Hydrogen Bonds Hold Together Disk-Shaped Self-Assembled Dendrimer

Stable organic structures the size of small proteins with interior cavities have been formed by the hydrogen-bond-driven self-assembly of "programmed" synthetic polymers known as dendrimers. University of Illinois chemists led by Steven C. Zimmerman, an organic chemist and affiliate of the University of Illinois Beckman Institute for Advanced Science and Technology, mimicked nature, creating a molecular self-assembly process in which six identical dendrimers interact via hydrogen bonding, forming a larger, hexameric structure. Zimmerman documented the creation of distinct disk-shaped assemblies—measuring 10 nm in diameter and 2 nm thick—in the February 23 issue of *Science*.

Previous syntheses of dendrimers involved a series of carbon-carbon, carbon-oxygen or peptide bonding, all of which have worked in making dendrimers. However, resulting structures contained defects and took on unpredictable sizes and shapes as they got bigger.

Zimmerman's use of more controllable hydrogen bonding interaction resulted in a two-layered structure in which two benzene rings in the center were each surrounded at 60° angles by six interconnected tetracarboxylyic acid branches. In analyzing the action of the dendrimers, the researchers unexpectedly found that the smaller, first-generation dendrimers would form linear structures, but subsequent larger generations were forced by their size to fold into desirable hexamers.

"We have demonstrated the fundamental principle for creating subunits that form together predictively into a larger and more stable single unit. Hydrogen bonds are the glue that hold it together," said Zimmerman.

SBIR Update

Advanced Refractory Technologies, Inc. (ART) (Buffalo, New York) is continuing its research efforts in advanced ceramic composites based on an award from the Department of Energy for a Phase I contract. The Phase I funding of $75,000 will be for a six-month effort on AlN-SiC composites which are expected to find widespread use in coal power generation applications, particularly heat exchangers.

Stable Mesoporous Silica Thin Film Synthesized Using Mica

Scientists from the University of Toronto and Imagetek Analytical Imaging in Toronto have synthesized thin films (~0.2–1.0 μm) of mesoporous silica on mica substrates, which remain stable upon removal from the substrate. The film consisted of $100H_2O{:}7.4HCl{:}0.11CTACl$ (cationic surfactant cetyltrimethylammonium chloride). After the synthesis mixture was prepared, 0.13–0.24 TEOS (silica source reagent, tetraethylorthosilicate) was added. The mixture was stirred for 2–3 minutes at room temperature then placed in a polypropylene bottle with the mica substrate where the film was formed at 80°C over a period of 1–2 hours to one week.

During the early stages, geometrical arrays of elongated micrometer-dimension mesoporous silica islands formed. As the crystals grew, a continuous mesoporous silica film formed. In the February 22 issue of *Nature*, the researchers reported, "An SEM [scanning electron microscope] image of a calcined thin film (540°C for 4 h in air) demonstrates that the macroscopic integrity of the film is maintained." The researchers suggest that crystal growth is regulated by charge- and structure-matching at the interface. "Assembly of silica-surfactant micellar species on the established mesoporous silica layers results in the continued growth of the film," they said.

Control System Developed to Monitor Surface Hardening of Steel Parts

Research conducted as a part of the U.S. government program Partnership for a New Generation of Vehicles has resulted in a system to control induction heat treatment, a process in which steel and cast iron parts are strengthened by heating them with an electromagnetic coil and cooling them with a water spray. Although the process has been used since World War II, there has been no way to continually monitor the parts and gauge the depth of the hardened surface.

Historically the quality control process was accomplished by heating the parts in batches and cutting apart samples for inspection. If the samples met the required specifications, the whole batch was accepted. Because there has been no way to monitor every part, some good parts were scrapped while bad parts may have gone undetected.

Working with Delphi Saginaw Steering Systems engineers, a team of researchers at Sandia National Laboratories developed a "closed loop" control system that monitors fundamental changes in the properties of the part. Using knowledge gained through computational modeling and materials characterization studies, the researchers developed a neural network controller that controls the depth and quality of the hardened surface as it is being heated. When the system detects the desired part condition, heating is halted and the part is "quenched" with a cooling spray of water.

"The new control system allows the manufacturer to produce parts that are more uniform and reproducible even if there are variations in material, factory environment, and handling procedures," said Russ Skocypec, Sandia manager of the project.

A Delphi Saginaw Steering Systems plant began using the system in August to produce shafts for front-drive axles in Saturn automobiles. Dave Hitz, chief process engineer at Delphi Saginaw Steering Systems, said the control system can be retrofitted to existing manufacturing systems at relatively little cost. The system also is energy efficient, providing a 40% savings over alternate hardening technologies, and it is environmentally benign, he said.

Solid Liquid Crystals Created as 3D Thin Films

Penn State researchers created a material they named helicoidal bianisotropic media, a cholesteric liquid crystal realized as a thin film. "Normal liquid crystals are somewhere between a solid and a liquid," said Akhlesh Lakhtakia, associate professor of engineering science and mechanics. "A helicoidal bianisotropic medium has a rigid backbone sculptured by nano-engineering."

Cholesteric liquid crystals pose a problem for theoretical electromagneticists because no general solution of the Maxwell equations for light propagation in them existed until recently. Lakhtakia said, "Only one special exact solution to the Maxwell equations in cholesterics was known, so I decided early in 1994 to determine what optical properties the material would have if a general solution were possible."

The material that Lakhtakia theoretically designed was a helicoidal or twisted material with specific electromagnetic propagation properties. The twist of this material would affect the way light and electromagnetic fields propagate through it and could be tailored for specific electromagnetic propagation. An associate, Russell Messier, professor of engineering science and mechanics, thought that by modulating the

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density of the material and switching the sample orientation rapidly, they could realize the theoretical material. Kevin Robbie and Michael Brett of the Department of Engineering at the University of Alberta, Edmonton, who have already made a herringbone-shaped thin film, fabricated the theoretical material.

The researchers from the University of Alberta manufactured the first thin films of a helicoidal bianisotropic medium from magnesium fluoride and calcium fluoride which they, along with Lakhtakia, reported in the November/December 1995 issue of the *Journal of Vacuum Science Technology*, Part A. To make the material the researchers used electron beam evaporation, then controlled the depositing vapor to create the twist. The films are highly porous and have a very strong backbone structure. Unlike liquid crystals, these nanoengineered thin films are likely to withstand wide temperature changes and high pressure. The researchers can control the form of the thin films to allow certain wavelengths of light to pass through, to polarize or focus light.

"The liquid crystal thermometers that currently exist can only cover a range of about 10 degrees," said Lakhtakia. "The new materials could make a true liquid crystal thermometer with a broad range because they are temperature stable."

Messier said that, in experiments, one-micrometer thin film can be fabricated within five minutes.

Researchers Fabricate Facsimile of 3D Objects via Computer Models

Researchers at Stanford University Computer Graphics Laboratory have demonstrated the capability to make and "fax" three-dimensional computer models of objects that are detailed enough to make accurate physical facsimiles of the original. During the week of January 22, the researchers scanned a 6-inch-high plastic sculpture of a "happy Buddha" and converted it into a three-dimensional computer model—a process that took about six hours. According to Marc Levoy, professor of computer science and electrical engineering and head of the three-dimensional fax project, the basic process began with placing the Buddha on a black platform. A line of ruby-red light traced the statue's surface as the platform carried it through the plane of laser light. Scans were made from dozens of different orientations to get enough information to convert them into a detailed three-dimensional computer model.

They then transmitted the model electronically to 3-D Systems in Valencia, California, a company that uses a commercial process called stereolithography to create plastic models. Over the weekend the company created a facsimile—a process that took 12 to 15 hours—and mailed it to the researchers.

Levoy's group has been working for several years to automate the process of producing high-quality, three-dimensional computer models of physical objects. The researchers began with a laser range scanner. By illuminating the object with laser light coming from one angle and recording it in a video camera from another angle, the scanner determines the distance of each point on the line of light by the process of triangulation. This information is stored in a "range image" that consists of a series of pixels, or points in a plane, each of which is associated with the distance of the surface at that point.

To go from range data to seamless, three-dimensional images, researchers must combine range images taken from a number of different viewpoints. The more complex the object, the more range images they need.

In their first effort, postdoctoral student W. Greg Turk, who is now at the University of North Carolina, began by converting each range image into a three-dimensional irregular polygon mesh that traces the object's surface as seen from each viewpoint.

Next, Turk developed an algorithm that aligns the different meshes accurately. There is frequently considerable overlap between meshes, so he also created a program that "eats away" at the mesh boundaries until the overlaps are eliminated. He then developed a routine that "zippers" the different meshes together, filling in gaps with new polygons as needed.

This produces a seamless three-dimensional mesh. These meshes can be very fine, with a single model containing hundreds of thousands of polygons.

"The polygon mesh does a pretty good job of capturing the surface, but it fails at extreme corners and sharp points," Levoy said. Turk's work was presented at the 1994 Siggraph meeting.

Since then, however, the Stanford researchers have developed a method that is as fast as the zippering approach, does not have its limitations, and can capture detail as small as 0.2 mm. This "volumetric" approach—developed by Brian Curless, a doctoral student in electrical engineering—begins by dividing up the space around the object into thousands of tiny cubes, dubbed voxels or volume pixels. Each voxel can have one of three values: occupied, unoccupied, and occupancy unknown. If a voxel is occupied, it is on the surface of the object. Curless developed an algorithm that takes the information in a range image and determines the state of the voxels that are visible from the image's viewpoint. Each successive range image fills in more of the voxels until a complete, three-dimensional representation of the object is built up. The result is a fuzzy, or probabilistic, representation of the object.

The last step is to extract the "most probable" surface from this representation using a contour extraction algorithm, called the marching cubes method by the researchers. The algorithm's author is Bill Lorensen, a senior scientist from General Electric, who is spending six months at Stanford working with Levoy's research group.

Yucca Mountain Lava Formations Evaluated by Cosmogenic Isotope Dating

John Gosse of Los Alamos National Laboratory Geology and Geochemistry Group outlined how he and others are working to improve the accuracy of cosmogenic isotope dating for geologic formations. When cosmic rays—high-energy particles streaking through space—enter the atmosphere, some of them interact with air molecules and produce secondary radiation. The rays and secondary radiation penetrate the surface of minerals and convert minuscule numbers of mineral atoms into new isotopes; for example, the radiation converts oxygen atoms to beryllium-10, a radioisotope. Scientists have found that by counting the number of beryllium-10 atoms in a rock sample, they can determine how long the rock has been on Earth's surface.

At the American Association for the Advancement of Science annual meeting in Baltimore in February, Gosse said that the research team used the technique to date lava formations and boulder deposits near Yucca Mountain, Nevada, a proposed underground repository for high-level nuclear waste. Using cosmogenic dating, Gosse determined that lava within 10 miles of the proposed repository site is about 880,000 years old. The age measurement agrees with other dating techniques, giving credence to cosmogenic dating.

He found that boulder deposits in the vicinity had not moved for hundreds of thousands of years and were eroding at a maximum rate of about 0.3 cm (0.12 inches) every thousand years. Age measurements for boulder deposits also agreed with other dating methods.

Production rates of cosmogenically produced isotopes vary with altitude, latitude, and time. Since cosmic rays are deflected by Earth's magnetic field toward the North and South Poles, geologic features at the equator have lower beryllium-10 production rates than features at the poles at similar altitudes. Because cosmogenic dating can be performed on rocks at particular altitudes and latitudes whose ages are known—lava flows that cooled on the surface at a known time, for example—production rate variations for those altitudes and latitudes can be accounted for and validated by computer models and other dating methods.

Generally, when the intensity of Earth's magnetic dipole field increases, the cosmogenic isotope production rate decreases; when the field intensity decreases, the isotope production rate increases. "Dependin on the age of a sample, field variations cai throw production rates off by more thai 20%," Gosse said. "If we had an accurat record of field variations, then we could better calibrate our production rates."

Gosse recently organized a workshop in Santa Fe, New Mexico, where he and others discussed strategies and problems for calibrating cosmogenic isotope production rates. Gosse said the method is worthy of refinement because it can be used in situations where other dating methods are impractical or unreliable. Some dating methods rely on specific sampling media, such as organic materials for radiocarbon dating; others, like potassium-argon dating, are limited by the slow decay rate of tested isotopes—resulting in a low abundance of isotopes, which makes accurate measurements difficult. Cosmogenic dating can be used for a variety of isotopes to provide a flexible, precise dating method.

GMR Found in $Tl_2Mn_2O_7$

Researchers from NEC Corporation have reported giant magnetoresistances (GMR) in $Tl_2Mn_2O_7$ with a pyrochlore structure. Through measurements of the Hall coefficient, researchers determined that the charge carriers are electrons as opposed to holes as in hole-doped perovskites.

Powder samples of $Tl_2Mn_2O_7$ were synthesized by solid-state reaction. A mixture of Tl_2O_3 was placed in a gold capsule and heated at 1020°C for a half hour, then cooled to room temperature before the pressure was released. Measurements of Hall coefficients revealed electron carriers in the material. Hall coefficients R_H observed at 260 and 315 K (above T_c) were approximately −6 to $-7 \times 10^{-1}cm^3$ per coulomb, and R_H values observed at 10 and 50 K were about $-2 \times 10^{-1}cm^3$ per coulomb. In their article in the January 4 issue of *Nature*, Y. Shimakawa, Y. Kubo, and T. Manako said that these Hall coefficients "correspond to 0.001–0.005 conduction electrons per formula unit, and strongly indicate that a very small number of electrons are doped into the Mn^+ state," which is in contrast with perovskite manganese oxides that exhibit approximately 0.18 holes per Mn ion. According to the researchers, oxygen deficiency ($Tl_2Mn_2O_{7-\delta}$), common in many types of pyrochlore compounds, produces the conduction electrons ı their material.

Research on Plasma Crystals Indicates Intermediate Vibrational State in Melting Process

Studying plasma crystals—a set of colloidal particles in a plasma exhibiting ordered crystallinity—with thicknesses of only a few lattice planes, researchers from Max-Planck-Institute für extraterrestrische Physik identified two fundamental intermediate stages of the melting process, including an unexpected vibrational phase. After the "flow and floe" stage, which the researchers described as characterized by islands of ordered crystalline structure (floes) and systematic directed particle motion (flows), a vibrational state occurs. Hubertus M. Thomas and Gregor E. Morfill report in the February 29 issue of *Nature* "growth in the orientational order and an increase in the thermal (vibrational) energy." As the material enters the "disordered" state as a function of gas pressure, the orientational order develops a secondary maximum that coincides with the vibrational state. The researchers said, "In this state, the particle surface density remains constant...at a somewhat higher (factor 1.06) value than the crystalline state. Thus the system has an 'equation of state' where the kinetic energy of the particles may increase by a factor ~100 at constant density."

WAND Detector Screens Waste for Low-Level Radioactivity

Researchers at Los Alamos National Laboratory have invented WAND (Waste Acceptance for Nonradioactive Disposal), an ultrasensitive detector that screens routine, low-density trash so it can be disposed of at a nonradioactive waste landfill. They specifically engineered WAND to detect the faintest possible radiation levels.

WAND allows workers to measure extremely low levels of radioactivity with little or no handling, reducing costs as well as risk of exposure if the trash is found to be radioactive.

Nonradioactive trash that workers have kept segregated from contaminated materials goes directly from the trash box through a commercial shredder, then into a hopper where an augur spreads it to a thickness of half an inch and meters the amount of waste dumped onto a small conveyor belt. The WAND detectors sit above the belt, shielded from most background radiation by lead. WAND's sensitive electronic system reduces background radiation by an additional 75%.

The instrument detects a broad energy range, from 10,000 eV up to 1.5 million eV. At the lower end of this range are hard-to-detect low-energy x-rays that are generated in all materials that emit alpha radiation, such as plutonium. WAND separates these low-energy x-rays from other signals, then amplifies them.

WAND separates signals given off by contaminated trash from the background radiation in real time for rapid inspection of large volumes and permits automated, hands-off inspection of all the material, not just the surface contamination that traditional alpha counters detect. The detector can locate plutonium concentrations as low as 0.13 nCi/g, or about one-thousandth of the upper limit for low-level waste.

If the waste is left in the cardboard box, WAND might miss small hot spots. But using the "shred and spread" method allows WAND to prove that waste contains no radioactive contamination since the detectors are extremely sensitive on material whose density is low and unshielded by a box.

"We've already demonstrated detection levels that are far more sensitive than anything commercially available," said co-developer Roland Hagan of the Nuclear Materials Technology Division. "And the instrument isn't specific only for plutonium; it can address nearly every other radioactive contaminant...except tritium." □

Correction: The April 1996 issue of *MRS Bulletin*, page 2, should have listed L.J. Schowalter as the Guest Editor.