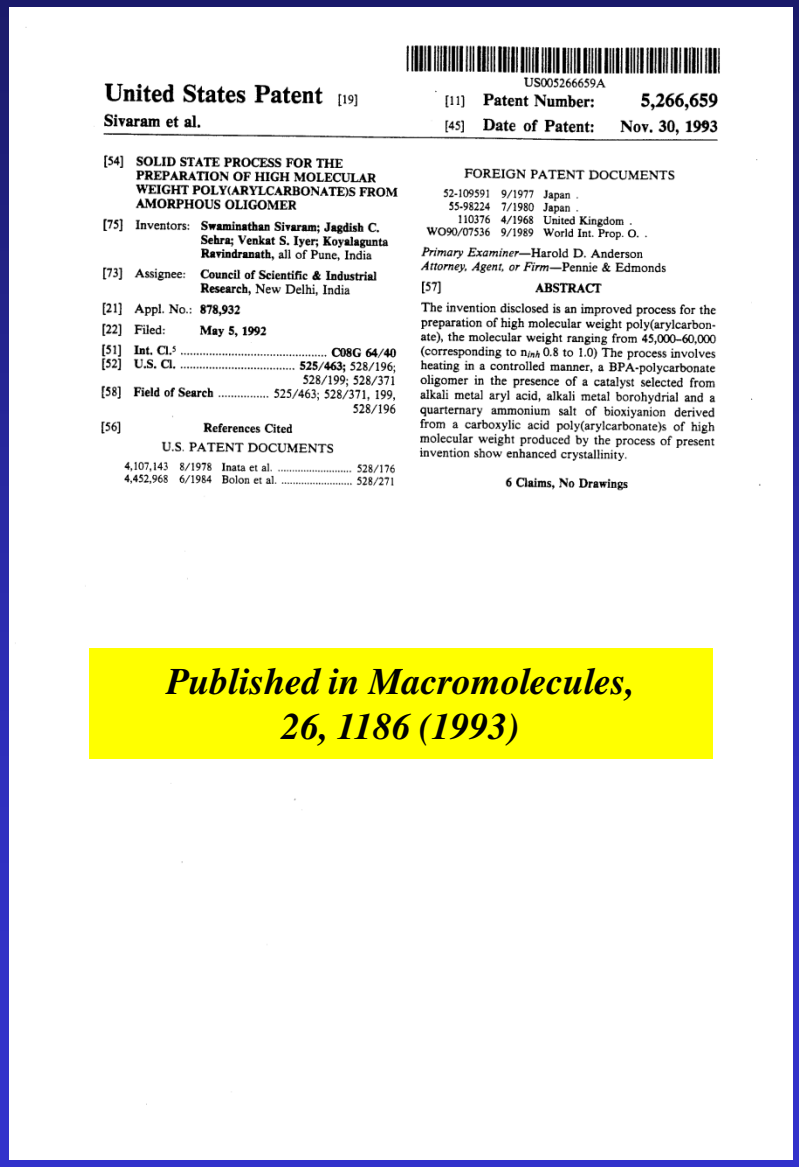
Over twenty five US patents in the broad area of polycondensation chemistry

Over 10 million dollars of income through patent licensing fee, royalties, research and consulting fee to NCL

The Beginning

This patent led to over ten years of very productive and exciting research in the area of polycarbonates, resulting in several PhD thesis, publications and industrial partnership with GE plastics. This also established the principle of "organic catalysis" for polymer synthesis

EARLY YEARS AT NCL : THE THRILL OF PATENTING



US005266659A

United States Patent [19]

Sivaram et al.

[11] **Patent Number: 5,266,659**

[45] **Date of Patent: Nov. 30, 1993**

[54] **SOLID STATE PROCESS FOR THE PREPARATION OF HIGH MOLECULAR WEIGHT POLY(ARYLCARBONATE)S FROM AMORPHOUS OLIGOMER**

[75] Inventors: **Swaminathan Sivaram; Jagdish C. Sehra; Venkat S. Iyer; Koyalagunta Ravindranath**, all of Pune, India

[73] Assignee: **Council of Scientific & Industrial Research**, New Delhi, India

[21] Appl. No.: **878,932**

[22] Filed: **May 5, 1992**

[51] **Int. Cl.**[5] **C08G 64/40**

[52] **U.S. Cl.** **525/463**; 528/196; 528/199; 528/371

[58] **Field of Search** 525/463; 528/371, 199, 528/196

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,107,143	8/1978	Inata et al.	528/176
4,452,968	6/1984	Bolon et al.	528/271

FOREIGN PATENT DOCUMENTS

52-109591	9/1977	Japan .
55-98224	7/1980	Japan .
110376	4/1968	United Kingdom .
WO90/07536	9/1989	World Int. Prop. O. .

Primary Examiner—Harold D. Anderson
Attorney, Agent, or Firm—Pennie & Edmonds

[57] **ABSTRACT**

The invention disclosed is an improved process for the preparation of high molecular weight poly(arylcarbonate), the molecular weight ranging from 45,000–60,000 (corresponding to n_{inh} 0.8 to 1.0) The process involves heating in a controlled manner, a BPA-polycarbonate oligomer in the presence of a catalyst selected from alkali metal aryl acid, alkali metal borohydrial and a quarternary ammonium salt of bioxiyanion derived from a carboxylic acid poly(arylcarbonate)s of high molecular weight produced by the process of present invention show enhanced crystallinity.

6 Claims, No Drawings

Published in Macromolecules, 26, 1186 (1993)

Genesis of CSIR 's IP Policy 1996

" The history of CSIR's recent patent successes has origins in the patent filed on May 5, 1992 by S.Sivaram et al of National Chemical Laboratory , Pune (US Pat 5,266,659 dated 30 November 1993) with the assignee as CSIR. This was followed by what was to be a milestone in Indian patenting history , when GE showed immense interest in the work pertaining to the NCL patent "

Current Science, 85, p.571, 10 September 2003

CREATING WEALTH OUT OF INTELLECTUAL PROPERTY

- Curiosity driven research initiated in 1989 in the area of high performance materials
- Research performed by Ph.D students
- Research aimed at new processes to make poly(carbonate)s and poly(ester - carbonate)s without phosgene and at substantially lower temperatures, than hitherto practised
- Research resulted in three Ph.D thesis, eight US patents and several publications
- Negotiations with GE Plastics initiated in 1993 for sale of patents on “as is where is” basis; negotiations concluded in 1995 with GE Plastics licensing all the NCL - CSIR patents
- Ratio of value earned to research cost ~ 100

First example of licensing from CSIR

From little acorns do tall oaks grow

United States Patent: 5,288,838 - Microsoft Internet Explorer

File Edit View Favorites Tools Help

Back Search Favorites History

Address

United States Patent

Sivaram , et al.

Preparation of polycarbonates with biocyanion catalyst

Abstract

The invention discloses an improved process for the preparation of aryl polycarbonates. The process involves reacting aryl carbonate and dihydric phenol in the melt phase with a catalyst belonging to the class of quaternary ammonium biocyanions having the general formula ##STR1## Wherein 'X' represents a carboxylate or a phenolate group or a mixture there of and 'R' represents alkyl or aryl.

Inventors: **Sivaram; Swaminathan** (Maharashtra, IN); **Sehra; Jagdish C.** (Maharashtra, IN); **Iyer; Venkat S.** (Maharashtra, IN); **Bhardwaj; Ishwar S.** (Gujarat, IN); **Satish; Sheo** (Gujarat, IN)

Assignee: **Council of Scientific & Industrial Research** (New Delhi, IN)

Appl. No.: **865951**

Filed: **April 9, 1992**

Current U.S. Class: **528/199**, 528/196, 528/198

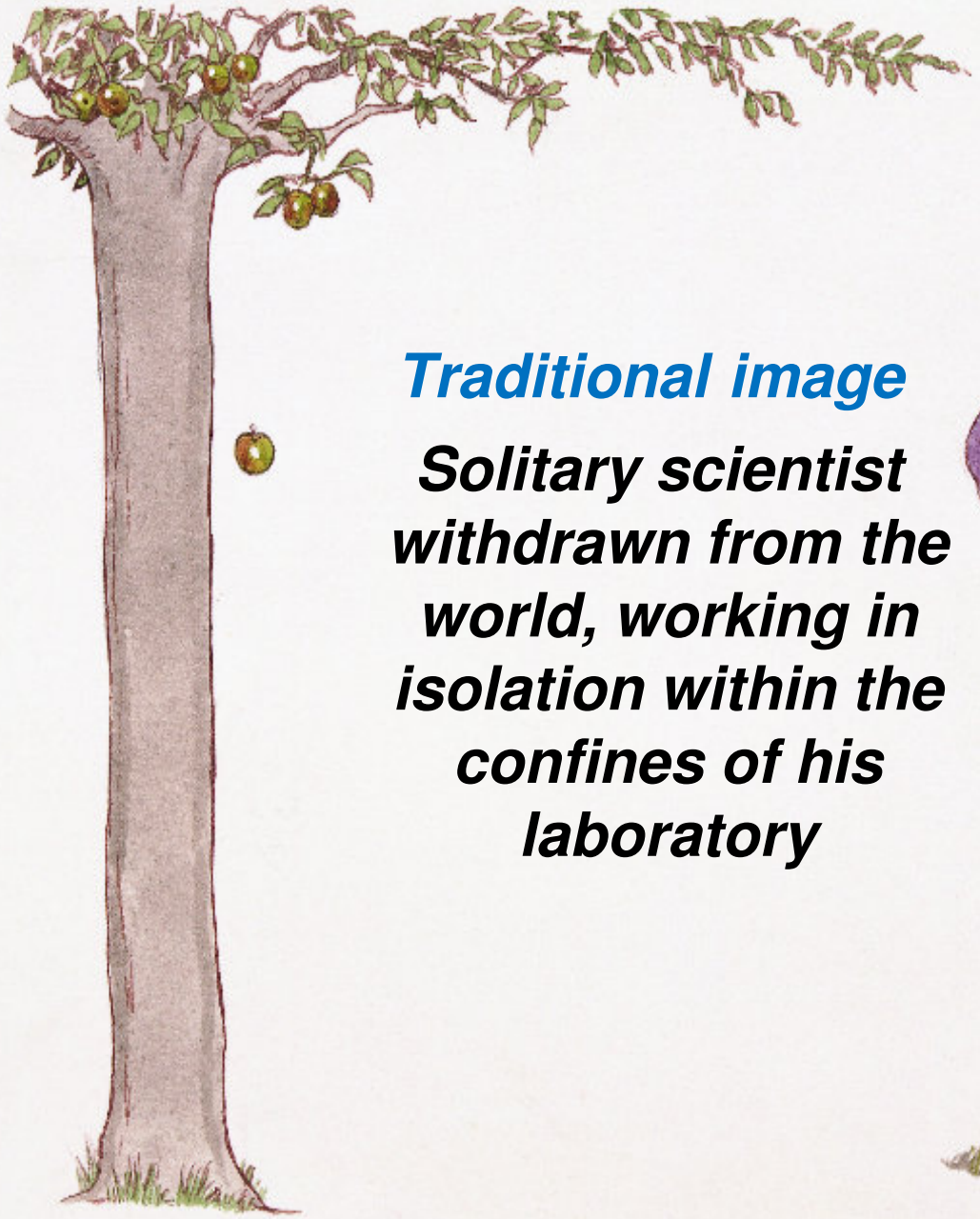
Int'l Class: C08G 064/30

Done Internet

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

Karl Ziegler

Nobel Address



Traditional image

Solitary scientist withdrawn from the world, working in isolation within the confines of his laboratory

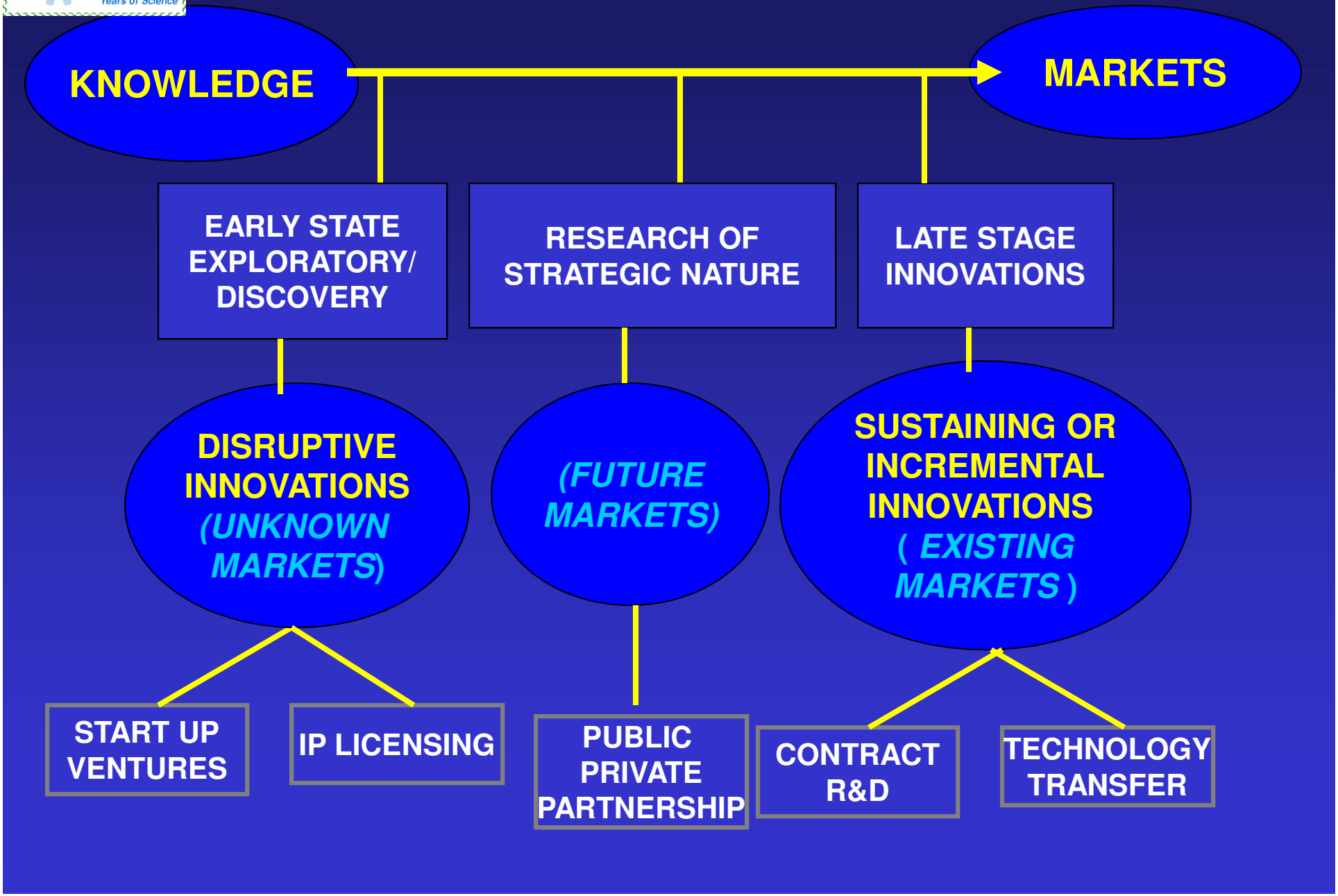
WHERE ARTS IS AHEAD...

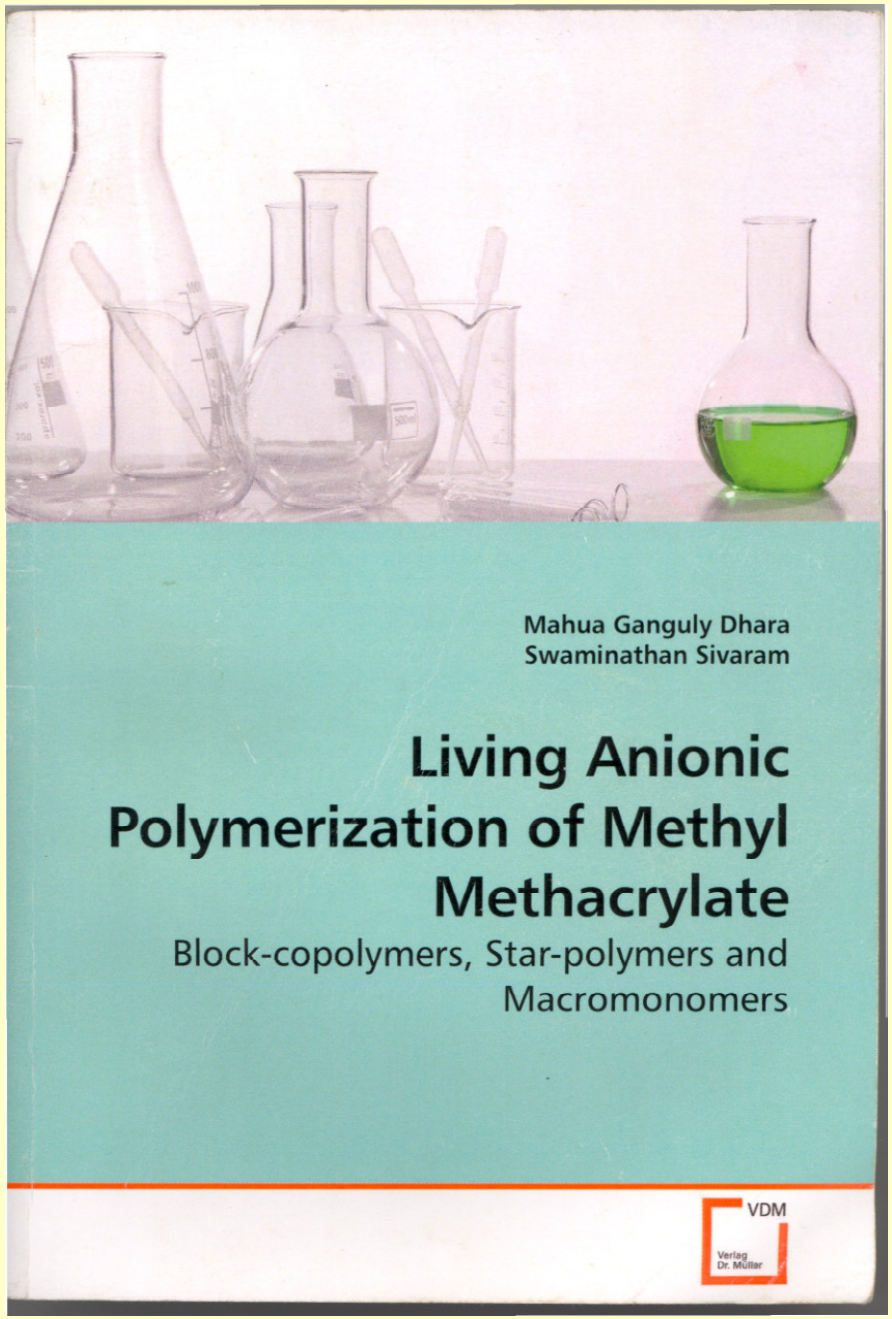
Organizing scientific research on the scale of big operatic and theatrical production is still something new in science

NATURE OF RESEARCH

EXPLORATORY	PRE-COMPETITIVE	TECHNOLOGY DEVELOPMENT
Output • Papers • IP • Ph.D. Thesis • Knowledge • Competence	**Output** • Papers • IP • Ph.D. Thesis • Concepts with market potentials	**Output** • Tech transfer (Royalty) • Lab to Market (Pre-serial A activities • Spin offs and Equity • IP licensing (Royalty/ License Fee)
• Unstructured research • Follow exciting ideas as they come	• Partially structured research • Follow key concepts which have potential utility	• Focus on innovation • Define delivery models • Connect solution with problems

LINKING KNOWLEDGE TO MARKETS





ACKNOWLEDGNENTS

All my students and colleagues at NCL

THANK YOU