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Question From the Classroom

By Bob Becker

Q: Why do water and oil not mix? I

always thought it was because oil was less dense than water, but my teacher said that water molecules would rather stick to other water molecules, and oil molecules would rather stick to other oil molecules, and that's why they don't mix. He says "like dissolves like". Which one of us is right?

A: A lot of people learn that oil floats on water because it is less dense, and they interpret this to mean that oil and water do not mix because oil is less dense. Its low density is what makes the oil end up on top of the water as they separate, but it's not what prevents the two liquids from mixing in the first place. For a better explanation, I have to side with your teacher on this one: The inability of water and oil to mix (also known as immiscibility) is a direct result of intermolecular "preferences", but it turns out that what your teacher is saying has a common misconception in it as well.

Before we get to that misconception, though, let's talk "polar". Not quite as in "north pole" but as in diametric, or in plain English, opposite ends. Molecules are held together by covalent bonds consisting of pairs of shared electrons. If one of the atoms in the bond pulls the electrons more strongly, that tends to attract the electrons toward its end of the molecule. This gives that electron-rich end a partially negative charge (δ^-) and the other end—the atom end where the electrons have made themselves scarce—a partially positive charge (δ^+). These attractions are known as dipole-dipole attractions. Particularly strong dipole-dipole forces are present among molecules where hydrogen is bound to an atom with a very strong pull on the shared electrons (namely, nitrogen, oxygen, and fluorine), and go by the name "hydrogen bonds". Water is an example of a molecule that forms hydrogen bonds. This is significant because it makes water molecules very sticky to one another with the (δ^-) end of one molecule attracted to the (δ^+) end of a neighboring molecule.

But what about the oil? The bonds within an oil molecule consist of pairs of electrons that are shared pretty equally between the participating atoms. The result? Because there are no (δ^-) and (δ^+) ends, these bonds are nonpo-



MIKE CIESIELSKI

lar and the molecule overall is considered to be nonpolar as well. There is, however, random movement of the electrons within these molecules, and this can lead to temporary lopsidedness in their charge distribution and produce momentary δ^+ and δ^- portions of the molecule. These, in turn, can lead to very weak attractive forces known as induced dipole-induced dipole, or London forces. Because hydrogen bonding in water contributes a substantial amount of cohesive energy, over and above the London forces present, water is a liquid, whereas other molecules of similar size but lacking water's polarity, such as methane, ethane, fluorine, or carbon dioxide, are gases at room temperature.

And now for the misconception: your teacher's explanation makes it sound as though the immiscibility of oil and water is one of mutual agreement and that there is no attraction existing between a water molecule and an oil molecule. Some teachers go as far as to say that oil and water molecules repel one another. In fact, the term often applied to nonpolar substances such as oil is "hydrophobic", which means "water fearing." The truth is that an oil molecule is very attracted to a water molecule—even more than it is to another oil molecule. Because the water molecule has a fixed polarity (a permanent dipole), it is much more capable of inducing a temporary dipole in a nearby oil molecule than is another nonpolar oil molecule. The (δ^+) end of the water molecule attracts the electrons in the oil molecule

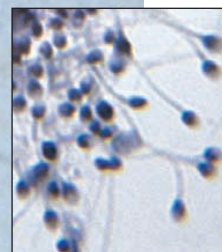


up close to it and this creates a (δ^-) end right there next to the water's (δ^+) end. Likewise, the (δ^-) end of the water molecule repels the electrons in the oil molecule to the far side, and this creates a (δ^+) end right there next to the water's (δ^-) end. These are known as dipole-induced dipole attractions, and they are significantly stronger than the induced-dipole-induced dipole attractions acting between two neighboring oil molecules.

What this means is, if you were an oil molecule, you would much rather surround yourself with water molecules than with others of your own kind. If that's the case, why then do oil and water not mix? If it were up to the oil, they would. But it turns out that the dipole-dipole attractions described above are so much stronger than dipole-induced dipole, that it is really the water molecules that are calling the shots. Water molecules are far too attracted to their own kind to ever allow any oil molecules to come in-between. In short, water molecules are very cliquish. They will allow other polar molecules such as ethanol or ammonia to enter their exclusive company, but a nonpolar molecule: no way! The only molecules that would associate with nonpolar molecules would be other nonpolar molecules.

So even though it's true: oil and water don't mix, it is hardly by mutual agreement. A really impressive illustration of this discrepancy occurs when a drop of water is placed on a nonpolar surface such as wax paper. The drop of water beads up into a sphere—barely touching the wax paper. One can almost visualize the water molecules all gathering together in their exclusive club, not wanting to associate with those lowly wax molecules at all! But when the tables are turned, and a drop of nonpolar liquid is placed on a polar surface, such as occurs when a drop of motor oil falls onto a wet pavement, a very different outcome is observed. Rather than beading up into a tiny sphere, the oil drop spreads out into an infinitesimally thin layer—this is what causes the cool concentric rainbow patterns. In this arrangement, each oil molecule is in minimum contact with other oil molecules, for which the attractions are so weak, and in maximum contact with the much more attractive water molecules.

In this way, like does dissolve like: Polar substances dissolve other polar substances, and nonpolar dissolve nonpolar, but for polar substances, it's a matter of preference and for nonpolar ones, it's more a matter of settling for what you can get! ▲



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The Dog Ate My Homework

and Other Gut-Wrenching Tales

By Michael Tinnesand

WANTED!



"Midge"

**Reward for Recovery
of \$180 Missing Cash**

You'd love Midge.

She's your ordinary,
fun-loving dalmatian
with a great
personality and one
bad habit. She loves
the taste of money,
paper money!

The crime

Recently, Midge's owners Kit and Steven were serving as hosts for a favorite singer/songwriter, an old acquaintance who was in town for a local concert. Things went well until the door to the guest bedroom was left ajar. Under normal circumstances the open door would not have been a problem, but for lovable Midge, it was a doorway to opportunity. There, on the bedside table was \$180 in cash and a check. So tempting! Not to mention delicious!

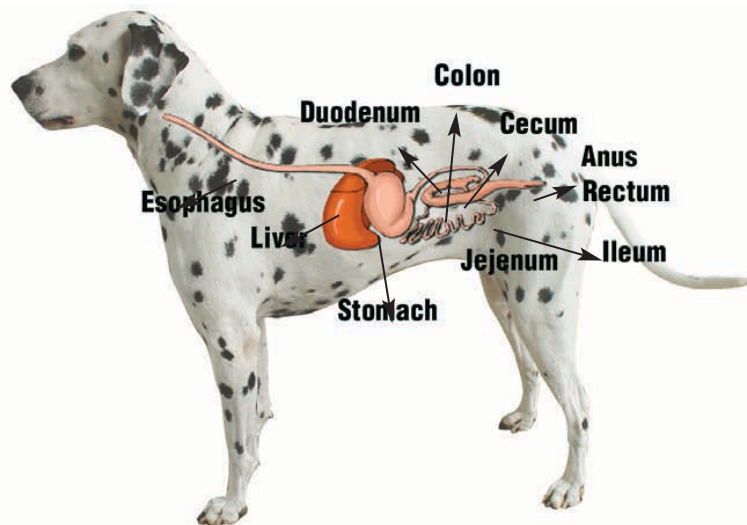
When the break-in was finally discovered, all that was left was a few shreds of the check. No sign of the \$180 cash. Thus, the wait began. For Kit and Steven, walking the dog took on an entirely new sense of pur-

pose. Picking up after Midge required an additional close inspection to see if any of the bills made it through her digestive system intact. The project gave "money laundering" a whole new meaning. Gross? Definitely. But luckily, there was some good chemistry working in favor of retrieving the cash.

The chemistry of digestion

At the most fundamental level, the biological processes of digestion and metabolism are all about the breaking and making of chemical bonds.

Basically, digestion consists of breaking food down into molecules small enough to diffuse through the thin walls of blood ves-



The digestive system of a dog.





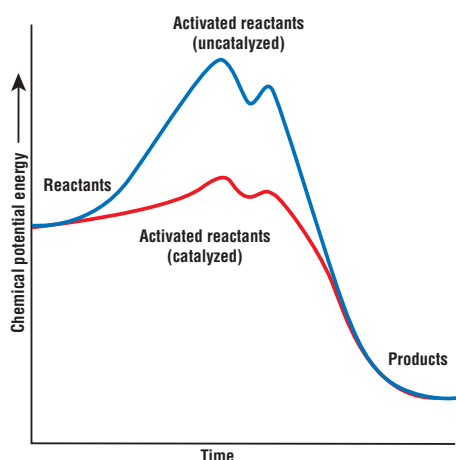
ACS STAFF

sels. After transport through the body, they cross over into tissues where they are absorbed and used by living cells.

Food is primarily composed of large biomolecules such as proteins, fats, and carbohydrates. The “breaking down” of food is the breaking of chemical bonds that hold the molecules of the food together. After the molecules of food are broken down into small enough pieces for cells to absorb them, they are either consumed completely for fuel or reassembled into new polymers and other molecules, according to the body’s own blueprint.

The process of breaking bonds in food includes a number of key steps. Except for animals like pythons who swallow their food whole, the process of digestion usually begins with a physical phase. Chewing breaks the food into smaller pieces, thereby exposing more surface area, which accelerates the process of digestion.

Next, most animals have some sort of specialized sac or pouch, such as a stomach, where serious digestion gets under way. In humans, a strong acid secreted by the stomach helps break down tough connective tissues and activates a set of biological catalysts called enzymes. Like all catalysts, enzymes greatly accelerate the rate of chemical reactions without being used up in the process. A single enzyme molecule can catalyze a reaction thousands of times. But that is not to say that an enzyme is able to catalyze thousands of different reactions. In fact, most enzymes catalyze single specific reactions.

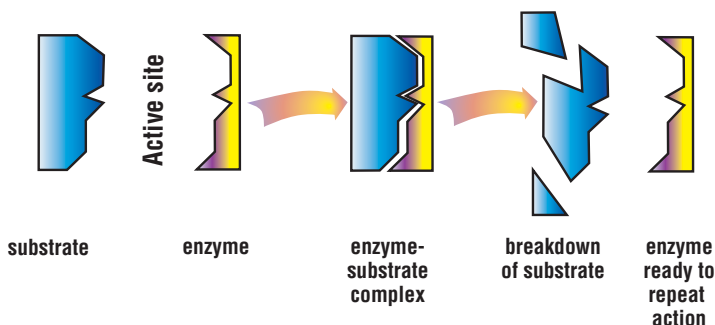


The red line in this graph shows the lower activation energy in a catalyzed reaction.

Enzymes lower the activation energy, the energy required to start the reaction, by securing the reactants in a geometrically favorable position. Held this way, the molecules react with little initial energy—less than if they had to rely on random collisions to bring them together. Once bonded, they are released, and the enzyme is free to act again.

Enzymes can also work to break bonds. In this case a single molecule fits with the enzyme in such a way that one particular bond is stressed. This stress lowers the energy requirement for breaking the bond.

Because the interactions between the enzyme and the substrate molecules are totally dependent on shapes, each reaction requires its own enzyme. Virtually all of the

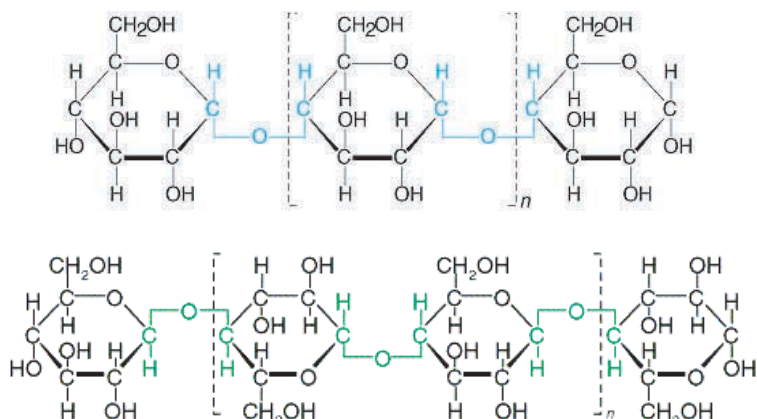


The lock and key model of enzyme action.

This is easier to understand once you understand how enzymes work. In what is often called the “lock and key” model, enzymes participate in chemical reactions based on the shape and structure of the reactants. An enzyme can join reactants (often called substrates) together by offering adjacent surface features where the reactants can fit. In this case, the enzyme makes it much easier for bonds to form in a reaction that is already energetically favorable.

chemical reactions that occur in living cells rely on one or more enzymes to allow them to occur at a useful rate. Just like each lock requires a key with just the right shape, each chemical reaction requires an enzyme with the right shape.

And all of this explains why Kit and Steven were optimistic about seeing their \$180 again, even after it had been subject to Midge’s digestive process and the accompanying onslaught of enzymes.



The only difference between starch top and cellulose bottom is the way the ring-shaped glucose molecules are connected (blue-colored bonds).



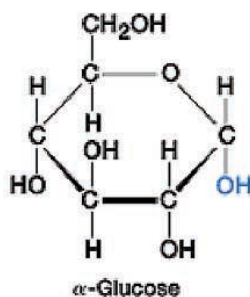
The paper currency is clearly intact after passing through the dog's digestive system.

Cellulose—defying digestion

The enzymes found in humans and other animals allow them to digest and metabolize many, but not all, biomolecules. Cellulose is one example of a molecule that defies digestion in many animals. This is an interesting exception because cellulose, a structural material found in plant cell walls, is made up of the same glucose subunits as digestible starch. Glucose is a simple sugar that provides fuel for most organisms. But the slight difference in the way the glucose molecules are hooked together in starch, compared with how they are hooked together in cellulose makes a big difference in their digestibility. Humans and many other higher animals have the enzyme required to break the bonds in starch, releasing glucose. But because the shape of the linkage is different in cellulose, the same enzyme will not work. In fact, where cellulose is concerned, humans do not have an enzyme that will work. Neither do dogs. Which brings us back to Midge.

Paper money is made of cellulose in the form of very high-quality cotton and linen fibers. This cellulose not only resists the chemical processes that are a part of digestion, but also withstands the mechanical breakdown—chewing and shredding—that is part of the digestive process.

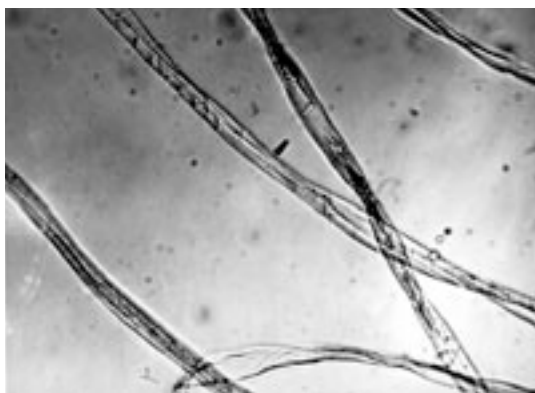
As it turns out, most humans eat a fair amount of cellulose in the form of fruits and vegetables. Although we cannot digest it, the cellulose serves as roughage or fiber that gives food bulk and keeps it moving through the digestive system. In the end, all of the undigested material ends up being eliminated as feces.



Glucose is fuel for most organisms and the building block for both starch and cellulose. Humans (and dogs) can break down starch into glucose but not cellulose.

The end ...

And so it was that Kit and Steven, with patience and endurance, were at last able to recover their \$180. Midge, like the goose that laid the golden egg, eventually passed all of the well-chewed bills in her feces.



Photomicrograph of cellulose fibers shows their linear nature.

Maybe you are wondering how animals such as cattle, sheep, deer, and goats thrive on a diet of grass or other cellulose-rich food. Can they digest cellulose when humans cannot? The answer is no. None of these animals have the enzymes required to digest cellu-

lose. Instead they rely on colonies of microorganisms living in their digestive systems. These simple microorganisms have the correct enzymes to digest the cellulose and to reassemble the products into starches and proteins. From these products, grazing animals acquire their nutrients. The special relationship between these animals and their resident microbes is called symbiosis—two organisms living with each other to the benefit of both.

As for Midge, it was a happy ending for all concerned. With the cash recovered, Midge eventually got out of the doghouse, and the songwriter was even inspired to write a new song to commemorate the entire affair.

So what are the chances—in the extremely rare case that a dog really DID eat your homework—that it might show up again undigested on the front lawn? Not good. The chemical processes that break down cellulose in the paper-making industry leaves a weaker form of cellulose in the product—so weak that there is little likelihood of it making its way through a dog's digestive system.

Better idea? Save to disk! Avoid magnets. But that's another story ... ▲



Michael Tinneland is the Associate Director of Academic Programs at ACS. His most recent article, "What's So Equal about Equilibrium", appeared in the September 2005 issue of *ChemMatters*.



BIOMIMICRY — Where Chemistry Lessons Come Naturally

By Kathryn E. Parent and Jennifer L. Young

Look around and you'll see many little chemical factories in nature that are nonpolluting and environmentally friendly. Inside a leaf or a bug, there lies some sophisticated chemistry, often turning out incredible materials that are the envy of today's chemists and engineers.

In fact, you might say that today's industrial chemists are developing a green thumb. Green chemistry is the design of chemical products and processes that reduce or eliminate the use and production of hazardous substances. Green chemists look for new ways to do chemistry that is benign by design, thus preventing pollution before it starts.

Why are chemists turning to nature for ideas? Think about it. Nature uses renewable sunlight for energy and recycled starting materials to make a lot of things. Organisms synthesize medicines, plastics, and all kinds of other useful materials without releasing toxic chemicals into the environment or using large amounts of heat or pressure. Nature's chemistry embodies many of the principles of green chemistry, using processes that have met the tests of time.

Scientists call the study of these natural chemical processes biomimicry, a term that means imitating life and involves applying nature's lessons to new human inventions. Janine Benyus, the author of *Biomimicry: Innovation Inspired by Nature*, calls it "the conscious emulation of life's genius". But that's not to say that every process in nature is nonpolluting. For example, it is well known that animals release carbon dioxide and methane, greenhouse gases, into the environment.

Although biomimicry is getting increased attention today, several famous inventions of the past were inspired

How do they do that? How do spiders spin a web that's stronger than steel? How do bombardier beetles launch chemical bombs at their enemies without hurting themselves? How do tiny mussels stick to rocks in the pounding surf? How do green plants generate a steady supply of safe and renewable energy?

by nature. Take the telephone, for instance. Alexander Graham Bell studied the human tongue and eardrum to help him design the first telephone. The Wright Brothers watched birds gliding in the wind for shaping airplane wings before taking the first flight. And nearly everyone is familiar with synthetic Velcro, which was inspired by the way the tiny hooks on seed pod burrs attach to the loops of thread in cloth.

Whether forms, processes, or systems, biology includes a wealth of ideas for chemists and engineers. When scientists apply the methods and systems practiced in nature to cutting-edge research challenges, creative and amazing scientific breakthroughs often occur.

Spiders spin webs stronger than steel

Dragline silk from a golden orb weaver spider is five times stronger than steel (when compared gram for gram),

and can absorb five times the impact force of Kevlar—the synthetic fiber of bullet-proof vests—without breaking. What's more, it can stretch 40% longer than its original length. For the spider, the durability and strength of silk means food. And for humans, it could mean an amazingly useful fiber that can be made from safer and less hazardous chemistry. Science writer Steve Miller describes the properties of good web fiber in a February 2001 *ChemMatters* article: "It must be strong enough to bear the weight of a bungee-jumping spider, flexible enough to withstand the impact of a flying insect, and stable enough to last for days. ... And it cannot require more raw material than the spider can replenish from ordinary food resources." Even the U.S. military has taken notice. The U.S. Army has interest in a manufactured version of dragline silk for applications such as catching fighter jets as they land on aircraft carriers.

How does a spider make such an incredible fiber that humans have not yet fully reproduced? Scientists are still studying the chemical composition of the spider's silk. Scientists know that spider silk is a protein and have identified the amino acids that are its building blocks. Glycine and alanine are the most abundant amino acids in the silk (see Figure 1). The three-dimensional structure of the fiber, which gives it the strength and flexibility, results from how the amino acid building blocks interact with each other. As a result of the diversity of amino acid interactions, some parts of the silk fiber are highly oriented, like uncooked spaghetti, and other parts are very nonoriented like cooked spaghetti.

To make the silk fiber, the spider synthesizes liquid protein by putting together the amino acid molecules and squeezes the protein through a spinneret (i.e., to spin the fiber). When it exits the spider, the soluble liquid protein becomes an insoluble, highly ordered, and extremely strong fiber. With this knowledge, scientists are trying to make a fiber that is similar to spider silk. This much is certain: spiders don't use the high pressures, high temperatures, or corrosive acids often used in chemical syntheses. In manufacturing Kevlar, for example, industrial chemists rely on hot concentrated sulfuric acid. Nylon fiber, used in ropes and cords for rock climbing and parachuting, is manufactured under conditions of high pressure and temperature. The golden orb weaver spider manages to produce a high-performance fiber using chemistry mild enough to occur inside their bodies.

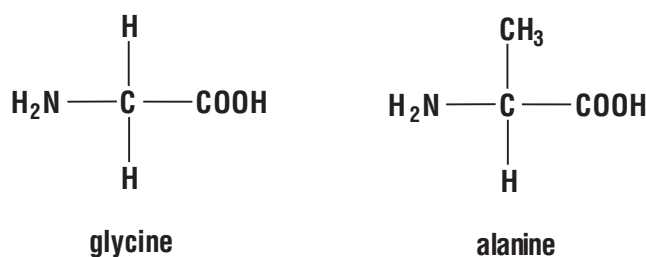


Figure 1. Chemical structures of glycine and alanine.

The bombardier beetle bomb



Bombardier beetles can fire, literally, a mixture of chemicals at predators. To prepare for attack, the beetles produce and store two chemicals, hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$) and hydrogen peroxide (H_2O_2).

When the mixture of chemicals is pushed from the storage reservoir into the firing chamber, enzymes in the chamber wall react to release free oxygen (O_2) and steam (H_2O). They also oxidize the hydroquinone to benzoquinone, which is an irritant (see Figure 2). The resulting reaction is extremely exothermic. Heat and pressure force the chemical spray out an opening in the beetles abdomen with a loud bang. "The chemistry is simple, but the biology is beautiful" said Jerrold Meinwald, a researcher at Cornell University. Despite the heat, pressure, and irritating chemicals emanating from its body, the beetle remains largely unaffected. Unfortunately, the news isn't as good for its enemies.

bile airbags, and unmanned aerial vehicles, though all of these are beyond the scope of his current study. "I think the natural world is full of excellent designs that we can learn from," McIntosh says.

Blue mussels make glue

Visit the seashore and you'll find mussels clinging steadfastly to rocks, despite the crashing surf. How do they do it? Professor J. Herbert Waite from the University of Delaware has been researching this question for more than 30 years. The mussels are able to apply their protein-based glue underwater, where it cures and sticks to nearly anything amidst the harsh ocean. "They do it with chemistry" Waite realizes. But so far, no chemist has successfully synthesized this incredible marine superglue. Clearly, the product would be a boon to boaters of all descriptions. With a glue like that, they would no longer have to dry-dock boats for repairs.

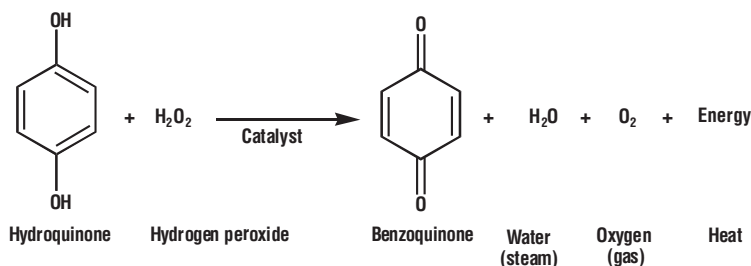


Figure 2. Oxidation of hydroquinone.

The March-April 2004 issue of *American Scientist* features the research of Andy McIntosh, a professor of thermodynamics and combustion theory at the University of Leeds in England. He is working to apply the bombardier beetle's methods to find a better way to reignite aircraft gas turbine engines. Beyond engine reigniters, McIntosh envisions future applications of the bombardier beetle's design, including rocket technology, automo-

Professor Kaichang Li, a wood chemistry expert at Oregon State University, used mussels as his model for developing a new soy-based wood adhesive. He explains, "Inspired by the strong and water-resistant binding of marine organisms such as mussels to rocks and other substances, we are investigating conversion of renewable natural resources such as soy protein, carbohydrates, and lignin to strong and water-resistant wood adhe-



PHOTO BY DAVE COWLES [HTTP://ROSARIO.WMC.EDU/INVERTS](http://rosario.wmc.edu/inverts)

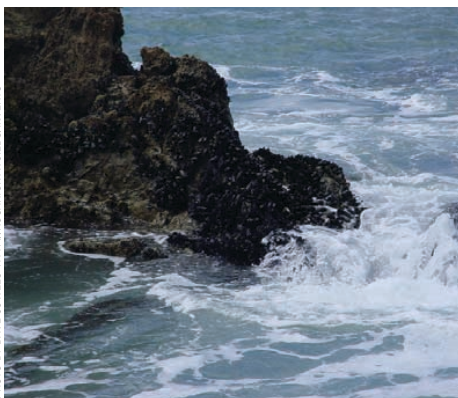


PHOTO BY DAVE COWLES [HTTP://ROSARIO.WMC.EDU/INVERTS](http://rosario.wmc.edu/inverts)

sives.” He noticed that the chemical structure of the proteins in the mussels’ glue included a lot of ringed hydroxyl chemical structures. By modifying soy protein (e.g., tofu) to incorporate more of these types of structures, Li has developed a new glue that is stronger and more

water-resistant than the traditional formaldehyde-based adhesives used to make plywood. Even better, the glue doesn’t release hazardous air emissions during manufacturing processes or from the finished plywood boards. That’s good news for the environment, for plywood manufacturers, and for consumers of plywood.

New directions in biomimicry research

Writer Alexandra Goho, in a *Science News Online* February 12, 2005, article, highlighted several chemists who are using nature for inspiration in their laboratories. For example, Dr. David Liu at Harvard University has found ways to use one of nature’s premier templates, DNA, like a molecular laboratory for synthesizing chemicals in miniscule batches. DNA controls the order and amount of chemicals that react during a given process, limiting the number of undesired by-products.

At Cornell University, Dr. Tyler McQuade looks to cell biology for inspiration to develop an assembly-line system to make drugs like Prozac. His microcapsule enzyme-mimic approach, controls the order in which reactions take place, minimizing separation and purification steps that typically generate large amounts of waste.

Dr. John Warner at the University of Massachusetts-Lowell recognizes seashells as models for lowering the energy required to produce solar cells. To make their shells, mollusks rely on small organic molecules to choreograph the assembly of calcium carbonate (CaCO_3) into elaborate mineral structures. When Warner looked at films of titanium dioxide (TiO_2), used as an alternative to silicon (Si) metal for solar material, he saw a resemblance to the structure of seashells. So, Warner



COURTESY OF PROF. KAICHANG LI, OREGON STATE UNIVERSITY

tried using small organic molecules with multiple carboxylic acids (RCOOH) to assemble titanium dioxide particles into films of solar material. He was able to accomplish it at room temperature, a tremendous energy savings over traditional manufacturing methods that require heating titanium dioxide (TiO_2) films at 500 °C.

The examples above show the incredible variety in the research chemists’ and engineers’ approach using biomimicry. Imagine what we can create, using examples in nature to find new and better ways to design materials, processes, and systems. ▲

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Kathryn E. Parent and Jennifer L. Young are staff of the American Chemical Society’s Green Chemistry Institute (www.greenchemistryinstitute.org).

The Consumer Product Safety Commission

The Consumer Product Safety Commission (CPSC) is the government agency responsible for protecting the American public from potential injury by more than 15,000 consumer products excluding cars, foods, and drugs. The CPSC issues product recalls and safety warnings; it also provides consumers with a forum for reporting safety products. For example, the CPSC was intimately involved with the recall of the some of the jewelry described in "Bling Zinger". For more information on the CPSC, visit <http://www.cpsc.gov/index.html>.

Not even asthma can stop Olympians from going for gold!

Exercise-induced asthma is fairly common, impacting up to one in five athletes. These athletes can suffer from shortness of breath, chest tightness, and wheezing either during or after exercise. Even Olympians aren't immune to this respiratory disease. According to the American



Academy of Asthma, Allergy and Immunology (AAAAI), up to one in six of these world class athletes suffer from asthma. For more information on exercise-induced asthma, its triggers, and symptom management, visit <http://www.aaaai.org/patients/publicedmat/tips/exerciseinducedasthma.stm>.

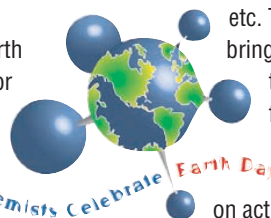
More on nanomotors

Synthetic nanomotors are an exciting and elegant creation at the interface of chemistry and physics. In "Nanomotors", the synthetic nanomotor created by Alex Zettl, professor of physics at UC Berkeley and his graduate students is described as a gold rotor attached to a carbon nanotube shaft. To view pictures and video of this 500-nm motor in action, visit http://www.berkeley.edu/news/media/releases/2003/07/23_motors.html.

Chemists celebrate Earth Day

That's right. The American Chemical Society will observe Earth Day on April 22. The theme for the 2006 celebration is "Dig It". The

community event for Chemists Celebrate Earth Day 2006 is "Plant It for the Planet." Celebrate the chemistry of the soil and plants by hosting activities that will benefit the community like planting flowers, trees, grass,



etc. This activity will bring the community together for a fun-filled day! To help celebrate the day, a series of hands-on activities are available for teachers and students at <http://chemistry.org/earthday>. ▲

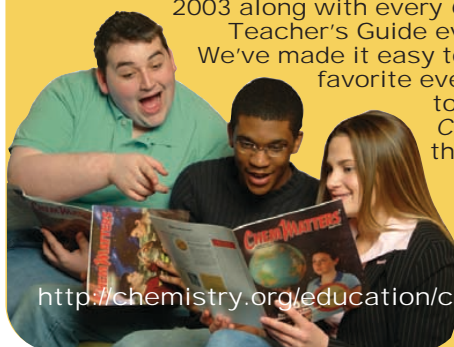
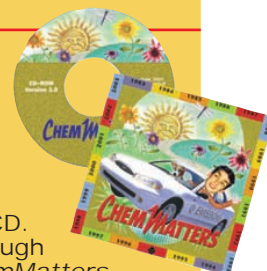
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