Conductive Polymers Recharged

With the problems that had blocked conductive polymer development now solved, the materials may find applications ranging from drug delivery to thermal windows to optical computing

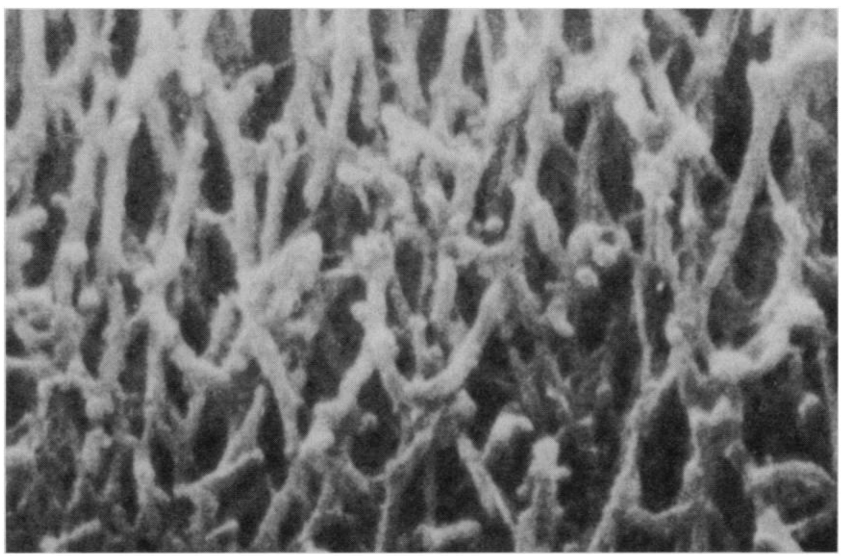
EIGHT YEARS AGO, at a press conference in New York City, twenty or so reporters crowded around a table as Alan G. MacDiarmid connected a small light bulb to two thin strips of golden plastic encased in Scotch tape. The bulb glowed, and so did the future of conductive polymers. "Within a decade or so, plastic batteries made from conductive polymers will have dozens of uses, from powering watches to replacing copper wire in airplanes, and will someday replace conventional batteries in most applications," announced MacDiarmid, an inorganic chemist at the University of Pennsylvania in Philadelphia. "We'll even have electric cars powered by lightweight plastic batteries incorporated right into the doors, roof, and other body panels."

Yet two years later, research on conductive polymers was itself in need of recharging. The materials that were to revolutionize the battery business had proved to be unstable and incapable of being worked into useful forms, with no solutions in sight. "Long-term applications may not be possible," predicted Sukant Tripathy, then manager of conductive polymer research at GTE.

Tripathy was wrong. Today, less than a decade later, the twin problems of stability and processibility have largely been solved (see box), and conductive polymers are entering the marketplace. Indeed, batteries with conductive polymer electrodes are already being sold in Japan and Europe.

But MacDiarmid was wrong, too. Perhaps the most striking thing about the conductive polymers is that most of their near-term markets have nothing to do with batteries. The plastic-powered automobile still lies far in the future. And yet Toyota, for instance, is testing a windshield made with a heat-reflecting coating of conductive polymer. The U.S. Defense Department is evaluating conductive polymer latexes as electromagnetic shields that can thwart spies' efforts to eavesdrop on conversations or electronic signals. Allied-Signal Research and Technology Corporation in Morristown, New Jersey, has developed a conductive polymer temperature sensor that indicates when frozen food has thawed. And in the operating room, nurses and surgeons may soon be wearing conductive polymer fibers in the form of antistatic clothing.

"I did get a little carried away with all the excitement over that first battery," admitted MacDiarmid. "But it's safe to say now, what with the developments of the past few years and the many different materials available today, that there really is a bright future for conductive polymers, mostly in novel areas that we can't yet foresee."



Plastic that conducts electricity. *Aligning polyacetylene fibers improves their conductivity.* [*Reprinted from* Scientific American]

Novel is right. Consider the possibility of devices that could deliver controlled amounts of drugs directly into a patient's skin over weeks or months. Because of the way conducting polymers are made, explains Larry L. Miller of the University of Minnesota in Minneapolis, they can be designed to release ions when an electric current is passed through them. In most instances, these ions are small. But according to Miller, it should be possible to design conducting polymers that release larger ions such as the positively charged ions of the drug dopamine.

But releasing a drug does no good if it cannot penetrate the skin and reach the blood stream. And any charged molecule, drug or otherwise, would not be able to penetrate the skin on its own. Enter transdermal iontophoresis, a process that should be able to electrochemically drive the drug ions through the skin as they are released. "What you need for iontophoresis is two electrodes attached to the skin and a small current," says Miller. "We can envision having the drug-loaded polymer as one of the electrodes of a small battery. Turning on the current between the electrodes would both release the drug when needed and drive it through the skin and into the blood stream."

A less exotic, but far larger application for the conductive polymers is as antistatic agents and electromagnetic shields. The carbon- and metal-filled polymers that now fill those roles are already billion-dollar markets, and demand is expected to grow 25 percent annually for the next decade.

For operating room personnel, antistatic clothing is needed to eliminate static discharges that can confound sensitive electrical monitors or even stun the heart during open heart surgery. In the computer industry, such clothing could reduce the number of computer chips and circuit boards ruined from static discharge. Conductive fabric could also be used to upholster office chairs, eliminating the static buildup that can damage computers in the workplace.

At present, static can only be warded off by frequent touching of a grounded mat that carries charge away from the body before it builds up to a potentially damaging level. But fibers coated with conductive polymers could do the trick continually and automatically, and that might make them big sellers. That's Hans Kuhn's hope. A chemist at the Milliken Corporation, a large textile company in South Carolina, Kuhn has developed a method for impregnating nylons and polyesters with a number of stable conductive polymers. Other chemists, such as Frank Karasz at the University of Massachusetts in Amherst, have created fibers made solely of conductive polymers. These fibers can be woven into fabrics or blended with more conventional fibers.

Another major arena for the new polymers involves protecting against electrical discharges on a much grander scale—lightning bolts. When lightning strikes a metal aircraft, the charge distributes itself over the entire metal skin, from which it gradually leaks into the atmosphere. But some airplanes, now mainly corporate-style jets, are being made of nonmetallic composite materials that cannot dissipate the electrical charge of a lightning bolt. Unless they are protected in some way, lightning could burn right through an aircraft's skin, possibly knocking the plane right out of the sky.

To prevent this, manufacturers now add conducting carbon fibers or metal flakes to the materials, but this adds weight and decreases their mechanical strength. That's why the Lockheed Corporation is making a big effort to develop conductive polymers that can be used to make airframes, although the exact amount of money they are spending is classified information.

Then there's the intriguing possibility that you could paint computer cabinets—or even entire buildings—with a conductive latex paint to keep electromagnetic radiation from leaking into the atmosphere, something the Defense Department is now testing. Perhaps the new U.S. embassy in Moscow can be salvaged by painting the entire building with a polypyrrole latex, thus trapping radio signals from bugging devices inside the building.

Los Alamos National Laboratory chemist Matt Aldissi does not find that idea far-fetched. He has come up with a way of making conductive latexes that could be sprayed onto surfaces of virtually any size. "You could paint the walls of a room with these materials," he says.

Aldissi has created conductive latexes by synthesizing the polymers in water mixed with a polymeric surfactant. As the polymer grows, it binds to the surfactant, forming a bilayer. Removing the water causes these layers to collapse into spherical latex particles that make a conducting film.

On another front, conductive polymers turn out to be useful not just for their ability

In Search of Stability

If some researchers were overly pessimistic about the practicality of conductive polymers in the early days, they had good reason to be. The materials' main drawbacks, which included poor stability in air and a stubborn resistance to being processed, seemed to be directly related to the electronic and chemical characteristics that made them conductive in the first place.

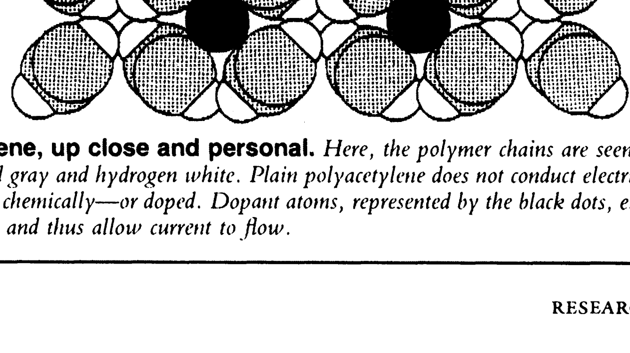
Consider the stability problem. All the known conductive polymers start out as a chain of carbon atoms connected by alternating single and double bonds. In that form, they are extremely weak conductors at best. However, researchers learned early on that when the materials are oxidized—stripped of a fraction of their electrons—their conductivity can rise by nine orders of magnitude or more. And therein lay the problem: the gaps left by the lost electrons provided a pathway for charge to be conducted down the polymer chain—and at the same time, made the polymer highly reactive with water, such as the humidity in air.

The conductive polymers' resistance to processing stemmed from the fact that they form rigid, tightly packed chains. This crowding was clearly essential if electrical charges were going to be able to jump from one molecule to the next as the current moved through the polymer. However, the tight packing also kept the polymer chains from intermixing with solvent molecules, which meant that the polymer as a whole was a hard, insoluble mass—and thus unprocessible.

During the 1980s, however, as researchers gained experience with the conductive polymers, the fixes proved surprisingly straightforward. Solving the stability problem proved as simple as incorporating less reactive atoms such as sulfur, nitrogen, and oxygen into the polymer backbone. For example, the first such polymer was polypyrrole, a chain of five-membered rings, each of which contains a nitrogen atom. Polypyrrole remains stable in the atmosphere indefinitely. Several Japanese firms, including Nippon Electric, are now selling high-frequency capacitors containing polypyrrole as the solid electrolyte. The analogous compounds with sulfur and oxygen atoms in the nitrogen position—polythiophene and polyfuran, respectively—have also proved stable and conductive.

Meanwhile, chemists were making a frontal attack on the processibility problem: they tried out dozens of different side chains to the basic polymers by trial and error, testing each version for solubility and conductivity. "It was brute-force chemistry, but it worked," said Lawrence W. Shacklette, senior research associate at the Allied-Signal Research and Technology Corporation in Morristown, New Jersey.

Finally, investigators also made striking improvements in the polymers' ability to conduct electricity. Back in the 1970s, the first polyacetylenes had conductivities only a fraction of a percent of copper's conductivity. This was high enough to be useful in many applications. Yet today, researchers make polyacetylene with conductivity approaching that of copper and other polymeric materials with conductivities that are only one or two orders of magnitude less conductive than copper. ■ **J.A.**



Lawrence W. Shacklette/Allied-Signal Corporation

Polyacetylene, up close and personal. *Here, the polymer chains are seen end on, with carbon colored gray and hydrogen white. Plain polyacetylene does not conduct electricity very well unless treated chemically—or doped. Dopant atoms, represented by the black dots, either donate or grab electrons and thus allow current to flow.*

to conduct electricity, but also for the unusual optical properties that some have. Among other applications, these polymers are now being considered for use in thermal windows that could either keep heat out or let it in, as needed.

Such polymers have been produced by chemists at Allied-Signal. In their nonconductive form they are bluish in color. In their conductive form, however, they are virtually transparent to the visible spectrum of light. They nonetheless absorb infrared radiation, and Allied-Signal researchers are exploiting this property to make heat-blocking window coatings. In hot climates, windows coated with the conductive polymer could help reduce air conditioning bills by keeping solar heat out of buildings and cars. In fact, Toyota is reportedly going to use the coating on its high-end automobiles.

In cold climates, the same material could be used for a more active type of thermal window. This application depends on the polymer's ability to change from a conducting to a nonconducting state and back again in response to an applied voltage.

The idea is to provide the coated windows with a built-in, light-controlled electrical circuit. In daylight, the circuit would keep the polymer in the clear, infrared-transparent state, letting heat in. But as the sun went down, or if the day was cloudy, the circuit would allow the polymer to revert to its bluish state, which is opaque to infrared radiation and would thus keeping heat from leaking out of the building.

The company is currently testing the long-term stability of these materials, for as project leader Lawrence W. Shacklette explains, "We're talking about architectural applications here, so the polymers have to be stable for 20 years or so."

The unusual optical properties of some conductive polymers may also make them useful in the embryonic field of optical computing, which is aimed at replacing microchips that operate with electricity with optical devices that would operate with pure light—at about 1000 times the speed.

This application of conductive polymers stems from their inherent nonlinearity. That is, the same chemical structure that enables these polymers to conduct electricity also interferes with the propagation of light through the material, thus forcing the speed of light to vary with the *intensity* of the light.

This effect is almost nonexistent in conventional materials such as glass and is relatively weak in the type of window coatings being tested by Allied-Signal. But it is very strong in certain other conductive polymers. And that, in turn, makes these materials attractive to optical computing researchers

For example, Bellcore of Livingston, New Jersey, the research and engineering consortium for the Bell operating companies, is testing several conductive polymers as optical switches—the optical counterparts of transistors. So far, the Bellcore group has demonstrated that the idea works, using polydiacetylene to create a device that allows pulse switching on a picosecond time scale. This material has exceptionally high optical nonlinearity, so that switching can be done with the cheap, but low-intensity dye lasers; most optical switches created to date require much more intense light to function properly.

Unfortunately, polydiacetylene, like all the other known nonlinear polymers, is a poor candidate for practical devices because it absorbs light as strongly as it distorts it. However, the Bellcore group is now searching for a conductive polymer that combines high nonlinearity with good transparency.

The one thing common to all these applications is that they only require low conductivities, a state that polymer chemists have found easy to achieve. However, highly conductive polymers may also be useful someday. Recently, Aldissi and his colleagues at Los Alamos have made substantial progress in that direction with a substituted polythiophene polymer that is not only highly conductive but is also water soluble.

These polythiophenes are essentially soaps, composed of an uncharged backbone and a long, charged side chain. When dissolved in water, the resulting solutions are cloudy, according to Aldissi, indicating that the polymer is in a liquid crystalline phase. Since liquid crystals are known to orient themselves in a magnetic field, Aldissi decided to see what would happen if he ran the polymer solution through a powerful magnet while removing the water.

"It was remarkable," Aldissi says. The resulting polymer had a conductivity only one order of magnitude less than that of copper. Aldissi has performed a similar feat with other polymers by synthesizing them in liquid crystal solvents and removing the solvent under a magnetic field while pulling on the material. Transmission electron microscopy shows that the majority of the polymer fibers created in this manner are aligned parallel to one another, but that some small fibrils remain disoriented. "Thus, we should be able to reach even higher conductivities," said Aldissi.

Another possible route to high conductivity comes from D. Fennell Evans and colleagues at the University of Minnesota, who have found (left) that polypyrrole has a crystalline form that might be very conductive indeed if made in bulk.

Where this and the other research on conducting polymers will lead is still a mystery. "The challenge with these materials," said GTE's Sandman, "is to find unique situations, unique applications, that conductive polymers can fit into by virtue of their unusual properties. They are never going to replace copper wire, but they don't have to in order to become a big success."

■ **JOSEPH ALPER**

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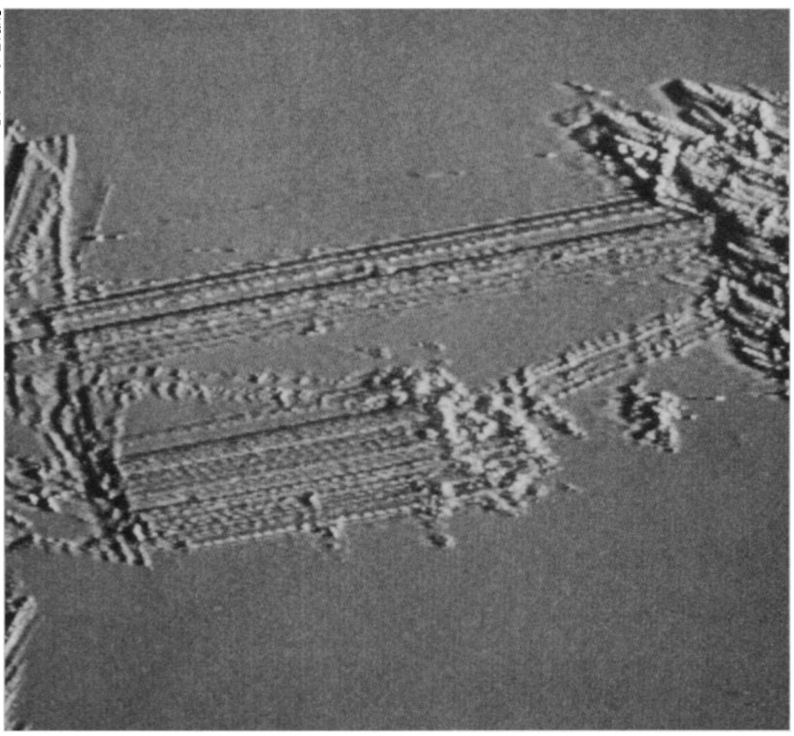

D. Fennel Evans

Microscopic crystals. *Until recently, conductive polymers as a group were thought to be amorphous. But this scanning tunneling micrograph of polypyrrole deposited on graphite shows that the compound can form helically twisted strands, which then crystallize. If the crystalline form could be made in bulk, its conductivity might be extremely high.*