FOUR DECADES IN CHEMISTRY : THE JOURNEY FROM MCC AND BEYOND

(A reflection on my personal and professional journey)

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Frontiers in Chemistry
A Conference to Commemorate the Birth Centenary of Professor S.V. Ananthakrishnan
Madras Christian College, Chennai
October 2, 2008

MCC Chennai 021008

THE BEGINNING OF A JOURNEY

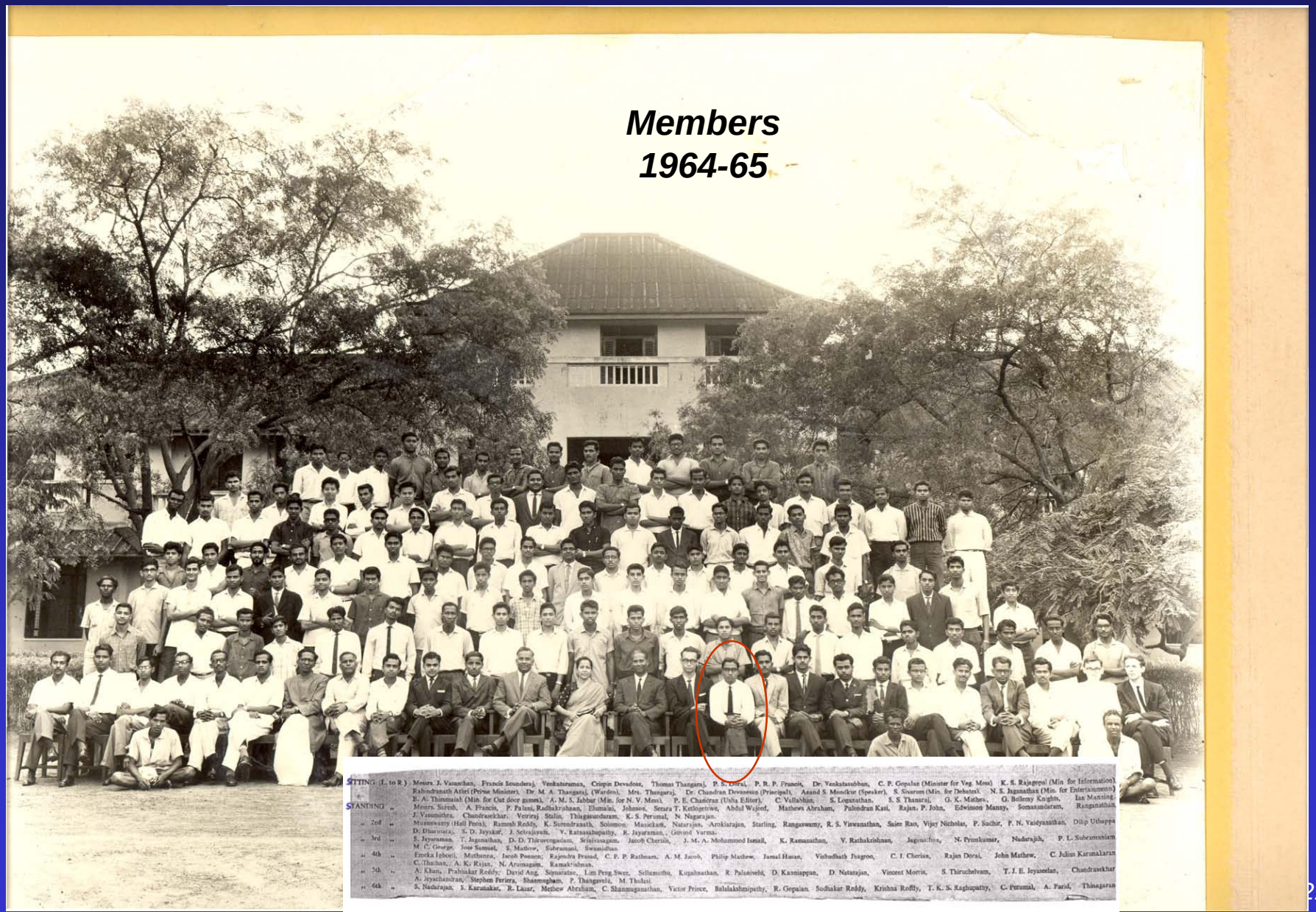
NEW DELHI TO MADRAS
May 1962

MY JOURNEY TO MADRAS CHRISTIAN COLLEGE

- Finished school at the age of fifteen and a half from the Delhi Higher Secondary Board; Age barred from admission to Delhi University
- Two of my uncles were alumnus of MCC in the late forties
- My father got an introduction to Professor Ananthakrishnan through family friends and sought his advice concerning my education
- I recall my first meeting with Professor Ananthakrishnan at his residence in the Campus along with my father. His advice must have convinced my father that MCC was the right place for me
- My inclination was to study Chemical Engineering ; failed to get admissions in either IIT`s or AC College of Technology
- The next best choice was Chemistry !

Lesson 1 : We rarely get what we want ; always make the best of second choice

ST. THOMAS'S HALL
MADRAS CHRISTIAN COLLEGE, TAMBARAM



SITTING (L. to R.) Messrs. J. Vasanthan, Francis Sounderaj, Venkatramana, Crispin Devadoss, Thomas Thangaraj, P. S. Desai, P. R. P. Francis, Dr. Venkatasubbiah, C. P. Gopalan (Minister for Veg. Mess) K. S. Rajagopal (Min. for Information), Rabindranath Attri (Prime Minister), Dr. M. A. Thangaraj (Warden), Mrs. Thangaraj, Dr. Chandran Devanesen (Principal), Anand S. Mondkur (Speaker), S. Sivarum (Min. for Debates), N. S. Jagnathan (Min. for Entertainments), B. Ai Thinmaiah (Min. for Out door games), A. M. S. Jabbar (Min. for N. V. Mess), P. E. Chaderan (Usha Editor), C. Vallabhan, S. Loganathan, S. S. Thanaraj, G. K. Mathew, G. Belleny Knights, Ian Manning.

STANDING Messrs. Suresh, A. Francis, P. Palani, Radhakrishnan, Ehamaiah, Johnson, Serara T. Kethgetswe, Abdul Wajeed, Mathews Abraham, Palendran Kasi, Rajan, P. John, Edwinson Manay, Somasundaram, Ranganathan, J. Vasumithra, Chandrasekhar, Vetriraj Stalin, Thiagasundaram, K. S. Perumal, N. Nagarajan.

2nd " Munuswamy (Hall Peon), Ramesh Reddy, K. Surendranath, Solomon Manickam, Natarajan, Arokiarajan, Starling, Rangaswamy, R. S. Viswanathan, Saier Rao, Vijay Nicholas, P. Sachir, P. N. Vaidyanathan, Dilip Uthappa

3rd " D. Dharmaraja, S. D. Jayakar, J. Selvajayam, V. Ratnasabapathy, R. Jayaraman, Govind Varma.

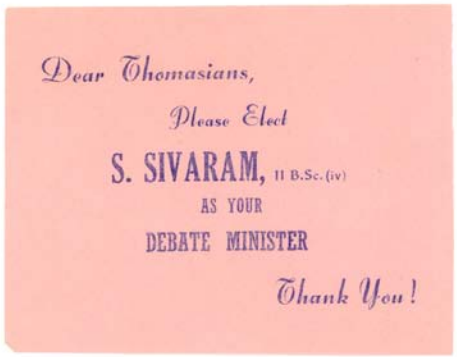
4th " S. Jeyaraman, T. Jagannathan, D. D. Thiruvengadam, Srinivasagam, Jacob Cherian, J. M. A. Mohammed Ismail, K. Ramanathan, V. Rathakrishnan, Jagannathan, N. Premkumar, Naderajah, P. L. Subramaniam, M. C. George, Jose Samuel, S. Mathew, Subramani, Swaminathan.

5th " Emeka Iyboili, Muthanna, Jacob Ponnen, Rajendra Prasad, C. P. P. Rathnam, A. M. Jacob, Philip Mathew, Jamal Hasan, Vishudath Jagroo, C. I. Cherian, Rajan Dorai, John Mathew, C. Julius Karunakaran, C. Thachan, A. K. Rajan, N. Arumugam, Ramakrishnan.

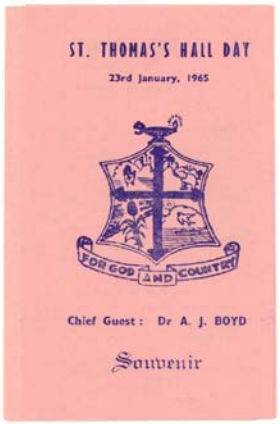
6th " A. Khan, Prabhakar Reddy, David Ang, Somaratne, Lim Peng Swee, Sellamuthu, Kugathasan, R. Palaniveli, D. Kannappan, D. Natarajan, Vincent Morris, S. Thiruchelvam, T. J. E. Jeyaseelan, Chandrasekhar A. Jeyachandran, Stephen Ferira, Shanmugham, P. Thangavelu, M. Thulasi.

7th " S. Nadarajan, S. Karunakar, R. Lazar, Mathew Abraham, C. Shanmuganathan, Victor Prince, Balalakshmipathy, R. Gopalan, Sudhakar Reddy, Krishna Reddy, T. K. S. Raghupathy, C. Perumal, A. Farid, Thiagarajan

HALL ELECTIONS : FIRST FORAYS IN LEADERSHIP SKILLS



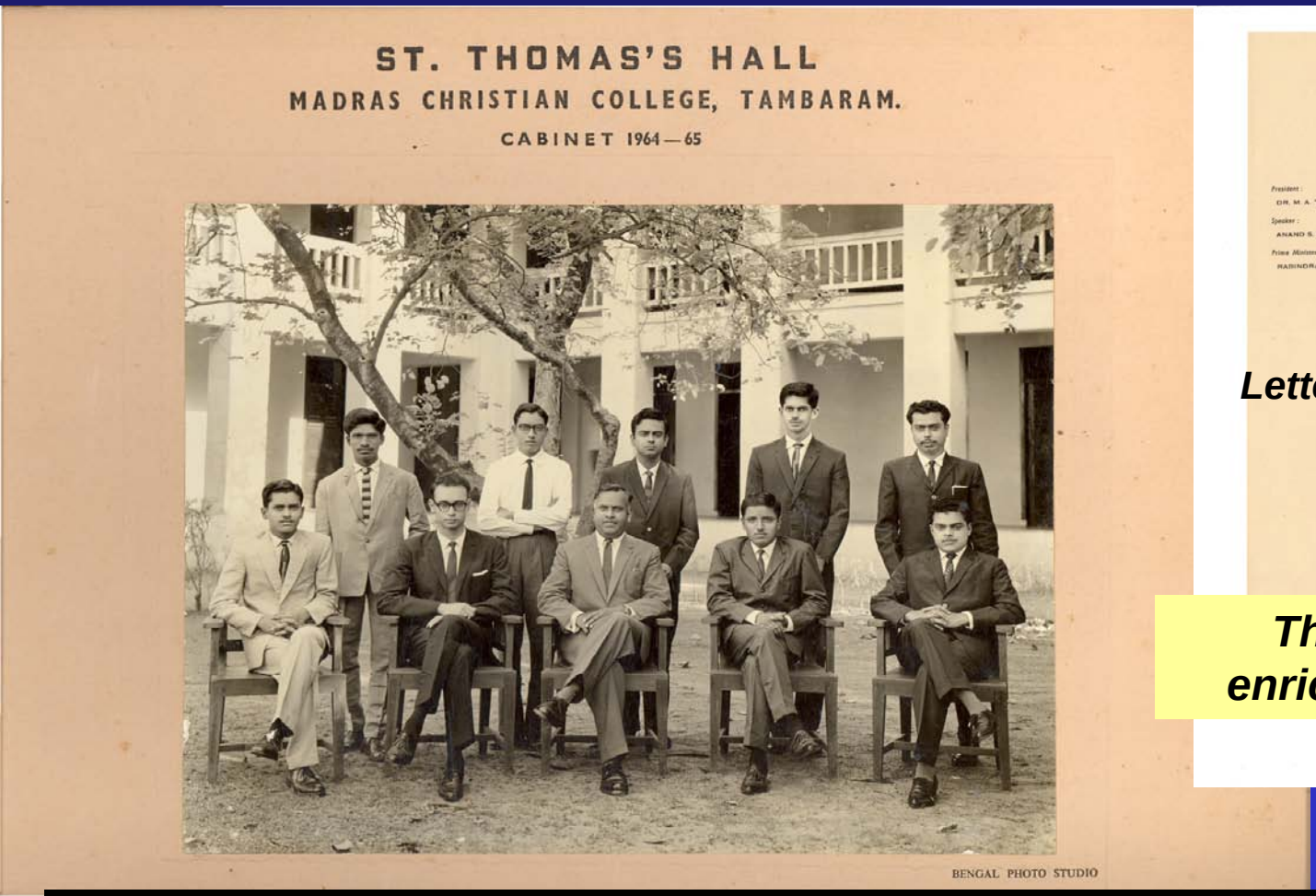
Learning the art of politics and winning popular votes

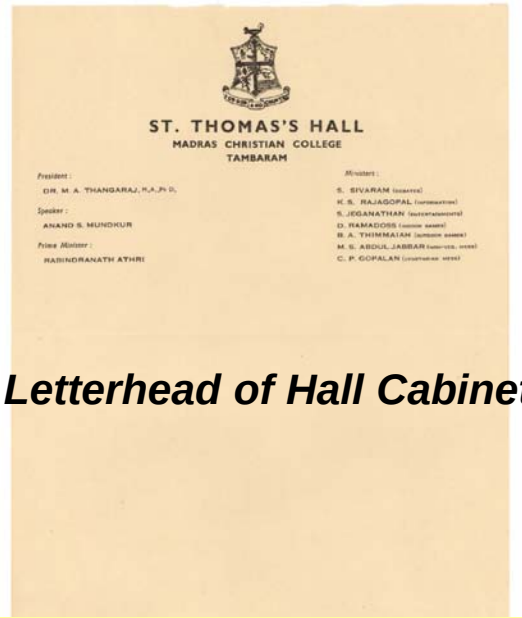


Organizing Hall Day
23 January 1965
Chief Guest : Dr A.J.Boyd

Lesson 2 : Provide early opportunities to learn leadership and organizational skills

THE PRIDE OF BEING A ST THOMASIAN !



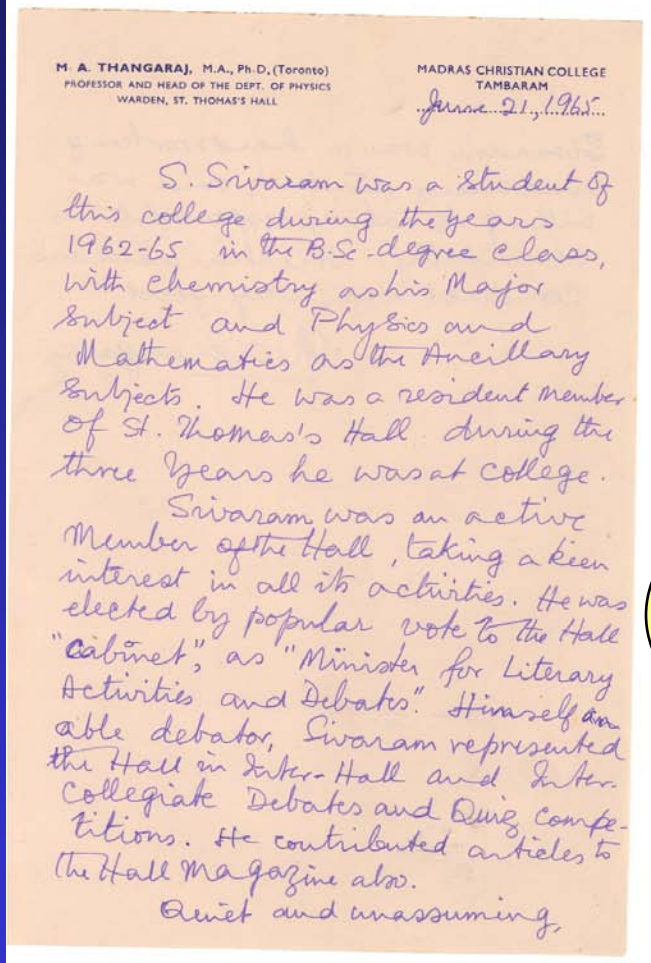


Letterhead of Hall Cabinet

Three years of life enriching experience !

Lesson 3 : Learning outside the classroom is more important than inside the classroom

A LETTER FROM DR M.A.THANGARAJ, WARDEN



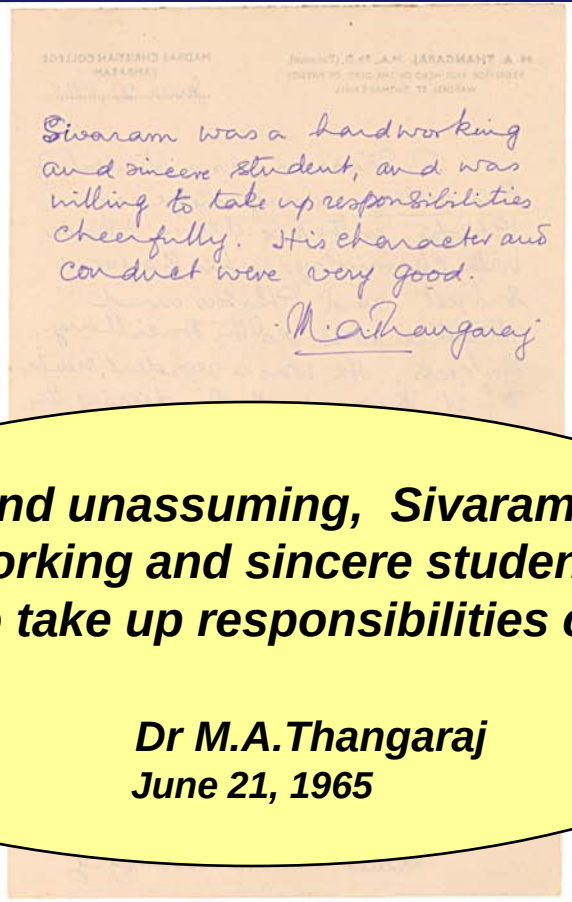
M. A. THANGARAJ, M.A., Ph.D. (Toronto)
PROFESSOR AND HEAD OF THE DEPT. OF PHYSICS
WARDEN, ST. THOMAS'S HALL

MADRAS CHRISTIAN COLLEGE
TAMBARAM
June 21, 1965

S. Sivaram was a student of this college during the years 1962-65 in the B.Sc. degree class, with chemistry as his Major subject and Physics and Mathematics as the Ancillary subjects. He was a resident member of St. Thomas's Hall during the three years he was at College.

Sivaram was an active Member of the Hall, taking a keen interest in all its activities. He was elected by popular vote to the Hall "Cabinet", as "Minister for Literary Activities and Debates". Himself an able debator, Sivaram represented the Hall in Inter-Hall and Inter-Collegiate Debates and Quiz competitions. He contributed articles to the Hall Magazine also.

Quiet and unassuming.



Sivaram was a hard working and sincere student, and was willing to take up responsibilities cheerfully. His character and conduct were very good.

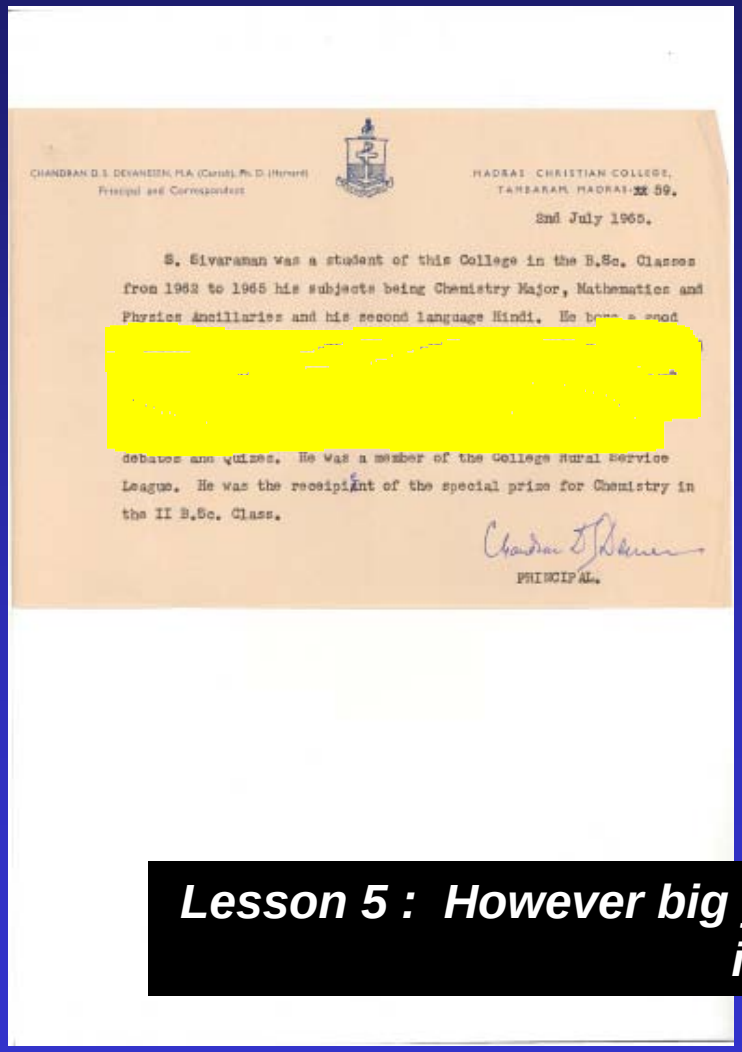
M. A. Thangaraj

"Quiet and unassuming, Sivaram was a hard working and sincere student and was willing to take up responsibilities cheerfully"

Dr M.A.Thangaraj
June 21, 1965

Lesson 4 : Be generous with praise ; It does wonders

A LETTER FROM THE PRINCIPAL



CHANDRAN D.S. DEVANESEN, M.A. (Cantab), Ph. D. (Harvard)
Principal and Correspondent

MADRAS CHRISTIAN COLLEGE,
TAMBARAM, MADRAS-59.

2nd July 1965.

S. Sivaraman was a student of this College in the B.Sc. Classes from 1962 to 1965 his subjects being Chemistry Major, Mathematics and Physics Ancillaries and his second language Hindi. He [redacted] debates and quizes. He was a member of the College Rural Service League. He was the receipient of the special prize for Chemistry in the II B.Sc. Class.

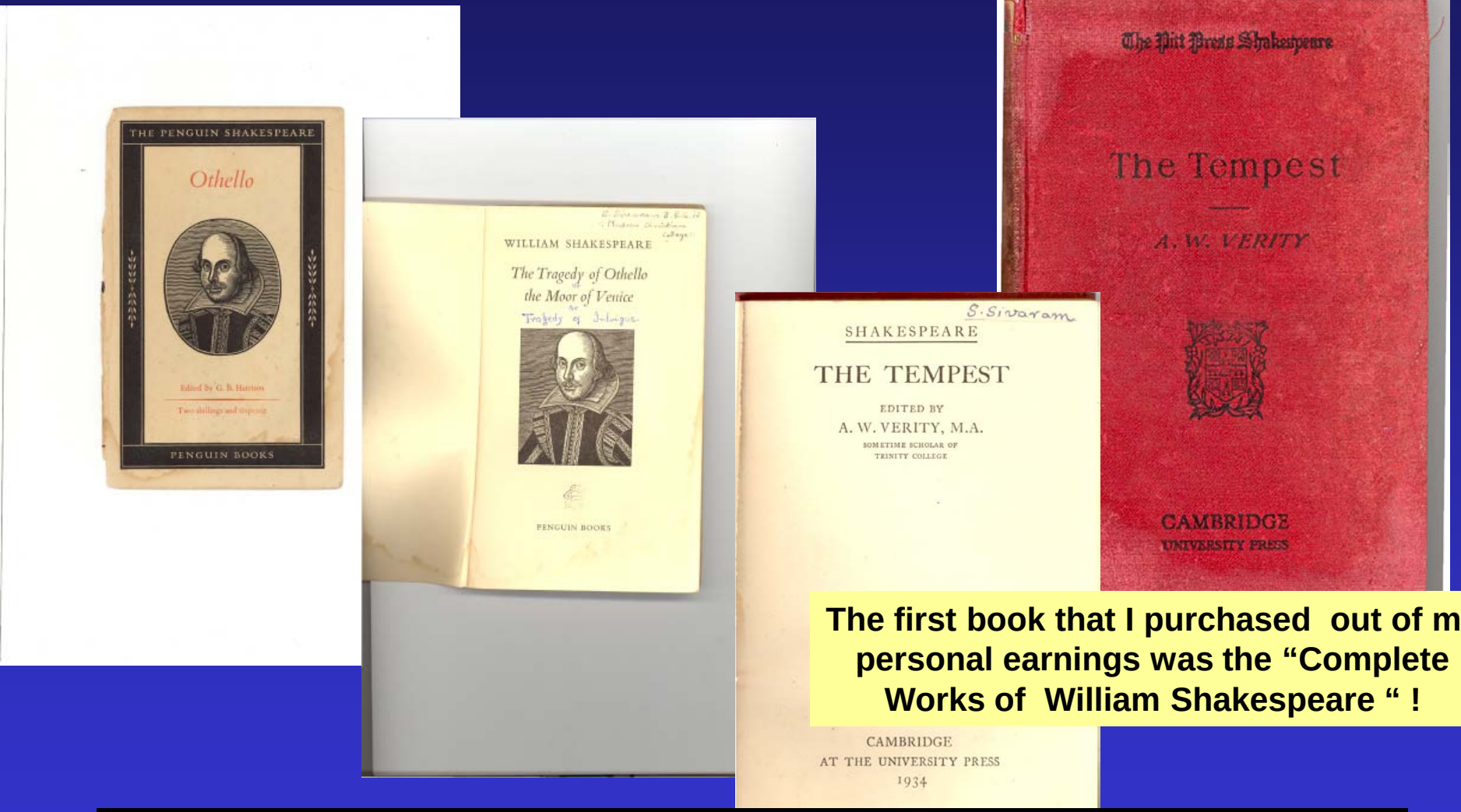
PRINCIPAL.

"The record of his class shows that he was a student of more than average ability and a steady worker"

Dr Chandran Devanesan
July 2.1965

Lesson 5 : However big you are , show that you care for everyone in your institution

THE BEAUTY OF THE WRITTEN WORD



The first book that I purchased out of my personal earnings was the "Complete Works of William Shakespeare " !

Lesson 6 : Teach to appreciate the beauty of the written word. Create the love for reading. Language is the window to the soul

THE BEAUTY OF THE WRITTEN WORD

- *सिंहासन हिल उठे राजवंशों ने भृकुटी तानी थी,*
  बूढ़े भारत में आई फिर से नयी जवानी थी,
  गुमी हुई आज़ादी की कीमत सबने पहचानी थी,
  दूर फिरंगी को करने की सबने मन में ठानी थी।
  चमक उठी सन सत्तावन में, वह तलवार पुरानी थी,
  बुंदेले हरबोलों के मुँह हमने सुनी कहानी थी,
  खूब लड़ी मर्दानी वह तो झाँसी वाली रानी थी।।

Harivansh Rai Bacchan

A life long love affair with books !

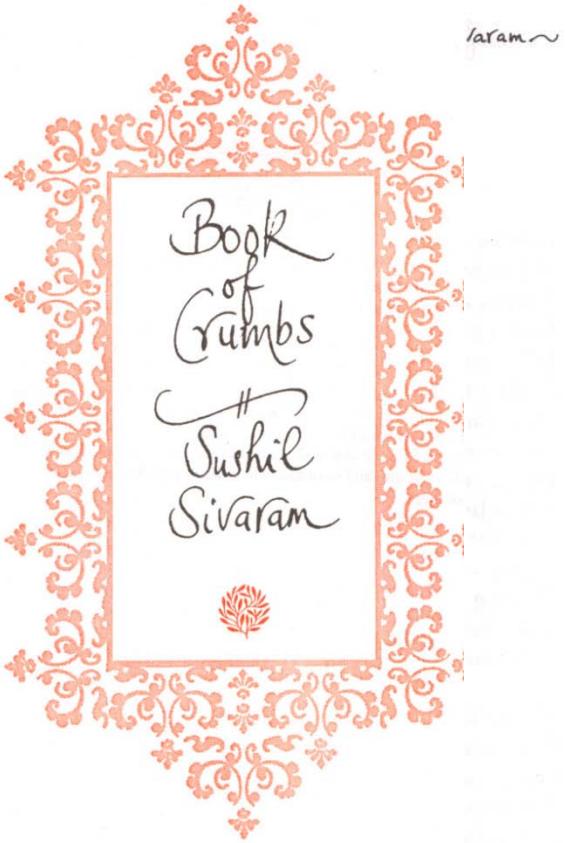
Subadhra Kumari Chauhan

मुसलमान औ' हिन्दू है दो, एक, मगर, उनका प्याला, एक, मगर, उनका मदिरालय, एक, मगर, उनकी हाला, दोनों रहते एक न जब तक मस्जिद मन्दिर में जाते, बैर बढ़ाते मस्जिद मन्दिर मेल कराती मधुशाला!।५०।

- **The Muslim and the Hindu are different, but they drink out of the same cup/ They drink at the same tavern, their wine is also the same/ They remain together so long as they stay away from the temple or mosque/ The temple and the mosque divide but the tavern only unites.**

LOVERS OF LITERATURE AND POETRY

Sushil : A writer and a poet



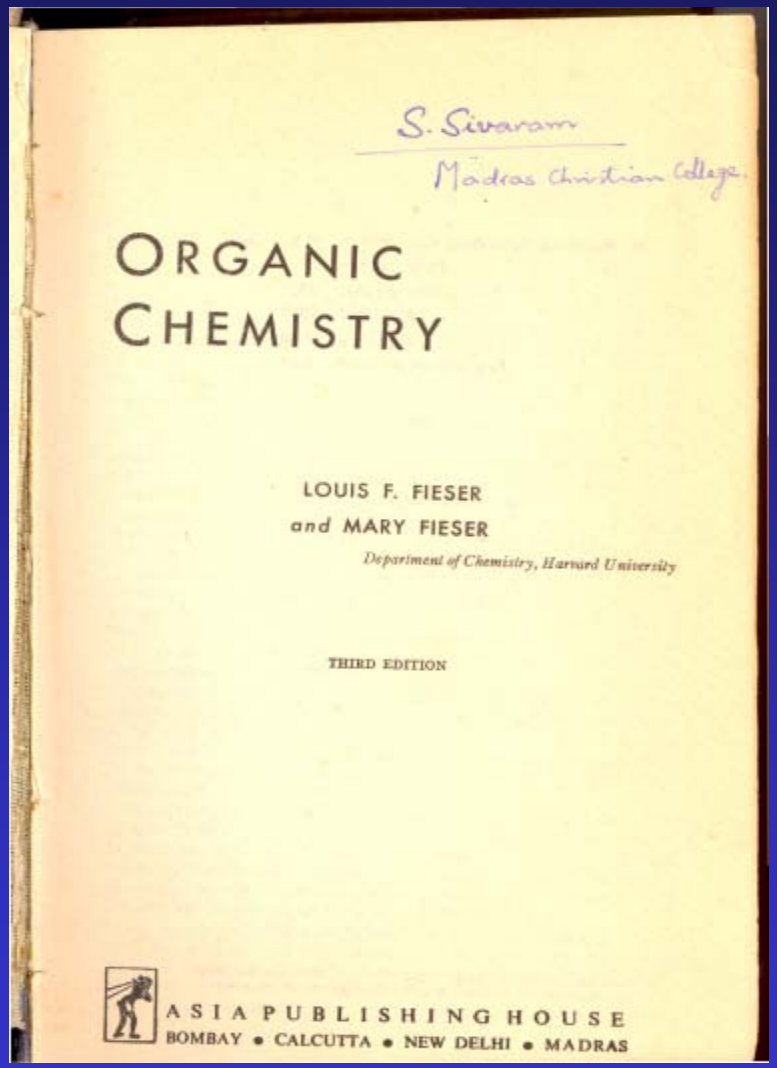
Rama : Literature, Art Historian and communicator

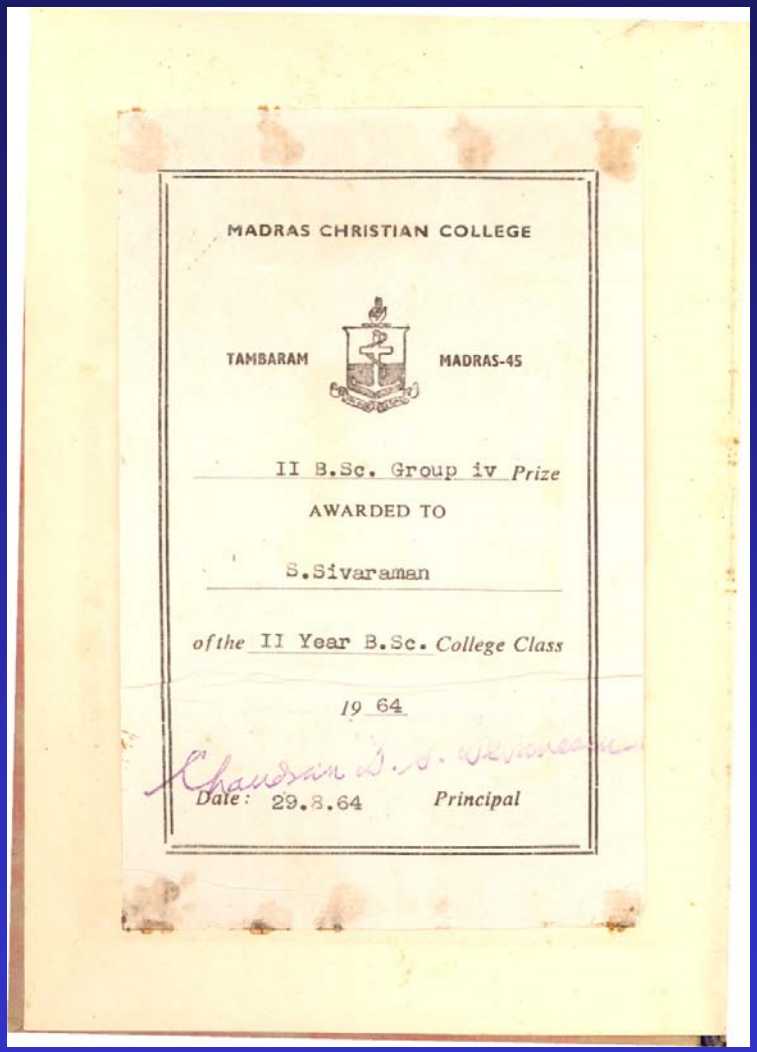
Book of Crumbs

Chemistry

You were wedded
To your polycarbonates.
In plastic satin,
Lotus stemmed siphon
Of chemical abstractions.
She was your whore,
A morning song –
Embalmed in turmeric and grey ash scent.
She was a spiritual crank
Of a rusted automobile,
Rotating
Like the little magnetic stirrer
At the bottom of our
Pyrex, conical flask.
Irony sitting pale,
On the Aldrich catalogue,
Schedules painted on the white board,
Teleconferences.
You couldn't hear my tear
Pelting within your outside,
For windows were sealed
And air-conditioners bellowed
Outside your inside.
Aboriginal pamphlets
Of hexagonal carbon double bonds
Like Fractal Geometry,
You left
You're lonely
Patents pending.

MY FIRST POSSESSION IN CHEMISTRY !





Lesson 7 : If you want to find out a person's real aptitude, give him a gift and ask him to select a book from a bookstore

EDUCATION AT MCC

- **Committed teachers who were genuinely interested in the student**
- **An ambience of research and scholarship**
- **Liberal education; apart from English and Hindi (prose and poetry) I had an opportunity to learn philosophy and economics; a class in moral instruction introduced me to the Old Testament ; led to a life long affair with books**
- **No early specialization**
- **A small class of just twenty !**
- **A compelling urge to excel !**

Lesson 8 : Teachers who are committed and show genuine interest in their pupil make good institutions great

THE INEVITABLE EXAMINATIONS !

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THREE-YEAR DEGREE COURSE

B.Sc. DEGREE EXAMINATION, APRIL 1965.

Part III—Branch IV—Chemistry Main—Group A

Paper I

THEORETICAL CHEMISTRY

Time: Three hours. *Maximum: 100 marks.*

Answer any FIVE questions.

All questions carry equal marks.

1. How was neutron discovered? Write an accou nuclear reactions brought about by neutrons. Ex any one use of a radioactive tracer in physico-che investigations.

2. What is meant by (*a*) molar refraction (*b*) molar polarization? How are these quantities u in the study of the structure of molecules?

3. How are the following results established:—

(*a*) α particles consist of helium nuclei.

(*b*) Ordinary water contains a small amou heavy water.

(*c*) Carbon dioxide is a linear molecule?

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THREE-YEAR DEGREE COURSE

B.Sc. DEGREE EXAMINATION, APRIL 1965.

Part III—Branch IV—Chemistry Main—Group A

Paper II

INORGANIC CHEMISTRY

Time: Three hours. *Maximum: 100 marks.*

Answer any FIVE questions.

All questions carry equal marks.

1. Describe Morley's experiment for the determination of the composition of water. Under what conditions does water react with the following:—sodium, magnesium, iron, chlorine, sodium peroxide and calcium oxide? Give equations.

2. How is pure hydrogen peroxide prepared? Mention its properties and uses. 25 c.c. of acidulated hydrogen peroxide solution required 20 c.c. of decinormal solution of potassium permanganate for complete oxidation. Calculate the volume of oxygen at N.T.P. produced during this reaction.

3. How is chlorine manufactured? What are its industrial applications?

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THREE-YEAR DEGREE COURSE

B.Sc. DEGREE EXAMINATION, APRIL 1965.

Part III—Branch IV—Chemistry Main—Group A

Paper IV

PHYSICAL CHEMISTRY

Time: Three hours. *Maximum: 100 marks.*

Answer any FIVE questions.

All questions carry equal marks.

1. State Dalton's Law of partial pressures. One g of nitrogen and one g of oxygen are put in a 2 litre flask at 27°C. Find (*a*) the partial pressure of each gas, (*b*) the total pressure and, (*c*) the composition of the mixture in mole percent.

2. Derive the equation $PV = 1/3\ m\ N\ \bar{C}^2$ for an ideal gas. Calculate the mean square velocity of oxygen at 0°C.

3. Explain Henry's Law of solubility of gases in liquids. What is Bunsen absorption coefficient? The Bunsen absorption coefficients of oxygen and nitrogen in water are 0.0283 and 0.0143 at 25°C. Calculate the volume of nitrogen and oxygen at S.T.P. dissolved in 100 c.c. of water, when the water is saturated with air at 25°C at (*a*) 1 atm pressure and (*b*) at 10 atm

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THREE-YEAR DEGREE COURSE

B.Sc. DEGREE EXAMINATION, APRIL 1965.

Part III—Branch IV—Chemistry Main—Group A

Paper III

ORGANIC CHEMISTRY

hours. *Maximum: 100 marks.*

Answer any FIVE questions.

ll questions carry equal marks.

re the following synthesised:—

Methyl glyoxal.

Leucine.

Acetonyl acetone.

Adipic acid?

g with nitrobenzene, how are the following

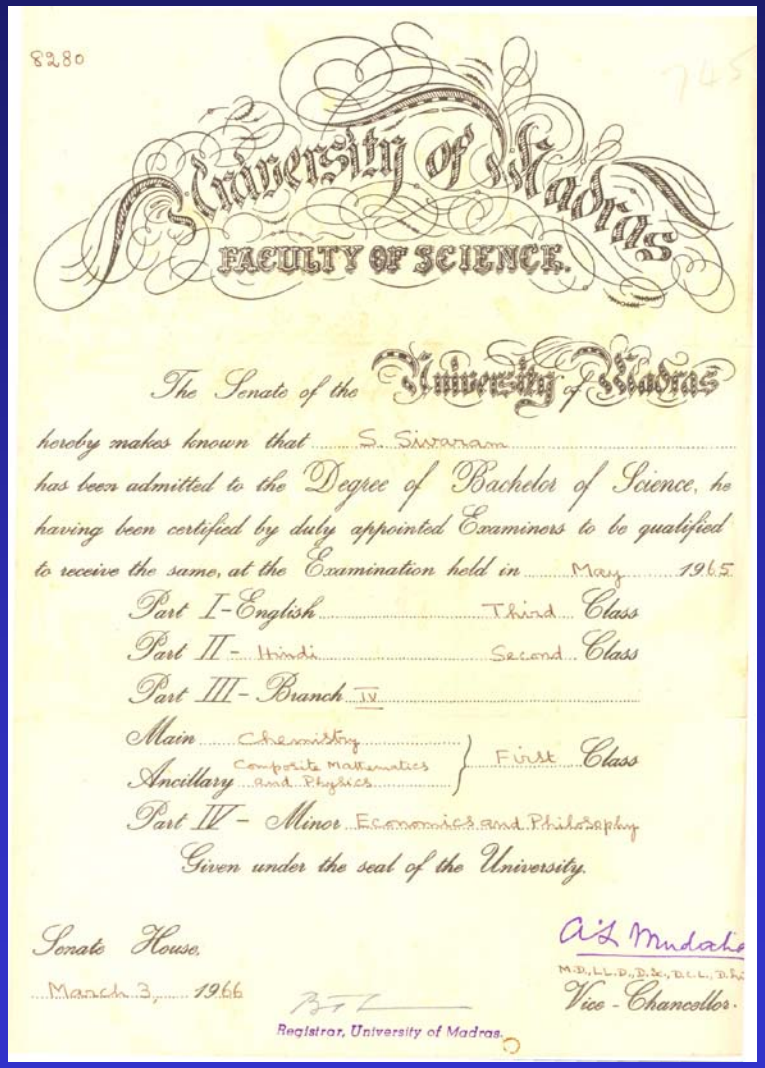
niline, azobenzene, benzidine and phenyl-

glycerol synthesised? Describe the action

dic acid, (*b*) potassium hydrogen sulphate

acid, upon glycerol on heating.

THE THRILL OF A PRIZED AQUISITION



University of Madras

FACULTY OF SCIENCE.

The Senate of the University of Madras

hereby makes known that S. Sivaram

has been admitted to the Degree of Bachelor of Science, he having been certified by duly appointed Examiners to be qualified to receive the same, at the Examination held in May 1965

Part I - English ..... Third Class

Part II - Hindi ..... Second Class

Part III - Branch IV

Main Chemistry

Ancillary Composite Mathematics and Physics } First Class

Part IV - Minor Economics and Philosophy

Given under the seal of the University.

Senate House,

March 3, 1966

A.L. Mudaliar

M.D., LL.D., D.Sc., D.C.L., D.Litt.

Vice-Chancellor.

Registrar, University of Madras.

March 3, 1966

- ***English : Third class***
- ***Hindi : Second class***
- ***Chemistry :First class***
- ***Physics and Mathematics (Ancillary) : First class***
- ***Philosophy and Economics (Minors)***

I left MCC, not merely armed with a degree but, with a preparation for life

Lesson 9 : A liberal education is far more important than learning a few subjects; You can rebuild a façade but can lay the foundation only once

IN DISTINGUISHED COMPANY !

A college which produces such men and women must have some great genes

E.C.G. Sudarshan

Prakash Karat

Indra Nooyi

M.V.George

T.N.Seshan

S. Radhakrishnan

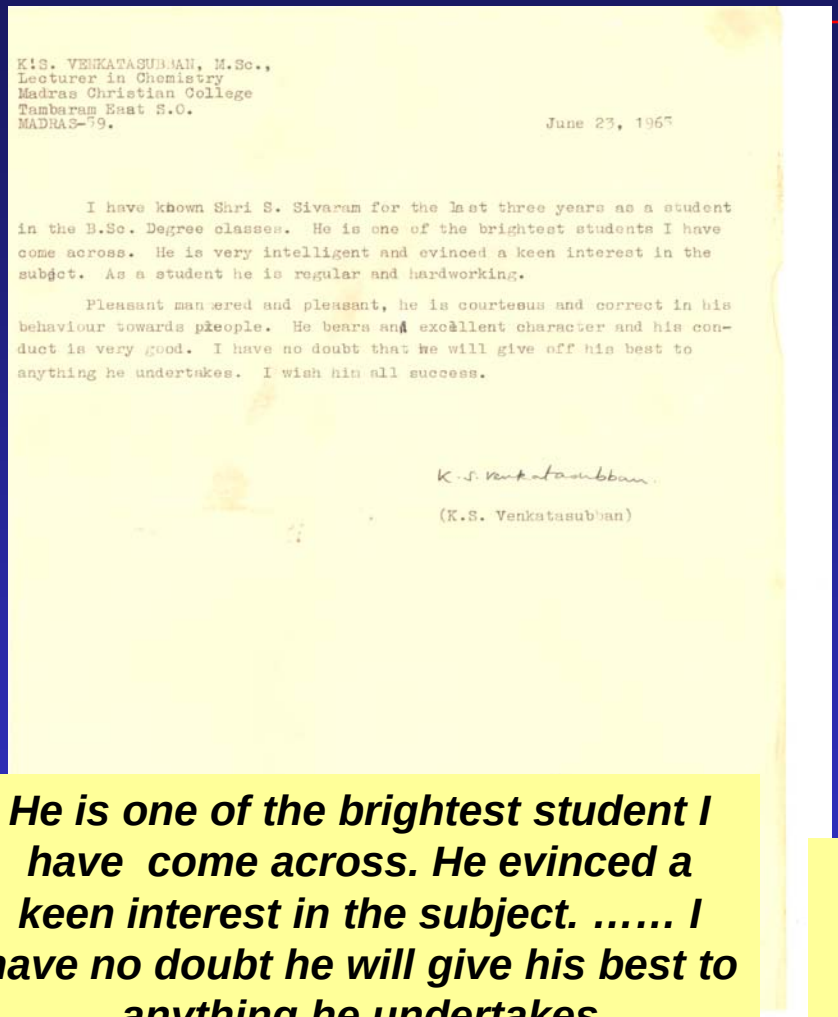
TIME TO SAY GOOD BYE

The class of `65 with Professor S.V.Ananthakrishnan

A rare photograph of a B. Sc Class with Professor Ananthakrishnan !

While addressing us at this valedictory function, SVA in his characteristic candidness said that not many of us will get far ahead in our lives !

GREATEST REWARDS FOR A STUDENT



K.S. VENKATASUBBAN, M.Sc.,
Lecturer in Chemistry
Madras Christian College
Tambaram East S.O.
MADRAS-59.

June 23, 1967

I have known Shri S. Sivaram for the last three years as a student in the B.Sc. Degree classes. He is one of the brightest students I have come across. He is very intelligent and evinced a keen interest in the subject. As a student he is regular and hardworking.

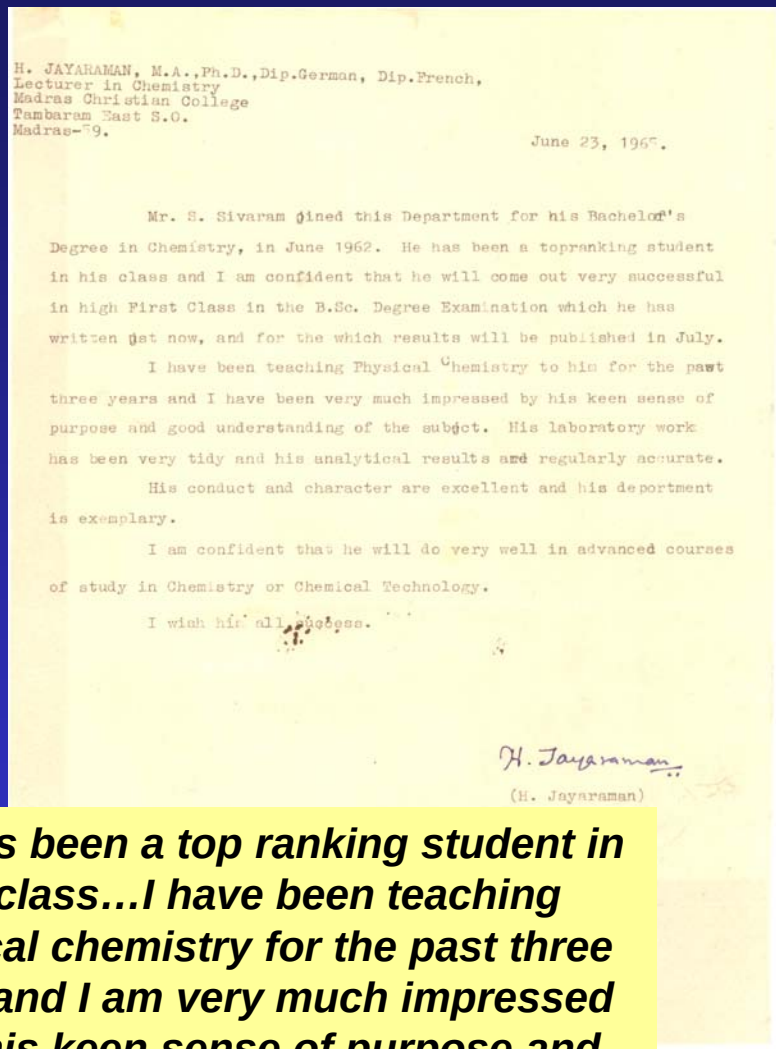
Pleasant mannered and pleasant, he is courteous and correct in his behaviour towards people. He bears an excellent character and his conduct is very good. I have no doubt that he will give off his best to anything he undertakes. I wish him all success.

K.S. Venkatasubban

(K.S. Venkatasubban)

He is one of the brightest student I have come across. He evinced a keen interest in the subject. …… I have no doubt he will give his best to anything he undertakes

K.S.Venkatasubban



H. JAYARAMAN, M.A.,Ph.D.,Dip.German, Dip.French,
Lecturer in Chemistry
Madras Christian College
Tambaram East S.O.
Madras-59.

June 23, 1967.

Mr. S. Sivaram joined this Department for his Bachelor's Degree in Chemistry, in June 1962. He has been a topranking student in his class and I am confident that he will come out very successful in high First Class in the B.Sc. Degree Examination which he has written just now, and for the which results will be published in July.

I have been teaching Physical Chemistry to him for the past three years and I have been very much impressed by his keen sense of purpose and good understanding of the subject. His laboratory work has been very tidy and his analytical results are regularly accurate.

His conduct and character are excellent and his deportment is exemplary.

I am confident that he will do very well in advanced courses of study in Chemistry or Chemical Technology.

I wish him all success.

H. Jayaraman

(H. Jayaraman)

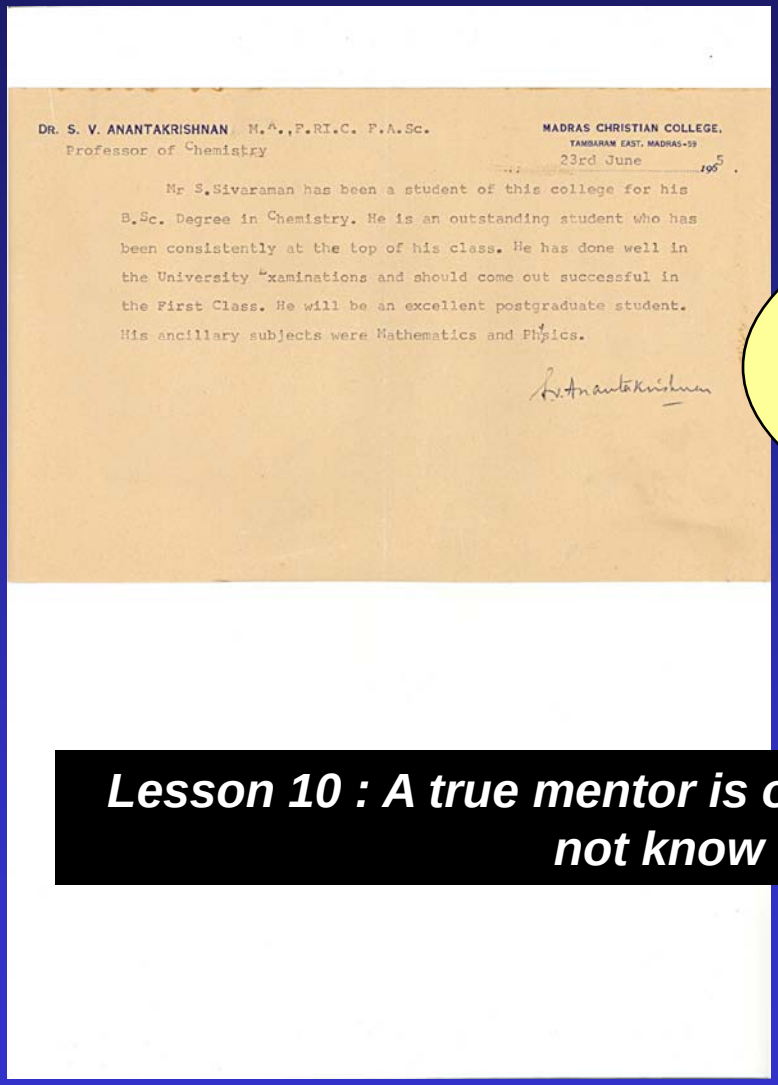
"He has been a top ranking student in his class…I have been teaching physical chemistry for the past three years and I am very much impressed with his keen sense of purpose and understanding of the subject"

H.Jayaraman

FROM MADRAS TO KANPUR

- **January 25, 1965 : The anti Hindi agitation begins all over the state of Madras**
- **Fuelled by politicians students are in the forefront of the agitation**
- **Colleges closed, examinations postponed and hostels vacated**
- **Postgraduate admissions possible only in Madras University**
- **An extraordinary intervention by SVA ; suggests that I try and seek admission to IIT Kanpur , where the Master's programme is commencing in 1965 ; tells me that IIT Kanpur has an outstanding faculty , including, two alumni of MCC – Professor M.V.George and Professor P.T. Narasimhan**
- **SVA gives me a letter of introduction to Professor P.T. Narasimhan and a letter of recommendation**

THE POWER OF THE TRUE MENTOR



DR. S. V. ANANTAKRISHNAN M.A.,P.RI.C. F.A.Sc.
Professor of Chemistry

MADRAS CHRISTIAN COLLEGE,
TAMBARAM EAST, MADRAS-59

23rd June 195[illegible].

Mr S.Sivaraman has been a student of this college for his B.Sc. Degree in Chemistry. He is an outstanding student who has been consistently at the top of his class. He has done well in the University Examinations and should come out successful in the First Class. He will be an excellent postgraduate student. His ancillary subjects were Mathematics and Physics.

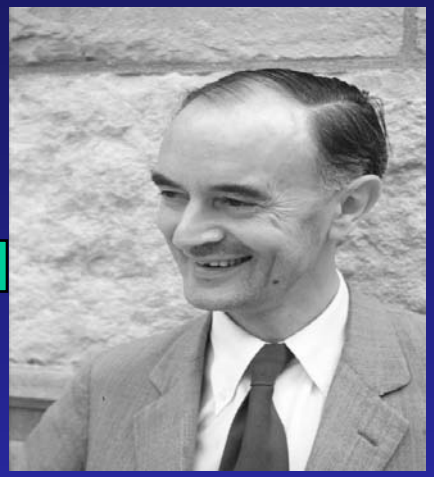
S.V.Anantakrishnan

"He has been an outstanding student who has been consistently at the top of his class. He has done well in the University examination and should come out successful in the first class He will be an excellent postgraduate student"

Lesson 10 : A true mentor is one who shows you the way when you do not know where you want to go

THE INGOLD CONNECTION

S.V.Ananthakrishnan
PhD with Professor Ingold
1908-89



Christopher K. Ingold
1893-70

The first book That I bought out of my personal earnings was "The Structure and Mechanism In Organic Chemistry", Second Edition, 1969, by C.K.Ingold

- **Ingold is considered to be the most influential chemist of the twentieth century**
- **The first organic chemist to use quantitative tools for the study of structure and reactivity ; the first physical organic chemist !**
- **Chemists use extensively the vocabulary of Ingold – nucleophilic, electrophilic, carbonium ion , R and S stereochemical notations , tautomerism, mesomerism , SN 1 and SN 2 mechanism; the use of curved arrows to indicate electron flow**
- **Role of steric and electronic factors in determining the reactivity of organic compounds**
- **Directive effects in aromatic substitution**
- **Kinetics of organic reactions and isotope effects to probe mechanisms**

ANANTAKRISHNAN AND INGOLD CITED IN GOULD`S BOOK

My love for this book connected me to the heritage of SVA

EDWIN S. GOULD

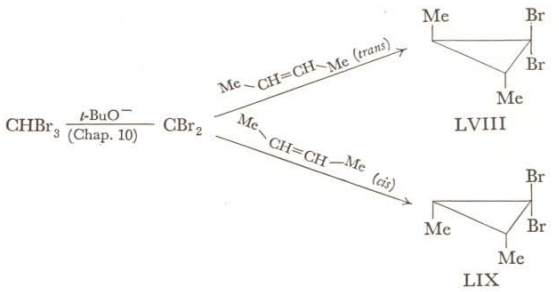
Stanford Research Institute

Mechanism and Structure in Organic Chemistry

This book has been purchased in the United States by the Kanpur Indo-American Program with dollar funds provided by the U.S.A.I.D. for use of students at the Indian Institute of Technology Kanpur. It has been sold at a subsidized price to a student at the IITK for his personal use. Sale of the book by the student to any person or any organization other than the IITK is a breach of the terms of the original sale of the book to the student.

HOLT, RINEHART AND WINSTON

New York - Chicago - San Francisco
Toronto - London



LVIII LIX

of olefins and their reactivities toward CBr_2 parallel the structure-reactivity relationships observed for heterolytic bromine addition[42(a)] and those for olefin epoxidation.[42(b)] The following reactivity sequence applies to all three types of addition reaction:[41]

$$Me_2C{=}CMe_2 > Me_2C{=}CHMe > Me_2C{=}CH_2 > \bigcirc \gg CH_2{=}CHCH{=}CH_2 >$$

$$\bigcirc \gg PhCH{=}CH_2 \gg PhCH_2CH{=}CH_2$$

On the other hand, these olefins follow a very different sequence with respect to their reactivity toward addition of CCl_3Br in the presence of peroxides,[42(c)] a reaction in which the C=C bond is attacked by a $Cl_3C\cdot$ radical (Chap. 16). Here the following order is observed:

$$CH_2{=}CH{-}CH{=}CH_2 > PhCH{=}CH_2 > Me_2C{=}CH_2 > Me_2C{=}CHMe >$$

$$\bigcirc > PhCH_2CH{=}CH_2 > \bigcirc$$

Thus, until more definitive evidence is available, we may infer that CBr_2 attacks as an electrophile rather than as a radical—that is, that it has zero unpaired electrons rather than two.

A somewhat similar question is associated with the familiar Diels-Alder reaction, which, the reader will recall, consists of the addition of a diene to a second unsaturated molecule—generally designated as a *dienophile* (which often, but not invariably, has one or more electron-attracting groups in conjugation

[41] (a) Ingold, *et al.*, *J. Chem. Soc.*, **1931**, 2354; **1935**, 984, 1396. (b) Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947). (c) Kharasch, *et al.*, *J. Org. Chem.*, **14**, 239, 537 (1949); **18**, 328 (1953).

PAPERS BY ANANTAKRISHNAN AND INGOLD
(from the Ph D thesis of SVA)

Addition of bromine to ethylene and substituted ethylenes : Role of methyl substituent on reactivity

226. *Influence of Substituents on the Additive Reactivity of Ethylene Derivatives. Part II. Effects of Catalysts on the Relative Rates of Addition of Bromine.*

By S. V. Anantakrishnan and Christopher K. Ingold.

The object of these researches is to determine, first, the effect of a single group, R, on the rate of reaction of R·CH:CH$_2$ towards addenda, and secondly, the rules under which such effects are compounded when several R's are simultaneously attached to the group C:C. When the electronic classification (nucleophilic or electrophilic) of the reagent is known, the influence on reaction rate should be capable of correlation with the modes of electron displacement characteristic of R.

Part I (Ingold and Ingold, J., 1931, 2354) commenced a study, which this paper continues, of the reactivity of ethylene derivatives towards the unambiguously electrophilic reagent, bromine. It was shown that the effect of substituents, R, could not in general be deduced by analogy with other reactions (tautomerism, aromatic substitution, etc.), because the polarisation and polarisability of a group contribute with different relative weights for every reaction, and it is impossible to tell in advance how these factors should be weighted in the addition reaction with bromine. It was also shown that the intrinsic effects of R's when present singly could not in general be deduced by an analysis of results for compounds in which several R's are present together: two activating groups could jointly deactivate, and *vice versa*. Theory defines the scope of these ambiguities, and it happens that most known results are affected by them. Therefore the authors of Part I sought to establish the fundamental relationships concerning group influence in the bromine addition reaction by choice of the proper examples, which, however, are not convenient for the purpose of detailed kinetic measurement. Accordingly, recourse was had to the com-

J. Chem. Soc, 1935

334. *Influence of Substituents on the Additive Reactivity of Ethylene Derivatives. Part III. Further Experiments on the Addition of Bromine in Solution.*

By S. V. Anantakrishnan and Christopher K. Ingold.

In this paper we report an extension of the investigation commenced in Part I (Ingold and Ingold, J., 1931, 2354) on the relative rates of addition of simple ethylene derivatives towards the electrophilic reagent, bromine. We have throughout standardised the catalytic conditions for this reaction by the method worked out in Part II (Anantakrishnan and Ingold, this vol., p. 984), a sufficient quantity of hydrogen bromide being added initially to cover up completely the autocatalysis of the reaction as well as any adventitious catalysis.

It was shown in Part I that the intrinsic effect of a given substituent on the reactivity of an ethylene bond towards a reagent such as bromine can be deduced only by reference to certain structural types. These may contain either just the single substituent under consideration or combinations of substituents subject to definite restrictions; for many combinations give rise to mutual effects which seriously distort, and may even invert, the separate effects of the groups. Theory, confirmed by observations as far as these have been extended, shows when it is possible for this to happen, and therefore indicates the structural types which may most profitably be studied.

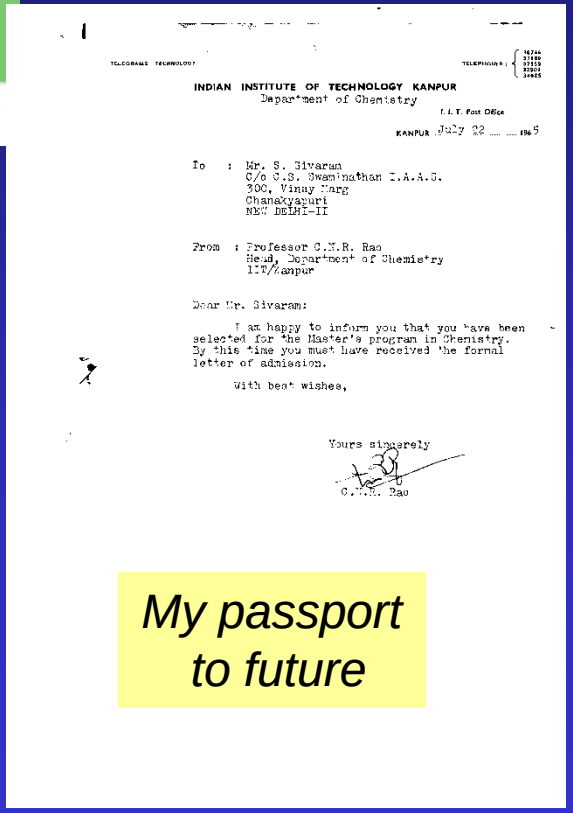
Lesson 11 : Knowledge is akin to insurance; You never know when you will need it.

DEPARTMENT OF CHEMISTRY, IIT KANPUR (1965-67)

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

DEPARTMENT OF CHEMISTRY, IIT KANPUR (1965-67)

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



INDIAN INSTITUTE OF TECHNOLOGY KANPUR
Department of Chemistry
I. I. T. Post Office
KANPUR July 22 1965

To : Mr. S. Sivaram
C/o C.S. Swaminathan I.A.A.S.
300, Vinay Marg
Chanakyapuri
NEW DELHI-11

From : Professor C.N.R. Rao
Head, Department of Chemistry
IIT/Kanpur

Dear Mr. Sivaram:

I am happy to inform you that you have been selected for the Master's program in Chemistry. By this time you must have received the formal letter of admission.

With best wishes,

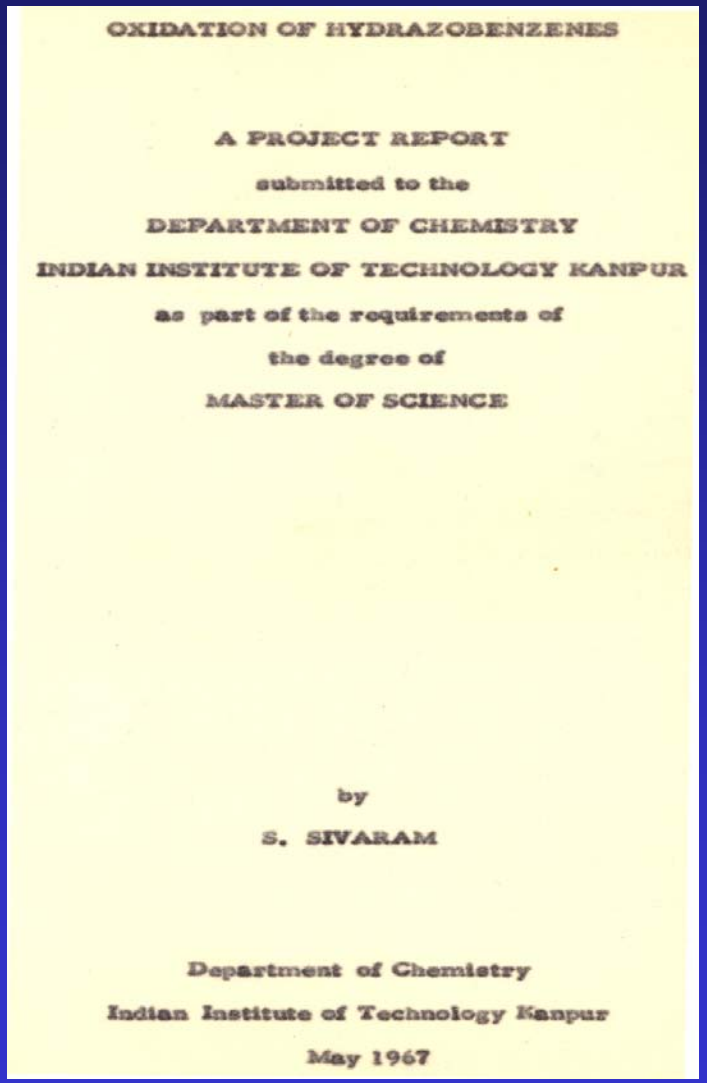
Yours sincerely

C.N.R. Rao

My passport to future

Lesson 12 : Teach less; encourage self learning; make learning a pleasure

THE FIRST TASTE OF RESEARCH



OXIDATION OF HYDRAZOBENZENES

A PROJECT REPORT

submitted to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

as part of the requirements of

the degree of

MASTER OF SCIENCE

by

S. SIVARAM

Department of Chemistry

Indian Institute of Technology Kanpur

May 1967

- Oxidation of hydrazobenzenes to azobenzenes using radical anions
- Na and K Naphthalene as radical anion source
- Effect of para substituent on the rate of oxidation
- Rate measured using a Beckman DU UV-Visible Spectrophotometer
- My little thesis undergoes about ten revisions in the hands of Professor M. V. George !

Lesson 13 : Pay attention to details; small things are important in science

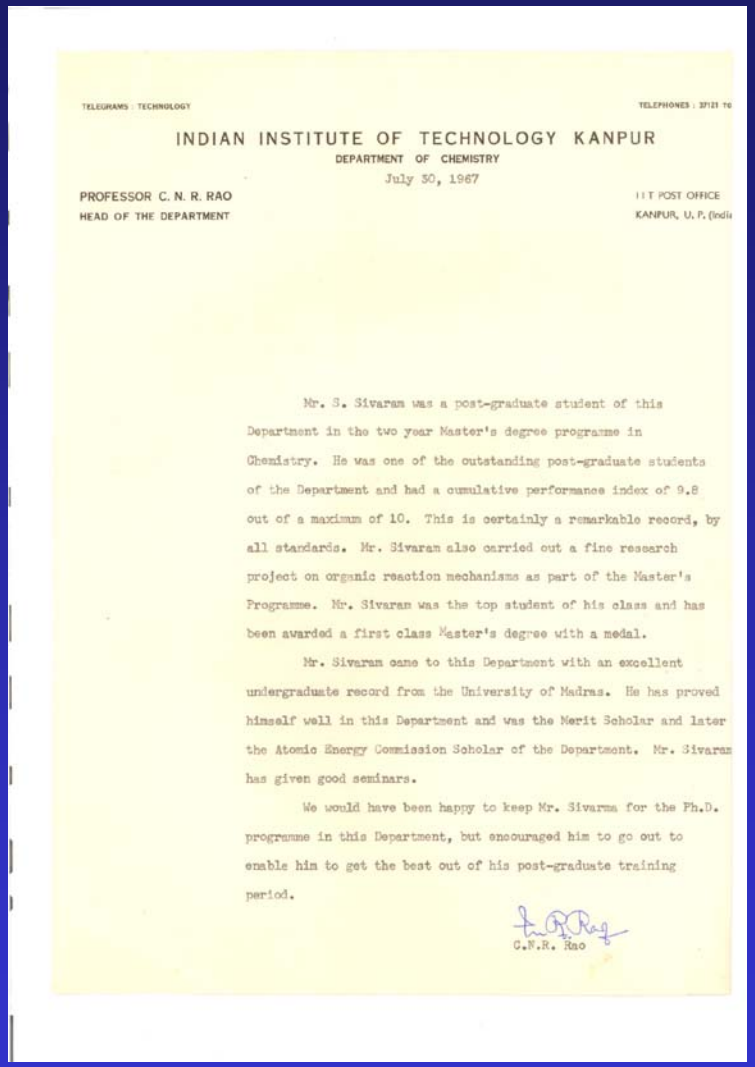
A MENTOR SETS THE COURSE (once again!)

Professor C. N. R. Rao

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

Lesson 14 : A true mentor is one who is more concerned about his student, not himself

A LETTER FROM PROFESSOR RAO



TELEGRAMS : TECHNOLOGY

TELEPHONES : 37121 TO

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

DEPARTMENT OF CHEMISTRY

July 30, 1967

PROFESSOR C. N. R. RAO
HEAD OF THE DEPARTMENT

I I T POST OFFICE
KANPUR, U. P. (India

Mr. S. Sivaram was a post-graduate student of this Department in the two year Master's degree programme in Chemistry. He was one of the outstanding post-graduate students of the Department and had a cumulative performance index of 9.8 out of a maximum of 10. This is certainly a remarkable record, by all standards. Mr. Sivaram also carried out a fine research project on organic reaction mechanisms as part of the Master's Programme. Mr. Sivaram was the top student of his class and has been awarded a first class Master's degree with a medal.

Mr. Sivaram came to this Department with an excellent undergraduate record from the University of Madras. He has proved himself well in this Department and was the Merit Scholar and later the Atomic Energy Commission Scholar of the Department. Mr. Sivaram has given good seminars.

We would have been happy to keep Mr. Sivarma for the Ph.D. programme in this Department, but encouraged him to go out to enable him to get the best out of his post-graduate training period.

C.N.R. Rao

"He was an outstanding postgraduate student of the department and had a cumulative performance index of 9.8 out of 10. This is certainly a remarkable record by all standards……..We would have been happy to keep Sivaram for the Ph D programme in this department, but encouraged him to go out to enable him to get the best out of his post graduate training period "

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

FROM KANPUR, INDIA TO W.LAFAYETTE, INDIANA, USA
August 1967

Purdue University

R. B. Wetherill Laboratories for Chemistry An ACS National Historic Landmark

PURDUE UNIVERSITY, DEPARTMENT OF CHEMISTRY, 1967-71

- **Professor Brown gives me a choice of two topics : Organoborane chemistry and carbonium ion chemistry; I choose the latter**
- **The die is cast . I am now on my way to becoming a physical organic chemist !**
- **Rich experience; learning to be independent in thought and action**
- **Heady days, great teachers (Nathan Kornblum, Robert Benkeser, Derek Davenport, Fred Mclafferty, Harry Morrison, Henry Feuer)**
- **Research and classroom learning**
- **Great friendships**

BRIDGED PHENONIUM ION OR EQUILIBRATING CARBONIUM ION ?

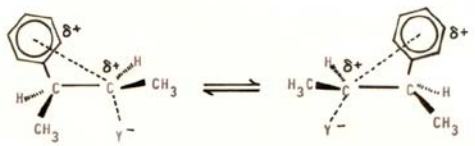


Figure 2. A Possible k_{Δ} Intermediate

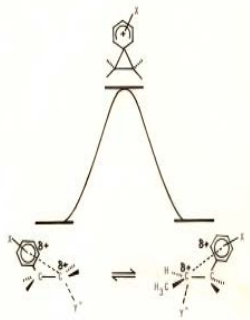
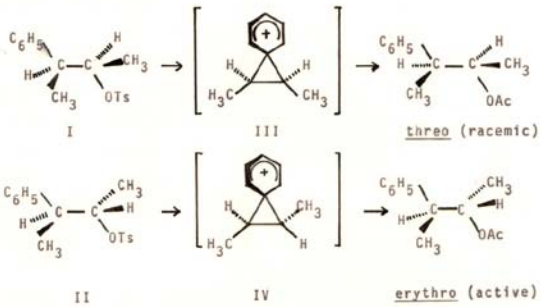


Figure 1. A Possible Intermediate in the Aryl Assisted Pathway

active products as shown in scheme 2.

Scheme 2

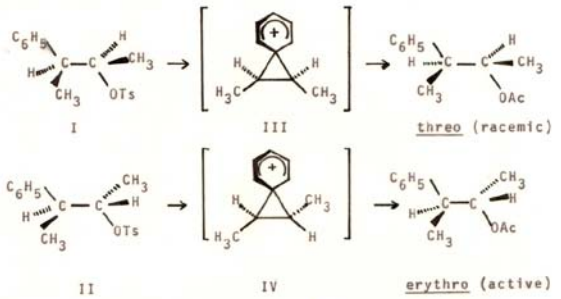


The initial simplicity of the phenonium ion theory, however, was largely lost when results of more detailed study on the rates and products became available. It was observed that the rate of racemization was considerably greater than the rate of acetolysis. This was attributed to ion pair return by Winstein and Schreiber.[10] The intermediacy of phenonium tosylate ion pairs were invoked to explain this observation. These ion pairs return to starting material as well as dissociate to products, all processes occurring with

RETENTION IN STEREOCHEMISTRY IS INCONSISTENT WITH A SYMMETRIC INTERMEDIATE

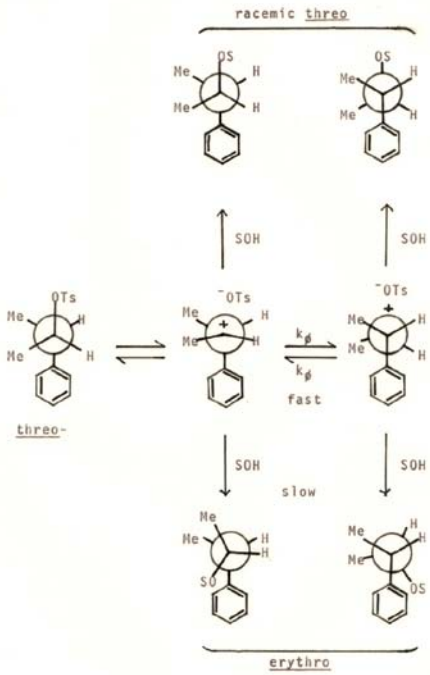
active products as shown in scheme 2.

Scheme 2

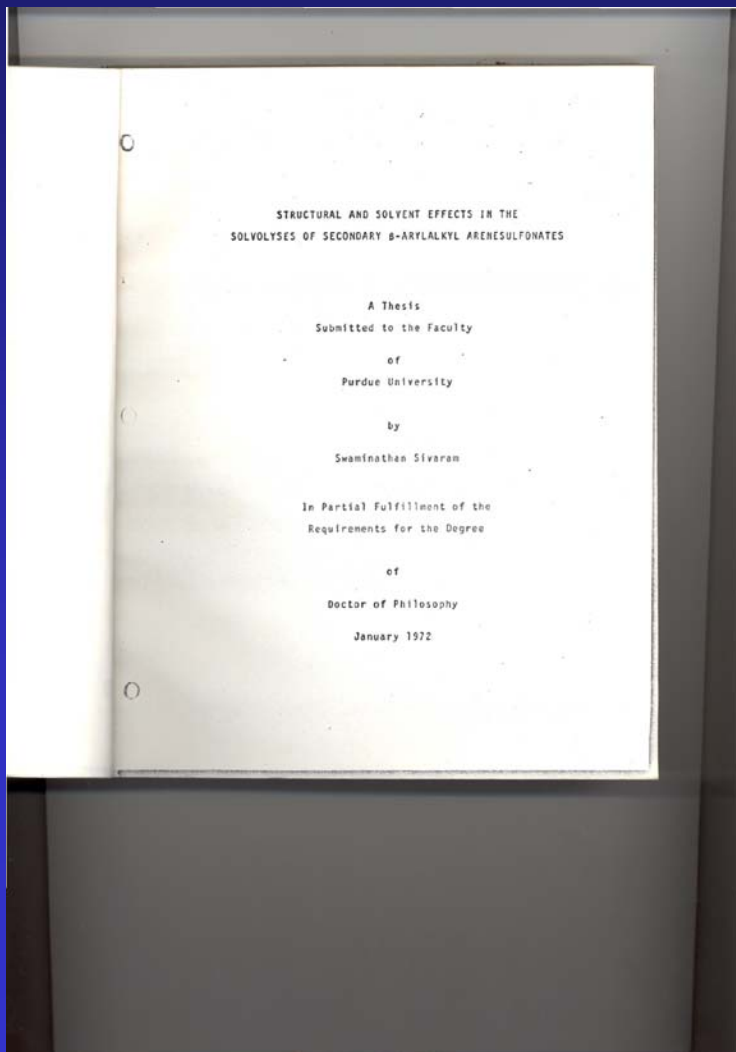


The initial simplicity of the phenonium ion theory, however, was largely lost when results of more detailed study on the rates and products became available. It was observed that the rate of racemization was considerably greater than the rate of acetolysis. This was attributed to ion pair return by Winstein and Schreiber.[10] The intermediacy of phenonium tosylate ion pairs were invoked to explain this observation. These ion pairs return to starting material as well as dissociate to products, all processes occurring with

Scheme 2



STRUCTURAL AND SOLVENT EFFECTS ON THE SOLVOLYSIS OF SECONDARY β- ARYLALKYL ARENESULFONATES

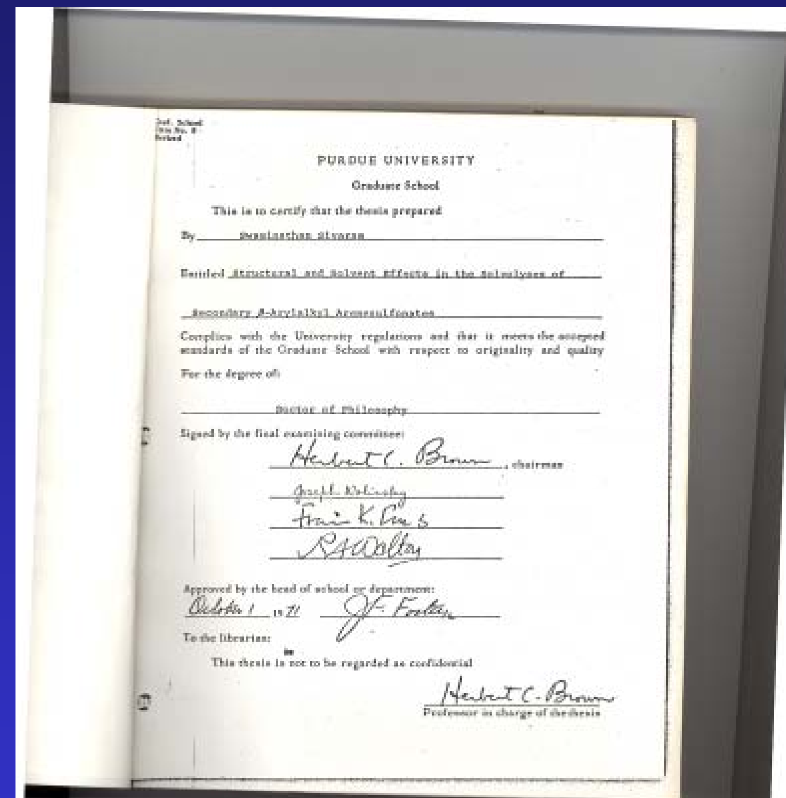


STRUCTURAL AND SOLVENT EFFECTS IN THE
SOLVOLYSES OF SECONDARY β-ARYLALKYL ARENESULFONATES

A Thesis
Submitted to the Faculty
of
Purdue University
by
Swaminathan Sivaram

In Partial Fulfillment of the
Requirements for the Degree
of
Doctor of Philosophy

January 1972



PURDUE UNIVERSITY
Graduate School

This is to certify that the thesis prepared

By Swaminathan Sivaram

Entitled Structural and Solvent Effects in the Solvolyses of Secondary β-Arylalkyl Arenesulfonates

Complies with the University regulations and that it meets the accepted standards of the Graduate School with respect to originality and quality

For the degree of:

Doctor of Philosophy

Signed by the final examining committee:

Herbert C. Brown, chairman

Approved by the head of school or department:

October 1 19 71

To the librarian:

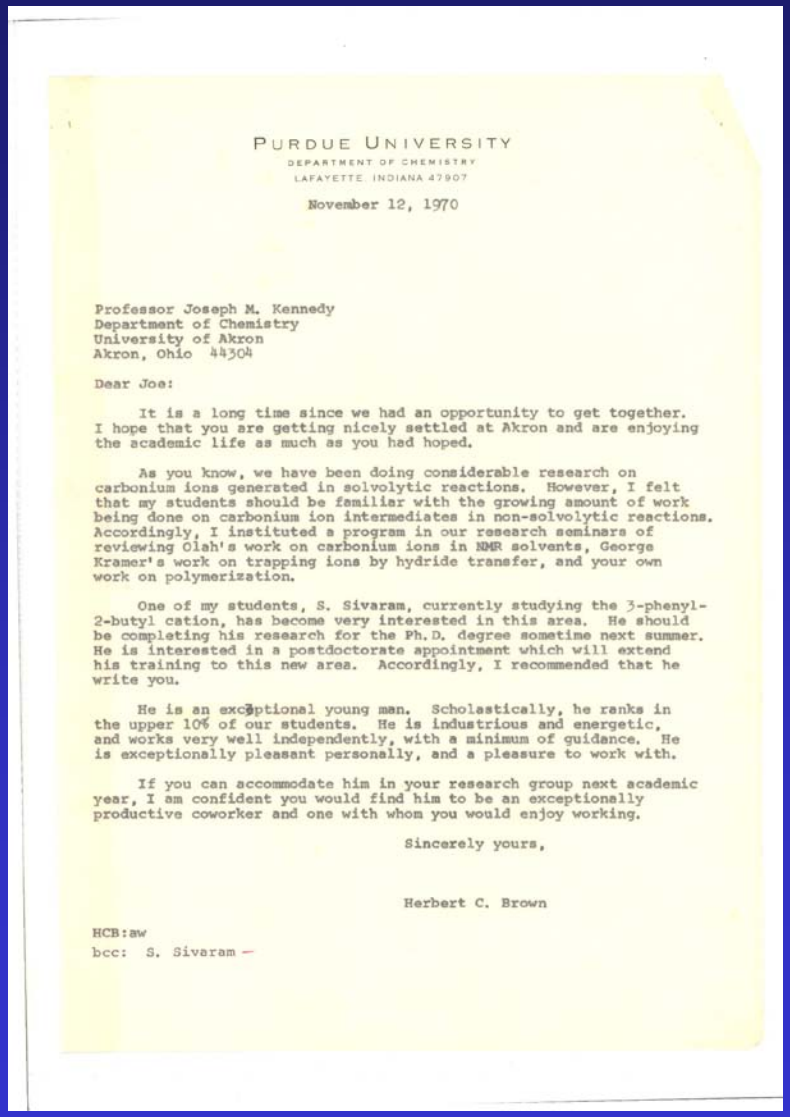
This thesis is not to be regarded as confidential

Herbert C. Brown
Professor in charge of thesis

OCTOBER 1, 1971

The Brown Research Group 1970

ANOTHER LETTER THAT SETS ME ON A NEW JOURNEY



PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

November 12, 1970

Professor Joseph M. Kennedy
Department of Chemistry
University of Akron
Akron, Ohio 44304

Dear Joe:

It is a long time since we had an opportunity to get together. I hope that you are getting nicely settled at Akron and are enjoying the academic life as much as you had hoped.

As you know, we have been doing considerable research on carbonium ions generated in solvolytic reactions. However, I felt that my students should be familiar with the growing amount of work being done on carbonium ion intermediates in non-solvolytic reactions. Accordingly, I instituted a program in our research seminars of reviewing Olah's work on carbonium ions in NMR solvents, George Kramer's work on trapping ions by hydride transfer, and your own work on polymerization.

One of my students, S. Sivaram, currently studying the 3-phenyl-2-butyl cation, has become very interested in this area. He should be completing his research for the Ph.D. degree sometime next summer. He is interested in a postdoctorate appointment which will extend his training to this new area. Accordingly, I recommended that he write you.

He is an exceptional young man. Scholastically, he ranks in the upper 10% of our students. He is industrious and energetic, and works very well independently, with a minimum of guidance. He is exceptionally pleasant personally, and a pleasure to work with.

If you can accommodate him in your research group next academic year, I am confident you would find him to be an exceptionally productive coworker and one with whom you would enjoy working.

Sincerely yours,

Herbert C. Brown

HCB:aw
bcc: S. Sivaram

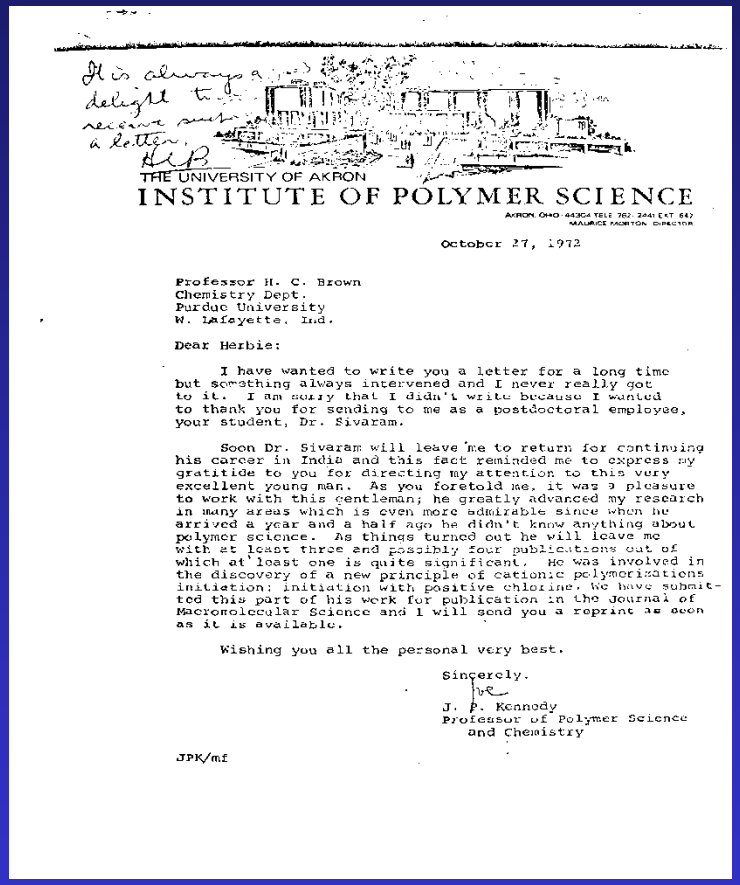
"One of my students Sivaram who is studying the 3-phenyl-2- butyl cation has become interested in your work on carbocationic polymerization. He should be completing his Ph D degree sometime this summer. Accordingly I recommended that he write to you.

He is an exceptional young man. Scholastically he ranks in the upper 10 % of our students. He is industrious and energetic and works well indpendently with a minimum of supervision

I am confident that you will find him to be an exceptionally productive coworker and one with whom you will enjoy working "

Professor H.C.Brown
November 12,1970

LETTER FROM PROFESSOR KENNEDY TO PROFESSOR BROWN OCTOBER 27, 1972



It is always a delight to receive such a letter, HCB

THE UNIVERSITY OF AKRON
INSTITUTE OF POLYMER SCIENCE
AKRON, OHIO 44304 TELE 762-3441 EXT 642
MAURICE MORTON, DIRECTOR

October 27, 1972

Professor H. C. Brown
Chemistry Dept.
Purdue University
W. Lafeyette, Ind.

Dear Herbie:

I have wanted to write you a letter for a long time but something always intervened and I never really got to it. I am sorry that I didn't write because I wanted to thank you for sending to me as a postdoctoral employee, your student, Dr. Sivaram.

Soon Dr. Sivaram will leave me to return for continuing his career in India and this fact reminded me to express my gratitide to you for directing my attention to this very excellent young man. As you foretold me, it was a pleasure to work with this gentleman; he greatly advanced my research in many areas which is even more admirable since when he arrived a year and a half ago he didn't know anything about polymer science. As things turned out he will leave me with at least three and possibly four publications out of which at least one is quite significant. He was involved in the discovery of a new principle of cationic polymerizations initiation: initiation with positive chlorine. We have submitted this part of his work for publication in the Journal of Macromolecular Science and I will send you a reprint as soon as it is available.

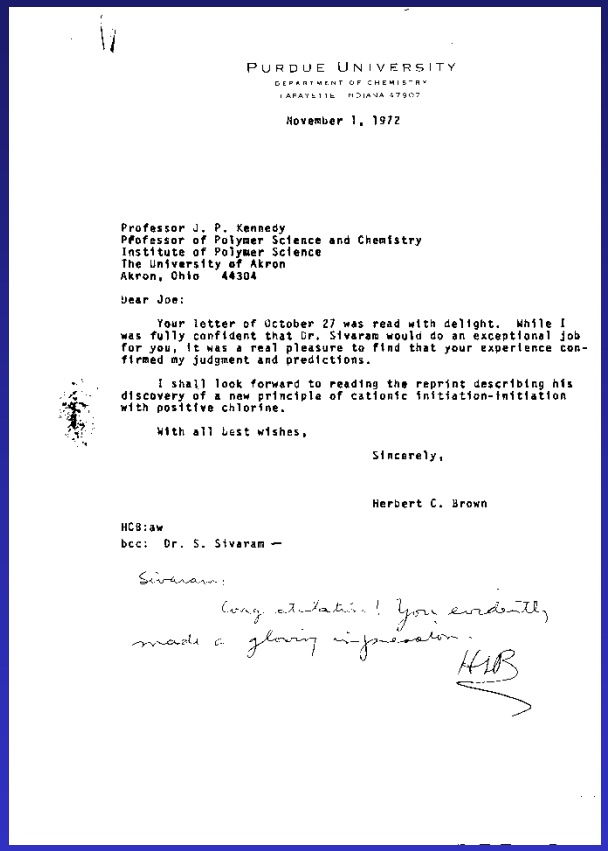
Wishing you all the personal very best.

Sincerely,

J. P. Kennedy
Professor of Polymer Science
and Chemistry

JPK/mf

""While I was fully confident that Sivaram would do an exceptional job for you it was a real pleasure to find out that your experience confirmed my judgment and predictions"



PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

November 1, 1972

Professor J. P. Kennedy
Professor of Polymer Science and Chemistry
Institute of Polymer Science
The University of Akron
Akron, Ohio 44304

Dear Joe:

Your letter of October 27 was read with delight. While I was fully confident that Dr. Sivaram would do an exceptional job for you, it was a real pleasure to find that your experience confirmed my judgment and predictions.

I shall look forward to reading the reprint describing his discovery of a new principle of cationic initiation-initiation with positive chlorine.

With all best wishes,

Sincerely,

Herbert C. Brown

HCB:aw
bcc: Dr. S. Sivaram —

Sivaram:
Congratulations! You evidently made a glowing impression.
HCB

Lesson 15 : There is no greater reward for a student than to know that he has lived up to his teacher' s expectations

LETTER FROM PROFESSOR BROWN DATED MARCH 24, 1998 AND E MAIL DATED JUNE 10, 1998

1393 H. C. BROWN BUILDING

PURDUE UNIVERSITY

HERBERT C. BROWN

March 24, 1998

Dr. S. Sivaram
CII/2 NCL Colony
Pune 411008
INDIA

My dear Sivaram:

From Rama's letter (undated), I learned of your latest honor, election to the Indian National Science Academy. It comes as no surprise. Indeed, I am puzzled as to why it took them so long. But then, I was not much younger (45) when I achieved the NAS!

Your life must be even more hectic than mine. But then, at 50, I had far more energy than at present. When I come home for lunch Sarah insists I have a 30 min. nap. I find it helps, but was unheard of when I was 50.

Sarah is equally busy, but she plans to write Rama as soon as she gets a little time. So I won't intrude.

With all best wishes to all of you,

Sincerely,

Herbert C. Brown

H. C. BROWN AND R. B. WETHERILL LABORATORIES OF CHEMISTRY
1393 BROWN BUILDING • WEST LAFAYETTE, IN 47907-1393 USA
PHONE: (765) 494-5316 • FAX: (765) 494-0239 • E-MAIL: hcbrown@chem.purdue.edu

From Rama's letter I learnt of your latest honor, election to the Indian National Science Academy. It comes as no surprise. I am puzzled as to why it took them so long. But then, I was not much younger (46) when I was elected to the National Academy of Sciences !

Congratulations!

Received: from CV3.CHEM.PURDUE.EDU (cv3.chem.purdue.edu [128.210.43.119]) by cms.ncl.res.in with SMTP (8.7.1/8.7.1) id CAA25538 for <sivaram@cms.ncl.res.in>; Thu, 11 Jun 1998 02:22:02 +0530 (IST)
Date: Thu, 11 Jun 1998 02:22:02 +0530 (IST)
Received: from [128.210.43.27] by CV3.CHEM.PURDUE.EDU with SMTP; Wed, 10 Jun 1998 15:51:25 -0500 (EST)
Message-ID: <l03110700b1a44cd920b2@[128.210.43.27]>
Mime-Version: 1.0
Content-Type: text/plain; charset="us-ascii"
To: sivaram@cms.ncl.res.in
From: "H. C. Brown" <hcbrown@chem.purdue.edu>
Subject: Congratulations!
X-UIDL: 897536418.008
X-Mozilla-Status: 8000

My dear Sivaram:

It is a rare experience to have a former student return to India and do research which attracts the attention of the academic community abroad. It is an even rarer experience for such research to attract the attention of industrial laboratories and organizations here to the point that joint research projects are initiated. Congratulations!

I shall look forward to seeing you on one of your upcoming trips to the US. Incidently, if you can manage to bring your wife along, Sarah would be especially delighted. On your last visit Sarah enjoyed her company enormously.

With all best wishes, sincerely,

Herbert C. Brown

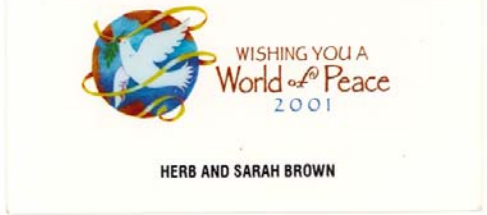
--

Prof. Herbert C. Brown
H. C. Brown and R. B. Wetherill
Laboratories of Chemistry
Purdue University
West Lafayette, Indiana 47907 USA
E-MAIL: hcbrown@chem.purdue.edu
FAX: 07-1-317-494-0239

It is a rare experience to have a former student return to India and do research which attracts the attention of the academic community abroad. It is an even rarer experience for such research to attract the attention of industrial research laboratories here to the point that joint research projects are initiated. Congratulations !

Lesson 16 : A true mentor is one who rejoices in the success of his student

I met Professor Brown for the last time in 2002 on his 90th Birthday ; he was visibly and genuinely proud that I had been appointed Director, NCL



From HCB, SBB, Tamar and Ronni (granddaughters) Celebrating HCB's 90th

CARBOCATIONIC POLYMERIZATION AT THE UNIVERSITY OF AKRON, INSTITUTE OF POLYMER SCIENCE (1971-73)

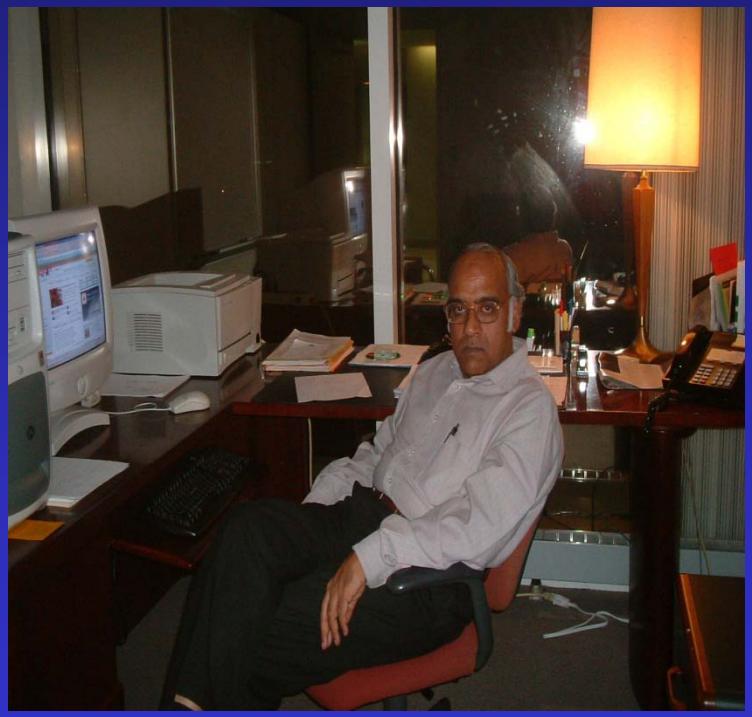
- **Polymerization of isobutene using cationic initiators**
- **Catalyzed addition of halogens to isobutylene for initiation of polymerization**
- **Mechanism of alkylation of t-butyl halides with alkylaluminums**
- **Alkylation of olefins with HCl / trimethylaluminum**
- **An opportunity to learn polymer science, both theory and practice**
- **Understand how chemistry becomes useful when used to make materials**

"It is exhilarating to explore, discover and understand……but it is no longer sufficient; chemistry not only has to be elegant but must also be useful"

Professor J.P.Kennedy

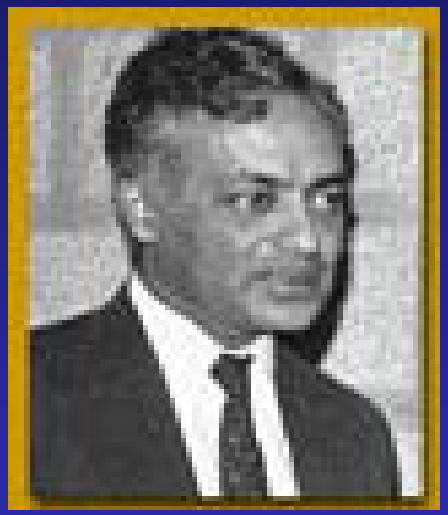
MEMORIES RELIVED : HAROLD A. MORTON DISTINGUISHED PROFESSOR AT THE UNIVERSITY OF AKRON IN FALL 2006

COLLEGE OF POLYMER SCIENCE AND ENGINEERING, THE UNIVERSITY OF AKRON (Fall 2006)



PROFESSOR KENNEDY AND INGRID KENNEDY, AKRON, NOVEMBER 2006

RETURN TO INDIA : TO INDIAN PETROCHEMICALS CORPORATION LIMITED, BARODA (1973-88)

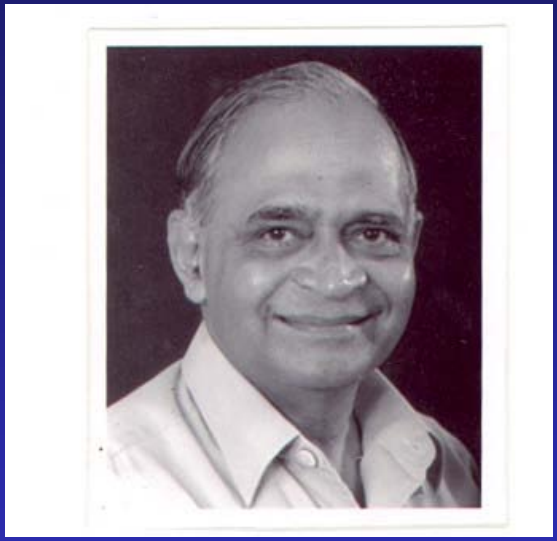


Dr S. Varadarajan
CMD, 1974-80
Taught me the principles of management and how to think big

- A career in industry
- Saw chemistry in action
- Established a research laboratory
- Initiated research in the area of Ziegler Natta Catalysts for Polyolefins
- Part of a team that developed a process for acrylic esters from acrylonitrile in collaboration with NCL
- Participated in the complete chain consisting of process development, process design, basic engineering and through commissioning of a 10,000 tpa plant at Baroda
- Participated in several technology acquisition activities

Dr P.G. Menon
Manager (R&D)
1973-1979
Initiated me into industrial R&D and taught me that no problem is too small to solve

ANOTHER INSPIRATIONAL MENTOR



Professor M. M. Sharma

- **Met him for the first time in 1973 in his crowded and modest office at the Department of Chemical Engineering, UDCT, Matunga, Bombay**
- **At a young age I was struck by his incredible breadth of knowledge, memory for facts, erudition and enthusiasm.**
- **Kindled my interests and taught valuable lessons in industrial chemistry, petrochemicals and catalysis; taught me the how to understand and value of technology**
- **Fortunate to have received his continuous mentorship for over four decades**

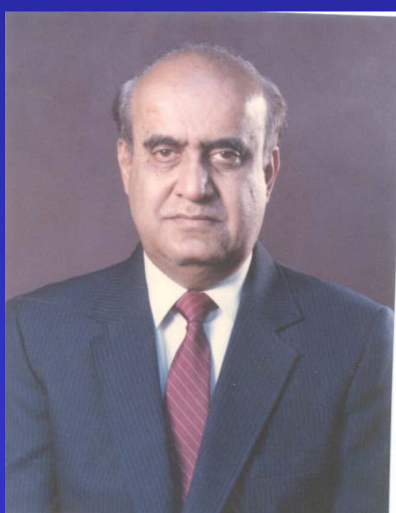
The most important lesson learnt

-Academic excellence and application of science in industry are not mutually exclusive

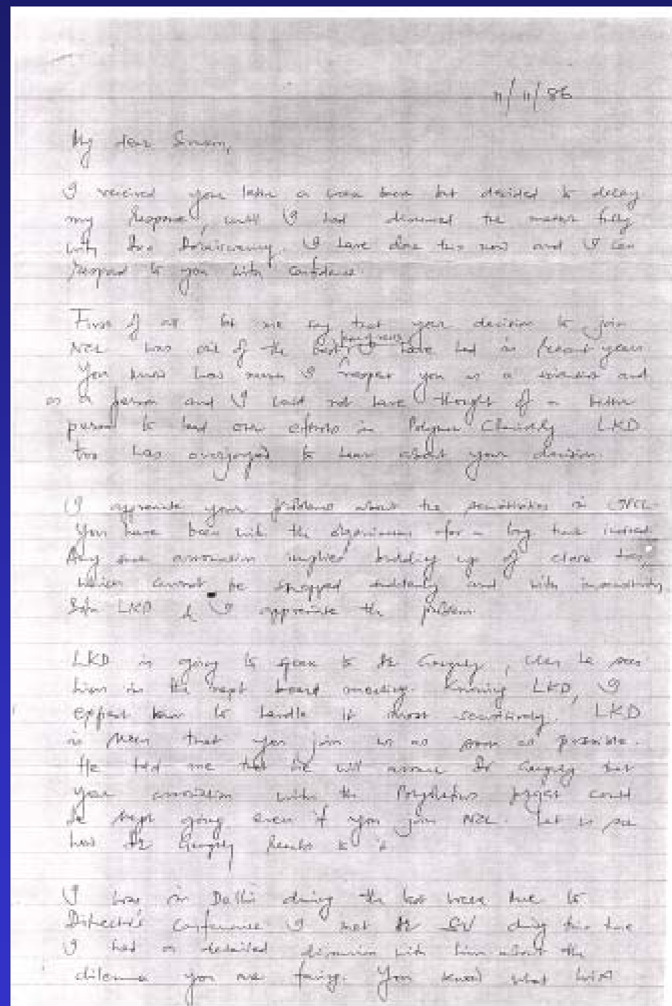
- Knowledge in depth and breadth is essential for becoming a successful professional

AN INVITATION TO JOIN NCL

Dr R. A. Mashelkar



Dr. L .K. Doraiswamy



11/11/86

My dear Sivaram,

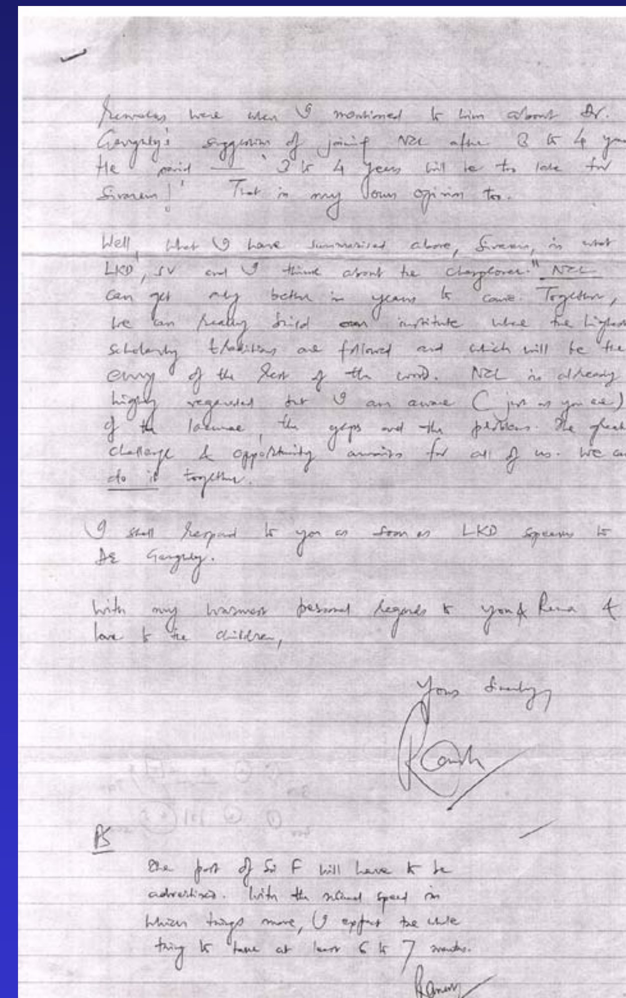
I received your letter a week back but decided to delay my response until I had discussed the matter fully with Doraiswamy. I have done this now and I can respond to you with confidence.

First of all let me say that your decision to join NCL has one of the best happenings we have had in recent years. You know how much I respect you as a scientist and as a person and I could not have thought of a better person to lead our efforts in Polymer Chemistry. LKD too was overjoyed to hear about your decision.

I appreciate your problems about the sensitivities in IPCL. You have been with the organisation for a long time indeed. Any such association implies building up of close ties which cannot be snapped suddenly and with insensitivity. Both LKD & I appreciate the problem.

LKD is going to speak to Dr Ganguly, when he sees him in the next board meeting. Knowing LKD, I expect him to handle it most sensitively. LKD is keen that you join us as soon as possible. He told me that he will assure Dr Ganguly that your association with the Polyolefins project could be kept going even if you join NCL. Let us see how Dr Ganguly reacts to it.

I was in Delhi during the last week due to Director's Conference. I met Dr SV during this time. I had a detailed discussion with him about the dilemma you are facing. You know what was



[illegible] here when I mentioned to him about Dr. Ganguly's suggestion of joining NCL after 3 to 4 years. He said '3 to 4 years will be too late for Sivaram!' That is my own opinion too.

Well, what I have summarised above, Sivaram, is what LKD, SV and I think about the changeover. NCL can get only better in years to come. Together, we can really build our institute where the highest scholarly traditions are followed and which will be the envy of the rest of the world. NCL is already highly regarded but I am aware (just as you are) of the lacunae, the gaps and the problems. The greater challenge & opportunity awaits for all of us. We can do it together.

I shall respond to you as soon as LKD speaks to Dr Ganguly.

With my warmest personal regards to you & Reena & love to the children,

Yours sincerely,

[signature]

PS

The post of Sci F will have to be advertised. With the normal speed in which things move, I expect the whole thing to take at least 6 to 7 months.

[initials]

A CALL ONE CAN HARDLY REFUSE

- *" NCL can only get better in the years to come. Together we can really build an institute where the highest traditions of scholarship are followed and which will be the envy of rest of the world. NCL is already highly regarded but I am aware of the lacunae, the gaps and the problems. The greatest challenge and opportunity awaits all of us. We can do it together "*

Dr R.A. Mashelkar F.R.S

- *Letter dated 11 November 1986*

NATIONAL CHEMICAL LABORATORY (1988 -2002)

- Leadership of Polymer Chemistry Division
- An opportunity to build the Division – Define programmes and philosophy
- Build a personal research program with PhD students – Mentoring
- NCL is a very competitive environment; only the best survive ! Highly decorated scientists
- Culture of patenting
- Collaboration with industry : Use new or known science to solve problems
- Opportunities for creating new science

A remarkable ambience for productive science; respect for scholarship and a distinguished lineage of remarkable leaders

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***

POLYESTERS AND POLYCARBONATES: SYNTHESIS,STRUCTURE AND PROPERTIES

- **Building diversity in aromatic polyesters : Structure and morphology**
- **Polycarbonates and co-polycarbonates : Synthesis via solid state polymerization**
- **Fully aliphatic polyesters as biodegradable polymers : Synthesis, structure and properties**

FUNCTIONAL POLYOLEFINS

IN-CHAIN FUNCTIONALIZATION

- **Copolymerization with a functional monomer**
- **Copolymerization with a precursor monomer with masked functionality which does not interfere in copolymerization**

CHAIN-END FUNCTIONALIZATION

- **Introduction of functional groups by chemical reaction on preformed polymer**

NATIONAL CHEMICAL LABORATORY (2002- present)

- **Challenge of management of one of the largest publicly funded laboratories in India**
- **Charting the future of the Laboratory**
- **Mentoring and nurturing younger scientists and students**
- **Resource management**
- **Building the pipeline for emerging science and technology**
- **Influence S&T policy of India**

SOME MOMENTS TO CHERISH

Professor Rao presenting the Silver Medal of the Chemical Research Society of India , 2002

Dr Mashelkar, President , presenting the Vishwakarma Medal. Indian National Science Academy, 2006

SOME MOMENTS TO CHERISH

President Abdul Kalam conferring Padma Shri , March 2006

LESSONS THAT I HAVE LEARNT

- **We rarely get what we want ; always make the best of second choice**
- **Provide early opportunities to learn leadership and organizational skills**
- **Learning outside the classroom is more important than inside the classroom**
- **Be generous with praise ; It does wonders**
- **However big you are, show that you care for everyone in your institution**
- **Teach to appreciate the beauty of the written word. Create the love for reading. Language is the window to the soul**
- **If you want to find out a person's real aptitude, give him a gift and ask him to select a book from a bookstore**
- **Teachers who are committed and show genuine interest in their pupil make good institutions great**

LESSONS THAT I HAVE LEARNT

- **A liberal education is far more important than learning a few subjects; You can rebuild a façade but can lay the foundation only once**
- **A true mentor is one who shows you the way when you do not know where you want to go**
- **Knowledge is akin to insurance; You never know when you will need it**
- **Teach less; encourage self learning; make learning a pleasure**
- **Pay attention to details; small things are important in science**
- **A true mentor is one who is more concerned about his student, not himself**
- **There is no greater reward for a student than to know that he has lived up to his teacher' s expectations**
- **A true mentor is one who rejoices in the success of his student**

LIFE`S LESSONS

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

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

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

Fitzgerald's Translation
Rubaiyat of Omar Khayyam

THANK YOU

Chennai 021008