New polymers harvest light to do chemistry

For many years people have used solar energy to heat household water, and more recently to generate electricity. A far older use of sunlight, though, involves doing chemistry. Plants and other photosynthetic organisms mastered this technology eons ago. Now come human chemists.

One of them is James E. Guillet at the University of Toronto. He sees a future in which sun-driven chemical reactions churn out liquid fuels during the brighter summer months for use during the less sunny Canadian winters. Guillet says his research also could lead to making vitamin D without using electricity-eating lamps, the usual practice today. Solar-inspired chemistry may even provide a means for clearing polychlorinated biphenyls (PCBs) and other pollutants from troubled waters.

The promise for carrying out such chemistry feats may rest in virus-sized polymer molecules developed by Guillet that behave like tiny antennae for gathering reaction-driving light energy. The same molecules, which become spherical when they dissolve in water, double as miniature vessels that attract and imprison other nearby organic molecules. They harvest light energy, then break apart the trapped molecules, forming different compounds. The polymers, which quicken certain reactions, resemble enzymes — biological polymers that throttle up biochemical reactions. Since the lab-made polymers use light to speed up reactions, Guillet calls them photozymes.

In the December MACROMOLECULES, he and two co-workers describe a new photozyme, poly(sodium styrenesulfonate-co-2-vinylnaphthalene), or PSSS-VN. "These things [photozymes] organize themselves in water in such a way as to scavenge any organic material in the water and subject it to a very large intensity of ultraviolet light," Guillet says.

In their paper, the researchers describe their use of PSSS-VN to break apart the compound 2-undecanone, used in perfumes. They observed a nine-fold increase in the rate of this reaction when compared to the same reaction without the photozyme. Although the ability to perform this photoreaction of 2-undecanone may not itself prove of practical importance, Guillet says the work demonstrates the principle of using solar energy to carry out organic chemical reactions in water. "It's rather important work," remarks Field Winslow, a chemist with AT&T Bell Laboratories in Murray Hill, N.J., and editor of MACROMOLECULES.

Electrically neutral organic molecules such as naphthalene (a chemical used for repelling moths and for making dyes, solvents and lubricants), 2-undecanone and the long carbon chains in vegetable oil do not mix well with water. For this reason, most laboratory reactions involving organic molecules have been done in neutral organic solvents, which are often toxic and expensive. Photozymes may enable chemists to use cheap, clean solar energy for carrying out many organic chemical reactions in cheap, clean water.

"Almost all of the organic chemicals that are made in the world are actually made in the presence of water because they're made in trees and plants," Guillet notes. Only in laboratory and industrial settings do organic solvents replace water as the standard reaction medium. Guillet argues that people should be able to mimic the ability of plants to make organic chemicals in water.

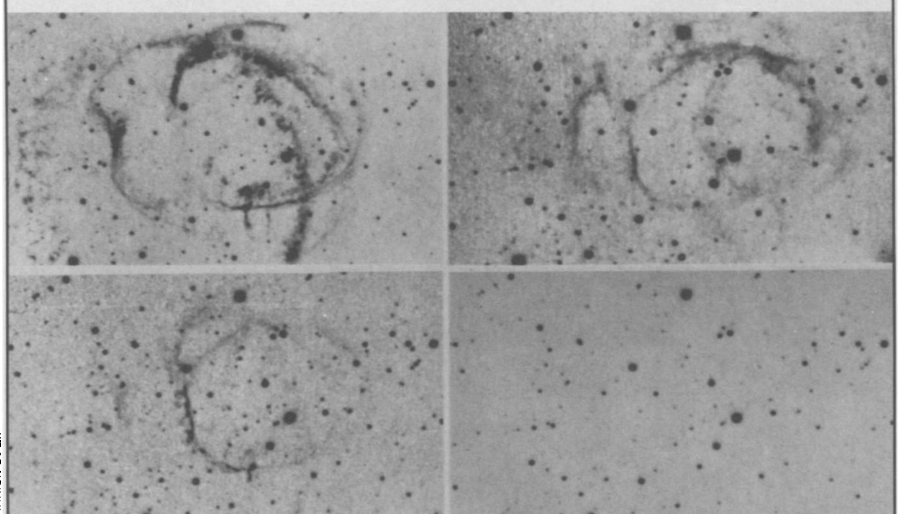
Green plants do it with the help of a cluster of 100 to 200 chlorophyll molecules, or "antennae pigments," to harvest light energy and transfer it to an active center where the first steps of photosynthesis occur. Guillet's team used two types of molecular building blocks to construct photozymes to gather light energy, in this case for catalyzing a reaction involving 2-undecanone.

The naphthalene-containing components of PSSS-VN absorb ultraviolet light. These parts of the photozyme also are hydrophobic. As a result, they cluster instead of allowing themselves to be surrounded by water molecules. This causes the stringy polymer molecules to pucker and curl into tiny spheres with neutral interiors quite receptive to other electrically neutral molecules such as 2-undecanone and PCBs. The other polymer parts, the sodium styrene sulfate components, make the spheres soluble in water. Curtis Frank, a chemical engineer at Stanford University who is familiar with Guillet's work, describes the dissolved photozymes as "lots of tiny reactors in an aqueous environment." Water also can serve as a "thermal sink" drawing away excess heat that might otherwise interfere with the reactions occurring inside the photozymes, he adds.

According to Guillet, photozymes such as PSSS-VN may be ideal for cleaning waters contaminated with PCBs or other organic pollutants such as polynuclear aromatics, which are suspected carcinogens. In laboratory preparations, Guillet says, the photozymes transform the pollutants into less troublesome compounds within a few hours. Nicholas Turro, a chemist at Columbia University in New York City, calls the work "first rate." He and others remark also that Guillet has a knack for getting his laboratory-proven concepts into practice.

— I. Amato

Filamentary signs of a second supernova



Winkler, et al.

The scattered residue of a supernova explosion provides a rare glimpse of material from the core of a massive star. In the case of the Puppis A supernova remnant, the unusual chemistry and apparent youth of a distinctive pattern of faint filaments near the remnant's center suggest a second supernova may have exploded within the original expanding shell of gas some 3,000 years later. P. Frank Winkler of Middlebury (Vt.) College and his colleagues provide evidence for that possibility in the Jan. 5 NATURE. Photographs taken through special filters at the Cerro Tololo Inter-American Observatory in Chile reveal three overlapping but separate sets of filaments, each with a characteristic chemical composition. One set (upper left) is dominated by nitrogen emissions, the second (upper right) by oxygen emissions and the third (lower left) by sulfur emissions. The fourth photograph (lower right) shows the region's appearance at a wavelength (6,100 angstroms) not dominated by emissions from specific elements.