

ments, the university sector and the IUCs, the potentials of space technology, etc. formed the nucleus of this highly personal talk which was deeply moving in places, especially where the speaker stressed the social impact of what technology can do.

The non-scientific but immensely enjoyable highlight of the Dedication Ceremony was the vocal musical concert in the North Indian classical style by Smt. Gangubai Hangal ably supported by her daughter Krishnabai.

The Dome at IUCAA has holes showing the bright star distribution as on 8 p.m. on 29 December 1988 the day that Yash Pal in his role as the UGC Chairman had unveiled the foundation stone of the Centre. Today some 15,000 square metres of excellent architecture stands on that empty site reflecting the vision of the architect Charles Correa. In his narration of the brief history of IUCAA at the Dedication Ceremony, the Director highlighted the goodwill of several friends and agencies, the dedica-

tion of those who worked here and, of course, several fortunate circumstances that made this achievement possible. The delightful buildings and the up-to-date facilities they house pose a stiff challenge to the IUCAA users: to produce high quality science that will match them in its excellence.

Jayant V. Narlikar, Inter-University Centre for Astronomy and Astrophysics, Pune.

RESEARCH NEWS

Conducting polymers — Newer avenues of application

S. Ramakrishnan

Polymers, by virtue of their light weight and greater ease of fabrication, have replaced and are continuing to replace metals in several areas of applications. Polymers have traditionally been considered good electrical insulators and a variety of their applications have been based upon this insulating property. However, for more than a decade now, researchers have shown that certain class of polymers which are conjugated (extended π -conjugation along the polymer backbone), exhibit semiconducting behaviour and can be doped (oxidized or reduced to create charge carriers) to give materials with conductivity as high as 10^5 S/cm (compare copper $\sigma_{rt} = 10^6$ S/cm). Due to the presence of this extended conjugation along the polymer backbone, the chains are rigid and possess strong interchain interactions resulting in insoluble, and infusible materials, which are difficult to process. More recently, however, it was demonstrated that when lateral substituents were introduced, even conjugated polymers can be made soluble (hence processable) without significant loss in their conductivity. One other problem that plagued this field from its inception, is the inherent instability of these polymers (especially in the doped form) to ambient conditions. Today conducting polymers that are stable even in the

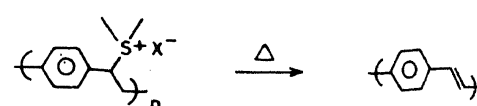
doped form have been prepared. This greater stability and enhanced processability of the new generation of conducting polymers has caused a resurgence of interest in this area. The realization that conducting polymers cannot compete with metals in traditional areas of application (due to their much lower conductivity) has caused researchers to concentrate on other areas of application that exploit the presence of extended conjugation in these polymers. Table 1 shows the structures and characteristics of some of the more important conducting polymers.

Polyacetylene, in view of possessing the simplest molecular framework, has attracted the most attention, especially of physicists, with an emphasis on understanding the mechanism of conduction. However, its insolubility, infusibility and poor environmental stability have rendered it rather unattractive for technological applications. The technologically relevant front runners belong to four families: polyaniline (PAN), polypyrroles (PPy), polythiophenes (PT) and polyphenylene vinylenes (PPV). While polyaniline may be considered as soluble in the neutral form, all other polymers are insoluble. However, laterally substituted derivatives of the later three classes are soluble in pristine form and are solution processable. PAN,

PPy and PT can be prepared either by chemical or electrochemical oxidation, the latter approach being often preferred as they result in polymeric films deposited on the anode surface, which can be removed to give free-standing films. The electrochemical method, in addition, may also be well suited for fabrication of microelectronic devices in which polymer films are directly deposited onto metal contacts. Although chemical oxidation yields powders, the reaction when done in the presence of surfactants in some cases, permits the preparation of emulsions, that upon drying form coherent films. In the case of the substituted derivatives, however, the chemical method is often preferred, as the resulting polymers are soluble, and hence can be purified and solution processed.

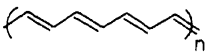
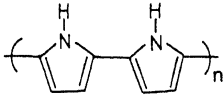
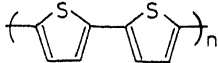
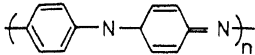
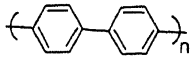
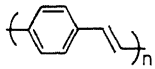
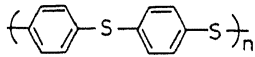
PPV has also attracted a lot of attention in recent years, due to the availability of a synthetic route that gives water soluble polyelectrolyte precursors which upon heating (about 200°C) under vacuum gives the wholly conjugated polymer (Scheme 1).

By virtue of this soluble precursor



Scheme 1.

Table 1. Conducting polymers

		Maximum conductivity (S/cm)	Stability	Processing
Polyacetylene		1.5×10^5	Reacts with air or fusible	Film not soluble
Polypyrrole		2000	Stable in conducting form	Film not soluble Derivatives are soluble
Polythiophene		100	Stable	Film not soluble Derivatives are soluble
Polyaniline		10	Stable	Slightly soluble Derivatives more soluble
Polyphenylene		1000	Stable	Powder, not soluble
Polyphenylene vinylene		1000	Stable undoped	Soluble Precursor or polymer
Polyphenylene sulphide		100	Doped only by strong oxidizing which are moisture-sensitive	Doped form soluble in AsF ₃

route, PPV films and fibres for a variety of applications are accessible. A recent demonstration of glass-PPV composites, via the sol-gel approach, for exploration of the fast third-order nonlinear response of PPV, is an excellent example of some of the possible avenues of application of such systems¹.

Two promising areas of applications of conducting polymers in electronics were discussed in a recent SAMPE conference² by Westinghouse chemists H. E. Saunders and K. F. Schoch: field effect transistors and electroluminescent devices.

One of the most widely studied devices based on conducting polymers has been field effect transistors (FETs). In addition to being a low cost material, a major reason for considering this application is for the use in flat liquid crystal panel displays in which each pixel is driven by an FET. Conducting polymers appear to be promising candidates for the development of a large array of FETs at low cost. A typical device structure that has been used with PAn and PTs is shown in Figure 1. In general, the primary limitation in use of conducting polymers in FETs is the low-carrier mobility in these systems resulting in a rather low cut-off frequency of 200 kHz (in comparison to 3 GHz for

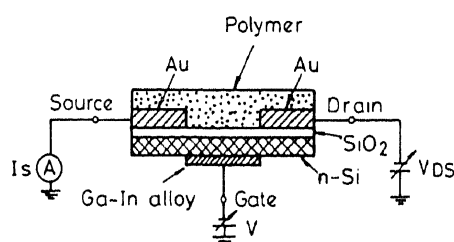


Figure 1.

doped silicon devices). By the use of a gate insulator with a high dielectric constant, such as cyanoethylpullan, a significant increase in the carrier mobilities has been achieved, and can lead to devices with cut-off frequencies of the order of 20 MHz. Further increase in carrier mobilities to raise the cut-off frequencies to the GHz level would enable the use of such devices to drive large area flat screen television. Construction of an all-polymer FET, would further require the use of polymer substrates and possibly highly conductive polymeric contact materials. Research along these directions are being carried out in various laboratories world-wide and it is expected that such devices will become possible in the next few years paving way for low cost large area flat panel displays.

The other exciting phenomenon that has caught the imagination of both

scientists and technologists alike is the phenomenon of electroluminescence in conducting polymers. Emission of light upon application of a voltage is termed electroluminescence. Light-emitting diode is an example of utilization of this phenomenon. It was recently demonstrated that PPV films can be used as the emissive layer in electroluminescent devices³. Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e. after thermal elimination of the precursor). Electrode materials are chosen with a low work function for use as negative, electron-injecting contact, and with a high work function as the positive hole-injecting contact. At least one of these layers must be semi-transparent for light emission normal to the plane of the device. Both indium-tin oxide and thin aluminium films (7-15 nm) have been used in this role. For polymer films, of about 100 nm, the forward voltages were as low as 10 V. Further improvements, using soluble PPV derivatives such as 2,5-dialkoxy PPV's and lower work function metals, particularly calcium, as the electron-injecting contact layer, has

resulted in a further drop in forward voltage to about 5 V, and an increase in the efficiency to about 1% (photons per electron injected). These devices are believed to operate by double charge injection of electrons and holes from the negative and positive electrodes, respectively. These singly charged excitations combine to form excitons which can then decay by photoemission. Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap. Enhancement of the photoemission efficiency and further lowering of forward operating voltage are two of the primary areas of current activity that is expected to

lead to improved devices of greater technological relevance.

The use of organic molecule-based systems for development of micro-electronic devices can lead to a greater control over their functional parameters due to better fine tunability of the molecular structure of these molecules. Organic polymers, in addition, have a further advantage that they are easier to fabricate into various device structures. This realization has led to the search for new polymeric structures that can replace active components in micro-electronic devices. Conjugated polymers exhibit a variety of interesting properties and form an important class of materials that is destined to make a significant contribution toward development of new and novel devices in the area of

microelectronics, data storage and optical signal processing.

1. Wung, C. J., Pang, Y., Prasad, P. N. and Karasz, F. E., *Polymer*, 1991, 32, 605.
2. Society for the Advancement of Materials and Process Engineering's 6th International Electronic Materials and Processes conference held in June 1992.
3. Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Friend, R. H., Burn, P. L. and Homes, A. B., *Nature*, 1990, 347, 605.

S. Ramakrishnan is in the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

How to reap what you did not sow — II

T. Ramakrishnan

The spectacular advances in recent times in genetic engineering and biotechnology owe their origin to the epoch-making discoveries in bacterial genetics and molecular biology in the forties and fifties of this century. The application of bacterial genetics to increasing the yield of plant products is at present engaging the attention of a number of plant molecular biologists all over the world. This development is not surprising since bacteria have been classified under plant kingdom and the discoveries in bacterial genetics should logically be extendable to plants.

One of the striking illustrations of this logic has been the discovery¹ that the amount of starch in plants like potato can be increased by the introduction of the ADP glucose pyrophosphorylase gene from the bacterium *Escherichia coli*.

Starch is the main storage carbohydrate in practically all plants and in several crops it is a major component of the harvest. During this decade the demand for starch has increased tremendously, mainly as a result of the development of high fructose syrup and ethanol in place of petrol for use in automobiles.

The enzymes involved in the synthesis of starch include adenosine diphosphate glucose pyrophosphorylase (ADPGPP) and starch synthase. ADPGPP has been proposed to play a central role in both plant starch synthesis as well as bacterial glycogen synthesis.

In *E. coli*, ADPGPP is encoded by the *glgC* gene. It is activated by fructose 1, 6-biphosphate (FbP), and inhibited by adenosine monophosphate (AMP) and inorganic phosphate (P_i). An *E. coli* K12 strain, 618, is available with a point mutation in the *glgC* gene (Gly₃₃₆-Asp). This gene is termed *glgC16*, and the gene product is less dependent on FbP and less inhibited by AMP and P_i . As a result, this strain accumulates about 33% more glycogen than the wild-type.

The plant ADPGPP is regulated positively by 3-phosphoglyceric acid (3PGA) and negatively by P_i , and shows homology to the *E. coli* enzyme. In this study the *E. coli glgC* gene was used to examine ADPGPP regulation; in order to minimize allosteric interactions, the *glgC16* gene was used.

First, since starch biosynthesis occurs in plastids, the *glgC16* gene product was fused to a modified chloroplast transit peptide (CTP), and targeted to plastids,

by incubating the radio-labelled protein with intact lettuce chloroplast preparations. Both uptake as well as processing of the fusion protein was confirmed.

The enzymatic activity of the CTP-*glgC16* gene product was examined in a transient assay. The gene, under control of the cauliflower mosaic virus-enhanced 35S (e35S) promoter and the polyadenylation signal derived from the nopaline synthase in plasmid pMON999 was electroporated into tobacco protoplasts. Activity specific to the bacterial enzyme was demonstrated, which was P_i -resistant.

Stable transformants were produced by mating the above plasmid containing a neomycin phosphotransferase gene as marker into *Agrobacterium tumefaciens* strain ASE, and subsequently transforming into tobacco, tomato and potato. An increase in starch content from an average of 3 to a maximum of 9-fold was detected.

However, it was found that constitutive expression of the CTP-*glgC16* gene under the 35S promoter inhibited plant growth and development, possibly by reducing sucrose availability for normal plant activities. It was possible to reverse this effect by growing a transgenic