

Swaminathan Sivaram

S. Sivaram is a polymer chemist at the National Chemical Laboratory (NCL), Pune. He obtained his Ph D from Purdue University, after his M Sc from the Indian Institute of Technology, Kanpur. Sivaram has worked both in academia and industry. He spearheaded several public–private partnerships as the Director of NCL, and also established a research group in polymer science at the institute. He is a fellow of the Indian National Science Academy, New Delhi; Indian Academy of Sciences, Bangalore; National Academy of Sciences, Allahabad; Indian National Academy of Engineering, New Delhi, and the Academy of Sciences for the Developing World, Trieste.



Sivaram is concerned about the fact that chemistry has become invisible to the common man, and believes that ‘it needs more powerful communicators as much as it needs a new breed of professionals’. Sivaram talks to *Current Science* about the evolution of polymer chemistry and his work in the field.

How has the field of polymer chemistry evolved over the years?

Polymer chemistry was born with the seminal contributions by Wallace Carothers in the early thirties when he showed that bond-forming reactions, when applied to di-functional molecules, lead to the formation of long macromolecular chains. This was a watershed moment since it meant that the techniques of rational organic synthesis could be applied to make macromolecules. In the early forties, Paul Flory showed that principles of physical chemistry, thermodynamics and statistical mechanics could be used to understand the kinetics and mechanism of polymer formation by both step-growth and chain-growth reactions.

During the last two decades, polymer chemistry has evolved and matured in two directions. One, in terms of synthesis and the other in terms of understanding structure. Polymers can now be synthesized by a variety of techniques with precision, namely with control over copolymer composition, molecular weight, distribution of molecular weights, functionalities and their precise location, sequence of monomer placements in block copolymers, stereochemistry, regiochemistry and topology. It is now also possible to probe the structure of macromolecules (both at a molecular and supra-molecular level) using several physical tools with a great degree of certainty.

Why and how did you choose to be a polymer chemist?

Till I completed my Ph D, I did not have any exposure to polymer chemistry. In the mid-sixties, this subject was never formally taught even in the graduate departments of chemistry in the US. Sadly, even today this is true. My Ph D thesis was in the area of physical organic chemistry, wherein, my preoccupation was to understand the structure of carbocations and nature of anchimeric assistance using chemical kinetics and stereochemical investigations. When I was about to finish my Ph D, I expressed a desire to my thesis advisor (Herbert C. Brown, Purdue University) to pursue postdoctoral research in an area different from my area of Ph D research. He then introduced me to a new faculty at the Institute of Polymer Science, the University of Akron, USA.

Reactive organic intermediates are key to the synthesis of polymers, and having spent four years understanding carbocations through solution chemistry, I was intrigued by the possibility that I could make use of them in creating new materials. Thus began my tryst with polymer chemistry. It was exhilarating to learn polymer science at the University of Akron. My project was to search for new carbocationic initiators for the polymerization of isobutylene to poly (isobutylene)s (Butyl rubber) at temperatures higher than usually practised. I realized that concepts of organic chemistry are not mere constructs of a chemist’s imagination, but help contribute to the making of useful materials. So began my lifelong fascination with polymers, first in industry and later in a national laboratory.

What have been your key contributions to polymer chemistry and areas of interests?

Our research has been focused on three broad themes, namely (a) new chemistry for the synthesis of high performance polymers, (b) controlled synthesis of polymers using the principles of ‘living’ polymerization and ‘catalyst design’, and (c) structure–property relationships in polymers.

We have explored controlled synthesis of polymers by free radical, anionic and Ziegler–Natta catalysts, chemistry of high performance polymers, surface modification of polymers, and synthesis, application and self-assembly of polymer nanoparticles. In the area of controlled polymer synthesis, the emphasis has been on the

design of new initiators capable of controlling polymer molecular weights, molecular weight distribution and chain end functionalities.

New catalysts are the key to the synthesis of high-performance polymers. New synthetic methods have been devised for high molecular weight aromatic poly(arylcarbonate)s, poly(arylester)s, poly(arylestercarbonate)s. More recently, the scope of solid state polymerization (SSP) in the preparation of high molecular weight polyesters and polycarbonates has been studied extensively. Structure and morphology of both the precursor oligomers and the final polymer by SSP have been investigated.

Polymer surfaces and interfaces offer a new dimension for property manipulation in polymers. Selective functionalization of poly (olefin) surfaces has been studied for imparting new properties such as barrier to hydrocarbon permeation and cell adhesion. Methods to introduce controlled porosities in polymers, both in the surface and the bulk, are under investigation.

What do you see as things that have changed in the field of polymer chemistry and what do you think lies in the future for the field?

Polymer chemistry has become truly an enabling science. Polymer chemists continue to be pre-occupied with creating new structures through synthesis. However, greater challenges wait in creating functions in synthetic polymers. Functional polymers have become important in many areas of contemporary applications, be it medicine, pharmaceuticals, energy, housing, transportation, water or environment. They are ubiquitous in information and communication technology products that we use every day.

Just like in other branches of chemistry, polymer chemists too are not merely asking what is it, but what does it do? Merely making a molecule is not enough anymore.

In many of these applications, polymers have to be used with other materials, namely inorganic, metals, biomolecules or natural polymers. Most functional materials are in some way either conjugates or hybrids. Consequently, polymer chemists will need greater understanding of surfaces and interfaces, since properties of dissimilar materials, in a hybrid or conjugate form, are determined by the molecular interaction at the interfaces. Polymers that self-assemble into large supra-molecular shapes and forms with hierarchical order, stimuli-responsive polymers, conjugated polymers with precise lengths, functional polymer networks, and other complex systems are becoming important in many applications. Complex polymer systems, using organized assemblies of block copolymers can be used to fabricate nanoscale objects. Polymeric systems with emergent properties are beginning to be better understood.

What kind of prospects do young polymer chemists have?

Polymer chemists have a bright future. Polymers are indispensable to human civilization, and their manufacture and consumption is expected to grow. Polymer chemists will continue to be contributors to both established and emerging science and technology. The world consumes over 250 mt of polymers today. The manufacturing technology, though mature, still requires new discoveries. Most of the polymers that we consume today come from fossil fuels. Is there a more sustainable basis for producing polymers? How can we use less polymers in the products we consume? Can we design polymers with an in-built trigger that will activate their degradation after a specified time? How can we make polymers truly biodegradable? In the emerging areas, polymer chemists can contribute to better methods of producing cleaner energy from either sun or hydrogen, help in producing potable water from sea water, enhance efficiency of water use in agriculture, create better drugs through targeted delivery, and create new prosthesis materials that can be implanted or substituted in a human body.

Polymer chemistry has given birth to materials such as plastics, which are a menace to the environment and health...

This is a wrong perception. No material is intrinsically good or bad. It is how we make use of it that makes it good or bad. Plastics are very useful materials without which we cannot live even for an hour. Yet, we should treat every material with the respect it deserves. We must promote more responsible use of materials through education and inculcating civic sense amongst our citizens. Plastics can be easily recycled, provided we can collect them post-consumer use. Every plastic has a defined method of disposal, defined by its 'cradle to grave' life-cycle analysis. Used plastic material still has most of the calorific energy content that was part of the raw material from which it was made. This energy can be recovered. There is also a need to ensure that the right materials are used for the right applications. Plastics have played a significant role in reducing the energy consumption and enhancing the sustainability of the environment in our planet, as both population and consumption have grown substantially during the past century.

The boundaries in different disciplines of science are blurring and at the same time there is increased specialization...

Polymer chemistry is also becoming a part of the larger tapestry of interdisciplinary sciences, where chemistry, physics and biology seamlessly interact. The breadth of the field will require greater focus on interdisciplinary research. Within the discipline, chemists, physicists and engineers will have to work collaboratively in seeking solutions. Collaboration outside of the discipline will also be needed, if polymer chemistry has to contribute to solving problems in energy, communication technologies, lighting, display systems, medicine and environmental stewardship.

What would you like to see changing about research in chemistry, and what would you convey to the young chemists?

Chemistry, over its two centuries of existence, has become invisible to the common man. Most people do not even realize how much their daily life is dependent on chemistry. I believe that the utilitarian aspects of chemistry have resulted in a loss of romance in the discipline. Chemistry needs to be reinvented, if we have to stay relevant and also attract bright young minds to practice the discipline.

At the bottom of this pyramid is education. If students do not get a taste of chemistry in all its dimensions at a very early age, it is unlikely that they will pursue it as a discipline. We need good teacher education, interesting textbooks and useful self-learning modules. In the universities and colleges, science education must become more integrative, wherein concepts are taught through examples drawn from all disciplines of science. Chemistry is, in the end, predominantly an experimental science. Young people must have the thrill of practising chemistry with their own hands early in their life.

At the apex of the pyramid is the spectacular vision of what polymer science can contribute to the well-being of over nine billion people on this planet. The history of polymer science over the past 70 years has established the discipline as one of the most worthwhile and useful branches of science. Even greater excitement waits the future generation of young men and women who choose to delve in this discipline.

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