POLYMER TECHNOLOGY

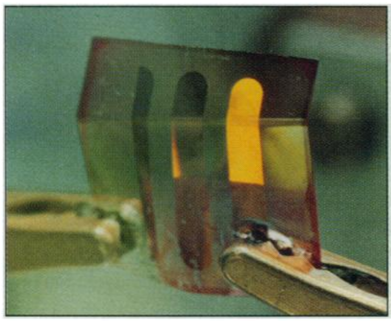
After Years in the Dark, Electric Plastic Finally Shines

The yellow-green glow in a lab at Cambridge University in 1990 was faint—yet, paradoxically, it was bright enough to illuminate an entire field, since that dim light promised to realize a decade-old dream for materials scientists: to create a generation of "plastic electronics."

The glow came from a piece of plastic—an organic material—through which physicist Richard Friend and his colleagues had passed an electric current; the result was the first polymer light-emitting diode, or LED. The reason for the excitement is that LEDs are a big-time commercial item. Normally made from inorganic semiconductors, they form the little red on/off lights on countless electronic gadgets. If they were small and cheap enough, however, they could have even more uses: An array of colored LEDs could display images and form flat plastic screens for computers or TVs. They could also replace traditional liquid crystal displays, which are limited to a small size.

Indeed, the lightness and toughness of electrically conducting plastics should be able to take them places conventional inorganic silicon technology cannot go. Imagine, for instance, a 10-foot-wide flat plastic panel on the wall that turns into a TV screen at the touch of a button. That kind of thing isn't here yet, but Friend's revelation, along with another crucial discovery at about the same time—the success of a French team in making a transistor from a similar plastic material (see box, next page)—began to move such fantasies closer to reality. And today the field is red hot: The Institute of Scientific Information's magazine *Science Watch* reported last September that among most cited scientific papers during the summer of 1993, five were papers on organic-polymer LEDs.

Much of the energy in the field is being poured into improving the efficiency of the plastic LED's and creating a full range of colors (the whole spectrum, from red to blue, is now possible). In spite of that work, there are big hurdles to clear before video games begin appearing on every wall. One is that after a few tens or occasionally hundreds of hours of operation, the current generation of LED's fade out. Many researchers are trying to extend the working life of the devices, but the underlying physics issues "are not fully understood," says electrical engineer David Braun of the Dutch electronics company Philips in Eindhoven, one of the competitors in the race. But many expert observers of the field predict that these obstacles will be overcome and that someday the glow from Richard Friend's lab may well be providing images on walls everywhere.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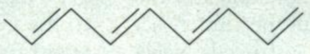
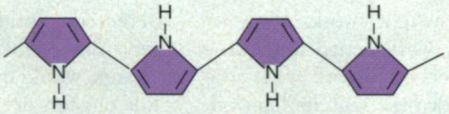
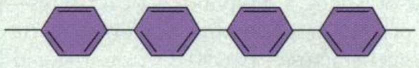
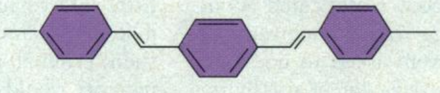
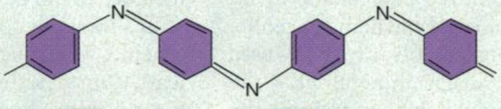
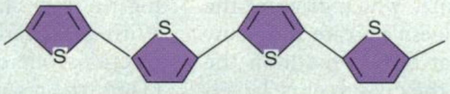
Flexible electronics. This light-emitting diode, made from PPV, a form of a conducting polymer, can be bent, a useful trait for commercial applications.

CONDUCTING POLYMERS

Polymer (date conductivity discovered)	Structure	Amps conducted per volt centimeter
Polyacetylene (1977)		1.7×10^{5}
Polypyrrol (1979)		7.5×10^{3}
Poly(*p*-phenylene) (1979)		10^{3}
Poly(*p*-phenylene-vinylene) (1979)		5×10^{3}
Polyaniline (1980)		200
Polythiophene (1981)		10^{3}
Other Conducting Materials		
Copper	good conductor	5.8×10^{7}
Silicon	semiconductor	4×10^{-4}
Quartz	insulator	2×10^{-17}

First light. If that does happen, it will be the culmination of a research project that began in 1977, when Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, then all at the University of Pennsylvania, discovered conducting, or "conjugated" polymers. Polymers are made by taking organic carbon-based molecules and linking them together in a chain. The chain is held together by covalent bonds, in which adjacent molecules share two electrons. A sample of a typical polymer would have a multitude of such chains, each made up of hundreds of the original molecular units, or monomers, and all tangled around each other—"an amorphous plate of spaghetti," according to Braun. It is this disordered structure, compared to the ordered arrangement of molecules in a crystal, that makes polymer plastics flexible. And that flexibility gave polymers loads of practical applications in everything from PVC window frames to nylon stockings.

One thing they didn't do, for the most part, is conduct electricity. Polyacetylene, the polymer used by the Pennsylvania group, did, but only with a bit of help. In this polymer, a carbon atom is connected to the next one in the chain by a single bond, and that atom is connected to the next by a double bond—two sets of electron pairs—and this alternating pattern continues on down the chain. The key to conductivity, the team discovered, was to add electrons to the chain by mixing atoms with spare electrons, such as sodium, lithium, or potassium, in with the polymer. These interloping atoms donate their spare electron to one of the nearby bonds in the polymer chain, introducing a very useful electronic instability.

If that electron settles on the first single bond, the bond now has three electrons. Electrons travel in pairs, so the free electron then grabs an electron from the adjacent double bond, leaving it with three electrons.

This effect can ripple down the chain, like a line of falling dominoes. If you then put a voltage across the polymer, all these dominoes will flip in unison, creating an electric current.

Remarkably, this neat trick also works if you add electron-deficient atoms or compounds, such as iodine or arsenic pentafluoride. These grab electrons from the chain, and that absence causes a similar effect on the bonds strung out along the polymer. What is more, in these conducting polymers, electrons can "jump" from one chain to another, so that electricity can move through a large sheet of polymer material.

The discovery that the addition of extra atoms or compounds, known as "dopants," would make polyacetylene conductive sparked a race among materials groups to find other polymers with the crucial alternating single and double bonds. Scientists hoped these polymers could replace metals as conductors throughout the electronics world. Other polymers were quickly found (see table on p. 1700), and the list continues to grow. Researchers have even been able to develop polymers whose bond arrangements permit limited conduction without the help of dopants. But despite their best efforts, researchers could not coax the conductivity of any of these polymers up to the levels of good conducting metals. Not only that, they proved unexpectedly difficult and expensive to produce, leaving researchers at a loss for practical applications. "The synthesis was not as easy as people first expected," says materials scientist Francis Garnier at the CNRS Laboratory of Molecular Materials in Thais near Paris. "The price is too high. It just doesn't fit for low added value applications."

A material in search of a use. The Cambridge breakthrough, however, gave the field a new direction. Rather than trying to use the polymers as simple conductors in place of metals, as they had originally, researchers began to focus on LEDs, in which the drawbacks of conducting polymers weren't as devastating. In LEDs, polymer conductivity needs to be low; in addition, the difficulties involved in manufacturing them are acceptable, since making the conventional inorganic semiconductor LEDs can be even more demanding.

Friend's group at the Cavendish Laboratory, along with colleagues from the chemistry department of Cambridge University, had begun to explore LEDs by looking at the luminescence of conducting polymers. Just like the luminous dial of a watch, if you expose some conducting polymers to light, they will glow—emitting their own light at a particular frequency, which is not necessarily the same as that of the incoming light.

The glow is produced by the interaction between the incoming light and the electrons in the polymer, and its wavelength is determined by the energy levels of those electrons. Electrons in any solid have different levels of energy, but within limits: there are ranges of energies—known as bands—that an electron is permitted to have and other bands that are forbidden to it by the laws of quantum mechanics. Most of the electrons in a polymer molecule sit in a low energy band. The next band up is generally empty, except for the electrons added by the dopant atoms (which are stuck in the higher band because the low band is full). But when there is an influx of photons, which inject additional energy into the system, electrons in the lower band get kicked upstairs to the upper band.

Switching on Plastic Transistors

In 1990, while a group of Cambridge scientists were busy lighting up conducting plastic (see main story), a group led by Francis Garnier at the CNRS Laboratory of Molecular Materials in Thais near Paris used a similar material to make another key electronic component: a transistor. While it's not getting as much attention as polymer LEDs, plastic transistors may make it into the market place first—which would make them the first fruit of a new generation of "plastic electronics."

Garnier's group used a short polymer, just 6 monomer units long, known as sexithiophene. A film of sexithiophene has conductivity levels close to those of semiconductors, somewhere between an insulator and a metal. This makes it useless as a conductor, but well suited for work in a transistor, which is a switch to turn a current on and off—and sexithiophene's low conductivity can be boosted sharply by an outside influence.

Garnier's group deposited a film of sexithiophene onto a piece of insulating plastic. The conductivity is low because the energies of all the electrons are confined by quantum mechanics into a specific energy band and their movement is severely limited because the band is so full—the switch is "off." But if you remove a few electrons, this also creates gaps, or "holes," which move around more quickly. These holes, which carry a positive charge, do the conducting.

To create more holes, the researchers place an electrode underneath the insulating layer and apply a voltage between it, as the negative electrode, and a positive electrode on top of the sexithiophene. The positive top electrode pulls electrons out of the polymer creating holes, which are then drawn down to the bottom of the sexithiophene film next to the insulator. They accumulate there in a thin layer, blocked by the insulator. If a voltage is then applied to a second top electrode, the holes form a current in this thin layer, moving along the film and into the other top electrode. The switch is "on."

"It's beautiful work," says Alan Heeger of the University of California, Santa Barbara, one of those working on plastic LEDs. Industry appears to agree. Garnier's group worked with researchers from the Dutch electronics company Philips to miniaturize the transistor, and Garnier has visited teams doing similar work at IBM and AT&T in the United States. There are lots of electronic gadgets in which transistors that are tough, light, and transparent would be highly desirable. They could, for instance, make liquid crystal displays more durable, since sexithiophene is much tougher than the type of silicon presently used for the screen circuits in these devices. "Mitsubishi may already have a prototype LCD with polymer circuits," says Garnier. And that would bring plastic electronics right to the edge of the marketplace.

–D.C.

They don't stay there for long, however. Electrons prefer lower energy states, and each newly promoted electron sheds its extra energy quickly, a move that allows it to drop back down into the hole in the low band it had just vacated. The extra energy is released either as a new photon or as heat. And the energy of the released photon, and hence its wavelength, is directly related to the size of the energy gap between the upper and lower bands. A large gap, for instance, means an electron has to acquire a lot of energy to be pushed across it; shedding that energy produces an energetic photon. Such photons have shorter wavelengths.

Friend's group had a hunch that they could create the same effect using an electric current instead of light. Their idea was to take a piece of polymer with no dopant atoms mixed in—so the upper band was empty—and attach electrodes to each side. Electrons will flow from a negative to a positive electrode, so when a voltage was put across the polymer, electrons moved into the plastic from the negative electrode. Because the lower energy band was full, these electrons took up residence in the upper band and were pulled by the voltage toward the positive electrode, all the while staying in the upper band. At the same time the positive electrode pulled electrons in the lower band out of the polymer—leaving vacancies, or holes, behind them. These lower band electrons take a step around these holes, one at a time, and this shuffling forward means that the holes effectively move backward toward the negative electrode. If one of these backward-moving holes happens to move past a forward-moving electron in the upper band, the electron may seize the moment—and a chance to move to lower energy—and drop down, emitting a photon.

The conducting polymer that made this happen was poly(*p*-phenylenevinylene), or PPV. The light it gave off will never replace the light bulb, but its glow can be seen in daylight. For materials scientists, that meant the possibility of building flat display screens from other materials besides the delicate and hard-to-manage liquid crystals that currently make up those displays. If polymer LEDs could be made to emit all colors, efficiently and reliably, and were cheap and easy to make, there was a fortune to be made.

Adding color to the field. And that realization made polymer LEDs a growth industry. "The LEDs are really promising and very exciting," says Heeger, now at the University of California, Santa Barbara (UCSB). His group, and others in Europe and Japan, set out to see whether they could make the polymers truly shine. One of the first tasks was to get the LEDs to emit different colors beyond the Cambridge group's yellow-green. This is done by altering the polymer so that the energy gap between the lower and upper energy bands creates photons of the right wavelength. Tuning a polymer to emit red light, for instance, which is a low-energy photon, requires a smaller energy gap. In 1991, Heeger's group was able to tweak the internal structure of PPV and produce red light. Blue light, on the other hand, has a higher energy, so the polymer needs a bigger band gap. In 1992, Gunther Leising's group at the Technical University of Graz in Austria achieved this with a larger-gapped polymer, poly(*p*-phenylene).

But color is only one hurdle; the other is efficiency—the proportion of electrons injected into the polymer that result in an emitted photon. The first polymer LEDs produced in Cambridge had efficiencies of only around 0.01%, low compared to a light bulb, in which about 10% of the introduced electrons produce photons. One reason lies in the electrodes that attach to the polymer. The electrodes are usually made of metal and they have their own energy bands, which don't match the bands in the polymer. And the energy bands in the most suitable metals are not at the right level for putting electrons into the upper band. The result: There are often holes in the lower band, but no upper band electrons to drop into them, and the material loses efficiency.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Plastic light. Conducting polymers can be made to emit light in a pattern.

Researchers are trying to solve this problem with different polymers and different electrode materials. Last October, Friend's group reported the highest efficiency yet attained: around 4%. They achieved it by constructing a two-layer LED out of two different polymers. One layer, from a family of conjugated polymers called poly(cyanoterephthalylidene)s, has energy bands closer to those in metals such as aluminum, making it easier to insert electrons into the upper energy band. The second layer is PPV, from which electrons are pulled into an indium tin oxide (ITO) contact, creating holes for the electrons to drop down into.

This bilayer arrangement also helps to bring electrons and holes together, since they tend to congregate at the junction between the two polymers. There's a slight energy band mismatch between the two materials, which hangs up both lines of electrons at the junction for a few extra fractions of a second, increasing the probability that an electron will find a hole. And an efficiency of 4% creates ample brightness for use in flat screen displays.

Lighting the way to market? These initial successes don't mean plastic displays will be on display any time soon. In particular, there's one large unsolved puzzle: how to make polymer LEDs last longer. Some polymers only glow for a few minutes before fading, others may last hundreds of hours, but to be useful to industry they must glow unfailingly for tens of thousands of hours. Researchers are still hunting for the reasons why the plastic LEDs fade so quickly; among the prime suspects are overheating and degrading the polymer with too high a current, and oxidative reactions between the polymer and the electrode which damage the material. But it's a tough problem. Says Philips' Braun, "I'm optimistic—but I'm not going to hold my breath."

Yet that optimism, as well as the patience, now pervades the field, since the other problems with LEDs were solved with time. Friend and Heeger have already set up companies for bringing commercial application of these polymers to light.

–Daniel Clery

PHYSICS

Building Bridges to the Nanoworld

Michael Roukes is not a musician, yet his conversations are seeded with references to guitar strings. Roukes is not an architect or civil engineer, either, although he often talks about building suspension bridges. Roukes is a physicist who, in his laboratories at the California Institute of Technology, is exploring the basic science behind nanofabrication, the creation of structures not much bigger than atoms or molecules. He and his colleagues are artfully carving up gallium arsenide and other semiconductors to construct some of the smallest freely suspended objects in the world. And these miniature structures are what Roukes compares to suspension bridges, guitar strings, and other oscillating mechanical systems.

These microscopic oscillators are, in Roukes' view, gateways into new physical domains. On a macroscopic scale, researchers understand reasonably well how heat and other forms of energy behave in various materials. Far below that scale, however, is largely terra incognita. But because Roukes' oscillators are so small, the slightest shifts in their energy, shape, or other physical characteristics have noticeable effects on their behavior, in the form of significant amplitude or frequency changes in their vibrations. Therefore, on these lilliputian bridges and strings Roukes will be able to trace whether heat flows differently than in macroscopic bulk materials, or how a single defect in a semiconductor crystal absorbs energy. Roukes also plans to use these structures to search for phonons, quantized lattice vibrations that are the fundamental units of heat. "We'd like to see the imprint of quantum mechanics," he says.

For the moment, this is all fundamental physics research, says Roukes, but eventually such information will be needed by nanotechnologists who dream of building electronic systems on the scale of individual molecules, or protein-sized machines that clean up pollution. Like engineers in the real world, they'll need to know how energy behaves in their tiny machines. Of a more immediate and practical nature, though, the Caltech group and their collaborators intend to use their minute oscillators to probe the nuclear or electron "spins" of just a few atoms deep within a material, an application that has intrigued some semiconductor manufacturers.

Because this research hovers in the area between applied and basic research, it has