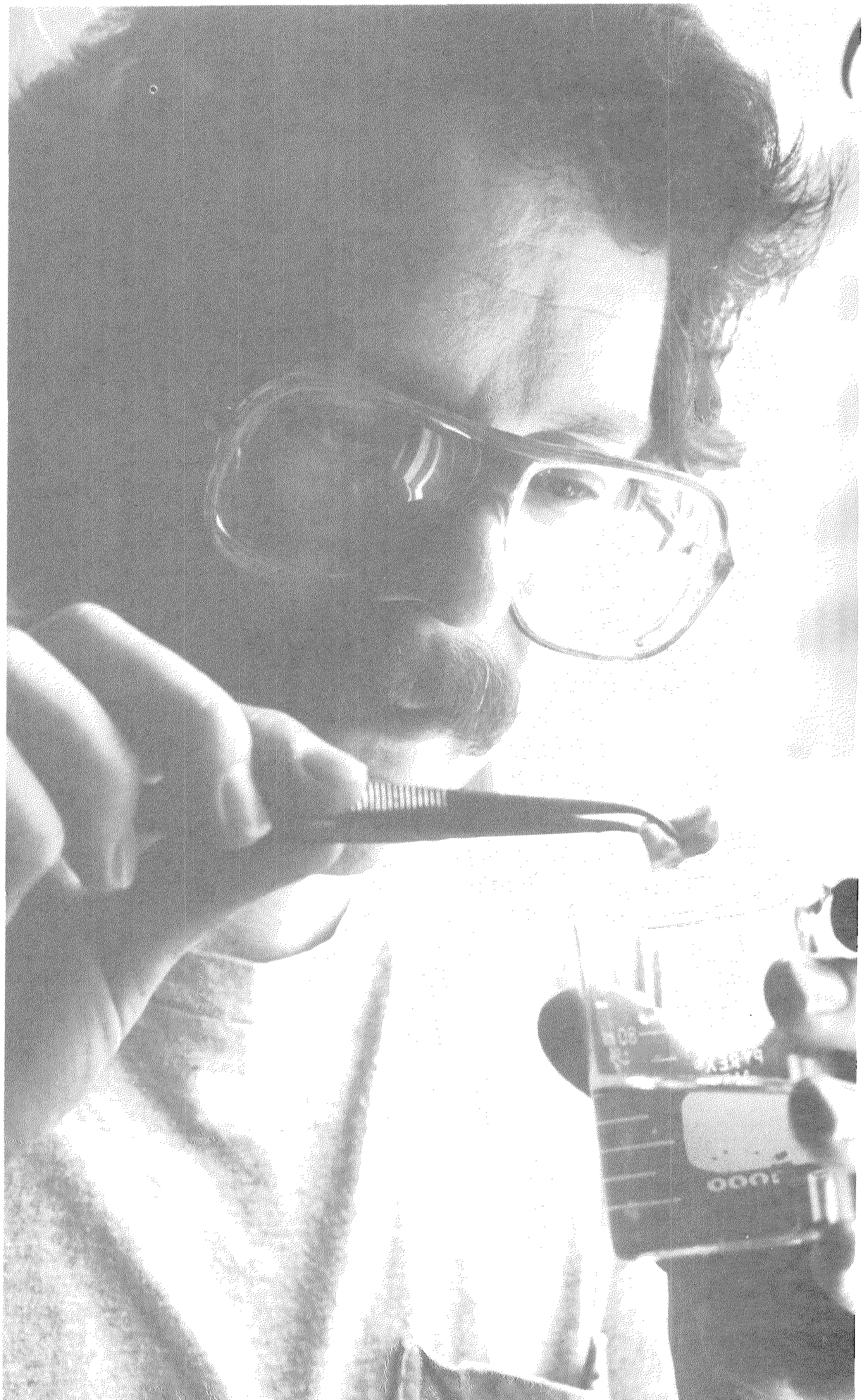
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Polymer's Progress

> *"What we need now are ways of making polymers with special properties."*

Graduate student Bruce Novak makes polymers that conduct ions the way cell membranes do.

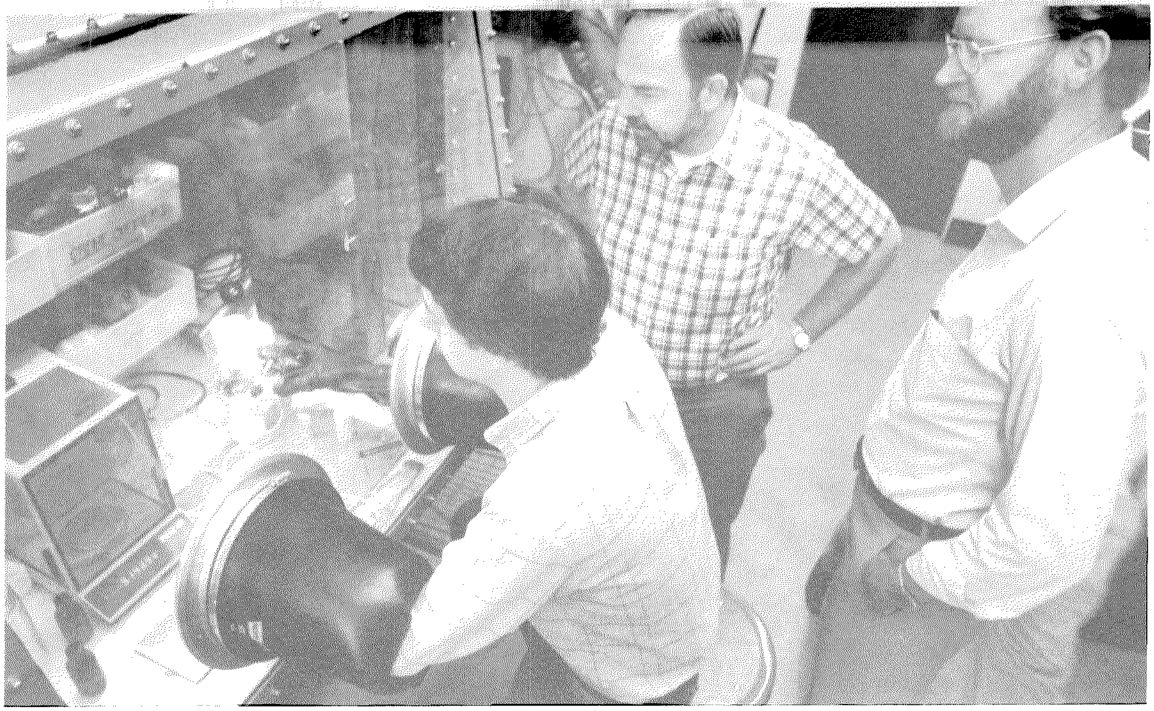
Ever since World War II, synthetic polymers have been an important part of our lives. (Natural polymers have always been part of our lives—proteins, starches, and polysaccharides are all polymers.) In general, a polymer is a large molecule created by linking many small molecules, called monomers, together. The polymer's great size gives it properties quite different from those of the monomer(s) that go into it—a single molecule of polyvinyl chloride (PVC) contains thousands of vinyl chloride monomers, yet PVC is a rigid, inert plastic used to make pipes, bottles, and other things, and vinyl chloride itself is a very reactive, poisonous gas. In the two generations since World War II, polymer chemists have gone from making substitutes for natural products (neoprene for rubber, nylon for silk) to making teflon, styrofoam, spandex, mylar, and a host of other substances Mother Nature never dreamed of.

Polymers are now so pervasive that one might think they've gone about as far as they can go. Not so, according to Professor of Chemistry Robert H. Grubbs. "Polymer synthesis has been directed at making stuff you can sell by the pound. What we need now are ways of making polymers with special properties, for applications where you only need a little bit of polymer. It's the difference between selling maleic anhydride [a basic industrial chemical] and selling a drug." Among the "drugs" under development in Grubbs's lab are polymers that conduct electricity and biological mimics that can transport ions through membranes. Molecules with even more exotic capabilities are on the drawing board.

"Our basic goal is to be able to sit down with our molecular models and a piece of paper or a computer terminal and design a polymer that has a certain molecular weight and certain kinds of functional groups, and then go into the lab and make it," Grubbs says. (A functional group is an atom or cluster of atoms that react as a unit. They dangle from the polymer's "backbone" and determine its chemical properties.) "In natural product synthesis," Grubbs continues, "you can draw a picture of a steroid, look up the right synthetic techniques, and make it. In polymer chemistry, these kinds of precise synthetic techniques are not generally available."

It's easy enough to make a polymer with the right functional groups, but well-nigh impossible to control its molecular weight precisely. Choosing the starting materials determines the polymer's functional groups. But the molecular weight (and thus the polymer's specific properties) depends on the number of monomers per polymer molecule—and on the statistical distribution of individual polymers around the average molecular weight. An ideal polymer would have exactly the same number of monomers per molecule. Real polymers tend to be distributed around the desired molecular weight, with the degree of variation as narrow as the laws of statistics, the chemist's skill, and the synthetic strategy will allow. The closer the actual distribution comes to the statistical ideal, the more "monodisperse" a polymer is said to be.

You can't change the laws of statistics, and chemists are only human, so any breakthroughs toward monodispersity must come from the syn-



Working with air- and water-sensitive chemicals takes special equipment. Graduate student Floyd Klavetter makes polyacetylene in a nitrogen-filled drybox as Professor Robert Grubbs (right) and Senior Research Associate in Chemistry William Schaefer look on.

Doing chemistry in a drybox is like planning a mission to the moon—contingencies need to be anticipated, and all conceivable supplies must be laid in before liftoff.

thetic strategy. There are two basic ways to make polymers: step synthesis and chain synthesis. Each has its own methods to control molecular weight.

Step synthesis builds up polymer molecules step by step. Two monomers make a dimer, three a trimer and so on; a dimer and a trimer make a pentamer, two pentamers a decamer. Every *n*-mer is reactive at both ends. *N*-mers continue to grow, step by step, until they become too unwieldy to mate with each other, or they precipitate out of solution, or they react with something else. During most of the reaction, small-mers will be forming middle-sized-mers. Polymers with the right molecular weight don't appear until the very end—usually when the reaction is better than 98 percent complete —when *n*-mers half the desired weight start to react with each other. The chemist stops the reaction after an elapsed time calculated to maximize yield in the desired weight range. If half-mers reacted exclusively with other half-mers, the product would be monodisperse. But half-mers react with *n*-mers of all sizes, so no matter where the reaction stops, many molecules will be over- or under-sized. The brakes are usually applied to a reaction by adding a molecule that reacts with the active ends, "capping" them. If the process dictates that the cap be added at the start of the reaction, the odds of an undersized polymer being capped prematurely also enters into the statistics. Or, if the polymer contains two monomers, the initial mixture can be adjusted to have a slight imbalance between them, with the shortfall calculated to make the reaction run out of steam at the right molecular weight. Nylon, polyester, polyurethane, and many resins are step polymers.

Chain synthesis, as the name implies, makes each polymer molecule in a single chain reaction. Chain polymers (which include polyethylene, polystyrene, PVC, and teflon) are often built by converting double bonds to single bonds, with the bonding electrons thus liberated being used to link two monomers. A chain reaction begins when an "initiator" creates an active site on a monomer. Then the active monomer adds other monomers onto itself in a chain reaction, building the polymer backbone. The reaction transfers the active site to each newly added monomer in turn, so the active site stays at the head of the growing molecule. If the active site eats something other than the monomer, the chain stops growing, but if the "something" reacts with another monomer to create a fresh active site, a new chain takes off—a process called chain transfer. The reaction finally ends when the active site swallows something that is neither a monomer nor a chain transfer agent, killing the active site. Each chain reaction is so fast that the polymer grows to maturity (and its active site dies) almost instantaneously. At any point in the reaction the vat contains dead full-grown polymers, prematurely dead undersized polymers, monomers, and a small quantity of initiator busily breeding new reactive centers. Unlike step polymerization, prolonging the reaction time does not increase the molecular weight but only improves the yield. Molecular weight control comes primarily through balancing the number

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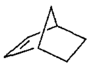

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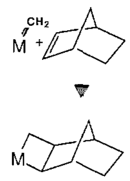

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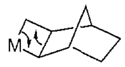

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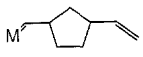

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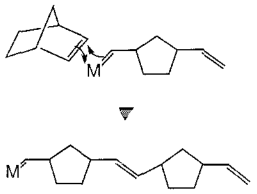

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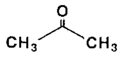

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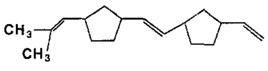

of chain transfer agents against the propagation rate, which is constant. The statistical weight distribution happens because the odds of a chain transfer agent hitting a growing chain of just the right length are fairly slim.

Most active sites are easily poisoned. They're unstable, reactive gluttons, and if a monomer doesn't come around quickly enough to suit them, they'll gobble up anything handy, including a solvent molecule, and die. A few, called "living systems," are more diet-conscious. They're comparatively stable, so they can afford to sit around and wait for their next meal. Grubbs's group has taken this idea one step further by developing temperature-dependent living systems. Unlike ordinary chain polymerizations, the active site in these systems sits on a catalyst molecule. The catalyst assembles monomers like an automatic riveter assembles steel plates. The temperature dependence makes it possible to start and stop the reaction at will, while the catalyst's specificity makes it invulnerable to chain transfer.

"We want to have a pretty rotten catalyst," Grubbs explains. "If you've got a rotten catalyst, then you can control it. If it's slow enough, you can make it very, very selective. For example, our titanium system is a miserable catalyst. It's not so miserable that it doesn't make exactly the right product, but it's miserable enough that it only works under a very special set of conditions. When we impose those conditions—we heat it to 65° C—it goes, and when we cool it to room temperature, it stops. It adds about 25 to 50 monomers per hour, so in 10 hours you can make a pretty good-sized polymer." The group has developed similar catalysts that add up to 1,000 monomers per hour. It's a trade-off—precise control versus speed. The catalyst's reactivity, or lack of it, governs another trade-off as well. The more aggressive the catalyst, the less reactive the monomer needs to be; but by the same token, the more likely the catalyst is to react with some other part of the monomer such as the functional groups that make the molecule desirable. The key, then, is to develop synthetic strategies that match monomer and catalyst.

"We've polymerized many cyclic monomers," Grubbs says. "The one we've studied most is norbornene, a reasonably strained monomer." Prospective monomers must meet a three-part standard: they must contain a carbon-carbon double bond; the double bond must be part of a ring system; and the ring must put a certain minimum strain on the double bond. A monomer falling short on any of the three criteria won't react. Norbornene (**1**), a tricyclic molecule whose three fused rings radiate from two shared carbons like the blades of an eggbeater, strains all its carbon-carbon bonds, but particularly the double bond.

The catalyst reacts through a process called ring-opening metathesis polymerization, or ROMP. The catalyst contains a metal ion, part of a metal-carbon double bond, that reacts with the monomer's strained double bond to produce a metallacycle (**2**). A metallacycle is a ring of carbon atoms incorporating a metal atom. These particular metallacycles are cyclobutanes—four atoms arranged in a square. Norbornene alleviates its strain by breaking the square and forming a new set of double bonds (**3**). When the square breaks open, so does the norbornene ring that contained the double bond. The remaining ring flattens out, relieving the strain. The product molecule (**4**) has a metal-carbon double bond that can form a new metallacycle with another norbornene (**5**). Whether the metal-carbon double bond or the metallacycle is the stable active site depends on the metal involved: titanium would rather wait as the metallacycle, while tungsten prefers the double bond. Both metals follow the same loop, but pause in different spots.

ROMP offers very precise molecular weight control. Unlike catalytic chain initiators, which turn out active centers (and thus polymer molecules) willy-nilly, each ROMP catalyst makes only one polymer molecule. Each molecule competes equally for monomer, and all grow at the same rate. All of the monomer eventually reacts, giving an almost completely monodisperse polymer. Once the monomer is gone, the catalyst can be turned off by adding a cap. The cap monomer (acetone, **6**) contains a carbonyl group—a carbon-oxygen double bond. The catalyst treats this double bond like a carbon-carbon double bond, reacting with it, but once the bond breaks, the catalyst is left holding the bag. The cap winds up on the polymer (**7**); the catalyst gets stuck with the oxygen atom and forms a very strong metal-oxygen double bond. No more metal-carbon double bond, no more reaction. To produce any given molecular weight, just multiply the number of monomers in one polymer molecule by the number of titanium atoms and add that amount of monomer.

Beside being monodisperse, the product is very clean. ROMP is very fussy about its monomer, and only produces one particular product. With a little care in solvent selection and purification to ensure that there is only the one potentially reactive double bond in the flask, product purity is easy to assure.

Some other monomers that graduate students

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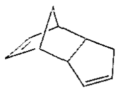

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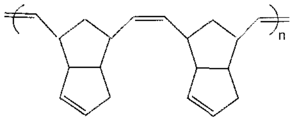

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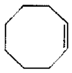

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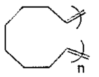

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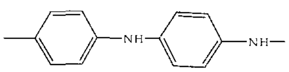

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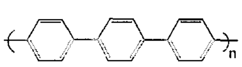

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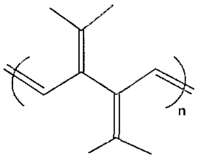

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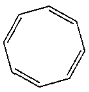

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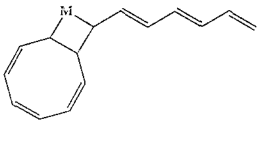

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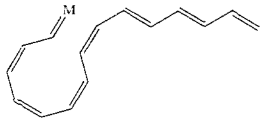

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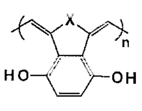

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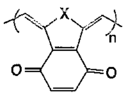


Eric Anslyn, Louis Cannizzo, and Laura Gilliom have tried successfully include dicyclopentadiene (8), which makes polydicyclopentadiene (9), and cyclooctene (10), which makes polycyclooctene (11). Polynorbornene is strong but flexible, and is widely added to the very soft rubbers used in certain flexible seals and roll covers. Polydicyclopentadiene is a strong but lightweight plastic used in snowmobile hoods and golf carts, among other things. Polycyclooctene is a thermosetting plastic which softens a few degrees above body temperature. It is used in the plastic casing for children's hearing aids: it can be remolded to fit the growing ear simply by dunking it in warm water and pressing it back into place.

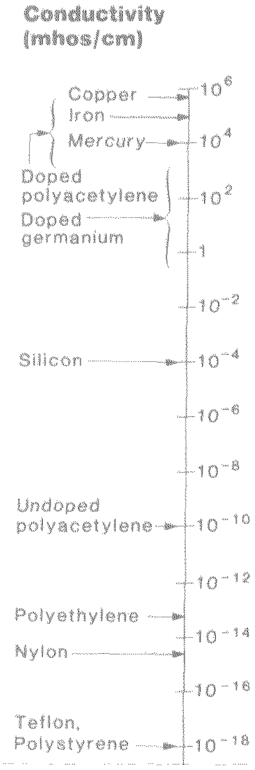
"So then the next question is what kind of monomers do you want to polymerize," Grubbs continues, "and what functional groups do you want the polymer to have? We are doing some that have interesting structural properties—elastomeric, crystalline, that sort of thing, but probably more interesting are the ones that do chemistry."

Chemists around the world are working on plastics that conduct electricity. (See box, p. 26.) A group at BASF has made a very-high-purity polyacetylene with a conductivity of about 147,000 mhos/cm, one-quarter that of copper by volume and twice that of copper by weight. The first commercial application hit the market in late 1987 when a coin-type rechargeable battery with electrodes of lithium and polyaniline (12)—a polyacetylene analog—went on sale in Japan. Even so, conducting polymers in general are very much in their infancy. One problem has to do with the starting material: polyacetylene, the granddaddy of conducting polymers, is made from acetylene gas, the explosive fuel used in welding torches. Polyacetylene also degrades slowly when exposed to air. Researchers are experimenting with protective laminations and with conjugated polymers related to polyacetylene, such as the polyaniline used in the battery. Graduate students Floyd Klavetter and Timothy Swager are looking at polyparaphenylene (13) and polydimethylenecyclobutene (14), for example, as well as polyacetylene. These polymers appear to have higher stability, but, unfortunately, lower conductivity.

Klavetter makes polyacetylene by ROMPing 1,3,5,7-cyclooctatetraene (COT, 15). COT has a ring of eight carbon atoms linked by alternating double and single bonds. The process works just like the polynorbornene reaction. The catalyst makes its square from one of the double bonds (16), and the opened rings link up to form new double bonds (17), producing a long, linear chain of alternating single and double bonds—polyacetylene. Since COT is a liquid at room temperature, it serves as its own solvent. This, along with the very specific nature of the reaction and its lack of side products, gives a very pure product. "We've got conductivities of up to 10^3 mho/cm so far," Grubbs says. "Copper's 6.4×10^5, so we're not far off. The hope is we'll be able to use some of the tricks the others used and see how well we do. Our purity, for example, should be higher, and our fabrication techniques are definitely much easier than theirs. We haven't stretched our films. That's one thing we're working on now. We're also starting to do our polymerizations under shear flow—making the liquid flow in one direction as we're polymerizing—and we hope that will align the chains."

Electrically conductive plastics have optically conductive properties as well.

Polyacetylene has proven to be a processing challenge in other ways: it is brittle, so it can't be machined, and it can't be melted and cast like thermoplastics, so it has to be synthesized in whatever shape it is to be used. The conventional method, polymerizing acetylene gas onto a catalyst-coated glass surface, gives a paper-thin film only 15 to 20 microns thick. As the polymer coats the glass, it covers the catalyst too, stopping the reaction. Furthermore, the catalyst, alkyl aluminum titanium oxide, is extremely corrosive. It devours most substrates other than glass. The catalyst has a weak stomach, though; any functional group on the substrate or impurity in the environment kills it.



The ROMP system has none of these drawbacks. The catalyst doesn't need a surface, but swims in the COT. The COT can be poured out as a sheet to make films of any desired thickness, or it can be poured into a container of any shape—the group has already made chunks of polyacetylene. The film can be deposited on different surfaces (glass, metal, plastics, and cellulose have been tried so far) because neither COT nor the catalyst seems interested in reacting outside the family. Among the various shapes produced to date are polyacetylene "wires" 1 mm in diameter, using thin teflon tubing as a mold. Such wires might eventually serve as prosthetic nerves.

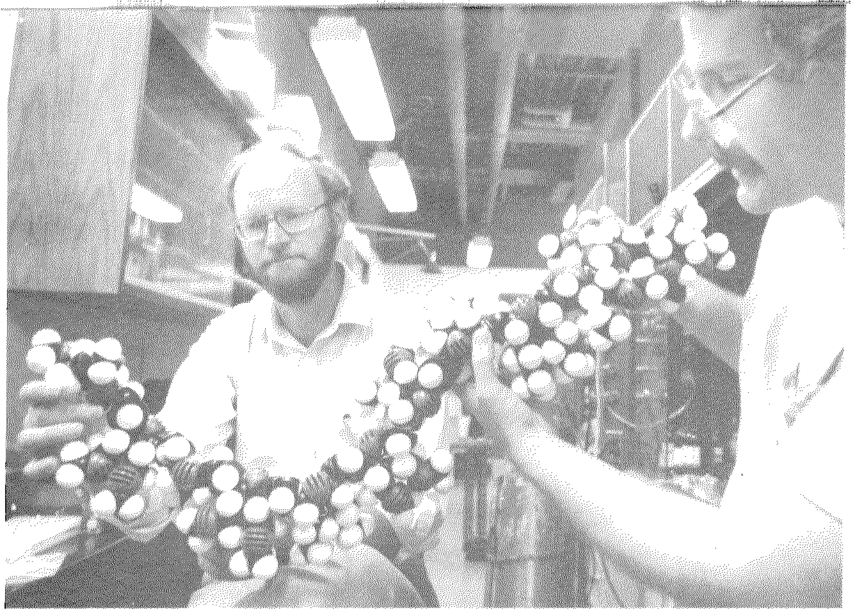
Polyacetylene films are a lustrous, highly reflective silver. Cyclooctatetraene is a yellow liquid. As the polymerization proceeds (15 to 45 seconds at room temperature, and a catalyst/COT ratio of about 1/100), the yellow darkens, turning orange, then red, magenta, and black before becoming a silver solid. Doping it with molecular iodine turns it black.

The way a polymer is doped has great influence on its electrical properties. The amount of dopant can be varied, but once added, it can't easily be removed. "One of the things we're doing now is designing built-in dopants that we can control," Grubbs says. Both molecules **18** and **19**, for example, have the alternating double bond-single bond backbone needed for conductivity. Molecule **18**'s backbone passes through a hydroquinone, a strongly delocalizing structure that should enhance electron mobility. Conversion to molecule **19** by oxidation creates a different double bond arrangement called a quinoid. "That changes the band gap significantly," says Grubbs, "so the conductivity will be controlled by how much of it we've oxidized. There's also an intermediate state called the hydroquinone anion radical, and that might be a dopant, too." A variable conductor could be used as a switch or a sensor.

Since light is an electromagnetic phenomenon, it may come as no surprise that electrically conductive plastics have optically conductive properties as well. As electrical conductivity changes, so do the optical properties. Such a plastic could be used to control the amount of light flowing through a fiber optic cable, or as a logic switch in the optical computers now being designed—chipless computers that think with light instead of electricity. In the nearer future, such a plastic could be used to protect people and equipment from damaging laser light—in the cockpit of an F-16, for example. "That might sound like an awfully expensive pair of sunglasses," Grubbs says, "but when you've got a pilot crashing a multi-million-dollar jet because someone shines a laser in his eye and blinds him, it's a pretty cheap pair of sunglasses." These optical properties are now being studied at Caltech's Jet Propulsion Laboratory by postdoc Seth Marder and JPL staff member Joe Perry.

Grubb's group is also making copolymers in which blocks of polyacetylene alternate with blocks of an insulator such as norbornene. Since partially doped polyacetylene acts as a semiconductor, such copolymers might eventually be used in electronic devices.

"It's easy to make blocks with a living system," Grubbs says. "We add A, and the system goes along until it runs out of A. Then it just sits there until we add B, and it starts up again. That's a nice straightforward way of doing things. We've also got a system that's living on both ends—you add A and get polymer growth in two directions, then if you add B you get a tri-block." Postdoc Wilhelm Risse is developing tri-block systems with "handles": the two end blocks play structural roles—orienting the mole-



Grubbs and Novak with a 3-D model of the "spinachy" ion-conducting polymer. This long molecule, when coiled up, puts all its oxygen atoms (slotted spheres) on its inner surface (opposite page, top), in position to attract and stabilize a positive ion (bottom).

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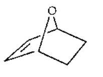

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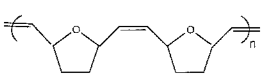

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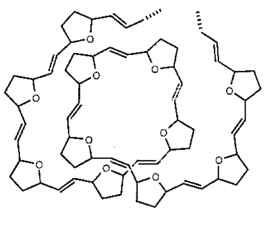


(22) "Spinach" not shown for clarity.

cule and anchoring it in position—while the middle block does chemistry. Making block polymers by other methods can be a tedious task. Reaction A must be stopped at the right time, and the A polymer separated from the reaction mixture and purified, before a new reaction with B can be started.

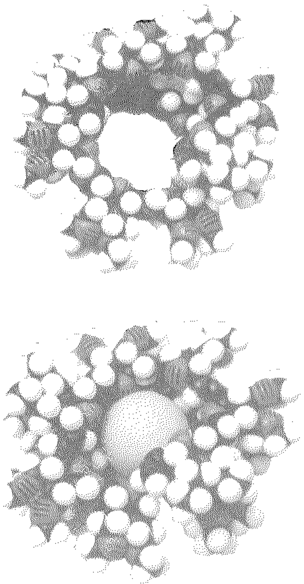
The group is working on polymers that conduct ions as well as electricity. In nature, ion-conducting polymers transport biologically important ions like calcium and sodium into and out of cells. In general, they are long proteins with a natural twist. They like to coil up into hollow tubes that penetrate the cell wall. The tube's outside is coated with fat-soluble groups that anchor the tube in the cell wall, while the inside is studded with oxygen or nitrogen atoms whose lone electron pairs attract and stabilize positive ions. The tube's inner diameter determines how big an ion it can carry, and natural ion conductors are quite selective—passing potassium but not sodium as an electrical impulse travels through a nerve, for example. These molecules may contain hundreds of amino acids in a specific sequence, however, so Grubbs's group is looking for polymers made from one simple repeating unit.

They are looking at polymers based on a norbornene analog called 7-oxanorbornene (20), in which a carbon atom in one ring has been replaced by an oxygen. After polymerization, the result is a string of five-membered, oxygen-containing rings called furans (21). "If you make a model of this polymer," Grubbs explains, "it has all these furans on the front, and all these methyl ethers hanging off the back. The methyl ethers are a sort of spinach that's left over from the synthetic technique. If all the spinach goes to the outside, putting all the oxygens in the middle, the molecule starts to make a helical channel with all the furans, which are really good ion stabilizers, on the inside—a channel just the right size to put an ion in." (22)

The group makes thin films using variations on this polymeric theme. They use the film as a barrier between two solutions in a test cell, and measure the membrane potential—the film's ability to transport ions between the solutions. The polymers now under study prefer to carry large positive ions. They do a good job of selecting cesium over sodium, but are not yet as selective as nature's design. "Once we know how to select an ion size, we'll incorporate these into tri-blocks," Grubbs says. The tri-blocks could then be used for membrane applications analogous to the ion channels in a cell wall.

"This is just the early stage," Grubbs says. "We sat down and designed this molecule two years ago. It took about a year and a half to make it, and now we're starting to look at its physical properties and ion-conducting properties. It's all been done by one graduate student, Bruce Novak." ROMP syntheses can fail if the ring includes something other than carbon. The catalyst, on the make for accessible electrons, may ignore the double bond in favor of the more tempting electron pairs on the non-carbon atom. Novak avoided this catalytic crossbreeding by developing a different, ruthenium-based ROMP catalyst.

It's not certain yet if the ruthenium ROMPer is "alive" or not. "It's not very well defined,"



"It's dynamite. It opens up a whole new area of organometallic chemistry."

Grubbs says. "We first made it by just adding ruthenium chloride to water. We're still trying to figure out what it made, but it's dynamite. It opens up a whole new area of organometallic chemistry."

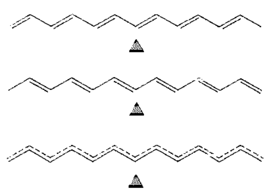
Most organometallics are hard to work with. They are air- and water-sensitive, and as a result must be handled in airtight dryboxes under an inert nitrogen atmosphere. A set of arm's-length gloves of heavy-duty rubber built into the front wall of the drybox allows the researcher to manipulate the material within, while watching the work through a thick plastic window. Just putting an empty test tube in the drybox is time-consuming. Everything entering the drybox passes through a built-in, double-doored airlock. The airlock must be pumped down to a vacuum and refilled with inert gas three times before the inner door to the drybox is opened. Doing chemistry in a drybox is like planning a mission to the moon—contingencies need to be anticipated, and all conceivable supplies must be laid in before liftoff. Otherwise the experiment could be on hold for 20 minutes for want of a spatula.

"But here's a catalyst we can just chuck in water and let sit on the lab bench overnight in the air—Pasadena air even—and then throw in the monomer and make stuff the next day," Grubbs says. "That's a pretty robust catalyst. We're doing emulsion polymerizations in water with it, and that's totally unheard-of using organometallics. That's been the fun part—it's been good fundamental research, understanding how bonds get made and broken. But after you've done all that, you've got people out there in industry who are pretty excited about all this. You can see the applications.

"We've got so many controls over the technique, we can start to tailor-make molecules now, I hope. With the new computer modeling programs you can ask questions about what structures are going to do, how things are going to coil, what effect changing cis-trans double bonds has, or hydrogenating double bonds, or putting more or less spinach on, whether you want fat spinach or skinny spinach, and so on. But once you've got a synthetic technique, you can start to dream and make molecules, and that's the whole point." This summer, the group will be launching a computer-aided design program for molecular synthesis.

"And that gets us into the next level," Grubbs continues. "When you build a polymer, you worry about putting together each individual bond in the molecule. Now you've got to worry about how the molecules stack together, and how they orient with respect to each other, which is essential for bulk properties like conductivity, magnetism, or ion transport." Since magnetism and conductivity are closely related, Grubbs and Associate Professor of Chemistry Dennis Dougherty are collaborating on the design and eventual synthesis of organic ferromagnets. Dougherty's group is experienced in designing molecules with high-spin states, a prerequisite for magnetism. The collaborators hope to make ferromagnetic plastics, permanent magnets, by tweaking the high-spin orientations. Superconducting plastics might also be possible—the conduction mechanism in doped polyacetylenes seems to resemble that of the new high-temperature superconductors.☐—*DS*

Acetylene was first polymerized in 1955. Polyacetylene turned out to be a dark, brittle film that crumbled into a powder with no particularly interesting properties. Then, in the early 1970s, a graduate student at the Tokyo Institute of Technology accidentally added a thousand times too much catalyst while preparing a batch of polyacetylene. The silvery film that resulted was a cross between aluminum foil and plastic wrap. It was lustrous and reflective like a metal, but stretched and flexed like plastic. Although this new and improved polyacetylene had some metallic properties, conductivity wasn't yet one of them. It was, in fact, an insulator, with a conductivity of about 10^{-10} reciprocal ohms (or mhos) per cm. By contrast, copper has a conductivity of about 5×10^5 mho/cm.



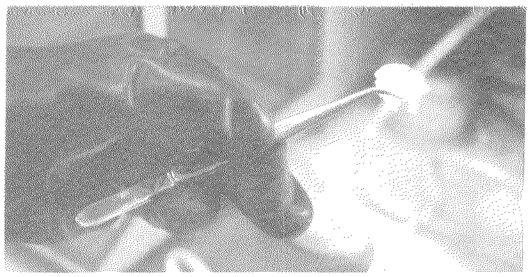
Delocalized electrons: the top two structures are equivalent, so the alternating double bonds blur into a continuous series of "1½ bonds."

Although polyacetylene didn't conduct electricity, it seemed reasonable to think it might somehow be made to. Polyacetylene is just a long chain of carbon-hydrogen units, linked together by alternating single and double bonds between successive carbon atoms—what chemists call a conjugated system. The arrangement can be thought of as a series of single bonds with an extra bond superimposed on alternate pairs of carbon atoms. To an electron in the extra bond, every carbon atom looks the same—it has one bond to a hydrogen atom, and one each to its neighboring carbon atoms. There is no atomic cue telling the extra bond which pair of carbons it should link, so it "delocalizes"—it tries to cover all the possibilities at once. As a result, each pair of double and single bonds is more like two "bonds-and-a-half," with the delocalized electrons smeared indeterminately across the system. If these highly mobile delocalized electrons could be persuaded to move in coordinated fashion, the system would conduct electricity.

In 1976, Hideki Shirakawa, in whose lab the shiny film had been made, working with Alan Heeger and Alan MacDiarmid of the University of Pennsylvania, discovered that adding iodine to the polymer increased its conductivity a billionfold. This process was christened "doping" by analogy to semiconductor preparation, and works along somewhat similar lines.

Although the details are still debated, the general scheme works as follows. Electrons in solids occupy certain discrete energy states called bands. An electron must have a certain energy in order to occupy a given band. Every band has a finite capacity, but within that capacity, the band may be full, partially full, or empty. Bands fill in order of their increasing energy. Metals conduct because their outermost occupied band, the valence band, is partially full. Insulators (including undoped semiconductors) have full valence bands. (It's like traffic flow through a parking lot—cars move freely when there are plenty of available spaces, but come to a standstill as the lot fills up.) The next available band, the conduction band, is empty, and is separated from the valence band by a sizeable energy difference, or band gap. (The band gap is smaller in semiconductors than in insulators.) Doping either adds electrons to the conduction band (called *n*-doping, because it gives the molecule a net negative charge), or removes electrons from the valence band (*p*-doping; the molecule gets a net positive charge). Either way, the electrons are free to flow. Iodine is a *p*-dopant, sodium is an *n*-dopant.

Unlike semiconductors, where the dopant actually replaces a silicon atom in the crystal matrix, dopants in conducting polymers insinuate themselves between adjoining polymer chains. The dopant exerts its influence by donating or removing electrons in the nearby portion of the chain. Unlike metallic conductors, the electrons do not flow in any direction with equal facility, but flow preferentially along the polymer chains. In fact, conductivity can be substantially enhanced by stretching the polymer before doping it, thereby maximizing chain alignment in the direction of stretch. The preferred orientation creates an anisotropic, or nonuniform, effect: conductivity can be a thousandfold greater in the preferred direction than perpendicular to it. No single molecule extends the entire length of a polymer sample, even after stretching, so some sort of chain-hopping is going on, but the conduction mechanism between chains remains a mystery.

Polyacetylene film