MEETING BRIEFS

Chemists Self-Assemble in Southern California

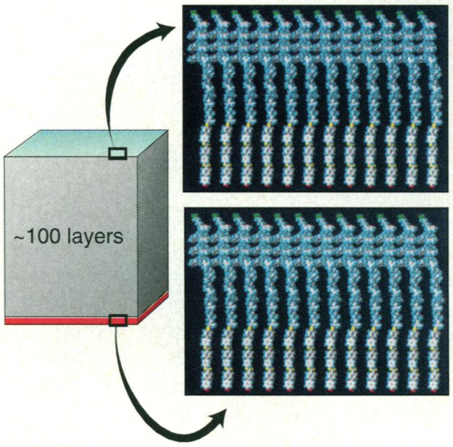
ANAHEIM, CALIFORNIA—Nearly 10,000 scientists gathered for the 209th national meeting of the American Chemical Society (ACS), held from 2 to 6 April. One piece of unwelcome news was that the ACS governance boards approved hikes in journal subscription prices for 1996. But researchers considered matters more physical than fiscal, listening to presentations on substances that self-construct, molecules that clean up after themselves, and DNA recovered from a stone, among other topics.

Self-Building Blocks

Chemists are in hot pursuit of a self-made world, where molecular building blocks put themselves together to form a wide variety of durable materials. It's not that scientists are lazy, but rather that self-assembly has tremendous advantages: It can, for instance, take place in a simple beaker or vat instead of a billion-dollar manufacturing plant. To date, however, most of these microengineering efforts have produced substances that are at most a few molecules thick. And that kind of arrangment has real drawbacks, because a single displaced molecule can puncture and destroy the thin material.

But at the ACS meeting, University of Illinois materials scientist Samuel Stupp reported that he and his colleagues have begun to move self-assembly into the thick of things. The researchers have developed a new class of polymers that build themselves into films containing up to 100 layers. And the researchers were able to vary the properties of the top and bottom film surfaces, making one side sticky while keeping the other slick. Stupp believes such self-assembling films could eventually prove useful as protective coatings for computer disks or to keep blood clots from forming on the inner walls of artificial blood vessels. Eventually, the technique could produce films with a variety of optical, electronic, or catalytic behaviors.

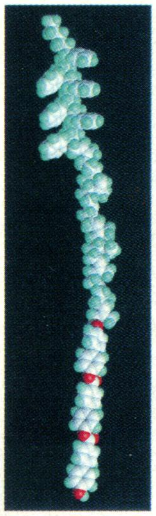
Other researchers are impressed with the early results."The approach is very elegant," says David Grainger, a professor of chemistry at Colorado State University in Fort Collins, who works with self-assembled materials. It is also, however, somewhat mysterious, for the researchers don't yet understand the mechanisms that allow the polymer layers to stack. And that understanding, Stupp says, is essential before they can move on to design layered films whose surfaces have other properties.



Pulling together. Molecules called "rodcoils" *(top right)* self-assemble into sheets, then stack into films 100 layers thick.

At the heart of these new self-assembling films are two-part molecules Stupp calls "rodcoils" because of their unique half-rigid, half-flexible structure. The coil portion consists of rubbery organic building blocks known as isoprenes, connected to another pliable set known as styrenes. A carboxilic acid group goes on the isoprene on one end of the coil, and this group is the linchpin of the molecule. It connects to the rod portion, composed of another series of chemical building blocks known as biphenyl esters, which lock into a rigid crystal structure. Finally, an ultrasticky phenolic group is placed on the far end of the rod, while the coil end holds a slippery methyl group.

Once the rodcoils are built, Stupp dissolves them in a common organic solvent, such as chloroform. As the solvent begins to evaporate, a weak intermolecular attraction, the van der Waals force, pulls neighboring rodcoils together. The rod ends line up side by side, because their pencillike shape allows them to share more van der Waals bonds than can the twisted coil components. This alignment forces the rodcoils into two-dimensional sheets with all the rod-ends on one side and all the coil-ends on the other. These sheets then begin to stack, up to 100 layers thick. And even with several molecules out of place, the structure as a whole remains intact.


SAMUEL STUPP

At this point, the researchers don't quite understand how the stacking comes about. "But we're trying hard to understand," says Stupp, because it should help them choose new functional groups to alter the surface properties of their films while retaining the ability of the polymer layers to stack. To investigate this mystery, the researchers are currently looking at the orientation of the polymer layers in the stacks in hopes that this will shed light on the mechanism that drives the stacking. If the sheets stack in paired layers, for example, with the phenolic surfaces in one layer facing their counterparts in the next layer, that would suggest that the attraction between sticky phenolic groups pulls neighboring sheets together, says Stupp. The researchers are trying to view the orientation of their polymer layers using a variety of imagers, including an electron and an atomic force microscope.

Even before this mystery is solved, the multidimensional assembly may have found some uses. One possibility is lubricating the inner surfaces of artificial blood vessels. Most artificial blood vessels are made from polymer fabrics, and small vessels commonly fail after a couple of years because proteins and blood cells build up along their interior walls. Stupp and his colleagues hope to prevent this clotting by making biocompatible rodcoil films with a sticky surface that binds to the inside wall of the artificial vessels, leaving a lubricating surface exposed. "We might even be able to make the entire vessel out of the rodcoil material," says Stupp. And that would be a slick feat indeed.

Cleaning Up White Paper

On paper, chlorine looks good. The chemical helps turn wood pulp into white paper sheets by breaking down the unwanted component, dark-colored lignin, leaving cellulose, which forms white fibers, virtually untouched. But, as always, what's on paper doesn't tell the whole story. In the real world, chlorine reacts with lignin byproducts to create potentially cancerous chemicals, such as dioxins, that wash from paper mills into rivers and streams.

Pushed by environmental laws, paper companies have been searching for less toxic agents that still make paper white. And in Anaheim, researchers at the U.S. Forest Service's Forest Products Laboratory (FPL) in Madison, Wisconsin, and Emory University in Atlanta unveiled newly formulated compounds that may fit the bill. Called polyoxometalates, or POMs, the compounds home in on lignin but create no toxic byproducts.

If POMs are as succesful on an industrial scale as they are at the lab bench, they "would appear to be very viable and attractive," says John Bergin, who heads research and development efforts at Consolidated Paper, a paper company in Wisconsin Rapids, Wisconsin. Adds Mark Floegel, who has been heading efforts by the environmental group Greenpeace to pressure industry to phase out chlorine: "At this point they sound better than the alternatives," such as ozone and peroxide, which can break down cellulose as well as lignin. Still, to be economically viable the POMs must be used over and over, and there are still some hitches in recycling the compounds.

Like chlorine, POMs are electron thieves, which is the key to their effectiveness. They steal electrons from the bonds holding lignin—a complex mesh made up primarily of carbon-based rings and oxygen—together. The weakened lignin mesh then breaks into fragments that can be washed out of the pulp. What is more, the POMs are selective in their theft; their pull for electrons is not strong enough to allow them to swipe the negative charges from cellulose.

The POM components responsible for the thievery are "transition metals" such as vanadium or manganese, which—with a slight positive charge—have a weak attraction for the negatively charged electrons of the atoms they encounter. But by themselves, transition metals are poor whiteners, as they can be unselective electron thieves and react with water to form compounds that give up their thieving ways altogether. To focus and sustain the metal atoms' thievery, chemists Ira Weinstock from the FPL and Craig Hill from Emory University incorporated them in molecular "cages" made from tungsten, silicon, and oxygen atoms. And in early tests, the researchers have shown that the POMs not only last in the presence of water but that lignin was the only wood pulp compound they affected.

Electron theft, however, is only half the battle, explains Hill. Once the POMs have stolen the electrons from lignin, they must give up their swag in order to be used again on a new batch of pulp. That's accomplished by heating the POMs and lignin fragments in oxygen-saturated water. Oxygen's strong positive charge pulls electrons from the POMs, leaving them ready to tackle a fresh batch of wood pulp. The electron transfer also transforms oxygen into superoxide. It triggers a series of reactions that break down lignin fragments into harmless carbon dioxide and water.

There are still some obstacles the POMs have to clear. One is cost. Bruce Sanborn, associate director for research and development at Consolidated Paper, says the POMs needed to bleach a ton of wood pulp are expected to cost millions of dollars compared to at most $60 for chlorine, although the POM cost is a one-time expense. Still, "at least 99.9% of the material will need to be recovered in order for the process to be economical," he says. In preliminary tests, the researchers have done even better, recycling up to 99.99% of the POMs, says Weinstock.

But these POMs face another problem. To be recyclable, POMs must be equally adept at taking lignin's electrons away and later giving them up to oxygen; right now the researchers have POM varieties that perform one task better than the other. So the researchers are now trying to come up with formulations with different combinations of transition metals, tungsten, oxygen, and silicon in their atomic cages, which are equally adept at both tasks. If they can do that and show that the new POMs are recoverable, the process of whitening may begin to look as good in practice as it does on paper.

Rock Paintings Yield DNA

Cave paintings have always held a pair of mysteries for archaeologists: How were they painted, and what did they mean to the painters? By providing a partial answer to the first question, researchers from Texas A&M University in College Station may have turned up clues to the second. In Anaheim, they presented an analysis of a pigment used in two 3000- to 4000-year-old rock paintings from Texas and reported they'd found ancient DNA. The molecules indicate that animal tissue—such as bone marrow—may have been used in the paint. More important, the DNA may be from a bison, and if it is, the painters must have gone to a great deal of trouble to get it, because bison were not found in the region at that time.

"It's very exciting work," says David Whitley, an archaeologist at the Rock Art Archive at the University of California, Los Angeles. "This technique gives us new insight into prehistoric religion." There's been a debate among anthropologists about whether such pictographs were elements of specialized religious practice or simply adornments to everyday life. If the painters took such pains to procure an ingredient, says Randall White, an archaeologist at New York University, that "would suggest that its use was motivated by a complex symbolic belief system."

The fact that any DNA was found at all came as something of a surprise, even to the researchers involved. "My colleagues told me that they thought it would be long gone," says Marvin Rowe, the Texas A&M analytical chemist who led the team. Most organic compounds degrade quickly in the presence of oxygen in the air. But while radiocarbon-dating the rock art—images thought to be shamans—the researchers noticed that much of the paintings were covered by thin layers of mineral deposits such as calcium carbonate. "So we reasoned that [the mineral deposits] might offer the DNA protection from complete degradation," says Rowe.

To isolate the DNA, the researchers started by taking small samples of the rock-art paint from the two paintings. They placed the flecks in a buffer solution to separate organic material from minerals and used the polymerase chain reaction to amplify a section of DNA from the histone 4 gene. This gene is found in most plants and animals, but not in bacteria, and the researchers targeted it, Rowe says, for two reasons. They wanted to eliminate the possibility that the DNA came from a modern bacterial contaminant. In addition, the gene varies enough among different plants and animals to allow the researchers to begin narrowing down the genetic contributor.


MARION HYMAN AND MARVIN ROWE

Secret ingredient. Analysis of pigments from ancient paintings like these, found along the Pecos River in Texas, turned up DNA, possibly from a bison.

When the researchers found and sequenced the DNA, they compared it to the known histone 4 sequences of a host of plants and animals. The sequence most closely resembled that of bison and deer. To double-check that they were not amplifying modern DNA introduced by accident, the group ran a series of controls, including an unsuccessful attempt to amplify DNA from unpainted flecks of the same rock. They were only able to get DNA from the paint.

The big question now is: bison or deer? By examining other genes in the prehistoric paint, Rowe says he believes his team will be able to isolate the exact species. And while not quite a religious experience, finding the answer will no doubt be a revelation.

–Robert F. Service